SYNTHESIS, CHARACTERISATION AND STRUCTURE DETERMINATION OF FLUORO- AND NON-FLUORO SCHIFF BASES AND THEIR METAL COMPLEXES

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STATEMENT

The accompanying thesis submitted for the degree of Ph.D. is based on work conducted by the author in the Department of Chemistry of the University of Leicester mainly during the period between September 1994 and September 1997.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by the references. None of the work has been submitted for another degree in this or any other University.

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DEDICATED TO

MUM AND DAD

WITH LOVE AND THANKS

ABSTRACT

SYNTHESIS, CHARACTERISATION AND STRUCTURE DETERMINATION OF FLUORO- AND NON-FLUORO SCHIFF BASES AND THEIR METAL COMPLEXES

Syeda R. Gilani

ABSTRACT

Schiff bases have been prepared from fluoro- and non-fluoro-substituted anilines with (a) salicaldehyde and substituted salicaldehydes and (b) acetylacetone and its trifluoro analogue. They were characterised by ultraviolet-visible, infrared, and NMR (^{1}H, ^{13}C, ^{19}F) spectroscopies, and by mass spectrometry. The crystal structures of several of these Schiff bases were determined by X-ray techniques. Several cobalt(II), cobalt(III), nickel(II) and copper(II) complexes of these ligands were prepared. Crystal structures were established for four of the copper(II) complexes; bond distances in the complexes have been compared with those in the respective free ligands. Inter- and intra-molecular hydrogen-bonding is significant in many of the Schiff bases, but not in the complexes.

Anhydrous bis(acetylacetonato)cobalt(II) was obtained, and its structure established by X-ray diffraction. It was found to be square-planar. Its bond lengths, bond angles, and geometry were compared with those for other metal(II) acetylacetonates [M(II) = Cr(II), Co(II), Ni(II), Cu(II), Zn(II)], in mononuclear, polynuclear, and hydrated forms.

CONTENTS:-

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION:-

The compounds which are called "Schiff bases" include various types, but this thesis is concerned mainly with the synthesis and characterisation of some novel Schiff bases derived from the condensation of either (a) salicylaldehyde and substituted salicylaldehydes or, (b) from β-diketones, with both fluoro-substituted anilines and with their non-fluoro hydrogen analogues and various metal chelates. The latter include Co(II), Co(III), Ni(II), and Cu(II) complexes.

The structures of the ligands and their Cu(II) complexes are determined by X-ray diffraction techniques. The bond lengths and bond angles of the ligands are compared with each other and with those in their respective Cu(II) complexes, to study the substituent effects in free and coordinated forms. The bond lengths and bond angles of complexes are also compared with each other and some other complexes with O,N donor ligands.

Anhydrous bis[acetylacetonato]Co(II) crystallised out during the attempts to synthesise complexes of Co(II) with acetylacetoimine by a template reaction. The structure of this novel anhydrous bis[acetylacetonato]Co(II) complex has been determined by X-ray techniques using the Fourier method and was found to be interesting because of its square planar geometry. Its bond lengths, bond angles and geometry were compared with other anhydrous, aqua monomers and polymers of M(II)[Cu(II), Co(II), Ni(II), Cr(II) and Zn(II)] complexes.

1.2 SCHIFF BASES :-

The condensation of primary amines with aldehydes and ketones gives products known as imines which contain a C=N double bond. These compounds rapidly decompose or polymerise unless there is at least one aryl group bonded to either nitrogen or carbon atom. These compounds were first reported by Schiff[1], and are therefore often referred to as Schiff bases. Imine formation is normally an acid catalysed process, a pH *versus* rate profile indicating that reaction is very slow at both high and low pH. At low pH there will be amine protonation, but a maximum rate is reached at weakly acidic pH (approximately 4.5)[2].

Due to several diverse systems of nomenclature, information on Schiff bases can also be found under the headings azomethine, anil, imine, ketimine and also as specific compounds such as benzylidene aniline can be found as benzalaniline, benzalanil or benzanil[3].

Aromatic aldehydes and ketones give quite stable Schiff bases with amines. Aromatic aldehydes react readily under mild conditions and at relatively low temperatures with or, if liquid, without a suitable solvent. With ketones, especially aromatic ones, higher temperatures and longer reaction times are usually required. In condensations of aromatic amines with aromatic aldehydes, electron-withdrawing substituents at the para position of the amine decrease the rate of the reaction, while increasing it when on the aldehyde[4].

The basicity of imines is increased by electron-donating substituents at the para-position, for example, 4-methyl and 4-methoxy groups, which tend to

increase the electron density at the nitrogen atom, and decreases with an electron-withdrawing substituent, such as a nitro group, at the para-position. Halogen substituents exert their expected effect in causing a withdrawal of electron density and hence in reducing the basic strength[5,6]. The basic character of the azomethine group is also revealed by the fact that in aprotic solvents, there is a tendency for the lone pair of electrons on the nitrogen atom to interact with hydroxylic compounds to yield hydrogen-bonded complexes.

1.3 SPECTROSCOPY OF SALICYLIDENEANILINES

Spectroscopic studies have largely been confined to ^{1}H NMR investigations of the keto-enol equilibria of the free bases. Percy and Thornton[7] reported an investigation of tautomeric equilibria in solutions of Schiff bases. It has been shown that the bases exist solely in the phenol-imine form in non-hydroxylic solvents at normal ambient temperatures. The strong intramolecular hydrogen-bonding present in the ligands leads to very broad and weak hydroxyl absorption in their IR spectra near 2700 cm^{-1}, so that the ^{1}H NMR spectra are more informative than IR spectra with respect to the nature of the O–H bonding. The electronic effects of the substituent may be transmitted to affect the strength of the hydrogen bond either *via* the conjugation through the heterocyclic ring or, more directly, by modifying the capacity of the nitrogen atom for participating in hydrogen-bonding.

1.3.1 UV

The UV spectra of compounds containing an unconjugated chromophore are characterised by bands due to n $\rightarrow$ π^* transitions in the range 235-272 nm. However, conjugation with alkene or aryl groups causes large changes in the spectrum, since strong bands due to $\pi \rightarrow \pi^*$ transitions cover the rather weak n$\rightarrow\pi^*$ absorptions. Minkin and coworkers suggested an enol structure for Schiff bases on the basis of UV and IR behaviour of a number of ortho-hydroxy aldehydes[8]. They showed that the $\pi \rightarrow \pi^*$ frequency of *N*-benzylidene aniline compounds is only very slightly affected by further substitution in the benzylidene or aniline rings, and therefore the six-membered H-bonded ring is strongly stabilised since it resists substituent effects which change the acidity of the hydroxy group and the basicity of the nitrogen atom. Tsuchida and Tsumaki[9] had noticed that the compounds having intramolecular hydrogen-bonding showed a band at ~400 nm, while in the compounds with no intramolecular hydrogen-bonding this band was absent.

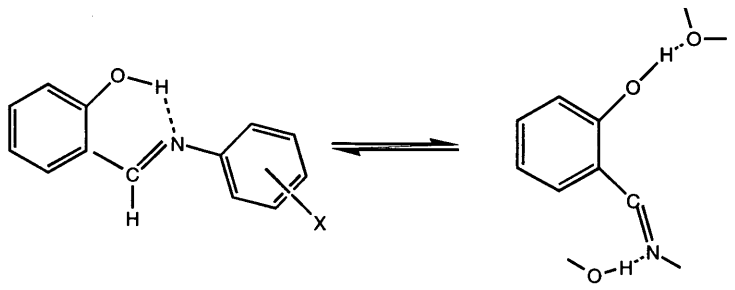

Figure 1.1

However, Kiss and Auer[10] had considered an alternative explanation that the band at ~400 nm is due to a tautomeric equilibrium involving enol-imine and keto-amine forms in solutions, which are represented in Fig. 1.2.

Figure 1.2

Other workers have favoured Kiss and Auer's interpretation[11-14] and the bands have been assigned to individual tautomers[15]; in this case both isomers are assumed to be present in the solid state.

Hydrogen-bonding generally results in a rather small red shift for the π to π^* band[12,14], the ~400 nm band is considerably displaced. Increasing the polarity of the solvent increases the ε_{max} of the ~400 nm band in a uniform fashion, although the wavelength of the absorption maximum does not change very much[15].

Many studies of the electronic spectra of bidentate N,O Schiff bases derived from chiral primary amines have been reported[16] in order to establish the absolute configuration of the amine. Three absorption bands, designated[17] I, II and III, at about 315, 255 and 215 nm respectively, are present in the electronic

absorption spectra of hexane solutions of the Schiff bases derived from salicylaldehyde and RNH_2 where R is a chiral group. These bands have been attributed to the C=N chromophore. As already pointed out, two additional bands, at about 400 and 280 nm, become apparent in polar solvents and have been attributed to the quinoid tautomer[18].

1.3.2 IR

The C=N stretching frequencies of the ligands occur in the region between 1680 and 1603 cm^{-1} when H, alkyl or aryl groups are bonded to the C and N atoms. The nature of the different substituents on these atoms determines the position of the stretching frequency in the above range, *e.g.* aryl groups on the C and N atoms cause a shift of frequency towards the lower part of the range[19]. Thus, for compounds such as ArCH=NR a frequency range of 1656-1631cm^{-1} has been reported[20]. Compounds of the type ArCH=NAr, with variously substituted aryl groups, exhibit a range of 1631-1613 cm^{-1} for ν(C=N)[21].

The presence of an OH group at the 2-position of the phenyl ring of the benzaldehyde effects a bathochromic shift. This has been attributed to intramolecular bond formation, with the benzenoid form being prevalent over the quinoid form (Fig 1.3). In these compounds, the phenolic C–O stretching vibration occurs between 1288 and 1265 cm^{-1}. Upon coordination to metal ions through both O and N, a decrease of the C=N frequency is generally observed.

1.3.3 NMR, MASS SPECTROMETRY AND X-RAY:-

NMR studies are mainly applied to elucidating the structural features of Schiff bases in solution. These studies are mainly concerned with Schiff bases derived from benzaldehyde and its derivatives, β-diketones, *o*-hydroxyacetophenones and *o*-hydroxyacetonaphthones. Data from ^{1}H NMR studies on ^{15}N-salicylidene aniline and related compounds provide independent evidence for an equilibrium between enol-imine and keto-amine tautomers[15].

Elias and Gillis[22] studied a series of substituted N-benzylidene anilines. They reported that the molecular ion was the base peak in every case for 4-substituted compounds, and that all underwent loss of the azomethine proton to yield an $(M-1)^{+}$ peak of variable intensity.

The crystal structures of some salicylidene anilines have been determined by several groups. The most interesting feature of these structures is intramolecular hydrogen-bonding[23]. They are known to show a self-isomerisation induced by an intramolecular proton transfer from the hydroxyl oxygen to the imine nitrogen through the O–H...N hydrogen bond[24]. Generally, it is seen that the salicylideneimine molecules are stacked in layers and are associated by an infinite chain of hydrogen-bonds[25].

1.4 SPECTROSCOPY OF ACETYLACETO IMINES:-

Bidentate Schiff bases derived from β-diketones have been shown to exist almost entirely as the tautomer (b) in Fig 1.4 in solution in common solvents. Proof of this structure has been obtained from the observed spin-spin splitting of the N-H proton by the protons of R[26-27](b) in Figure 1.4.

Similarly the condensation products of amines with 1-hydroxy-2-acetonaphthone and 2-hydroxy-1-naphthaldehyde, in a 1:1 ratio, have been shown to be ketoamines, the quinoid forms being preferred over the enol forms. The ^{15}N NMR spectra of the above Schiff bases confirmed these assignments and the temperature dependence of the spectra gave information on the tautomeric equilibria[28].

The Schiff bases derived from hydroxymethylene ketones (Fig 1.3) exhibit tautomers (b) and (c), but not (a), in a variety of solvents. The ratio of the two isomers is influenced by the substituent R[29].

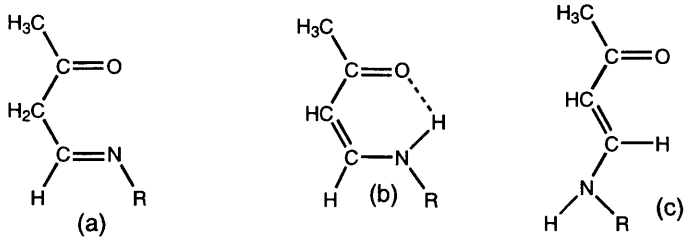

Figure 1.3

Similarly, a recent NMR study of the formylcamphor derivatives (d)-(f) in Fig 1.5 showed that the tautomer distribution was very strongly solvent dependent, and also that spectral changes occured with time. Thus, (e) (Fig. 1.4) is the most abundant in $CHCl_3$ while (f) is the most stable in acetone. In benzene solution the ratio (e)/(f) varied from 1/10 to 10/1 during 24 h. No evidence of the tautomer (d) was obtained[30].

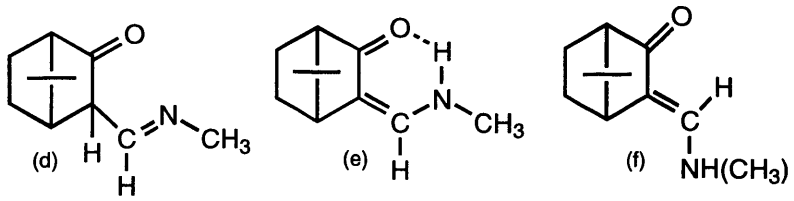

Figure 1.4

NMR results show that all these compounds exist in solution as the enolimine tautomers. In addition, an electron-withdrawing R substituent reduces the magnetic shielding of the hydroxyl proton. In contrast, the C=N stretching frequencies do not appear to be influenced by the nature of the R group in a systematic way. Upon coordination to transition metals the C=N stretching frequencies at about 1620 cm^{-1} decrease, whereas those at about 1575 cm^{-1} increase. On the other hand, the two bands assigned to the C-O stretching frequency increase by about 30 and 40 cm^{-1} [7].

Dudek and Holm[27] studied the ^1H resonance spectra of a number of compounds obtained from the 1:1 condensation of a β-diketone with a mono

amine. Of the three tautomeric possibilities, these compounds exist predominantly in the keto-amine form(R = CH_3, R′ = substituted aryl group).

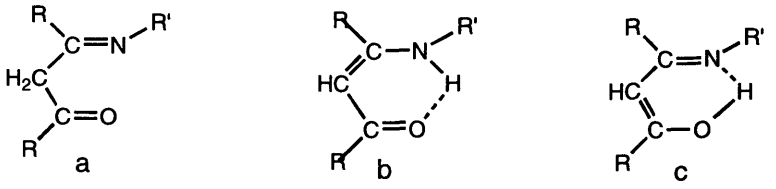

Figure 1.5

Proof of this structure is obtained from the observed spin-spin splitting of N–H with the α-protons of R. The position of the tautomeric equilibrium could not be altered by large changes in the nature of the solvent nor by the substituent R. The preferential existence of the keto-amine form over the keto-imine and enol-imine forms is ascribed to greater stabilisation through resonance and hydrogen-bonding.

Such tautomerisation in the solid state has been suggested to be responsible for the thermochromism of many crystalline anils[31].

McCarthy and Martell[32] reported the NMR spectra of β-diketone diimine Schiff bases and several of their diamagnetic nickel(II) and palladium(II) chelates. The spectra indicate that all of the ligands studied exist mainly in the keto-amine form.

1.5 COMPLEXES:-

Despite the considerable number of papers which have appeared on the structure of Schiff base metal complexes, a relatively small number of the free ligands have been structurally characterised. Metal complexes, with a general formula ML_n [where L = SAL or AcAc] (Figure 1.6, 1.8), of these organic ligands have been prepared and studied for many years. Various methods have been employed for their characterisation and for determining the structure of the complexes, including determinations of magnetic moment, electronic spectra and nuclear magnetic resonance spectra, in addition to elemental analysis and molecular weight determinations.

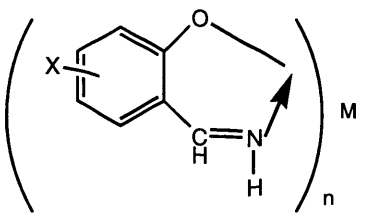

Figure 1.6

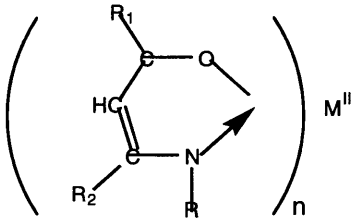

Figure 1.7

Salicylaldimines react with bivalent metal ions to form complexes $M(OC_6H_4CH{:}NR)_2$. Such complexes have been isolated for nickel[33], copper[33,34] and cobalt[35,36], and their magnetic properties[37,38], absorption spectra[38] and dipole moments[39] have been studied. Only a few Schiff bases commonly used as ligands have been prepared and characterised in the uncomplexed state, metal complexes have generally been directly obtained by other procedures[40]. A large

group of bidentate Schiff bases utilised as metal ligands is characterised by having a NO donor set. Since, in the free ligands, the oxygen is often present as an OH group, these ligands generally act as chelating mono anions.

The most characteristic respect in which ligands containing the C=N bond show basic properties is in the formation of complexes with metals. These complexes provide some very characteristic series of co-ordination compounds, and consequently a large number of them have been prepared and their properties examined and compared. The basic strength of the C=N group is insufficient by itself to permit the formation of stable complexes by simple co-ordination of the lone pair to the metal atom. Therefore, a functional group with a replaceable hydrogen atom, preferably a hydroxyl group, is required, near the C=N group, for the formation of a five or six membered ring by chelation to the metal atom[41].

Among the simplest imine compounds are salicylaldimines. The salicylaldimine complexes can often be made either by direct interaction between the metal ion and the appropriate Schiff base in alcoholic solution, in the presence of a base such as NaOH or sodium acetate, or by refluxing salicylaldehyde complexes of the metal with a slight excess of a primary amine in non-aqueous solvent.

The co-ordination complexes formed with divalent metal ions are of considerable interest as they vary in structure from coplanar to tetrahedral, not only depending on the nature of the divalent metal involved, but also on the nature of the substituent on the nitrogen atom and the substituents on the aromatic ring of the salicylaldimine molecule.

Difficulty has been reported in the preparation of cobalt(II) complexes with salicylidene-arylimines bearing substituents in the aryl ring ortho to imino-nitrogen: compounds can be readily prepared from bases containing meta- or para- substituents, and complexes of copper and nickel can be prepared with all three kinds of substituent present. In order to explain this behaviour it has been suggested that Co(II) complexes of this kind prefer a tetrahedral arrangement of ligands, and ortho-substituents in the arylimine ring system, for steric reasons, prevent the most stable configuration from being adopted, so that crystalline products cannot be isolated. Nickel and copper complexes exist preferentially in a planar configuration and such compounds show a greatly reduced steric hindrance to chelation. The development of brown-yellow colours after oxidation of reaction mixtures of Co(II) and either ortho- or meta-substituted salicylidenearylimines indicates that coordination of some kind does occur in solution even though pure products could not be isolated[42].

The presence of two different kinds of coordinating atom on each ligand, *viz.,* oxygen and nitrogen, allows the existence of structural isomers for the octahedral Co(III) complexes. As one molecule is unable to span opposite corners of the octahedron, only two geometric isomers of these tris ligand Co(III) complexes would be expected to exist. These are the fac-form in which the nitrogen atoms all occupy corners opposite to an oxygen atom, and mer-form in which one pair of nitrogen atoms occupy corners opposite to one another. In fact one form has been isolated in each case, and dipole moment[43] and NMR[44]

evidence indicates that this is the mer form, as would be predicted from steric considerations. There is also the possibility of positional isomerism among salicylaldimine complexes containing aryl substituents attached to the nitrogen atom, depending upon whether the substituents are in the ortho-, meta-, or para-position[45]. The copper(II) complexes having a d^9 configuration have one unpaired electron in both the planar and tetrahedral complexes and are paramagnetic.

The keto tautomer is rather unusual, since it has been previously shown that Schiff bases derived from salicylaldehyde prefer form (a)[Fig. 1.5]. When such Schiff bases coordinate to the metal as monoanionic ligands the C-N and C-O bond lengths undergo variations which are in agreement with the IR spectroscopic result reported in the previous section.

X-ray diffraction studies show that an N-phenyl group causes considerable distortion from overall coplanarity in the molecule[46-48]. In the solid state the Ni(II) complexes of N-aryl salicylaldimines are all either diamagnetic or paramagnetic. For a series of metal complexes of Schiff bases derived from salicylaldehyde, the C-N and C-O bond length have mean values of 1.295 and 1.312 Å respectively[49].

As expected, comparison of these data with those relative to the free ligands shows that the shortening of the C-O distance corresponds to a small, but significant, lengthening of the C=N distance. This is in agreement with the amount of variation of the corresponding stretching frequencies of C-N and C-O bonds upon coordination to a metal.

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CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF SUBSTITUTED SALICYLIDENEANILINES

2.1 INTRODUCTION:-

A Schiff base is a nitrogen analogue of an aldehyde or ketone in which the C=O group is replaced by a C=N-R group[1]. A large group of Schiff bases are utilised as metal ligands. They may be mono, bi, tri, tetra or multidentate having, for example, N, NO, N_2, N_2O, N_2S, NO_2, NSO or N_2O_2 donor sets. In the case of monodentate Schiff base ligands the basic strength of the C=N group is not sufficient to obtain stable complexes by coordination of the imino nitrogen atom to a metal ion. Hence only the presence of at least one other donor atom, suitably near the nitrogen atom, generally stabilises the metal-nitrogen bond through formation of chelate ring. Some examples of Schiff base whose anions can act as bi, tri, or tetradentate ligands are shown in Figures 2.1, 2.2 and 2.3.

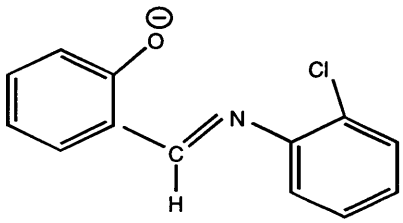


Figure 2.1 *Bidentate NO donor set*

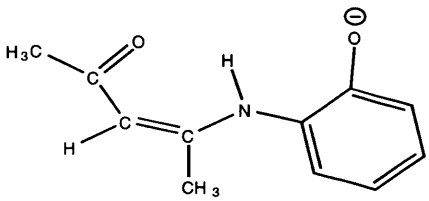


Figure 2.2 *Tridentate NO_2 donor set*

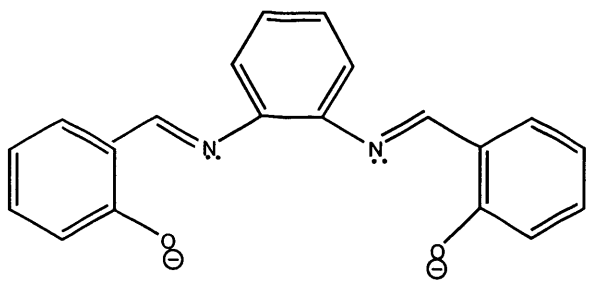


Figure 2.3 *Tetradentate N_2O_2 donor set*

Most of the chelates of Schiff base ligands are synthesised by template reactions in which the carbonyl oxygen first reacts with a metal ion to give an intermediate complex which then reacts with a basic nitrogen, i.e. $-NH_2$ group, donor to give a Schiff base ligand complex.

Bidentate Schiff bases utilised as ligands are usually characterised by having an NO or N_2 donor set, for example, azo and azomethine ligands. Since the oxygen is often present as an OH group, these ligands generally act as mono anions[2].

The most studied bidentate Schiff bases containing an NO donor set are those derived from substituted salicylaldehyde derivatives, for example, salicylideneaniline (Figure 2.4) and salicylidene-p-toluidine (Figure 2.5).

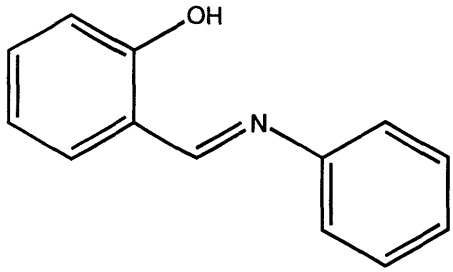


Figure 2.4 SAL

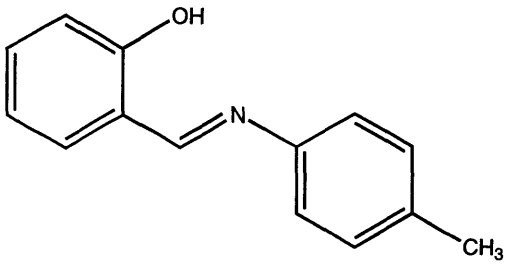


Figure 2.5 SAL4(CH_3)

Sacconi and co-workers reported[3] that the hydroxyl oxygen atom, under particular circumstances, may bridge two metal atoms as tridentate ligands that favour the formation of binuclear complexes. Countryman *et al.* reported the structure and magnetic properties of copper halide adducts of some binuclear copper Schiff base complexes[4] (Figure 2.6).

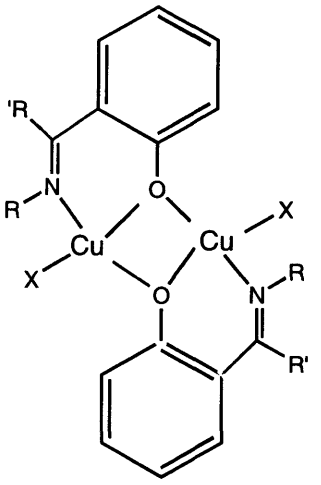


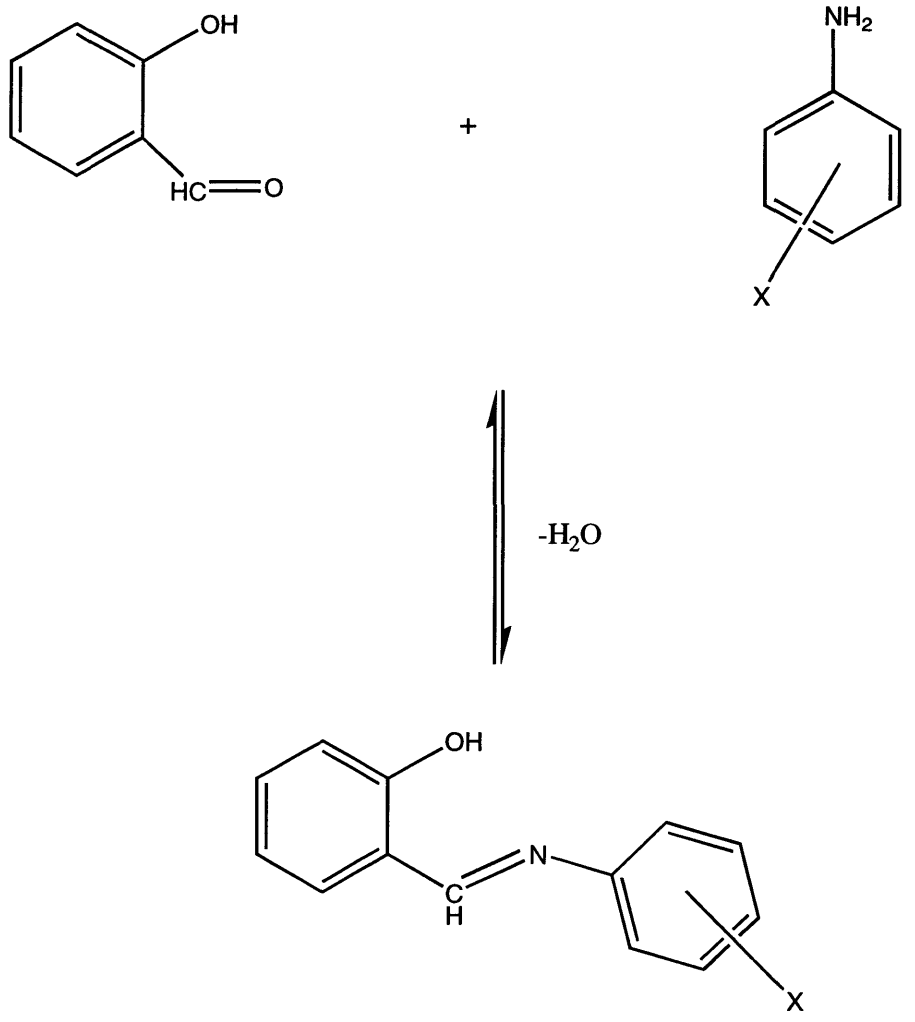
Figure 2.6 *Binuclear copper complex*

As they have been widely used as ligands in many transition metal complexes[5], the NMR spectra of many Schiff bases derived from substituted salicylaldehydes and primary amines have been reported[6]. The electron-withdrawing substituent group has been shown to reduce the magnetic shielding of the hydroxyl proton.

2.2 PREPARATION OF SCHIFF BASES:-

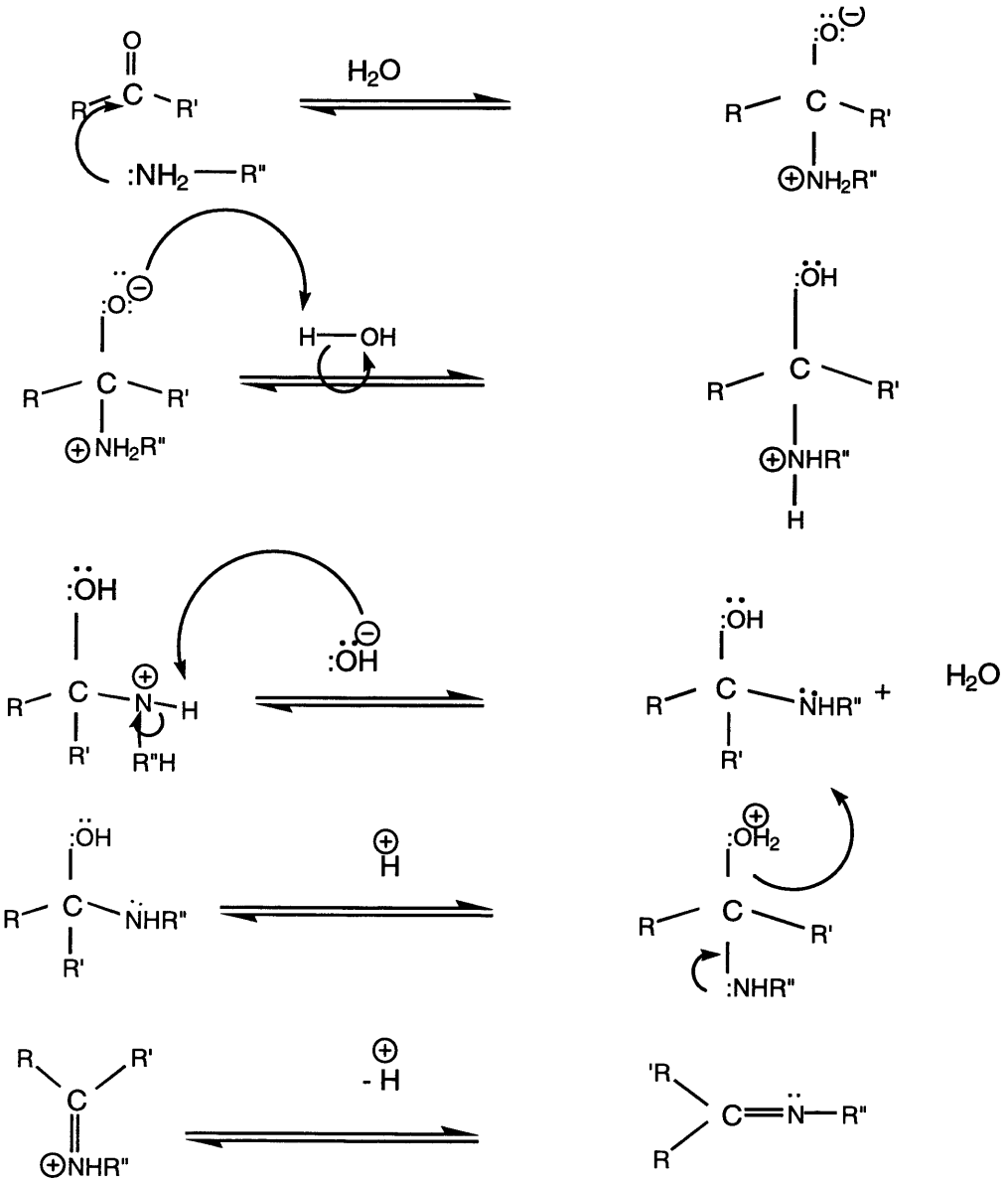
A number of Schiff bases have been synthesised in this work by reacting salicylaldehyde with different fluoro-anilines and their non-fluoro hydrogen-analogues. They are shown in Table 2.1. The reaction and its mechanism are given in the following sections.

2.3 GENERAL REACTION:-



2.4 REACTION MECHANISM:-

The reaction mechanism is[7]



2.5 EXPERIMENTAL:-

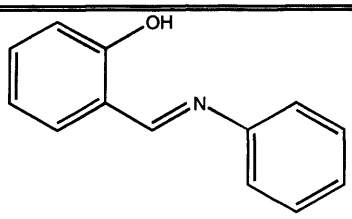
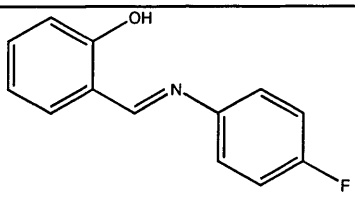
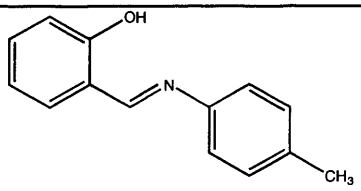
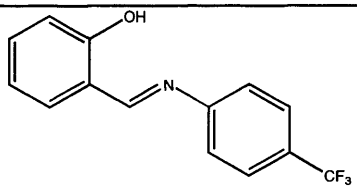
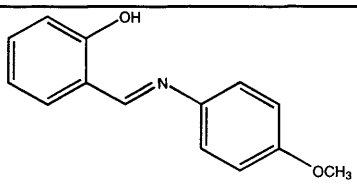
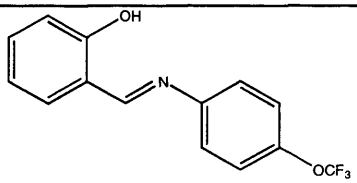
All NMR spectra were recorded on a Bruker AM250 MHz spectrometer, I.R. spectra on a Perkin Elmer 580B and UV spectra on a Beckmann DU 650 spectrometer. Mass spectrometry was undertaken on a Kratos concept double focussing mass spectrometer by Dr. G. Eaton. All chemicals were used as obtained from Aldrich.

2.6 GENERAL METHOD OF PREPARATION:-

To an ethanolic solution of salicylaldehyde(one molar, 25ml) a few drops of pH 5.0 solution (HCl + NaOH) were added to protonate the aldehyde. Into this acidic aldehydic solution, an ethanolic solution of the substituted aniline(one molar, 25ml)[calculated amounts are given in Table 2.1 for each ligand] was added in several small portions, in a one to one ratio. The reaction mixture was then stirred and refluxed for an hour. After refluxing, it was allowed to cool down slowly. After cooling, precipitation began. The resulting precipitate was washed with water, filtered off by suction and dried using a vacuum desiccator. The dried precipitates were recrystallised from a CH_2Cl_2/n-hexane (1:10) mixture.

2.7 LIST OF SALICYLIDENEANILINES PREPARED:-

TABLE 2.1

Structure Formulae	Molecular Formula	Abbreviations Used	Amounts Used gm
	$C_{13}H_{11}NO$	SAL	sa[i] = 3.05 an[ii] = 2.32
	$C_{13}H_{10}FNO$	SAL4F	sa = 3.05 4Fan = 2.78
	$C_{14}H_{13}NO$	SAL4(CH_3)	sa = 3.07 4(CH_3)an = 2.68
	$C_{14}H_{10}F_3NO$	SAL4(CF_3)	sa = 3.07 4(CF_3)an = 4.03
	$C_{14}H_{13}NO_2$	SAL4(OCH_3)	sa = 3.07 4(OCH_3)an = 3.08
	$C_{14}H_{10}F_3NO_2$	SAL4(OCF_3)	sa = 3.07 4(OCF_3)an = 4.43

Structure Formulae	Molecular Formula	Abbreviations Used	Amounts Used gm
	$C_{15}H_{15}NO$	SAL3,5 $(CH_3)_2$	sa = 3.07 3,5$(CH_3)_2$an = 3.03
	$C_{15}H_9F_6NO$	SAL3,5 $(CF_3)_2$	sa = 3.07 3,5$(CF_3)_2$an = 5.73
	$C_{13}H_6F_5NO$	SAL F_5	sa = 3.07 F_5an = 4.58
	$C_{13}H_{12}FNO$	SAL 3F,4(CH_3)	sa = 3.07 3F,4(CH_3)an = 3.13
	$C_{15}H_{15}NO$	SAL3,4 (CH_3)	sa = 3.07 3,4(CH_3)an = 3.03
	$C_{13}H_{10}ClNO$	SAL4Cl	sa = 3.07 4Clan = 3.19
	$C_{13}H_9Cl_2NO$	5(Cl) SAL4Cl	5Clsa = 3.92 4Clan = 3.19

Structure Formulae	Molecular Formula	Abbreviations Used	Amounts Used gm
	$C_{13}H_{10}N_2O_3$	SAL4(NO_2)	sa = 3.07 4(NO_2)an = 3.45
	$C_{13}H_9N_3O_5$	5(NO_2) SAL4(NO_2)	5(NO_2)sa = 4.18 4(NO_2)an = 3.45
	$C_{14}H_{11}NO_3$	SAL4 (COOH)	sa = 3.07 4(COOH)an = 3.43
	$C_{13}H_{11}NO_4S$	SAL4(SO_3H)	sa = 3.07 4(SO_3H)an 4.33
	$C_{20}H_{16}N_2O_2$	BispSAL	sa = 6.10 4(NH_2)an = 2.70
	$C_{20}H_{16}N_2O_2$	BisoSAL	sa = 6.10 2(NH_2)an = 2.70

i = Salicyaldehyde, ii = Aniline

2.8 RESULTS AND DISCUSSION:-

All the compounds have been characterised by various techniques including melting points (Table 2.2) and elemental analyses (Table 2.3). ^{1}H NMR (Table 2.4) and ^{13}C-DEPT. NMR (Table 2.5) and ^{19}F NMR (Table 2.6) spectroscopies were also carried out as were mass spectrometry (Table 2.7), I.R. spectroscopy (Table 8) and U.V. spectroscopy (Table 2.2).

2.8.1 PHYSICAL CHARACTERISATION

TABLE 2.2

Abbreviation Used	Molecular Formula	Melting Points ^{0}C	Colour/ State	% Yield	λmax* /nm
SAL	$C_{13}H_{11}NO$	46	Dark yellow crystals	76	356
SAL4F	$C_{13}H_{10}FNO$	78	Dark yellow needles	65	323
SAL F_5	$C_{13}H_6F_5NO$	120	Light yellow needles	69	325
SAL3F,4(CH_3)	$C_{14}H_{12}FNO$	86	Bright yellow needles	62	343
SAL4(CH_3)	$C_{14}H_{13}NO$	92	Dark yellow needles	78	322
SAL4(CF_3)	$C_{14}H_{10}F_3NO$	104	Light yellow flakes	54	350
SAL4(OCH_3)	$C_{14}H_{13}NO_2$	80	Bright yellow powder	67	297
SAL4(OCF_3)	$C_{14}H_{13}F_3NO_2$	70	Dark yellow needles	58	341

Abbreviation Used	Molecular Formula	Melting Points ^0C	Colour/ State	% Yield	λmax* /nm
SAL3,5$(CH_3)_2$	$C_{15}H_{15}NO$	68	Light yellow crystals	35	326
SAL3,5$(OCF_3)_2$	$C_{15}H_9F_6NO$	90	Dark yellow crystals	36	317
SAL3,4(CH3)	$C_{15}H_{15}NO$	66	Dark yellow powder	63	346
SAL4Cl	$C_{13}H_{10}ClNO$	108	Light yellow needles	76	318
5(Cl)SAL4Cl	$C_{13}H_9C_{l2}NO$	145	Bright yellow crystals	85	324
SAL4(NO_2)	$C_{13}H_{10}N_2O_3$	160	Orange crystals	77	381
5(NO_2) SAL4(NO_2)	$C_{13}H_9N_3O_5$	225	Yellow crystals	68	384
SAL4(COOH)	$C_{14}H_{11}NO_3$	270	Bright yellow crystals	84	378
SAL4(SO_3H)	$C_{13}H_{11}NO_4S$	245	Mustard powder	55	324
BispSAL	$C_{20}H_{16}N_2O_2$	218	Orange crystals	89	314
BisoSAL	$C_{20}H_{16}N_2O_2$	160	Light brown crystals	67	328

* = Solvent used was 50% ethanol/water mixture.

2.8.2 ELEMENTAL ANALYSES:-

TABLE 2.3

Compounds	**% C**		**% H**		**% N**	
	Calc.	**Found**	**Calc.**	**Found**	**Calc.**	**Found**
SAL4(OCF_3)	59.57	59.80	3.55	3.54	4.96	5.08
SAL4(CF_3)	63.16	63.45	3.76	3.89	5.26	5.26
SAL3,5(CF_3)	53.89	54.06	2.69	2.66	4.19	4.20
5(Cl)SAL4(Cl)	58.87	58.74	3.4	3.14	5.28	5.24
SAL4(COOH)	69.70	69.56	4.56	4.55	5.81	5.89

All the compounds investigated by elemental analysis were found to be anhydrous and free of solvent molecules. This is consistent with previous work described in the literature.

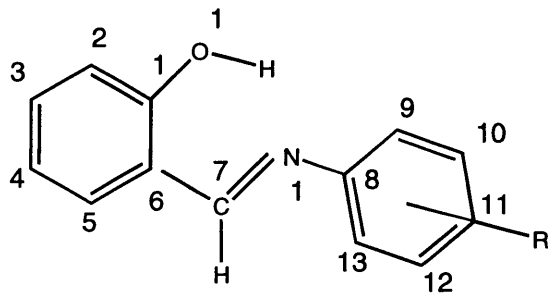


Figure 2.7 *The numbering of the hydrogen atoms in ^1H NMR*

2.8.3 ^{1}H NMR

TABLE 4. **^{1}H NMR DATA** [Recorded in $CDCl_3$]

Compounds	Peaks Assigned	δ	Integral	Multip-licity
SAL.	Ar.H	7.05-7.87	9	m
	C_7H	8.76	1	s
	O_1H	13.42	1	s
SAL4F	Ar.H	7.11-7.61	8	m
	C_7H	8.78	1	s
	O_1H	13.32	1	s
SALF $_5$	Ar.H	6.88-7.43	4	m
	C_7H	8.75	1	s
	O_1H	12.19	1	s
SAL3F,4(CH_3)	CH_3	2.29-2.30	3	d (J=1.89)
	Ar.H	6.91-7.41	8	m
	C_7H	8.59		s
	O_1H	13.09	1	s
SAL4(CH_3)	CH_3	2.31	3	s
	Ar.H	6.79-7.33	8	m
	C_7H	8.76	1	s
	O_1H	13.33	1	s
SAL4(CF $_3$)	Ar.H	6.79-7.56	8	m
	C_7H	8.47	1	s
	O_1H	12.69	1	s
SAL.4(OCH_3)	OCH_3	3.66-3.72	3	s
	Ar.H	6.63-7.56	9	m
	C_7H	8.53	1	s
	O_1H	13.37	1	s

Compounds	Peaks Assigned	δ	Integral	Multip-licity
SAL4(OCF_3)	Ar.H	7.03-7.53	8	m
	C_7H	8.69	1	s
	O_1H	13.07	1	s
SAL3,5(CH_3)	CH_3	2.21-2.49	6	s
	Ar.H	6.89-7.53	7	m
	C_7H	8.57	1	s
	O_1H	13.36	0	s
SAL3,5(CF_3)$_2$	Ar.H	6.89-7.72	7	m
	C_7H	8.583	1	s
	O_1H	12.37	1	s
SAL3,4(CH_3)$_2$	CH_3	2.36	3	s
	CH_3	2.34	3	s
	Ar.H	6.89-7.44	7	m
	C_7H	8.67	1	s
	O_1H	13.52	1	s
SAL4(Cl)	Ar.H	6.92-7.43	8	m
	C_7H	8.59	1	s
	O_1H	13.03	1	s
5(Cl)SAL4Cl	Ar.H	7.42-6.95	7	m
	C_7H	8.53	1	s
	O_1H	13.01	1	s
SAL4(NO_2)	Ar.H	6.69-8.96	8	m
	C_7H	9.8	1	s
	O_1H	11.02	1	s
5(NO_2)SAL 4(NO_2)	Ar.H	6.50-6.67	3	m
		7.84-8.31	4	m
	C_7H	7.14-7.18	1	s
	O_1H	10.24	1	s
SAL4(COOH)	COOH	2.79	1	b.s
	Ar.H	6.92-8.09	8	m
	C_7H	8.95	1	s
	O_1H	12.85	1	s
SAL4(SO_3H)	SO_3H	2.78	1	s
	Ar. ^1H	7.14-8.54	8	m
	C_7H	9.25	1	s
	O_1H	10.51	1	s
BispSAL	Ar.^1H	6.68-7.42	6	m
	CH	8.66	1	s
	OH	13.06	1	s
BisoSAL	Ar.^1H	6.82-7.54	6	m
	C_7H	8.63	1	s
	O_1H	13.041	1	s

DISCUSSION:-

In the NMR spectra there is a singlet for the –CH proton at approximately 8.6 ppm as expected, except for the $-NO_2$ (SAL4(NO_2)) and –SO_3H (SAL4(SO_3H)) substituted molecules. In the case of SAL4NO_2 and SAL4(SO_3H) the –CH proton appeared in the region 9.0 - 10.0 ppm; with 5(NO_2)SAL4(NO_2) the –CH proton appeared at 7.14 - 7.18 ppm, this may be due to the electronic effect of the substituents. In all the spectra recorded there is a singlet in the region 12.0- 13.5 ppm corresponding to the –OH proton except for the -NO_2 substituted molecules [SAL4(NO_2 and 5(NO_2)SAL4(NO_2)]. In these, the nitro group shifted the -OH peak towards lower field and it appeared in the region 10.0-11.0 ppm. This may be due to the inductive effect of the -NO_2 group. There was a multiplet for the aromatic protons in the region 6.5 - 7.8 ppm, for all the molecules as expected. Singlets of -OH and -CH of SAL and complete ^{1}H NMR spectra of SAL and SAL4F are given in Figures 2.8 an 2.9 and 2.10 respectively.

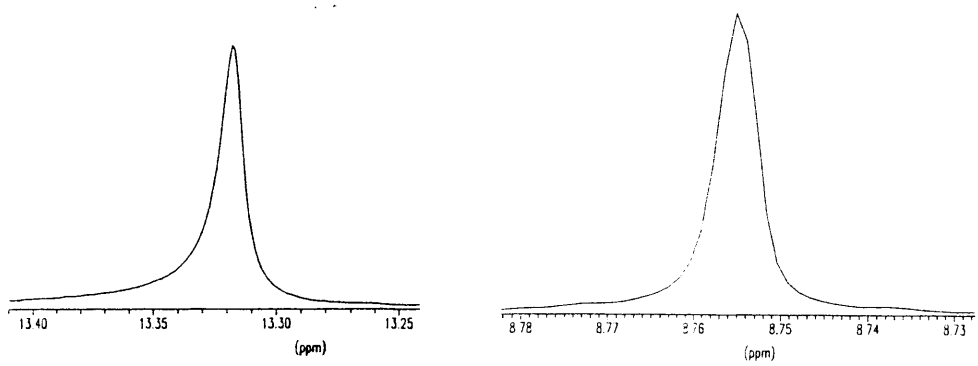


Figure 2.8 *-OH Singlet of SAL* *-CH Singlet of SAL*

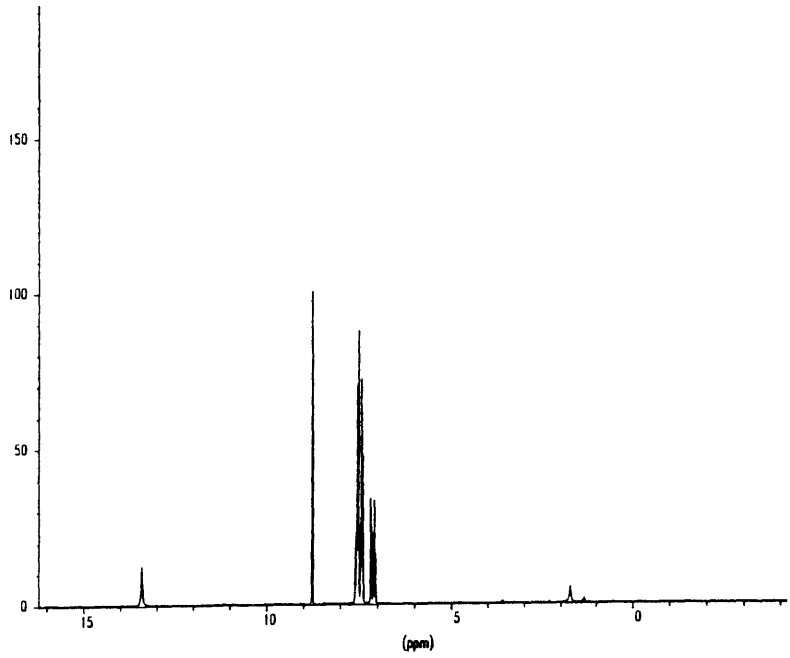


Figure 2.9 *^{1}H NMR Spectrum of SAL*

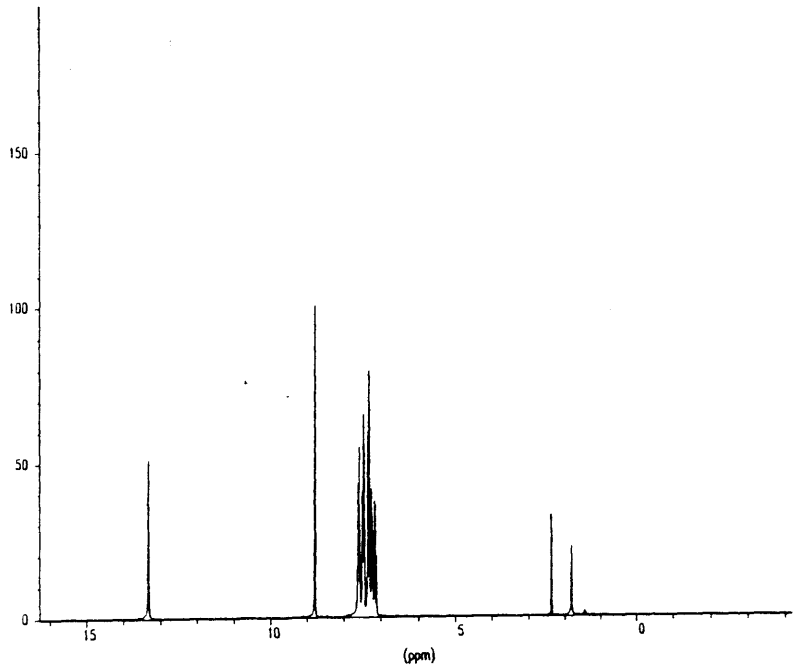


Figure 2.10 *^{1}H NMR Spectrum of SAL4F*

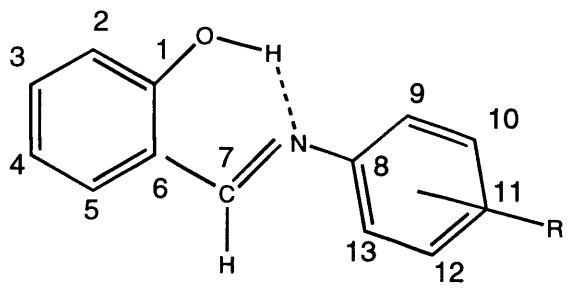


Figure 2.11 *The numbering of the carbons in ^{13}C-DEPT NMR*

2.8.4 ^{13}C-DEPT. NMR DATA [Recorded in $CDCl_3$]

TABLE 2.5

Compounds	Peaks Assigned	δ Values
SAL	C_7H C_6 C_1 C_8 Ar $C_{9\text{-}13}$	163.1 119.7 149.9 161.6 117.7, 119.5, 121.6, 127.4, 129.9, 132.6
SAL4F	C_7H C_8 C_1 C_6 C_{11} Ar $C_{9\text{-}10,12\text{-}13}$	162.4 161.0 149.9 144.6 159.7 116.0, 116.5, 117.2, 119.1, 122.5, 122.7, 132.3, 133.2
SAL4(OCF_3)	C_7H C_8 C_{11} C_1 OCF_3 C_6 Ar $C_{9\text{-}10,12\text{-}13}$	163.5 147.8 118.4 119.0 161.1 147.2 117.4, 119.3, 122.1, 122.4, 122.5, 132.5, 133.6
SAL4(CF_3)	C_7H CF_3 C_1 C_8 C_{11} C_6 Ar $C_{9\text{-}10,12\text{-}13}$	164.5 127.9, 128.4, 129.0 151.6 161.2 122.0 118.9 117.4, 119.4, 121.5, 126.7, 130.6, 133.9,

Compounds	Peaks Assigned	δ Values
SAL3,5(CF_3)$_2$	C_7H CF_3 C_1 C_8, C_6 $C_{10,12}$ Ar $C_{9,11,13}$	165.7 132.2, 132.7, 133.2, 133.8 150.2 161.3, 162.9 118.6, 120.9, 125.3, 129.6 117.6, 119.6, 121.5, 121.6, 133.1, 134.6, 120.1, 120.2
SAL4Cl	C_7H C_8 C_{11} C_1 C_6 Ar$C_{9\text{-}10,11\text{-}12}$	163.4 161.5 119.4 147.4 132.9 117.7, 119.6, 129.9, 132.8, 133.9
5(Cl)SAL4(Cl)	C_7H C_8 C_1 C_6 $C_{4,11}$ Ar $C_{9\text{-}10,11\text{-}12}$	161.4 159.4 146.3 119.6 123.6 118.7, 122.3, 129.4, 131.1, 133.0
SAL4(SO_3H)	CH C_8 C_1 C_{11} C_6 Ar $C_{9\text{-}10,11\text{-}12}$	165.2 167.2 160.7 152.5 129.2 117.1, 119.7, 121.9, 131.1, 133.0, 134.2
BispSAL	C_7H C_8 C_1 C_6 Ar C	163.7 161.3 142.5 119.2 117.5, 119.0, 119.7, 127.7, 132.3, 133.3
SAL4(COOH)	$-C_7H$ –COOH C_{11} C_8 C_1 C_6 Ar $C_{9\text{-}10,11\text{-}12}$	164.6 206.3 166.7 160.1 151.9 129.1 112.4, 116.7, 121.4, 128.7, 130.6, 131.1, 132.5, 133.7, 136.3
SALF_5	C_7H C_8 C_6 C_1 $C_{9,13}$ $C_{10,12}$ C_{11} Ar CH	170.6 161.5 118.7 143.1 141.3, 138.2 136.2, 135.8 123.5 117.8, 119.6, 133.3, 135.0

Compounds	Peaks Assigned	δ Values
BisoSAL	C_7H C_8 C_1 C_6 Ar C	163.7 161.3 142.5 119.2 117.5, 119.0, 119.7, 127.7, 132.3, 133.3
SAL3,5$(CH_3)_2$	CH_3 C_7H C_8 C_1 C_6 $C_{10,12}$ Ar $C_{9,11,13}$	21.8 162.6 161.7 148.8 119.8 139.5 117.7, 118.9, 119.4, 119.4, 129.1, 132.7, 133.4
SAL4(OCH_3)	OCH_3 C_7H C_8 C_1 C_{11} C_6 Ar $C_{9\text{-}10,11\text{-}12}$	55.5 160.4 161.0 158.8 141.4 119.4 114.6, 117.1, 119.0, 122.3, 131.9, 132.7
SAL4(CH_3)	CH_3 C_7H C_8 C_{11} C_1 Ar $C_{9\text{-}10,11\text{-}12}$	21.0 161.7 161.1 119.3 136.9 145.8 117.2, 119.0, 121.0, 130.0, 132.1, 132.9
5(NO_2)SAL4(NO_2)	C_7H $C_{4,11}$ C_8 C_1 C_6 Ar $C_{9\text{-}10,11\text{-}12}$	194.6 171.5, 171.8 161.3 145.2 141.2 118.0, 124.1, 128.1, 129.8, 130.7, 131.7
SAL3,4(CH_3)	$-CH_3$ C_7H C_1 $C_{10,11}$ C_6 C_8 Ar $C_{9,11,13}$	19.4, 19.9 161.5 119.3 135.6, 137.7 146.1 161.1 117.2, 118.2, 118.9, 122.5, 130.5, 132.0, 132.8
SAL3F,4(CH_3)	CH_3 C_7 C_8 C_{11} C_{10} C_6 C_1 Ar $C_{9,13}$	14.3 162.6 163.5 123.4,123.7 147.6, 147.8 159.6 161.1 107.5, 108.1, 116.9, 117.3, 132.0, 132.4, 133.3,

Compounds	Peaks Assigned	δ Values
SAL4(NO_2)	C_7H C_8 C_{11} C_6 C_1 Ar $C_{9\text{-}10,11\text{-}12}$	165.4 161.1 154.2 118.2 118.7 146.1 117.5, 119.6, 121.9, 125, 133.0, 134.5

All the compounds gave satisfactory ^{13}C-DEPT NMR spectra, peaks were as expected for all the carbons in comparison with the previous work present in the literature[8-10]. ^{13}C NMR spectrum of SAL4F is given in Figure 2.12.

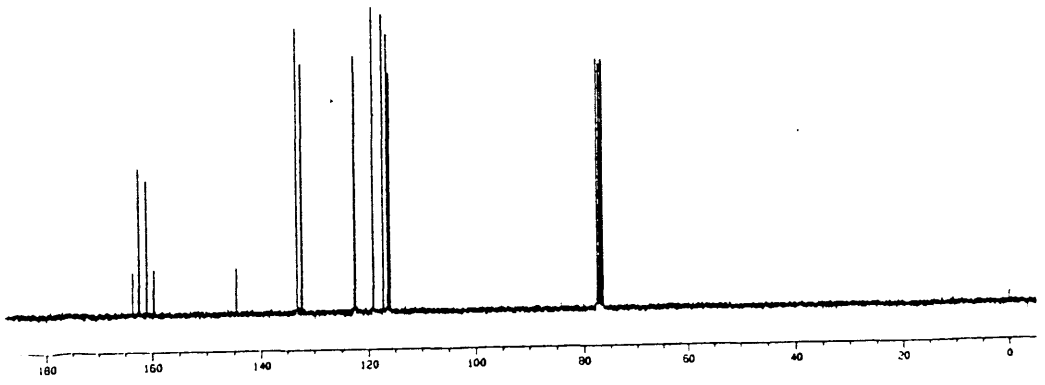
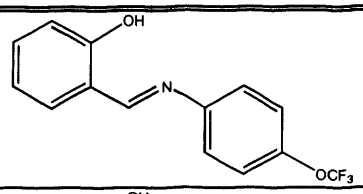
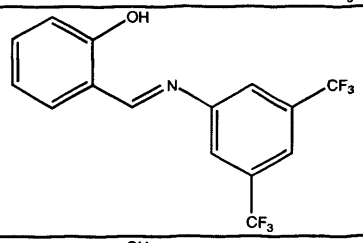
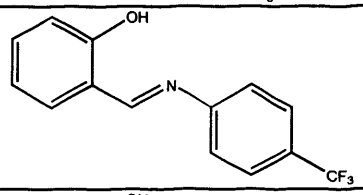
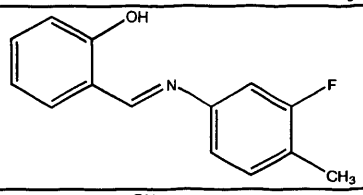
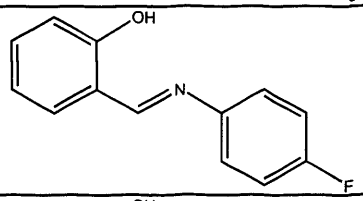
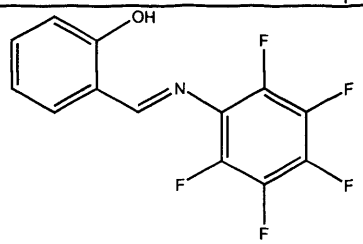


Figure 2.12 *^{13}C NMR Spectrum of SAL4F*

2.8.5 ^{19}F NMR DATA [Recorded in $CDCl_3$]

TABLE 2.6

Structural Formula	Reference	δ	M*	J
	Coupled Decoupled	-58.405 -58.427	s s	-
	Coupled Decoupled	-63.312 -63.332	s s	-
	Coupled Decoupled	-62.587 -62.607	s s	-
	Coupled Decoupled	-118.14--118.3 -118.20	t s	8.52
	Coupled Decoupled	-116.01--115.9 -115.96	Quintet s	4.49
	Coupled F_1,F_5 F_3 F_2,F_4 Decoupled F_1,F_5 F_3 F_2,F_4	 -152.39--152.3 -158.7--158.5 -162.8--162.6 -152.4--152.3 -158.7--158.41 -162.81--162.6	 dd t ddd dd t ddd	 7.63 21.57 6.31 7.59 21.61 6.42

* M = Multiplicity

DISCUSSION:-

^{19}F NMR decoupled and coupled spectra were recorded for the F-substituted molecules. The chemical shift for $SALF_5$ gave a doublet of doublets(dd), triplet(t), and a doublet of doublets of doublets(ddd) at -152.39 to -152.3, -158.7 to -158.5,-162.8 to -162.6 respectively. These peaks are highfield compared to the other molecules studied during this work, this is probably due to the complete substitution of hydrogen by fluorine atoms on the ring. For all other molecules, the peaks were in the expected region.

2.8.6 MASS SPECTROMETRY:-

All the salicylidene anilines prepared were characterised by a variety of mass spectroscopic techniques including +FAB (Fast Atomic Bombardment), EI (Electron Ionisation) or E Spray (Electron Spray) mass spectroscopies, as required by the nature of the compound. All gave strong peaks corresponding to the molecular ion, no significant fragmentation was observed, because the expected fragments were too small for the mass spectrum detection.

TABLE 2.7 MASS SPECTROSCOPIC DATA

Compounds	Calculated Mass	Ions Observed
SAL.	197.21	+FAB MH^+ 198
SAL4F	215.2	+FAB M^+ 216
$SALF_5$	287.0	+FAB M^+ 288
SAL3F,4Me	229.11	+FAB M^+230
SAL4(CH_3)	211.0	EI M^+ 211 (Nonpolar, Volatile, Stable)
SAL4(CF_3)	265.117	E. Spray MH^+ 266 Polar
SAL4(OCH_3)	227.11	+FAB M^+ 228
SAL4(OCF_3)	281.19	+FAB MH^+ 282
SAL3,5$(CH_3)_2$	225.0	+FAB M^+ 226
SAL3,5$(CF_3)_2$	333.158	+FAB M^+ 334
SAL3,4$(CH_3)_2$	225.11	+FAB M^+226
SAL4Cl	231.45	+FAB 232 mixture of M^+, 233MH^+

Compounds	Calculated Mass	Ions Observed
5(Cl)SAL4(Cl)	265.9	+FAB M^+ 265
SAL4(NO_2)	242.0	+FAB MH^+ 243, M^+ 242
5(NO_2)SAL4(NO_2)	287.0	+FAB MH^+ 288, EI M^+ 287
SAL4(COOH)	241.2	+FAB. Mixture of M^+ and MH^+ 241
SAL4(SO_3H)	277.21	+FAB. MH^+ 278
BispSAL	316.33	+FAB and EI M^+316
BisoSAL	316.33	+FAB MH^+ 317

Mass spectra of SAL and SAL4F are given in Figure 2.13 and 2.14 respectively.

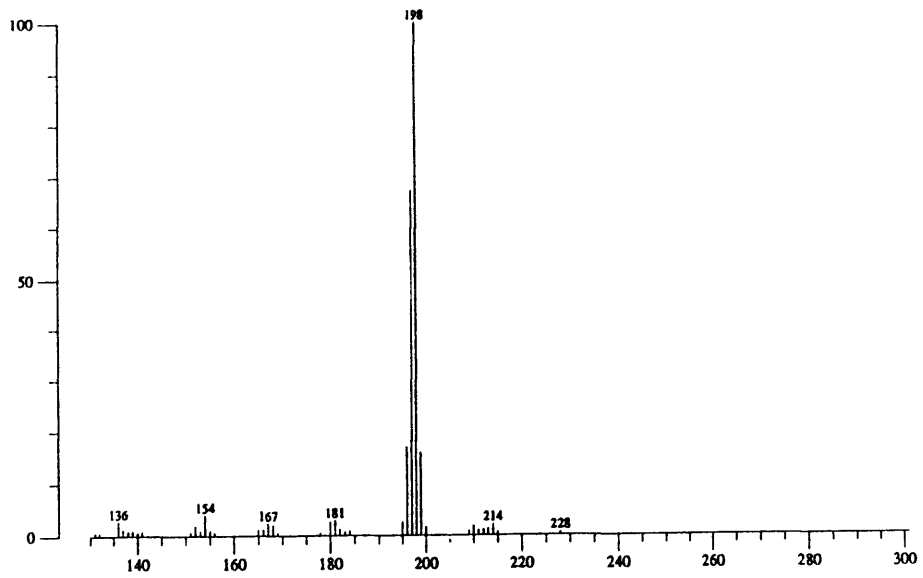


Figure 2.13 *Mass Spectrum of SAL*

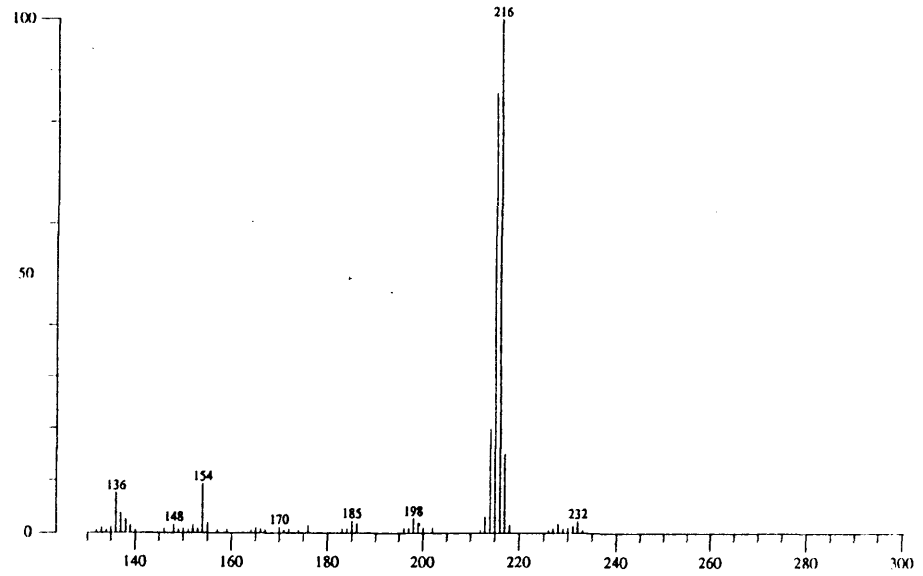


Figure 2.14 *Mass Spectrum of SAL4F*

2.8.7 I.R. DATA(Recorded as solutions in CH_2Cl_2)

TABLE 2.8

Compound	C–H	C–H	← Stretches →						Other
	(Stretch)	(bend)	C=N	N–C	O–H	C–O	C=C	C–F	Bands
SAL.	3040,2980m, 2680,2400m	680,760,840,890s, 1030,1070,1110w	1610s	1360w	4000,3740, 3680w	1265,1140m, 1180s	1575,1450 1480,1600 1400s		2680,2400 m
SAL4F	3100,2700w	900,840,790,1110 980 w	1610s	1360m	4000,3710m	1230,1275s	1570, 1480s	1180, 1150s	2700w
SAL4(CH_3)	3060,2970m 2680,2450m	670,780,840, 880s,1040, 1070w	1610s	1360m	4000,3740, 3660w	1260,1150w, 1180s	1570,1450 1460, 1600s		2680,2450 m
SAL4(CF_3)	3035,2970s, 2650m	758,870,m 980,1010, 1030m	1590s	1370w	4000,3740, 3680m	1240,127011 80,1140s	1550,1425 1610s	1060, 1100, 1200s	2650m

Compound	C–H	C–H	← Stretches →						Other
	(Stretch)	(bend)	C=N	N–C	O–H	C–O	C=C	C–F	Bands
SALp(OCH_3)	3040,2980s,	680,760,840 890s,980s, 1030,1100m	1610s	1360w	3090,3810s	1240,129011 80,1150s	1500, 1450s		
SAL4(OCF_3)	3040s,	690,750,860, 975,1010, 1030m	1600s	1350w	3940,3740, 3680w	1330,1250s	1570, 1480m	1200, 1100, 1050s	2400,2300 w
SAL3,5$(CH_3)_2$	3050m,2900,	730,790w, 950,1030m	1640m	1350w	3790,3650m	1250,120011 40s	1620, 1500, 1480s		
SAL3,5$(CF_3)_2$	3070s,	740,840,890s,980, 1010, 1030m	1580, 1600s	1350s	3940s	1310m	1570,1510, 1410, 1380s	1180, 1100s	2400m
SALF_5	3070,2950m	690,740,900m, 1100,1150m	1610s	1380m	3640m	1210,1300s	1450, 1530, 1600m	950, 1000 s	2750m
SAL3F,4(CH_3)	3040,2980m	690,760,890s, 1050,1120w	1610 m	1360w	3850m	1250,1280s	1570,1480 1450 s	1180w	2680,2500 m

Compound	C–H	C–H	←		Stretches		→		Other
	(Stretch)	(bend)	C=N	N–C	O–H	C–O	C=C	C–F	Bands
SAL3,4(CH_3)	3070.3110m	690,840m, 1040,1090w	1610s	1410m	3970,3890m	1270,1150s	1410, 1490s 1600m		2600,2500 m
SAL4Cl	3040,2970m	670,780,890s, 1040,1080 m	1610s	1380m	3940,3780m	1270, 1150m	1480, 1650m		2670,2450 m
5(CL)SAL4(Cl)	3070,2950m,	660,790s, 1050,1070m	1620s	1390m	3950,3790m	1280, 1150m	1470, 1680m		2590m
SAL4(NO_2) [N–O 1570s]	3060m	900m,980, 1030w	1620s	1340s	3740,3810m	1250, 1160m, 1180 s	1520, 1580s, 1480 m		2640w
5(NO_2) SAL4(NO_2) [N–O 1570,1560s]	3080m	1040,970, 920m	1630s	1330s	3730,3820s	1265, 1160m, 1185s	1520,1575s ,1470m		2675w

Compound	C–H	C–H	← Stretches →						Other
	(Stretch)	(bend)	C=N	N–C	O–H	C–O	C=C	C–F	Bands
SAL4(COOH)	3050,2960m	680,750,890s, 1020,1060m	1620s	1355s	3920,3750, 3670m	1265,1150m, 1170s	1570,1460 1490s,1650 1400m		2680w
SAL4(SO_3H)	3040,2970,	680,870s,1030, 1050s	1580s	1340m	3890,3770s	1250,1210m, 1180w	1580,1490s 1665w		2650m
BispSAL	3030,2960,	670,870,1040s	1610m	1330m	3880s	1240,1220, 1170m	1680, 1590m		2680m
BisoSAL	3040,2970	680,860,1050	1610m	1340m	3870s	1230,1250, 1180m	1670, 1570m		2680m

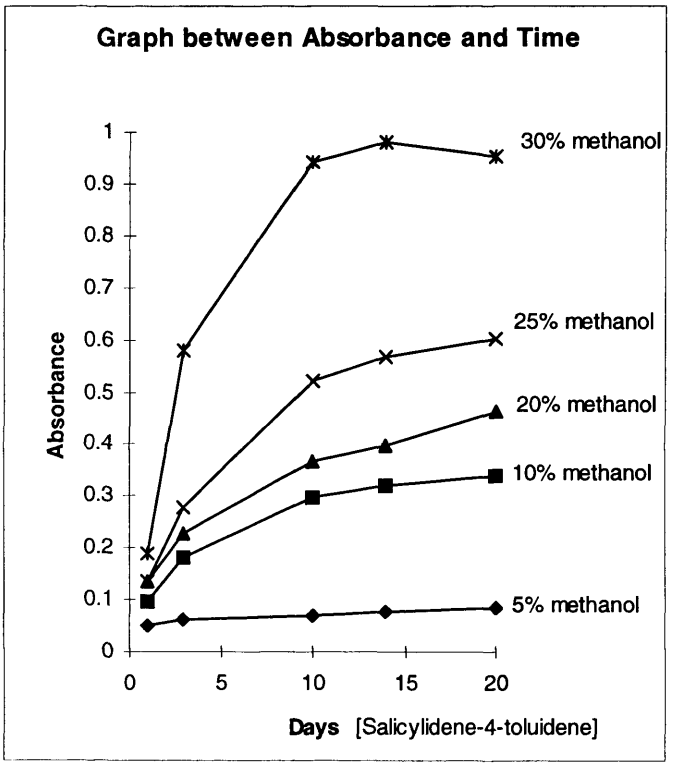
I.R. DISCUSSION:-

All the salicylideneanilines were characterised by I.R. spectroscopy. The I.R. spectra were recorded as solutions in CH_2Cl_2 against a CH_2Cl_2 blank. All the characteristic bonds in the compounds gave satisfactory bands in their respective region. No significant shift from the expected value for each band was observed, in comparison with the previous work present in the literature[8-13].

Salicylideneanilines have two aromatic rings, one aldehydic and other of aniline. They gave stretching vibrations in the region 3100-2800 cm^{-1}, and their deformations are in the 1600-1450 cm^{-1} region. The out-of-plane bends are in the 650-1000 cm^{-1} region. The C=N bond gave a strong band in the region of 1690-1600cm^{-1}. The C–N, C–O, C=C and C–F bonds gave bands in the region of 1600-1000 cm^{-1}. The –OH bond gave a medium to weak broad band in the region of 4000-3700 cm^{-1}, which indicates the presence of hydrogen-bonding between hydroxyl hydrogen and imine nitrogen, except for SAL3,5$(CF_3)_2$. This compound gave a strong -OH band which indicates the absence of hydrogen-bonding in SAL3,5$(CF_3)_2$.

2.8.8 U.V. SCANS:

U.V. scans of the solutions of the ligands at different concentrations(10%, 20%, 25%, 30%) in methanol/water mixtures were recorded over a period of time. A graph of absorbance plotted against time gave an ascending curve, showing the solubilisation in progress. The plot straightened after a certain time indicating saturation of the solution. There was no change in the wavelength of maximum absorption, and no new peak at any other wavelength appeared. Thus it was concluded that the compounds were stable in solution.



2.9 CONCLUSION:-

The preparation of these ligands was straightforward. Most were isolated as crystals, and were easily recrystallised for purification.

They are air and hydrolytically stable in solid and solution forms. No significant effect of electron donating or electron withdrawing subsitituent groups on the properties of the ligands was found.

2.10 REFERENCES:-

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CHAPTER 3

STRUCTURE DETERMINATION OF SOME NOVEL SUBSTITUTED SALICYLIDENEANILINES

3.1 INTRODUCTION:-

This chapter describes the structures of some novel salicylidene aniline derivatives (Figure 3.1) which were determined by single crystal X-ray diffraction. The synthesis and characterisation of these compounds were given in Chapter 2. Information concerning bond lengths, bond angles and inter- and intramolecular hydrogen-bonding has been gathered.

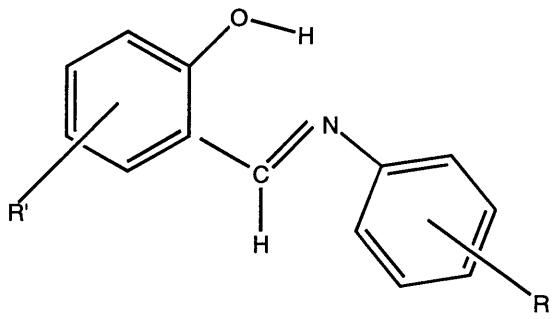


Figure 3.1

3.2 LITERATURE SURVEY:-

Several groups[1-6] have determined structures of salicylideneaniline and its derivatives. Destro *et al*[7]. reported the structure of salicylidene aniline itself (SAL)[Figure 3.2], Tenon *et al*[8]. reported the structure of N-(5-hydroxysalicylidene)-2,4,6-trimethylaniline [Figure 3.3] (5(OH)SAL2,4,6 $(CH_3)_2$), while Bregman[9-10] and co-workers published the structures of N-5-chlorosalicylideneaniline(5ClSAL) [Figure 3.4] and 2-chloro-salicylideneaniline (SAL2Cl) [Figure 3.5]. Inabe[11] and coworkers reported the structure of N-tetrachlorosalicylideneaniline [Figure 3.6](Cl_4SAL). Burgess *et al*[12]. solved the structure of salicylidene-4-nitroaniline[Figure 3.7](SALp(NO_2). All the molecules have a hydrogen bond between the hydroxyl hydrogen and nitrogen. Selected bond lengths and bond angles of some structures, from the literature, are given in Table 3.1 and Table 3.2 respectively. The numbering of carbon atoms is given in Figure 3.12.

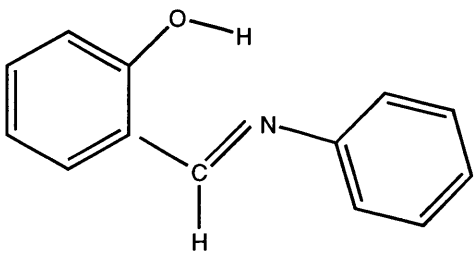


Figure. 3.2 *SAL*

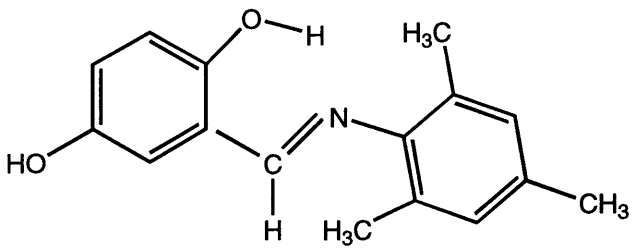


Figure. 3.3 *5(OH)SAL2,4,6(CH₃)*

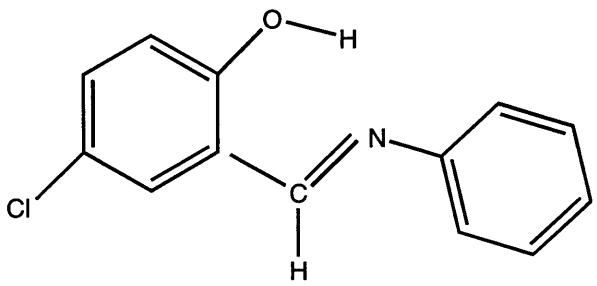


Figure. 3.4 *5ClSAL*

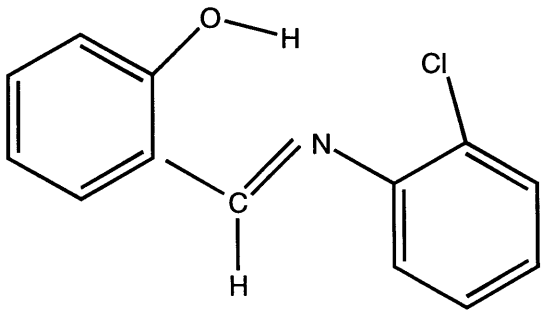


Figure 3.5 *SAL2Cl*

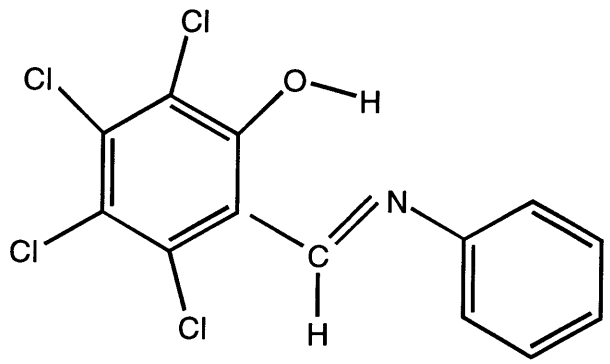


Figure 3.6 *Cl_4SAL*

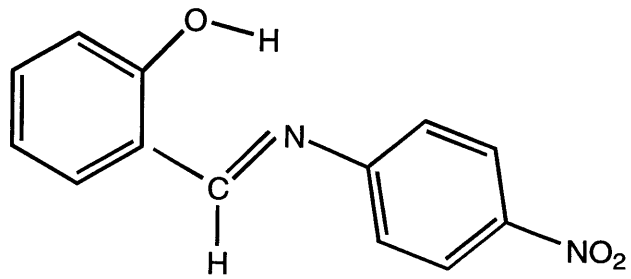


Figure 3.7 *$SALp(NO_2)$*

X-ray crystallographic structures of SAL4(NO_2), (5-(OH)SAL,2,4,6($CH3)_3$), and Cl_4SAL (from the literature) are given in Figures 3.8, 3.9, 3.10, and 3.11

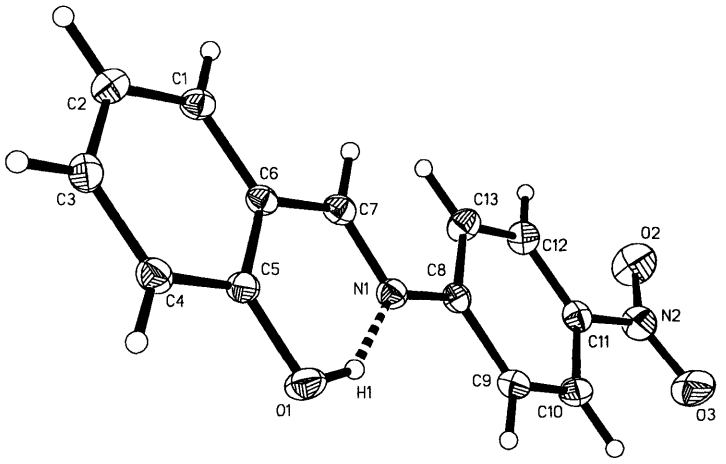


Figure 3.8 *SAL4NO$_2$*

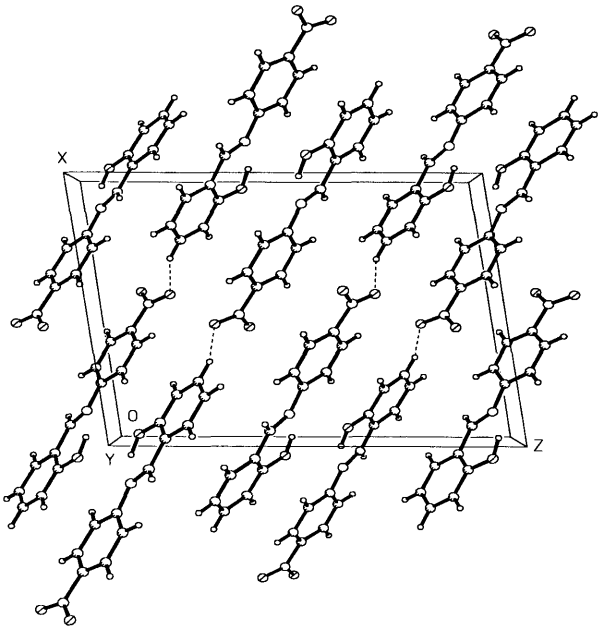


Figure 3.9 *Packing Diagram of SAL4NO$_2$*

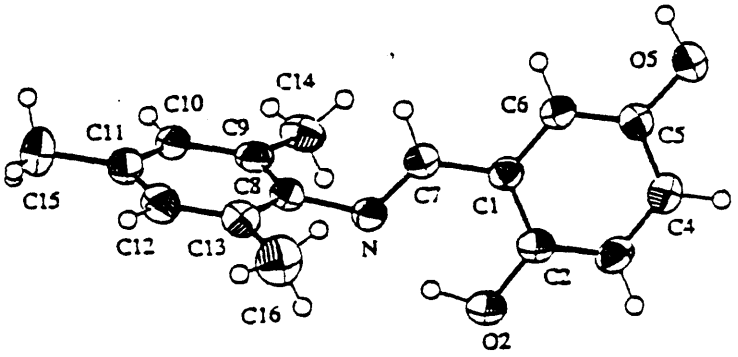


Figure 3.10 *(5-(OH)SAL,2,4,6(CH$_3$)$_3$)*

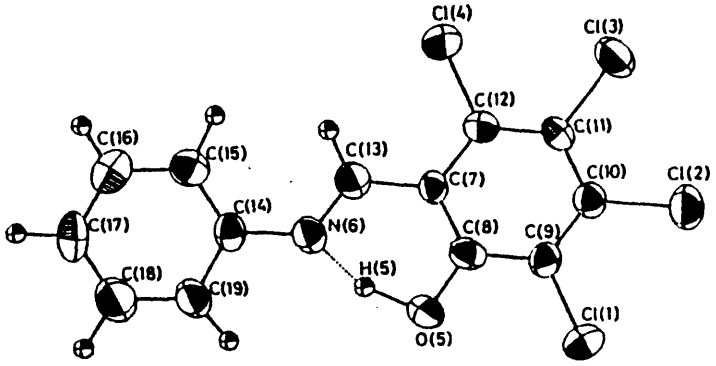


Figure 3.11 *Cl$_4$SAL*

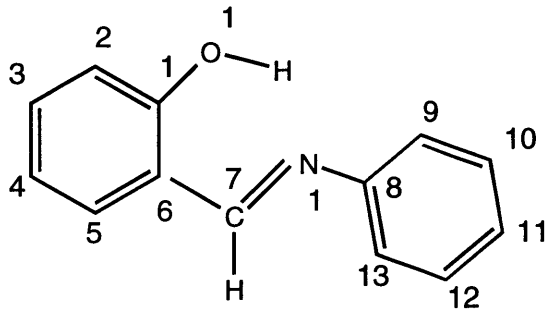


Figure 3.12

Bonds	SAL	5ClSAL	SAL2Cl	Cl_4SAL	SALp(NO_2)
C(7)-N(1)	1.262(8)	1.270(5)	1.288(4)	1.298(9)	1.287(2)
C(6)-C(7)	1.529(5)	1.444(6)	1.452(4)	1.435(9)	1.443(3)
C(8)-N(1)	1.466(5)	1.419(5)	1.421(4)	1.414(9)	1.412(2)
C(1)-O(1)	1.320(7)	1.351(5)	1.365(4)	1.332(8)	1.352(2)
C(6)-C(5)	-	1.407(6)	1.400(4)	1.422(9)	1.399(3)
C(1)-C(6)	-	1.418(6)	1.391(4)	1.412(9)	1.409(3)
C(8)-C(9)	-	1.410(6)	1.384(4)	1.390(10)	1.388(3)
C(8)-C(13)	-	1.387(6)	1.381(4)	1.390(10)	1.398(3)
H...N	-	-	-	1.38(9)	1.797(24)
O...N	2.598(8)	2.584	2.609	2.5717(7)	2.645(3)
O-H		1.15	1.04	1.18(9)	

Table 3.1 *Selected Bond Lengths of **SAL, 5ClSAL, SAL2Cl, Cl_4SAL** and **SAL4(NO_2)** taken from the literature, spaces left blank where details are not given in the literature.*

Angles	SAL	5ClSAL	SAL2Cl	Cl4SAL	SALp(NO_2)
C(5)-C(6)-C(7)	105.1(3)	120.3	119.0	121.5(6)	118.8(2)
C(5)-C(6)-C(1)	-	118.2	118.6	117.8(6)	118.7(2)
C(1)-C(6)-C(7)	135.3(3)	121.5	122.0	120.7(6)	122.5(2)
C(6)-C(1)-C(2)	-	119.8	120.6	120.3(6)	119.6(2)
C(6)-C(1)-O(1)	107.1(3)	120.5	121.3	120.8(6)	121.4(2)
C(2)-C(1)-O(1)	132.(9)	119.6	118.1	118.8(6)	119.0(2)
C(6)-C(7)-N(1)	113.3(6)	121.7	121.4	120.2(6)	122.1(2)
C(7)-N(1)-C(8)	113.0(6)	122.3	118.9	123.6(6)	121.2(2)
N(1)-C(8)-C(9)	100.2(3)	124,3	121.2	124.1(6)	116.2(2)
N(1)-C(8)-C(13)	139.9(3)	116.1	120.2	116.0(6)	124.9(2)
C(9)-C(8)-C(13)	-	119.6	118.5	120.0(7)	118.9(2)

Table 3.2 *Selected Bond Angles of SAL, 5ClSAL, SAL2Cl, Cl_4SAL, SAL4(NO_2) taken from the literature, the spaces left blank where details are not given in the literature.*

3.3 METHODS OF CRYSTALLISATION:-

Crystals of these Schiff bases were grown using a number of crystallising methods as described below.

3.3.1 BY SUBLIMATION:-

For sublimation, the cold finger technique was used. The sample was introduced into the outer jacket and the finger was filled with a solid CO_2 and acetone mixture. The temperature difference between the outer jacket and cold finger was maintained at approximately 40 ^{0}C.

By this method very pure flaky crystals were obtained, which could not be used for X-ray analysis.

3.3.2 BY SLOW COOLING:-

The sample was refluxed in ethanol for half an hour and then allowed to cool, first within the heating mantle and then in cold water into which ice was added in small portions. When the temperature was in the range of 5 - 10 ^{0}C crystals appeared. However, the crystals were very large and were stacked together and were not suitable for X-ray analysis.

3.3.3 BY MIXTURE OF SOLVENTS:-

(a) *By slow evaporation at low temperature:*

A number of solvent mixtures were tried, for example, ethanol/n-hexane, CH_2Cl_2/n-hexane and ether/n-hexane. Crystals appeared in ethanol/n-hexane and CH_2Cl_2/n-hexane mixtures on slow evaporation at 0-5 ^{0}C which were suitable for X-ray analysis.

(b) *By adding cold solvent into a hot ligand solution:*

The sample was dissolved in a small volume of ethanol, in which it was very soluble. This solution was heated to reflux temperature, then the other solvent (usually n-hexane) was added dropwise down the condenser until turbidity was seen, then a few drops of the first solvent were added to clear the turbidity. The solution was allowed to cool slowly. On cooling flaky crystals appeared, which were not suitable for X-ray analysis.

3.3.4 BY SLOW EVAPORATION:-

The sample was dissolved either in CH_2Cl_2 or ethanol, in a sample tube having three small holes in its top, and was left at 5 °C for several weeks. As the solvent evaporated crystals appeared at the bottom of the tube. The solvent was then drawn out with a fine pipette, leaving crystals which were good enough for X-ray analysis.

3.4 EXPERIMENTAL:-

All X-ray structure determinations were done on a Siemens P4 X-ray diffractometer by Dr. J. Fawcett.

3.5 SALICYLIDENEANILINE DERIVATIVES:-

Seven of the ligands prepared for this work have been investigated using X-ray crystallography. Their formulae are shown in Figures 3.13, 3.14, 3.15, 3.16, and 3.17.

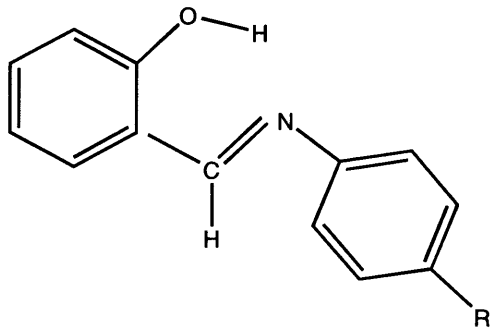


Figure 3.13

R =	OCF_3	SAL4(OCF_3)
	F	SAL4F
	CH_3	SAL4(CH_3)

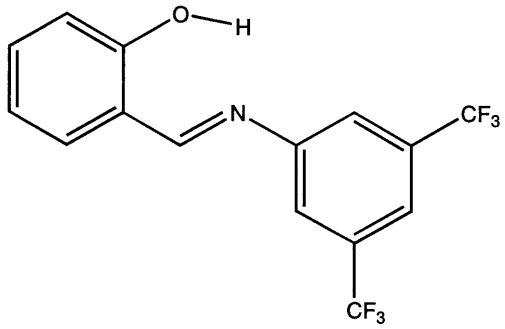


Figure 3.14 *SAL3,5(CF_3)$_2$*

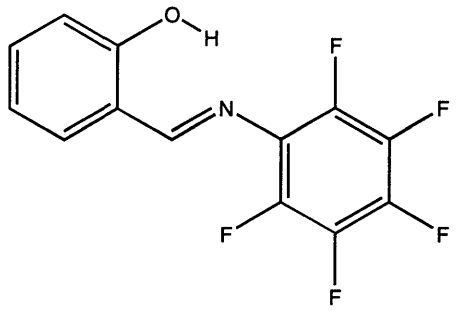


Figure 3.15 *SALF$_5$*

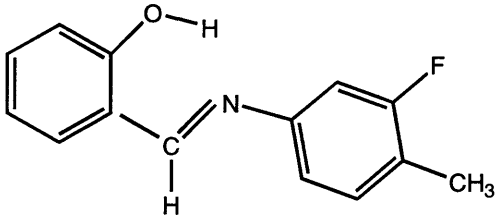


Figure 3.16 *SAL3F,4(CH$_3$)*

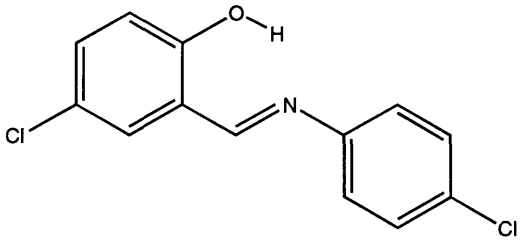


Figure 3.17 *5ClSAL4Cl*

3.6 RESULTS AND DISCUSSION:-

3.6.1 SAL3,5(CF_3)$_2$:-

SAL3,5(CF_3)$_2$ was crystallised from a CH_2Cl_2/n-hexane mixture, at low temperature(0-5 ^{0}C), as dark yellow crystals. Its crystal system is monoclinic. The molecular structure is shown in Figure 3.18. The packing and 3D stereo pair diagrams are shown in Figures 3.19 and 3.20 repectively. Unlike other SAL structures no intramolecular hydrogen-bonding between the hydroxyl hydrogen and nitrogen is found. This may be due to the electron-withdrawing effect of the –CF_3 groups or due to the steric hindrance caused by the presence of two bulky groups on the same ring. The oxygen nitrogen bond distance in this case is 2.631(10) Å, which is similar to the compounds with hydrogen-bonding. Selected bond lengths and bond angles for SAL3,5(CF_3)$_2$ are shown in Tables 3.3 and 3.4 respectively.

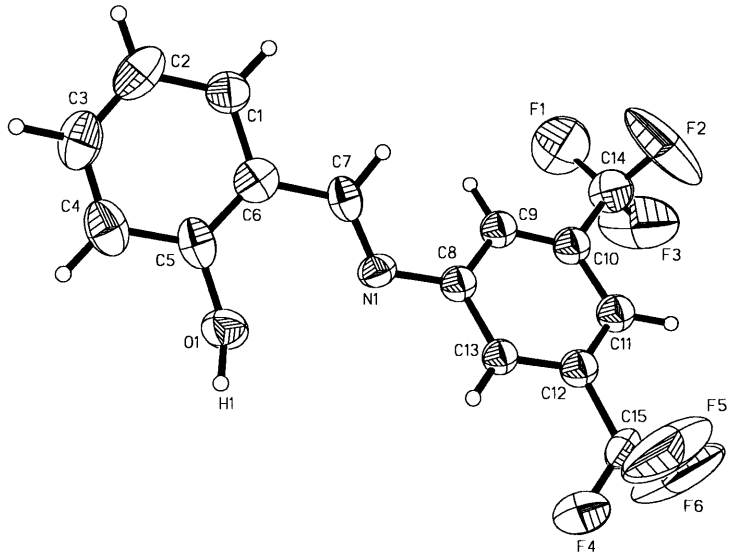


Figure 3.18 *Structure diagram of SAL3,5(CF_3)$_2$*

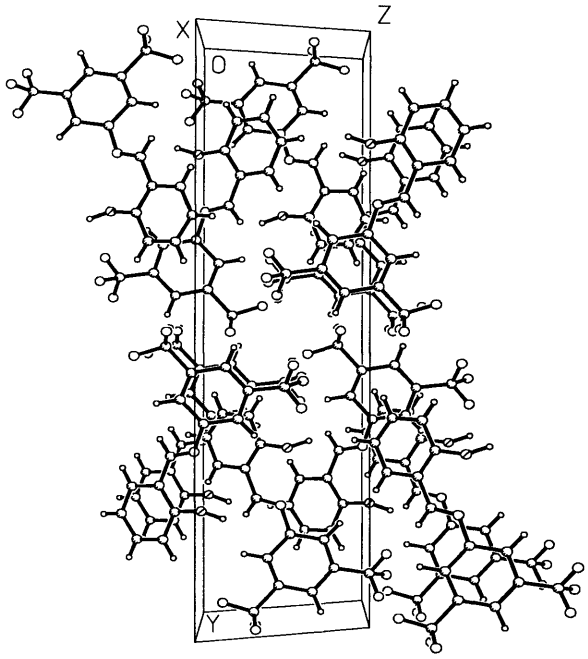


Figure 3.19 *Packing diagram of SAL3,5(CF_3)$_2$*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
N(1)-C(7)	1.254(13)	N(1)-C(8)	1.374(12)
C(1)-C(6)	1.438(13)	C(4)-C(5)	1.403(17)
C(5)-C(6)	1.372(16)	C(6)-C(7)	1.463(16)
C(8)-C(9)	1.407(14)	C(8)-C(13)	1.406(12)
C(9)-C(10)	1.323(14)	C(10)-C(11)	1.397(13)
C(10)-C(14)	1.538(13)	C(11)-C(12)	1.361(15)
C(12)-C(13)	1.353(14)	C(12)-C(15)	1.457(10)
O(1)-C(5)	1.413(13)	O(1)-Ha(1)	0.922(10)

Table 3.3 *Selected Bond Lengths of SAL3,5(CF_3)$_2$*

	Angles[°]		Angles[°]
C(7)-N(1)-C(8)	122.7(8)	C(2)-C(1)-C(6)	119.6(11)
O(1)-C(5)-C(6)	117.8(9)	O(1)-C(5)-C(4)	117.8(10)
C(1)-C(6)-C(5)	117.6(11)	C(4)-C(5)-C(6)	123.8(10)
C(5)-C(6)-C(7)	123.6(9)	C(1)-C(6)-C(7)	118.8(10)
N(1)-C(8)-C(9)	123.6(8)	N(1)-C(8)-C(13)	118.4(9)
N(1)-C(7)-C(6)	124.5(9)	C(8)-C(9)-C(10)	120.1(9)
C(9)-C(8)-C(13)	118.1(9)	C(9)-C(10)-C(14)	120.6(8)
C(9)-C(10)-C(11)	122.4(10)	C(10)-C(11)-C(12)	117.4(9)
C(11)-C(10)-C(14)	117.0(8)	C(11)-C(12)-C(15)	119.0(9)
C(11)-C(12)-C(13)	122.6(9)	C(8)-C(13)-C(12)	119.4(9)
C(13)-C(12)-C(15)	118/3(9)		

Table 3.4 *Selected Bond Angles of SAL3,5(CF_3)$_2$*

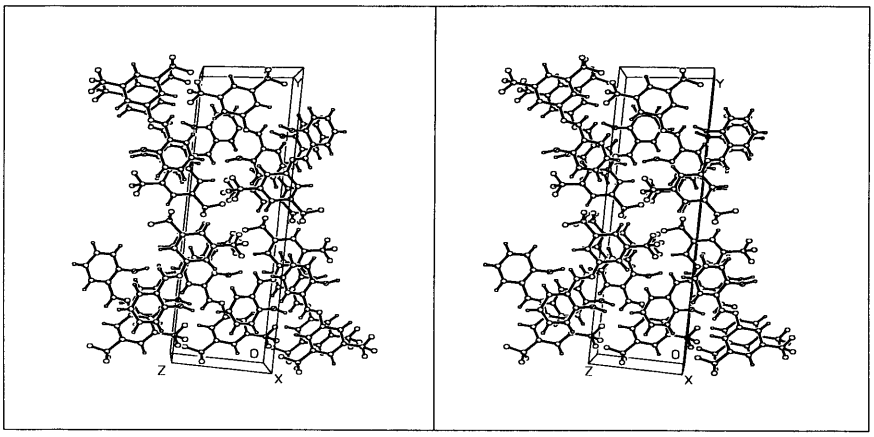


Figure 3.20 *3D Stereo pair of SAL3,5(CF_3)$_2$*

3.6.2 SAL3F,4(CH_3)

SAL3F,4(CH_3) was crystallised from CH_2Cl_2 by slow evaporation at low temperature (0-5 ^{0}C), giving yellow needles. Its crystal system is monoclinic. The molecular structure diagram is shown in Figure 3.21. The fluorine atom is disordered with equal probability at the two meta aniline ring positions. The packing and 3D stereo pair diagrams are shown in Figures 3.22 and 3.23 respectively. It is a planar molecule, packed in layers. There is intramolecular hydrogen-bonding between the hydroxyl hydrogen and the nitrogen having a bonding length of 1.729 Å, the distance between oxygen and nitrogen is 2.600 Å. These molecules were found to be aligned such that the hydroxyl oxygen of one molecule was facing the methylene proton of the other, having a distance of 2.640 Å, which is larger than the sum of the van der Waals radii (2.26 Å[13]). Selected bond lengths and bond angles are given in Tables 3.5 and 3.6 respectively.

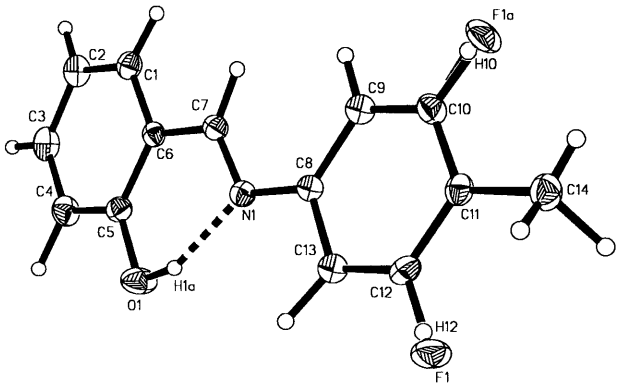


Figure 3.21 *Structure diagram of SAL3F,4(CH_3)*

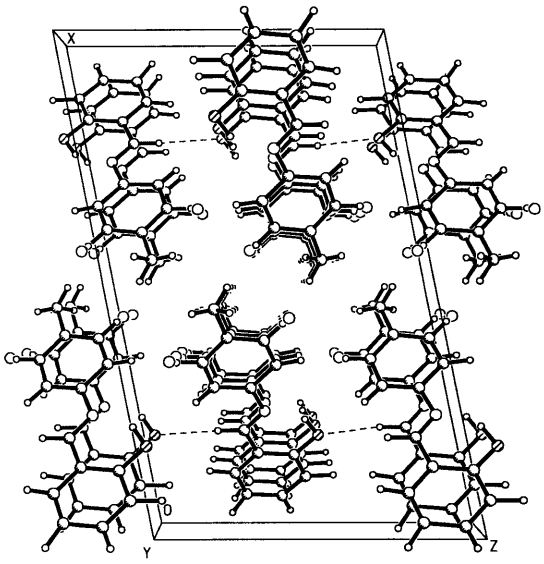


Figure 3.22 *Packing diagram of SAL3F,4(CH_3)*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
F(1)-C(12)	1.323(4)	O(1)-C(5)	1.354(4)
N(1)-C(7)	1.274(4)	N(1)-C(8)	1.419(4)
C(4)-C(5)	1.391(4)	C(5)-C(6)	1.402(4)
C(6)-C(7)	1.452(4)	C(8)-C(13)	1.382(4)
C(1)-C(6)	1.397(4)	C(10)-C(11)	1.383(4)
C(8)-C(9)	1.397(4)	C(9)-C(10)	1.372(4)
C(11)-C(12)	1.385(4)	C(12)-C(13)	1.377(4)
C(11)-C(14)	1.504(4)	O(1)-H	0.974

Table 3.5 *Selected Bond Lengths of SAL3F,4(CH_3)*

	Angles[°]		Angles[°]
C(7)-N(1)-C(8)	121.5(3)	O(1)-C(5)-C(4)	118.7(3)
O(1)-C(5)-C(6)	121.2(3)	C(4)-C(5)-C(6)	120.1(3)
C(1)-C(6)-C(5)	118.1(3)	C(1)-C(6)-C(7)	120.4(3)
C(5)-C(6)-C(7)	121.5(3)	N(1)-C(7)-C(6)	122.1(3)
C(13)-C(8)-C(9)	118.4(3)	C(13)-C(8)-N(1)	116.4(3)
C(9)-C(8)-N(1)	125.2(3)	C(10)-C(11)-C(12)	114.6(3)
C(10)-C(11)-C(14)	123.3(3)	C(12)-C(11)-C(14)	122.0(3)
F(1)-C(12)-C(13)	119.1(3)		

Table 3.6 *Selected Bond Angles of* ***SAL3F,4(CH$_3$)***

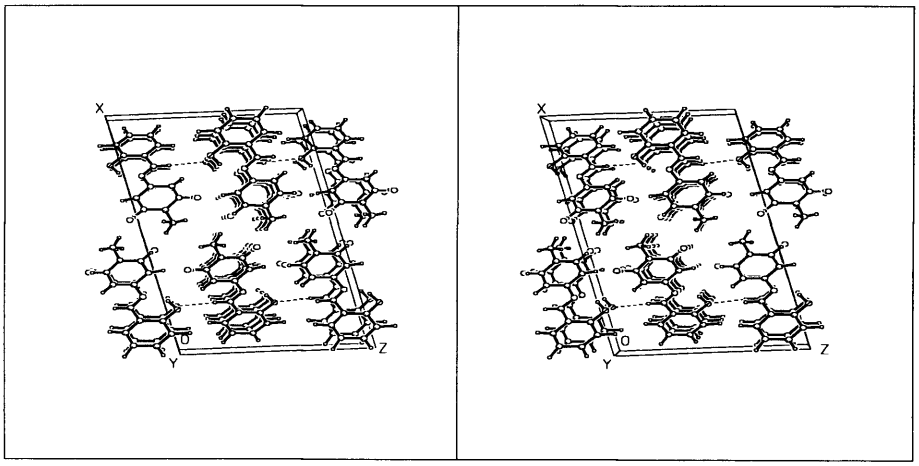


Figure 3.23 *3D Stereo pair of 3F,4(CH$_3$)*

3.6.3 SAL4(OCF_3)

SAL4(OCF_3) was crystallised from CH_2Cl_2 by slow evaporation at low temperature (0-5 ^{0}C), to give yellow blocks. Its crystal structure is monoclinic. The structure diagram is given in Figure 3.24. There is a strong intramolecular hydrogen-bond between the hydroxyl hydrogen and the nitrogen, its bond length is 1.622(6) Å, but no intermolecular hydrogen-bonding is present in this case. The oxygen-nitrogen distance is 2.603(6) Å. This molecule is packed in the form of layers such that the aldehydic ring of one is above the aldehydic ring of the other. The packing and 3D stereo pair diagrams are shown in Figures 3.25 and 3.26 respectively. Selected bond lengths and bond angles are given in Tables 3.7 and 3.8 respectively.

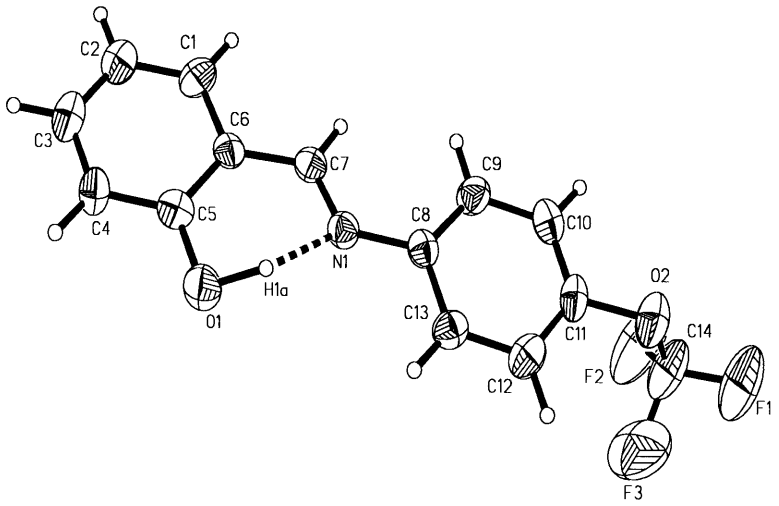


Figure 3.24 *Structure diagram of SAL4(OCF_3)*

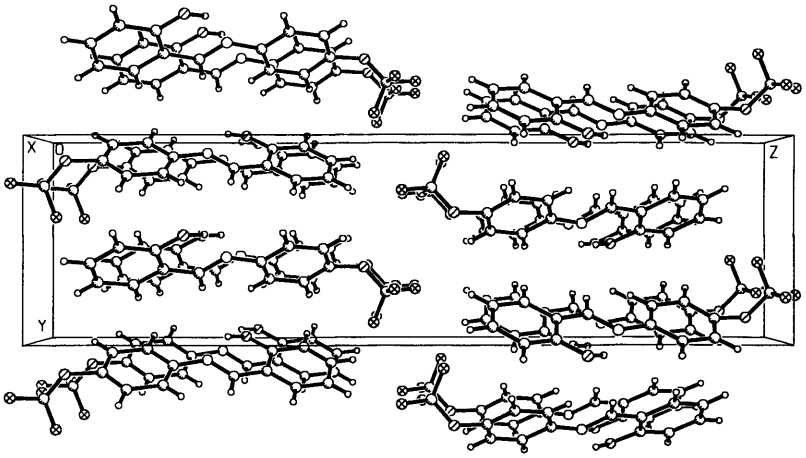


Figure 3.25 *Packing diagram of SAL4(OCF$_3$)*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
N(1)-C(7)	1.289(7)	N(1)-C(8)	1.415(7)
O(1)-C(5)	1.350(8)	O(2)-C(11)	1.417(8)
O(2)-C(14)	1.318(12)	C(1)-C(6)	1.414(9)
C(4)-C(6)	1.373(9)	C(5)-C(6)	1.403(8)
C(6)-C(7)	1.440(8)	C(8)-C(9)	1.371(9)
C(8)-C(13)	1.388(8)	C(9)-C(10)	1.392(9)
C(10)-C(11)	1.349(10)	C(11)-C(12)	1.374(11)
O(1)-H	1.092(6)	C(12)-C(13)	1.365(9)

Table 3.7 *Selected Bond Lengths of SAL4(OCF$_3$)*

	Angles[°]		Angles[°]
C(7)-N(1)-C(8)	122.7(5)	O(1)-C(5)-C(4)	119.7(6)
O(1)-C(5)-C(6)	120.2(6)	C(4)-C(5)-C(6)	120.1(6)
C(1)-C(6)-C(5)	117.5(5)	C(1)-C(6)-C(7)	119.3(5)
C(5)-C(6)-C(7)	123.1(5)	N(1)-C(7)-C(6)	120.9(5)
N(1)-C(8)-C(9)	125.8(5)	N(1)-C(8)-C(13)	115.5(5)
C(9)-C(8)-C(13)	118.7(5)	O(2)-C(11)-C(10)	118.2(7)
O(2)-C(11)-C(12)	118.9(6)	C(10)-C(11)-C(12)	122.8(6)

Table 3.8 *Selected Bond Angles of SAL4(OCF$_3$)*

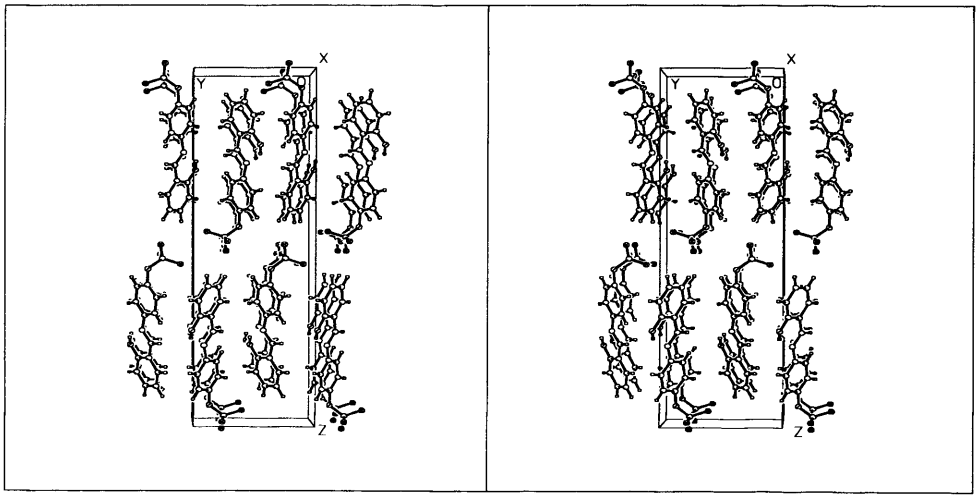


Figure 3.26 *3D Stereo pair of SAL4(OCF$_3$)*

3.6.4 SAL4F

SAL4F was crystallised from a 50% CH_2Cl_2/n-hexane mixture by slow evaporation at low temperature (0-5 ^{0}C), to give lemon yellow needles. Its crystal system is monoclinic. The structure diagram is given in Figure 3.27. There is a strong intra-molecular hydrogen-bonding present between the hydroxyl hydrogen and the nitrogen having bond length 1.744(3) Å, the oxygen-nitrogen bond distance is 2.619(3) Å, but no intermolecular hydrogen bond was observed. These molecules are planar and packed in layers such that the aldehydic ring of one molecule faces the anil ring of the other. The packing and 3D stereo pair diagrams are shown in Figures 3.28 and 3.29 respectively. Selected bond lengths and bond angles are given in Tables 3.9 and 3.10 respectively.

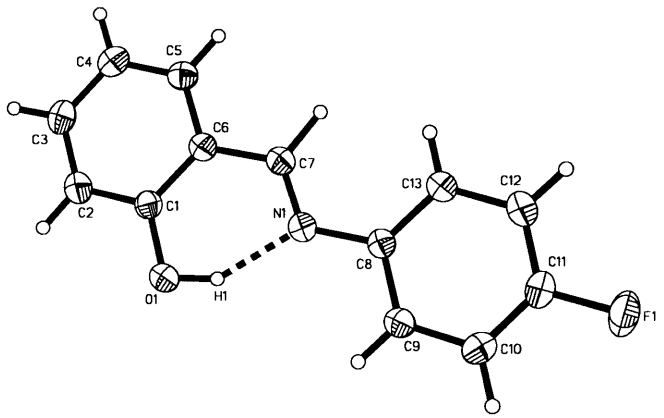


Figure 3.27 *Structure diagram of SAL4F*

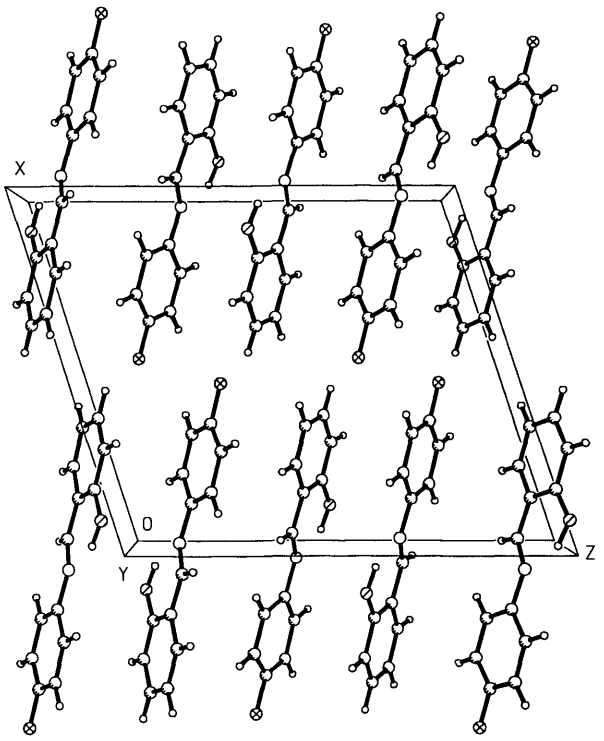


Figure 3.28 *Packing diagram of SAL4F*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(1)-C(2)	1.388(3)	O(1)-C(1)	1.354(2)
C(1)-C(6)	1.406(2)	C(5)-C(6)	1.395(2)
C(6)-C(7)	1.447(2)	N(1)-C(7)	1.273(2)
N(1)-C(8)	1.419(2)	C(8)-C(9)	1.377(2)
C(8)-C(13)	1.394(2)	C(10)-C(11)	1.366(3)
C(11)-F(1)	1.362(2)	C(11)-C(12)	1.365(3)
O(1)-H	0.969(4)		

Table 3.9 *Selected Bond Lengths of SAL4F*

	Angles[°]		Angles[°]
O(1)-C(1)-C(2)	118.7(2)	O(1)-C(1)-C(6)	121.5(2)
C(2)-C(1)-C(6)	119.8(2)	C(5)-C(6)-C(1)	118.5(2)
C(5)-C(6)-C(7)	119.8(2)	C(1)-C(6)-C(7)	121.8(2)
N(1)-C(7)-C(6)	122.1(2)	C(7)-N(1)-C(8)	122.9(2)
C(9)-C(8)-N(1)	116.1(2)	C(13)-C(8)-N(1)	124.8(2)
C(12)-C(11)-C(10)	122.8(2)	F(1)-C(11)-C(10)	118.7(2)
F(1)-C(11)-C(12)	118.5(2)	C(9)-C(8)-C(13)	119.1(2)

Table 3.10 *Selected Bond Angles [°] of SAL4F*

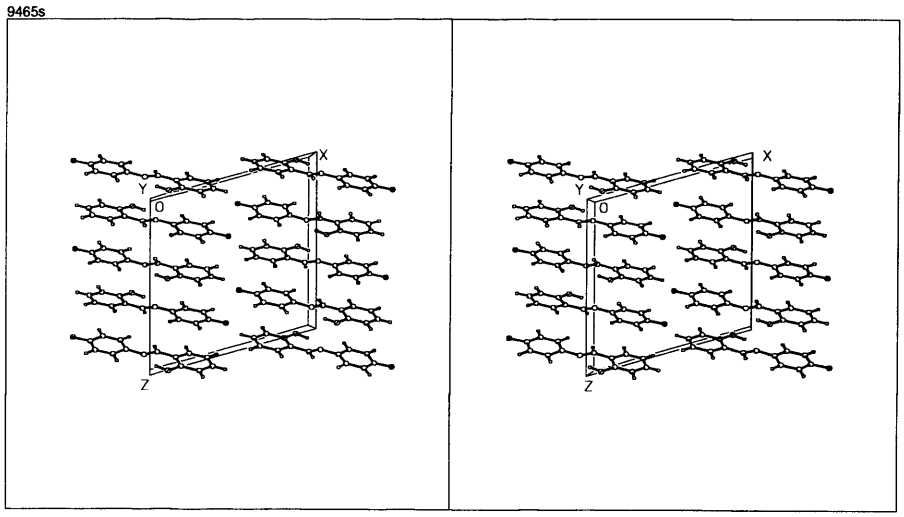


Figure 3.29 *3D Stereo pair of SAL4F*

3.6.5 SAL4(CH_3):-

SAL4(CH_3) was crystallised from ethanol by slow evaporation at low temperature 0-5 ^{0}C to give bright yellow needles. Its crystal structure is monoclinic. The structure diagram is given in Figure 3.30. There is a strong intramolecular hydrogen-bond between the hydroxyl hydrogen and nitrogen, and this is reflected in the fact that its bond length is 1.455 Å. No intermolecular hydrogen-bonding is present in this case. The oxygen to nitrogen distance is 2.597 Å. This structure was first solved by Aldoshin *et al*[14] but with high e.s.d. values, in the range of 0.02 Å and their R value was 0.052. The structure solved in this work has lower e.s.d. values in the range of 0.005 Å and its R value is 0.048. The packing and 3D stereo pair diagrams are shown in Figures 3.31 and 3.32 respectively. Selected bond lengths and bond angles are given in Tables 3.11 and 3.12 respectively.

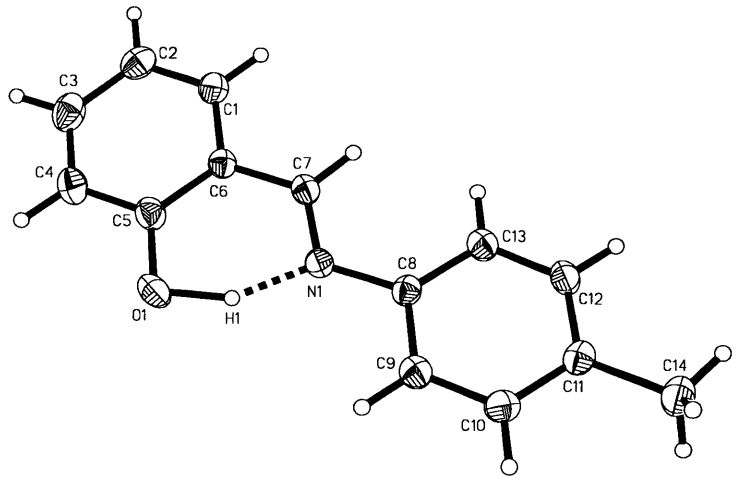


Figure 3.30 *Structure diagram of SAL4(CH_3)*

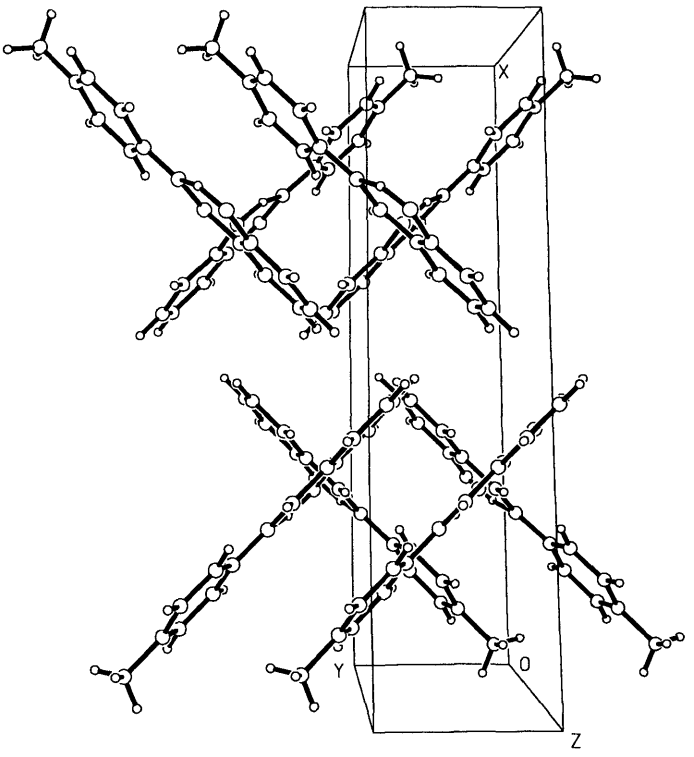


Figure 3.31 *Packing diagram of SAL4(CH_3)*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(4)-C(5)	1.391(6) *[1.398(6)]*	C(6)-C(7)	1.448(5) *[1.453(6)]*
C(5)-O(1)	1.349(5) *[1.345(6)]*	C(7)-N(1)	1.282(5) *[1.294(6)]*
C(5)-C(6)	1.393(6) *[1.401(6)]*	N(1)-C(8)	1.420(5) *[1.419(6)]*
C(6)-C(1)	1.396(5) *[1.398(6)]*	C(8)-C(9)	1.382(5) *[1.395(6)]*
C(10)-C(11)	1.384(6) *[1.395(5)]*	C(8)-C(13)	1.392(6) *[1.380(6)]*
C(11)-C(12)	1.378(5) *[1.385(6)]*	C(11)-C(14)	1.511(6) *[1.503(6)]*

Table 3.11 *Selected Bond Lengths of SAL4(CH_3)*
Values from the literature[14] are given in italics.

	Angles[°]		Angles[°]
C(4)-C(5)-O(1)	119.2(4)	C(4)-C(5)-C(6)	119.7(4)
O(1)-C(5)-C(6)	121.1(4)	C(1)-C(6)-C(5)	118.8(4)
C(1)-C(6)-C(7)	119.4(4)	C(5)-C(6)-C(7)	121.9(3)
C(6)-C(7)-N(1)	122.0(4)	C(7)-N(1)-C(8)	121.7(3)
N(1)-C(8)-C(9)	116.5(3)	N(1)-C(8)-C(13)	124.9(3)
C(9)-C(8)-C(13)	118.6(4)	C(10)-C(11)-C(12)	117.4(4)
C(10)-C(11)-C(14)	121.1(3)	C(12)-C(11)-C(14)	121.5(4)

Table 3.12 *Selected Bond Angles of SAL4(CH_3)*

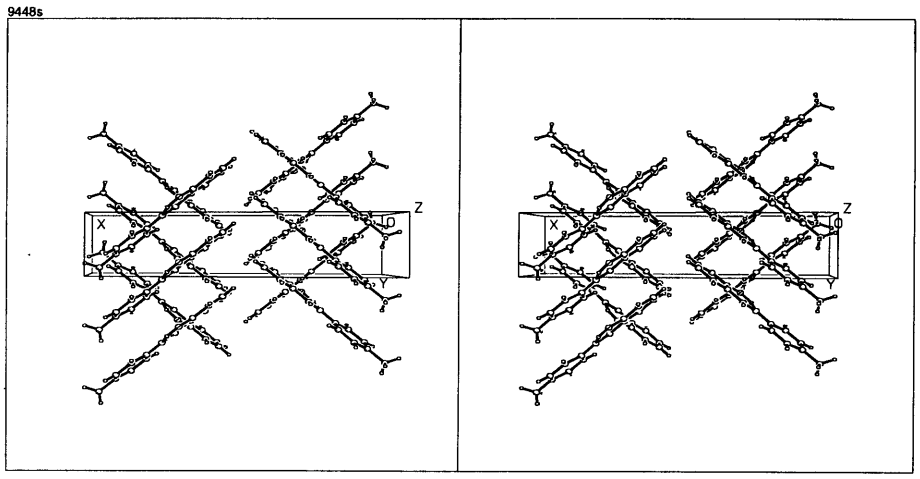


Figure 3.32 *3D Stereo pair of SAL4(CH_3)*

3.6.6 $SALF_5$

$SALF_5$ was crystallised from ethanol by slow evaporation at low temperature (0 to 5 ^0C) giving light yellow needles. Its crystal system is monoclinic. The structure diagram is given in Figure 3.34. This structure was first solved by Lindeman[15] in 1981 but the e.s.d. values were high, up to of 0.012 Å, and refinement R was 0.054. The structure solved in this work has lower e.s.d. values up to of 0.003 Å, and R value is 0.034. The molecules are packed in layers such that the aldehydic phenyl ring is above the anil phenyl ring of another molecule. There is a strong intramolecular hydrogen-bond present between the hydroxyl-hydrogen and nitrogen which is reflected by its bond length [1.722 Å]. Its packing and 3D stereo pair diagrams are in Figures 3.35 and 3.36 respectively . The oxygen-nitrogen bond distance in this case is 2.616 Å. Selected bond lengths and bond angles are given in Tables 3.13 and 3.14 respectively.

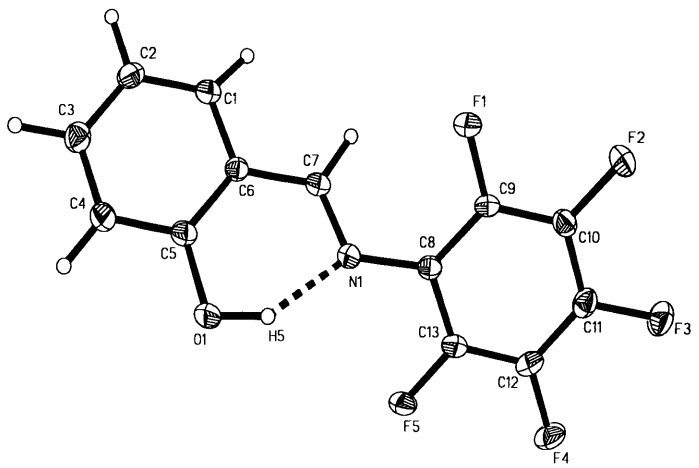


Figure 3.34 *Structure diagram of $SALF_5$*

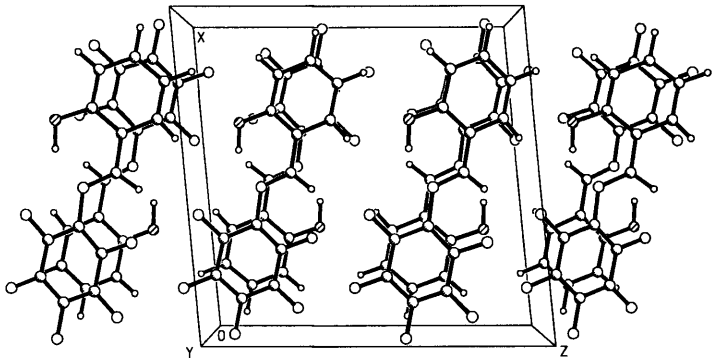


Figure 3.35 *Packing diagram of $SALF_5$*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
O(1)-C(5)	1.353(2) *[1.359(8)]*	C(5)-C(6)	1.407(3) *[1.422(8)]*
C(6)-C(1)	1.401(3) *[1.392(9)]*	C(6)-C(7)	1.441(3) *[1.426(9)]*
N(1)-C(7)	1.285(2) *[1.279(9)]*	N(1)-C(8)	1.407(2) *[1.387(8)]*
C(8)-C(9)	1.387(3) *[1.394(10)]*	C(8)-C(13)	1.388(3) *[1.382(9)]*
C(12)-C(11)	1.372(3) *[1.356(11)]*	C(11)-C(10)	1.374(3) *[1.372(11)]*
C(11)-F(3)	1.342(2) *[1.368(8)]*	C(13)-F(5)	1.342(2) *[1.355(9)]*
C(9)-F(1)	1.347(2) *[1.341(7)]*		

Table 3.13 *Selected Bond Lengths of $SALF_5$*
Values from the literature[15] are given in italics

	Angles[°]		Angles[°]
O(1)-C(5)-C(4)	118.3(2)	C(4)-C(5)-C(6)	119.8(2)
O(1)-C(5)-C(6)	121.9(2)	C(1)-C(6)-C(7)	119.4(2)
C(1)-C(6)-C(5)	118.8(2)	C(5)-C(6)-C(7)	121.8(2)
C(6)-C(7)-N(1)	121.9(2)	C(7)-N(1)-C(8)	120.2(2)
N(1)-C(8)-C(9)	124.5(2)	N(1)-C(8)-C(13)	118.5(2)
C(8)-C(13)-F(5)	118.7(2)	C(8)-C(9)-F(1)	120.0(2)
C(12)-C(11)-C(10)	120.2(2)	C(10)-C(11)-F(3)	119.7(2)
C(12)-C(11)-F(3)	120.1(2)	C(9)-C(8)-C(13)	116.7(2)

Table 3.14 *Selected Bond Angles of* $SALF_5$

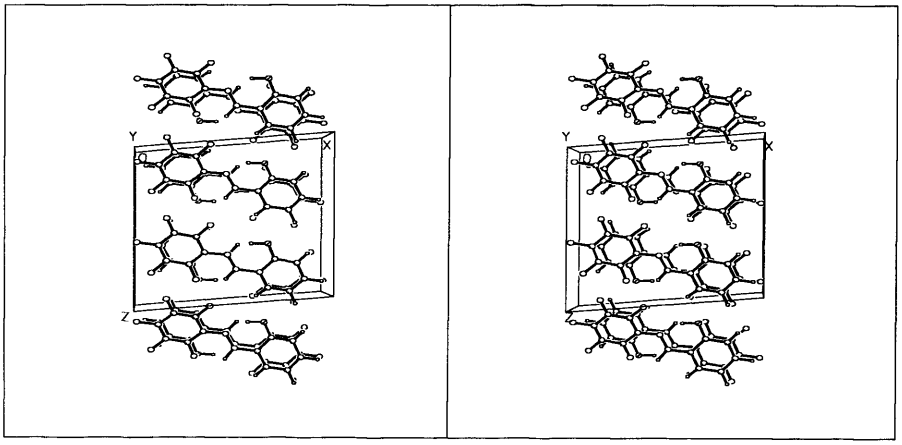


Figure 3.36 *3D Stereo pair of* $SALF_5$

3.6.7 5ClSAL4Cl

5ClSAL4Cl was crystallised from ethanol by slow evaporation at low temperature (0-5 ^{0}C), to give yellow blocks. Its crystal stucture is monoclinic. The structure diagram is given in Figure 3.37. There is a strong intramolecular hydrogen-bond between the hydroxyl-hydrogen and nitrogen, its bond length being 1.716 Å. The oxygen-nitrogen bond distance is 2.594 Å. The packing and 3D stereo pair diagrams are given in Figures 3.38 and 3.39 respectively. Selected bond lengths and bond angles are given in Tables 3.15 and 3.16 respectively.

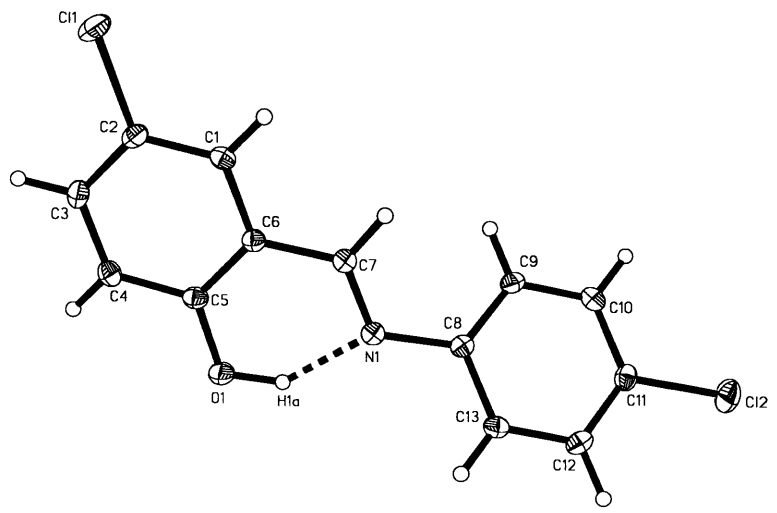


Figure 3.37 *Structure diagram of 5ClSAL4Cl*

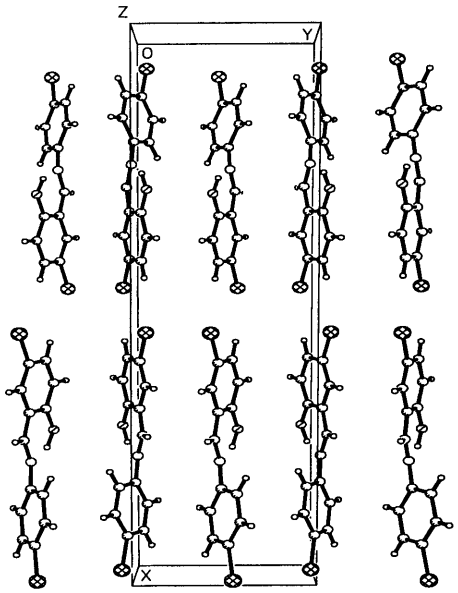


Figure 3.38 *Packing diagram of 5ClSAL4Cl*

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(4-C(5)	1.390(3)	C(5)-C(6)	1.411(3)
C(5)-O(1)	1.352(3)	C(1)-C(6)	1.396(3)
C(6)-C(7)	1.447(3)	C(1)-C(2)	1.367(3)
N(1)-C(8)	1.419(3)	C(7)-N(1)	1.281(3)
C(8)-C(13)	1.388(3)	C(8)-C(9)	1.388(3)
C(11)-C(12)	1.381(4)	C(10)-C(11)	1.380(4)
C(2)-Cl(1)	1.741(2)	C(11)-Cl(2)	1.740(2)
O(1)-H	1.007		

Table 3.15 *Selected Bond Lengths of 5ClSAL4Cl*

	Angles[°]		Angles[°]
C(4)-C(5)-O(1)	119.0(2)	C(4)-C(5)-C(6)	119.7(2)
O(1)-C(5)-C(6)	121.3(2)	C(5)-C(6)-C(1)	118.6(2)
C(1)-C(6)-C(7)	120.2(2)	C(5)-C(6)-C(7)	121.3(2)
C(1)-C(2)-C(3)	121.1(2)	C(1)-C(2)-Cl(1)	119.5(2)
Cl(1)-C(2)-C(3)	119.3(2)	C(6)-C(7)-N(1)	121.7(2)
C(7)-N(1)-C(8)	120.4(2)	C(9)-C(8)-C(13)	119.5(2)
N(1)-C(8)-C(9)	121.8(2)	N(1)-C(8)-C(13)	118.5(2)
C(10)-C(11)-C(12)	121.3(2)	C(10)-C(11)-Cl(2)	118.8(2)
Cl(2)-C(11)-C(12)	119.9(2)	O(1)-H(1)a...N(1)	143.3

Table 3.16 *Selected Bond Angles of 5ClSAL4Cl*

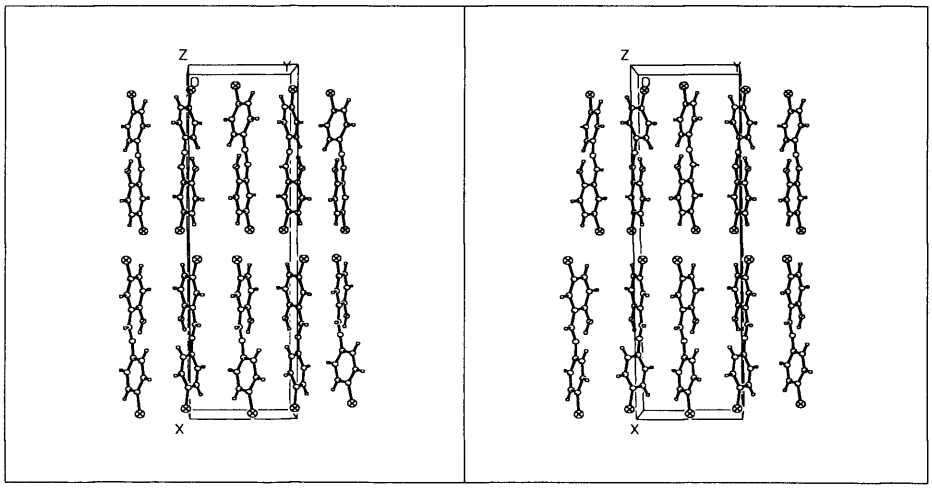


Figure 3.39 *3D Stereo pair of 5ClSAL4Cl*

3.7 DISCUSSION:-

The majority of the salicylideneanilines show strong intramolecular hydrogen bonding, the exception being SAL3,5$(CF_3)_2$. It was assumed that this is due to the electron-withdrawing effect of the two -CF_3 groups and steric hindrance. For confirmation of the steric effect, the angles between the planes of (OH)C_6H_4CH= and =NC_6H_3[3,5$(CF_3)_2$], in all the molecules, were calculated (Table 3.18) but no significant change was observed. The hydrogen-bonding is strongest in the case of the methyl substituted compound (SAL4(CH_3)), which has a N.....H distance of 1.46 Å. It is 1.62 Å in the case of SAL4(OCF_3), but in the other compounds its value is ≈1.70 Å. It can be seen that all the compounds having fluorine directly substituted on the ring show weak hydrogen-bonding as compared to the compounds not having such fluoro-substituents. For example, in the case of SAL4(OCF_3), the oxygen is in between the ring and the trifluoromethyl group. The bond distances between hydroxyl-oxygen and nitrogen is ≈2.6 Å(which is the predicted bond distance for O-H...N bonding[16-17])in all the compounds even in SAL3,5$(CF_3)_2$ where there is no hydrogen-bonding at all. In some structures weak intermolecular hydrogen-bonding is present, for example in SAL3,5$(CF_3)_2$), SALF_5 and 5ClSAL4Cl.

All these ligands have very similar bond lengths and bond angles. This implies that there is no significant fluoro or non-fluoro substituent effect on the bond lengths and bond angles. There is no significant substituent effect on hydrogen-bonds except in case of methyl-substituted compound SAL4(CH_3) which

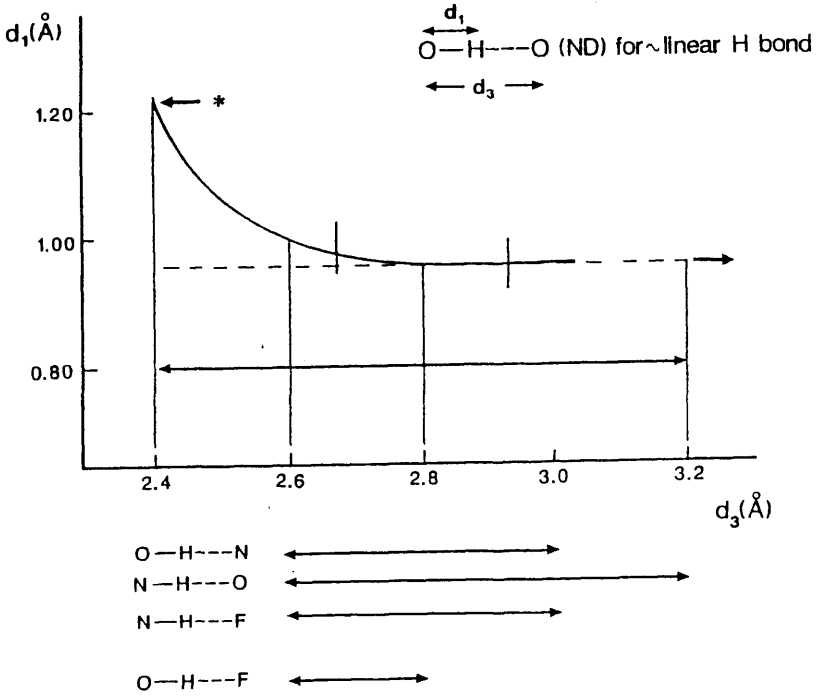
has a strong hydrogen-bond having bond length 1.455 Å. This is to be expected as there is no substituent effect noticed in the structures previously reported in the literature, for example SAL4(NO_2), 5ClSAL, SAL2Cl and Cl_4SAL[3-6](Table 3.19 and 3.20). The N...O, O-H, N...H, OH...N and the difference of O-H and N...H is given in Table 3.17 and the expected range[18] of a hydrogen-bond is given in Graph 3.1.

Compounds	N...H-O [°]	N...O Å	N...H Å	O-H Å	Diff.Å .N...H/O-H
SAL3,5(CF_3)$_2$	-	2.631	-	0.922	-
SAL4(OCF_3)	146	2.603	1.622	1.092	0.53
SAL3F,4(CH_3)	147	2.60	1.729	0.974	0.755
SAL4F	148	2.617	1.744	0.969	0.755
SAL4(CH_3)	149	2.597	1.455	1.237	0.218
SALF_5	144	2.616	1.722	1.018	0.704
5ClSAL4Cl	143	2.594	1.716	1.007	0.709

Table 3.17 *Represents hydrogen bonding of SAL3,5(CF_3)$_2$, SAL4(OCF_3), SAL3F,4(CH_3), SAL4F, SAL4(CH_3), SALF_5 and 5ClSAL4Cl*

Compounds	Angles [°]
SAL3,5$(CF_3)_2$	152.8
SAL4F	2.1
SALF_5	40.1
SAL4(CH_3)	6.4
SAL3F,4(CH_3)	5.8
SAL4(OCF_3)	2.7
5ClSAL4Cl	42.6

Table 3.17 *Angles between the $(OH)C_6H_4CH=$ and $=NC_6H_3R$ planes*



Graph 3.1

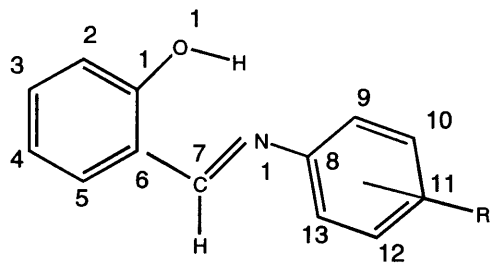
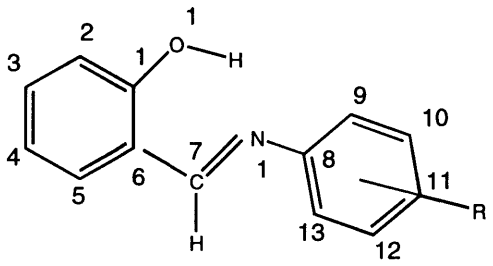


Figure 3.32 *Represents the numbering of carbon atoms*

BONDS	SAL3,5 $(CF_3)_2$)	SAL3F,4 (CH_3)	SAL4 (OCF_3)	SAL4F	SAL4 (CH_3)	SALF5	5ClSA L4Cl
C(7)-N(1)	1.254(13)	1.274(4)	1.289(7)	1.273(2)	1.282	1.285(2)	1.281(3)
C(6)-C(7)	1.463(16)	1.452(4)	1.440(8)	1.447(2)	1.448(5)	1.441(3)	1.447(3)
C(8)-N(1)	1.374(12)	1.419(4)	1.415(7)	1.419(2)	1.420(5)	1.407(2)	1.419(3)
C(1)-O(1)	1.413(13)	1.354(4)	1.350(8)	1.354(2)	1.349(5)	1.353(2)	1.352(3)
C(6)-C(5)	1.438(13)	1.397(4)	1.414(9)	1.39592)	1.396(5)	1.401(3)	1.396(3)
C(1)-C(6)	1.372(16)	1.402(4)	1.403(8)	1.406(2)	1.393(6)	1.407(3)	1.411(3)
C(8)-C(9)	1.407(14)	1.397(4)	1.371(9)	1.377(2)	1.382(5)	1.387(3)	1.388(3)
C(8)-C(13)	1.406(12)	1.382(4)	1.388(8)	1.394(2)	1.392(6)	1.388(3)	1.388(3)
H...N	-	1.729	1.622(6)	1.744(3)	1.455	1.722	1.716
O...N	2.631(10)	2.600	2.603(6)	2.619(3)	2.597	2.616	2.594

Table 3.18 *Selected Bond lengths Å of* **SAL3,5$(CF_3)_2$, SAL3F,4(CH_3), SAL4(OCF_3), SAL4F, SAL4(CH_3), SALF$_5$** and **5ClSAL4Cl**



ANGLES[°]	SAL3,5 $(CF_3)_2$	SAL3F, 4(CH_3)	SAL4 (OCF_3)	SAL4F	SAL4 (CH_3)	SALF$_5$	5ClSA L4Cl
C(5)-C(6)-C(7)	118.8(10)	120.4(30	119.3(5)	119.8(2)	119.4(4)	119.4(2)	120.2(2)
C(5)-C(6)-C(1)	117.6(11)	121.2(30	117.5(5)	118.5(2)	118.8(4)	118.8(2)	118.6(2)
C(1)-C(6)-C(7)	123.6(8)	121.5(3)	123.1(5)	121.8(2)	121.9(3)	121.8(2)	121.3(2)
C(6)-C(1)-C(2)	123.8(10)	120.1(3)	120.1(6)	119.8(2)	119.7(4)	119.8(2)	119.7(2)
C(6)-C(1)-O(1)	117.8(9)	121.2(3)	120.2(6)	121.5(2)	121.1(4)	121.9(2)	121.3(2)
C(2)-C(1)-O(1)	117.8(10)	118.7(3)	119.7(6)	118.7(2)	119.2(4)	118.3(2)	119.0(2)
C(6)-C(7)-N(1)	124.5(9)	122.1(3)	120.9(5)	122.1(2)	122.0(4)	121.9(2)	121.7(2)
C(7)-N(1)-C(8)	122.7(8)	121.5(3)	122.7(5)	122.9(2)	121.7(3)	120.2(2)	120.4(2)
N(1)-C(8)-C(9)	123.6(8)	125.2(3)	125.8(5)	116.1(2)	116.5(3)	124.5(2)	121.8(2)
N(1)-C(8)-C(13)	118.4(9)	116.4(3)	115.5(5)	124.8(2)	124.9(3)	118.5(2)	118.5(2)
C(9)-C(8)-C(13)	118.1(9)	118.4(3)	118.7(5)	119.1(2)	118.6(4)	116.7(2)	119.5(2)

Table 3.19 *Selected Bond Angles[°] of* **SAL3,5(CF_3), SAL3F,4(CH_3), SAL4(OCF_3), SAL4F, SAL4(CH_3), SALF$_5$** and **5ClSAL4Cl.**

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CHAPTER 4

SYNTHESIS AND CHARACTERISATION OF SOME SUBSTITUTED 4-ANILINO-PENTA-3-EN-2-ONES

4.1 INTRODUCTION:-

The first reaction of a β-diketone with an amino compound was carried out in 1885 by Fisher and Bülow[1]. Simple substituted anilines and aryl amines condense readily with several β-diketones to give β-amino-α,β-unsaturated ketones[2], but the condensation of alkyl amines with β-diketones is difficult[3]. It is generally known that compounds having a Schiff base bonding, C=N, are affected by hydrogen ions in solution.[4]

Ueno and Martell[5-6] have reported the preparation and IR spectra of some α,β-unsaturated-β-ketoamines and several corresponding metal chelates. They suggested three possible forms, A, B and C in Figure 4.1, for the α,β-unsaturated-β-ketoamines in solutions.

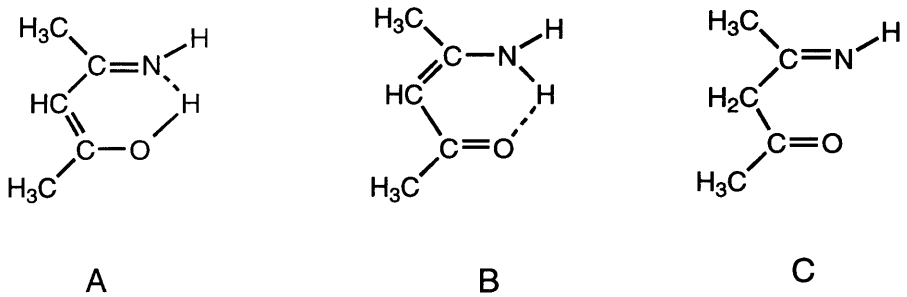


Figure 4.1

They concluded that a tautomeric equilibrium exists between the forms corresponding to A and B. Cromwell *et al.*[7] presented convincing evidence for structure B on the basis of their IR studies, which was supported by Holtzclaw and coworkers[8]. Dudek and coworkers[9-11] reported NMR studies of 4-amino-3-pentene-2-ones which confirm the presence of structure B in solution.

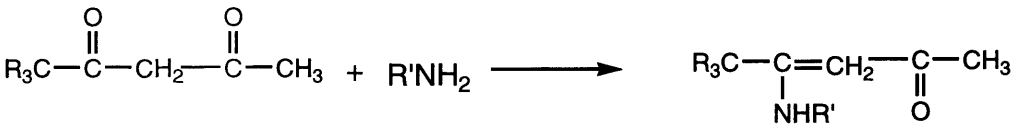
As these compounds contain two reactive functional groups which are also activating groups, so there are reactions which depend on the activated methylene hydrogen as well as the usual reactions of the keto and amino groups which are expected with such substances. In general the β-aminoketones are stable at elevated temperatures or in the presence of acids. The β-aminoketones, like β-amino acids, show a tendency to reform the α,β-unsaturated carbonyl compound.[13-14]

4.2 PREPARATION OF KETOANILINES:-

Ketoanilines have been prepared by reacting diketones (2,4-pentanedione and 1,1,1-trifluoro-2,4-pentanedione) with a variety of fluoro-anilines and their non-fluoro hydrogen-analogues. They are illustrated in Table 4.1.

4.3 GENERAL REACTION:-

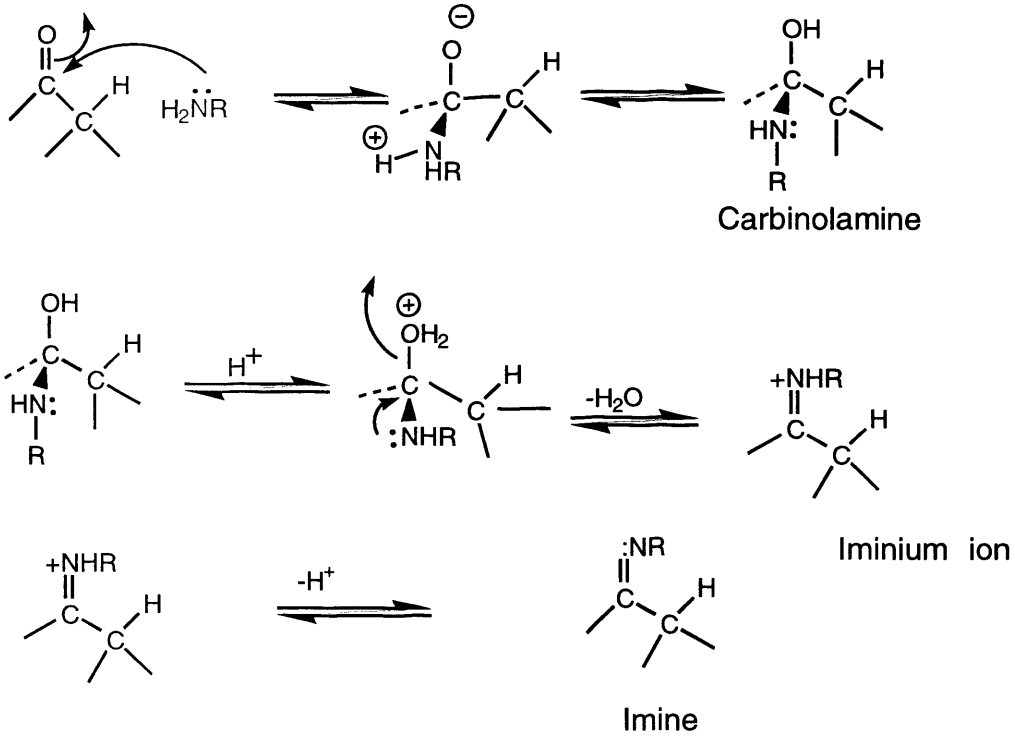
The reaction is



(R=H,F, R'=C_6H_5) Ketoaniline

4.4 REACTION MECHANISM:-

Ketoanilines are formed by a reversible, acid-catalysed process involving nucleophilic attack on the carbonyl group by the primary amine, followed by transfer of a proton from nitrogen to oxygen to yield a neutral carbinolamine. Protonation of the carbinolamine oxygen by the acid catalyst present converts the hydroxyl into a better leaving group, and loss of water produces an iminium ion. Loss of a proton then gives the final product and regenerates the acid catalyst. The maximum reaction rate is obtained at pH 4.5, because at low pH protonation of aldehyde or ketones, and at high pH protonation of aniline, takes place.



4.5 EXPERIMENTAL:-

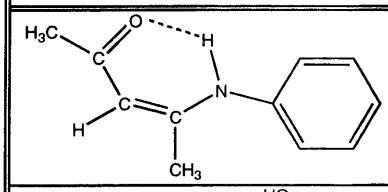
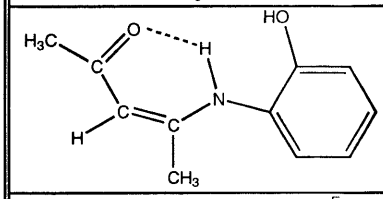
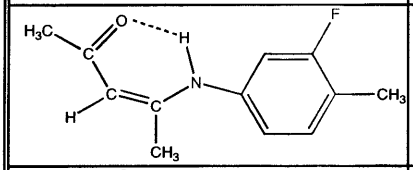
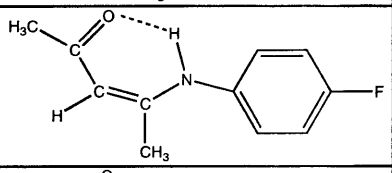
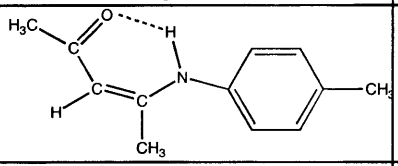
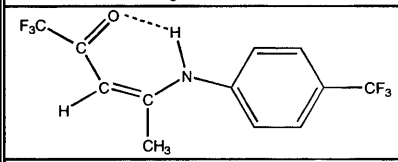
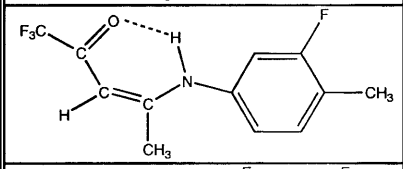
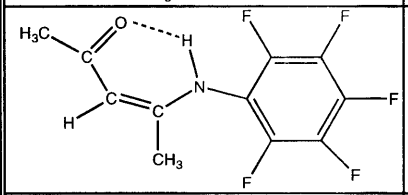
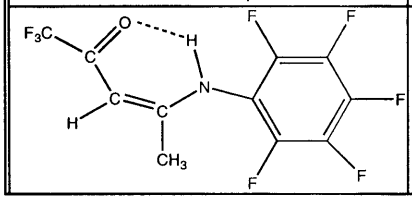
All the solvents used were of analytical grade, all other chemicals were from Aldrich, and used as such. All NMR [Tables 4.4, 4.5 and 4.6] spectra were recorded on a Bruker AM250 MHz spectrometer, infra-red (I.R.) spectra [Table 4.8] on a Perkin Elmer 580B and ultra-violet (U.V.) spectra [Table 4.2] on a Beckmann DU650 spectrophotometer. Mass spectrometry [Table 4.7] was undertaken on a Kratos concept double focusing mass spectrometer by Dr. G. Eaton. All elemental analyses [Table 4.3] were done by Butterworth Laboratories, Teddington.

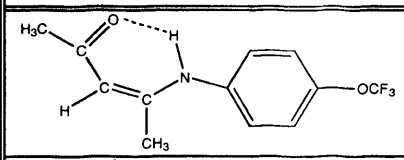
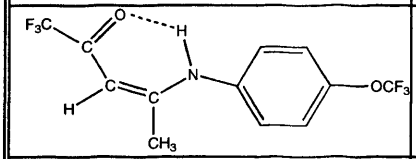
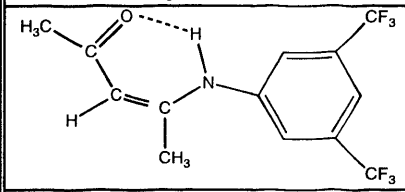
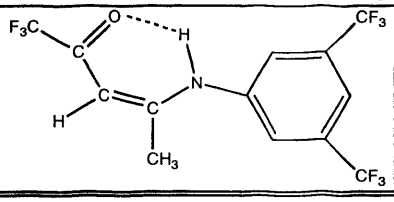
4.6 GENERAL METHOD OF PREPARATION:-

Two ethanolic solutions, of diketone [1M, 25ml] and of substituted aniline [1M, 25ml](calculated amounts are given in Table 4.1), were mixed, in several small portions, in a one to one ratio. The reaction mixture was then stirred and refluxed for an hour. After refluxing, it was allowed to cool slowly. After cooling precipitation began. The resulting precipitates were dark brown in colour and were very impure. All the isolated compounds were purified first by sublimation, using the cold finger method, in which the temperature of the finger was maintained at -30 to -40 ^{0}C with a solid CO_2/acetone mixture. The temperature of the outer jacket was kept 5-10 ^{0}C below the melting point of the respective ligand. Recrystallisation was then carried out in CH_2Cl_2 solution by slow evaporation [by placing the solution in a tube with a perforated cover in a fridge for several days] at low temperature (0 to 5 ^{0}C). A list of the diketoimines prepared with the abbreviations used is given in Table 4.1.

4.7 LIST OF KETOAMINES PREPARED

TABLE 4.1

Structural Formulae	Molecular Formulae	Abbreviation Used	Amounts Used gm
	$C_{13}H_{13}NO$	AcAcA	Aa = 2.50 an = 2.32
	$C_{11}H_{13}NO$	AcAc2(OH)A	Ac = 2.50 2(OH)an = 2.73
	$C_{12}H_{14}FNO$	AcAc3F4MeA	Ac = 2.50 3F,4(CH_3)an = 3.13
	$C_{11}H_{12}FNO$	AcAc4FA	Ac = 2.50 4Fan = 2.78
	$C_{12}H_{15}NO$	AcAc4(CH_3)	An = 2.50 4(CH_3)an = 2.68
	$C_{12}H_9F_6NO$	(CF_3)AcAc4(CF_3)	1CF_3An = 3.85 4(CF_3)an = 4.03
	$C_{12}H_{11}F_4NO$	(CF_3)AcAc3F4MeA	1(CF_3)An = 3.85 3F,4(CH_3)an = 3.13
	$C_{11}H_{14}F_5NO$	AcAcF_5A	Ac = 2.50 F_5an = 4.58
	$C_{11}H_5F_8NO$	(CF_3)AcAcF_5A	1(CF_3)Ac = 3.85 F_5an = 4.58

Structural Formulae	Molecular Formulae	Abbreviation Used	Amounts Used gm
	$C_{12}H_{12}F_3NO_2$	AcAc4(OCF_3)	Ac = 2.50 4(OCF_3)an = 4.43
	$C_{12}H_9F_6NO_2$	(CF_3)AcAc4(OCF_3)	1(CF_3)Ac = 3.85 4(OCF_3)an = 4.43
	$C_{13}H_{11}F_6NO$	AcAc3,5(CF_3)$_2$	Ac = 2.50 3,5(CF_3)$_2$an = 5.73
	$C_{13}H_8F_9NO$	(CF_3)AcAc3,5(CF_3)$_2$	1(CF_3)Ac = 3.85 3,5(CF_3)$_2$an = 5.73

4.8 RESULTS AND DISCUSSION:-

All the compounds have been characterised by a variety of techniques including melting points (Table 4.2), elemental analyses (Table 4.3) ^{1}H NMR spectra (Table 4.4), ^{13}C-DEPT. NMR spectra (Table 4.5) and ^{19}F NMR spectra (Table 6). +FAB(Fast atom bombardment) mass spectra (Table 4.7), I.R. spectra (Table 4.8) and U.V. spectra (Table 4.2) have also been recorded.

4.8.1 PHYSICAL CHARACTERISATION

TABLE 4.2

Abbreviations Used	Molecular Formula	M.P. ^{0}C	Colour/ State	% Yield	λmax (EtOH)
AcAcA	$C_{11}H_{13}NO$	45	White crystals	28	323.5
AcAc2(OH)A	$C_{11}H_{13}NO_2$	170	Light brown needles	65	322.0
AcAc3F,4(CH_3)A	$C_{12}H_{14}FNO$	65	White crystals	23	324.0
AcAc4(F)A	$C_{11}H_{12}FNO$	47	White crystals	62	320.0
AcAc4(CH_3)A	$C_{12}H_{15}NO$	63	White crystals	53	321.0
CF_3AcAc4(CF_3)A	$C_{12}H_9F_6NO$	95	White crystals	71	332.0
CF_3AcAc3F,4(CH_3)A	$C_{12}H_{11}F_4NO$	72	White crystals	71	328.0
CF_3AcAcF_5A	$C_{11}H_5F_8NO$	120	White crystals	26	318.0
AcAcF_5A	$C_{11}H_8F_5NO$	93	White crystals	11	308.0

Abbreviations Used	Molecular Formula	M.P. ^0C	Colour/ State	% Yield	λmax (EtOH)
AcAc4(OCF_3)A	$C_{12}H_{12}F_3NO_2$	55	White crystals	68	323.0
CF_3AcAc4(OCF_3)A	$C_{12}H_9F_6NO_2$	60	White crystals	23	358.0
CF_3AcAc3,5(CF_3)$_2$A	$C_{13}H_8F_9NO$	105	White crystals	22	328.0
AcAc3,5(CF_3)$_2$A	$C_{13}H_{11}F_6NO$	98	White crystals	19	329.0

4.8.2 ELEMENTAL ANALYSIS

TABLE 4.3

Comp-pounds	% C		% H		% N	
	Calculated	Found	Calculated	Found	Calculated	Found
AcAc4(F)A	68.4	68.81	6.2	6.39	7.3	7.49
AcAc3F, 4(CH_3)A	69.57	69.20	6.76	6.53	6.67	6.64
AcAc4 (OCF_3)A	55.59	55.89	4.69	4.78	5.46	5.40
CF_3AcAcF_5A	41.38	41.76	1.57	1.60	4.39	4.46
CF3AcAc 4(CF3)A	48.5	48.45	3.1	3.37	4.7	4.66
CF_3AcAc3F4 (CH_3)A	55.17	55.14	4.22	4.30	5.36	5.31

All the above compounds were anhydrous which is consistent with those previously reported in the literature for similar derivatives.

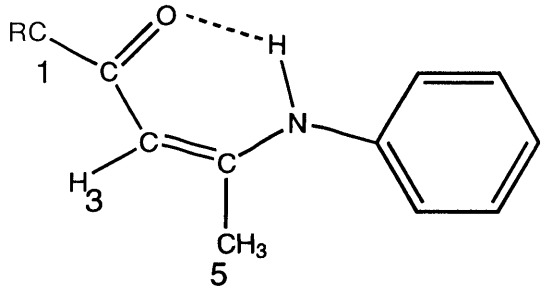


Figure 4.2 *Numbering of the Hydrogen Atoms in the ^1H NMR*

4.8.3 ^{1}H NMR DATA

TABLE 4.4

Abbreviation Used	Peaks Assigned	δ	Integral	Multiplicity
AcAcA	NH	12.49	1	s
	Ar H	7.86-6.65	6	m
	C_3H	5.19	1	s
	CH_3	2.24, 1.98	3,3	s,s
AcAc2(OH)	NH	11.73	1	s
	OH	8.48	1	s
	Ar H	7.38-6.68	4	m
	C_3H	5.19	1	s
	CH_3	2.36,1.25	3,3	s,s
AcAc3F,4(CH_3)A	NH	12.24	1	s
	Ar H	7.27-6.97	3	m
	C_3H	5.19	1	s
	CH_3	2.51,1.96,1.21	3,3,3	s,s,s
AcAc4(F)A	NH	12.37	1	s
	Ar H	7.06-6.69	4	m
	C_3H	5.40	1	s
	CH_3	2.39,1.84	3,3	s,s
AcAc4(CH_3)A	NH	12.40	1	s
	Ar H	7.44-6.8	4	m
	C_3H	5.29	1	s
	CH_3	2.60,2.15,1.69	3,3,3	s,s,s

Abbreviation Used	Peaks Assigned	δ	Integral	Multiplicity
$CF_3AcAc4(CF_3)A$	NH	12.65	1	s
	Ar H	8.03-6.68	4	m
	C_3H	5.62	1	s
	CH_3	2.19	3	s
$1CF_3AcAc3F4(CH_3)$ A	NH	12.52	1	s
	Ar H	7.38-6.41	3	m
	C_3H	5.55	1	s
	CH_3	2.29,1.98	3,3	s,s
$AcAcF_5A$	NH	11.846	1	s
	C_3H	5.324	1	s
	CH_3	2.103,2.08	3,3	s,s
$1CF_3AcAcF_5A$	NH	11.97	1	s
	C_3H	5.73	1	s
	CH_3	2.14	3	s
$AcAc4(OCF_3)A$	NH	12.65	1	s
	Ar H	7.43-6.48	4	m
	C_3H	5.29	1	s
	CH_3	2.29,1.91	3,3	s,s
$1CF_3AcAc4(OCF_3)A$	NH	12.55	1	s
	Ar H	7.45-6.65	4	m
	C_3H	5.57	1	s
	CH_3	2.37-2.05	3	s
$1CF_3AcAc3,5(CF_3)_2$	NH	12.54	1	s
	Ar. H	7.73-6.91	3	m
	C_3H	5.57	1	s
	CH_3	2.09	3	s
$AcAc3,5(CF_3)_2$	NH	12.6	1	s
	Ar. H	7.54-6.92	3	m
	C_3H	5.24	1	s
	CH_3	2.05,1.99	3,3	s,s

^{1}H NMR DISCUSSION:-

In the NMR spectra for these molecules, there is a singlet for NH at approximately 12.45 ppm, and a singlet for the methylene -CH proton approximately at 5.5 ppm. There is also a multiplet for the aromatic protons in the region 6.5-7.8 ppm.These are assigned according to the suggested region for such proton in the literature[14-16].

According to the structure of acetylacetoimines, in ^{1}H NMR studies there is no $-CH_2$ signal at ≈5.0 ppm, rather there is a singlet in the region 5.19-5.59 ppm giving an integrated value of one and also there is a singlet for a -NH proton in the region 11.7-12.6 ppm also with an integrated value of one. This implies that one of the methylene protons is shifted from carbon C_3 (Figure 4.2) to the nitrogen, shifting the double bond to C_3. With the majority of ligands the -NH proton appeared in the region 11.6-12.7 ppm, except for AcAc2(OH)A and two penta-fluoro substituted ligands. In the case of the fluoro-substituted ligands this shift may be due to the strong electron-withdrawing effect of fluorine which is present on the ring, directly attached to the ring carbon. In the case of AcAc2(OH)A, this shift may be due to the inductive effect of the -OH group or may be due to the *ortho* effect of -OH group, or indeed may be a combination of both.

Aromatic protons in all the molecules appear in their expected region of 6.25-7.5 ppm, except for $1CF_3AcAc4CF_3A$. In this case peaks are in the region 6.68-8.03 ppm, this may be due to the $-CF_3$ group, but no such shift is present in case of $1CF_3AcAc3,5(CF_3)A$ and $AcAc3,5(CF_3)A$, where there are two $-CF_3$ groups present at the phenyl ring. The remaining protons gave peaks in their expected regions. -NH and -CH Singlets of AcAcA and complete ^1H NMR spectra of AcAcA and AcAc4FA are given in Figure 4.3 and 4.4 and 4.5 respectively.

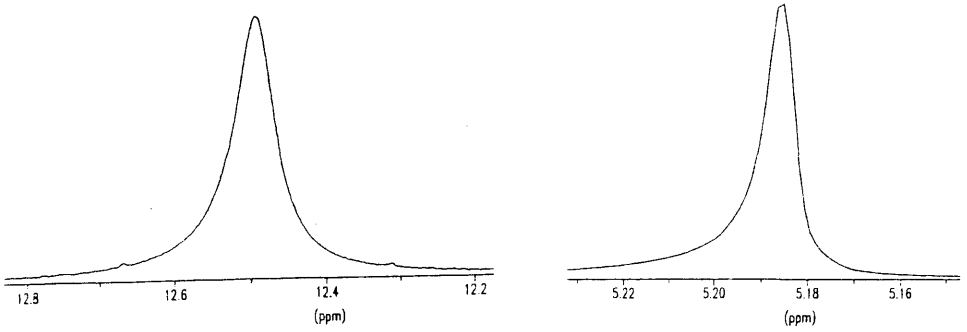


Figure 4.3 *-NH Singlet of AcAcA* *-CH Singlet of AcAcA*

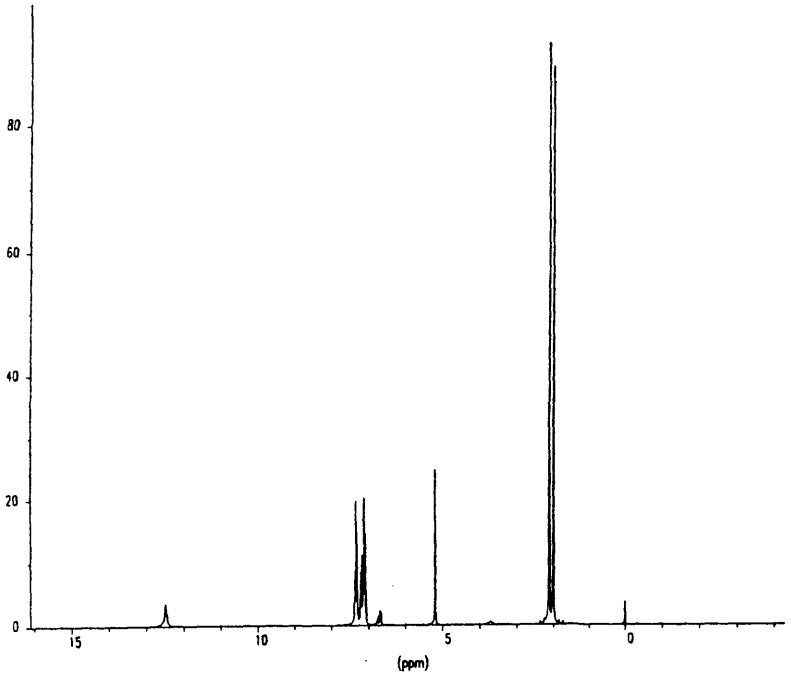


Figure 4.4 *^{1}H NMR Spectrum of AcAcA*

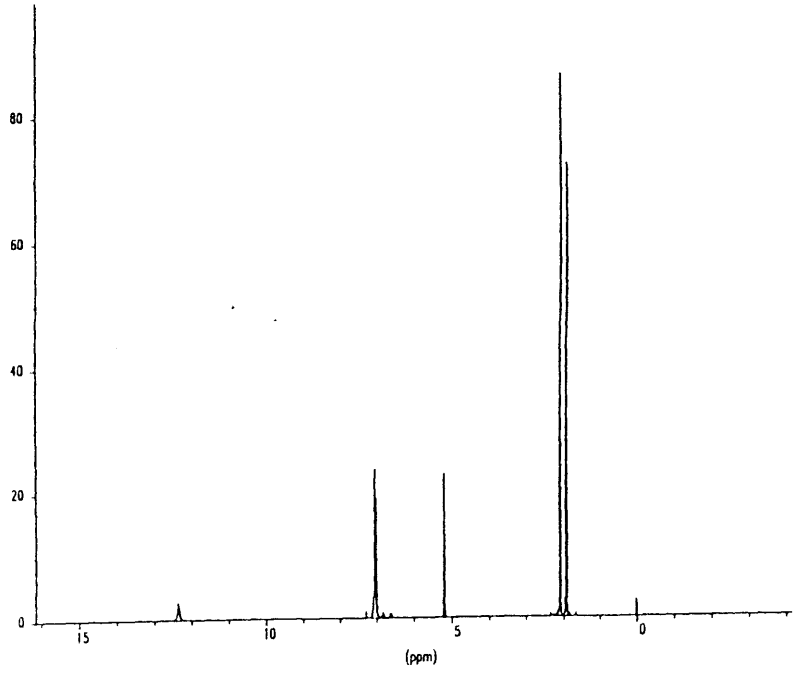


Figure 4.5 *^{1}H NMR Spectrum of AcAc4FA*

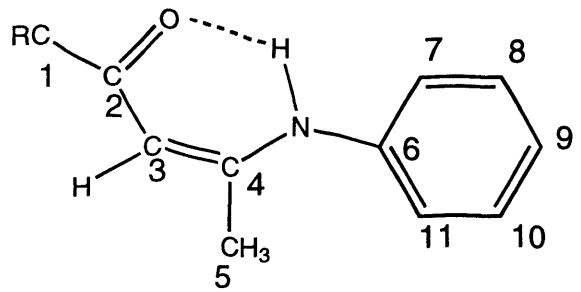


Figure 4.6 *Numbering of the carbons in ^{13}C-DEPT NMR*

4.8.4 ^{13}C DEPT. NMR DATA

TABLE 4.5

Compounds	Peaks Assigned	δ
AcAcA	$C_{1,5}$	20.3,29.6
	C_3	98.0
	C_2	196.5
	C_4	160.5
	C_6	142.3
	Ar $C_{7\text{-}11}$	115.5,118.8,125.1,126.0,129.7
$1CF_3AcAc4(OCF_3)A$	C_5	20.3,
	C_3	91.4
	C_9	118.4-119.7 (d, J- 320.81Hz)
	C_4	148.1
	C_6	135.6
	C_2	167.8
	C_1F_3	176.3-177.9 (q, J- 123.39Hz)
	OCF_3	114.3-115.1 (d, J- 197.48Hz)
	Ar $C_{7\text{-}8,10\text{-}11}$	122.5,126.8
$AcAc4(OCF_3)$	$C_{1,5}$	20.2,29.6
	C_3	98.6
	OCF_3	115.8
	C_6	146.9
	C_9	137.9
	C_4	160.1
	C_2	197.1
	Ar $C_{7\text{-}8,10\text{-}11}$	122.2,122.8,122.9,126.2
AcAc4(F)A	$C_{1,5}$	20.0,29.5
	C_3	97.9
	C_6	135.1
	C_4	160.8
	C_9	162.9
	C_2	196.7
	Ar $C_{7\text{-}9,10\text{-}11}$	116.1,116.5,127.1,127.7

Compounds	Peaks Assigned	δ
$1CF_3AcAc4(CF_3)A$	C_5	20.5
	C_3	92.0
	C_4	140.3
	C_6	125.9
	C_2	167.1
	C_9	-119.6-121.5 (d, J- 468.87Hz)
	CF_3	128.5-130.1 (q,J- 124.56Hz)
	C_1F_3	176.2-178.2 (q, J- 124.21Hz)
	Ar $C_{7\text{-}9,10\text{-}11}$	125.9,126.7,126.8,126.9
$1CF_3AcAc3F,4(CH_3)A$	C_5	20.7
	CH_3	14.7
	C_3	91.5
	C_8	124.7-124.9 (q, J- 49.37Hz)
	C_1F_3	176.15-177.35 (q, J- 98.71Hz)
	C_4	163.4
	C_2	168.2
	C_6	159.5
	C_9	136.4
	Ar $C_{7,10\text{-}11}$	112.5,112.9,121.1,132.4,132.5
$AcAc3F,4(CH_3)A$	$C_{1,5}$	20.9,29.2
	C_9	14.5
	C_3	98.3
	C_4	160.3
	C_6	159.5
	C_8	138.2,138.3
	C_9	122.3,122.5
	Ar $C_{7,10\text{-}11}$	111.2,111.8,120.5,131.9,132.0
$AcAc4(CH_3)A$	$C_{1,5}$	20.9,29.1
	C_9	19.8
	C_2	195.9
	C_3	97.2
	C_4	160.7
	C_6	136.1
	C_9	135.5
	Ar $C_{7\text{-}8,10\text{-}11}$	124.9,129.7
$AcAcF_5A$	$C_{1,5}$	19.3,29.8
	C_2	207.4
	C_3	100.1
	C_4	198.5
	C_6	160.23
	$C_{7\text{-}11}$	135.6,146.53,143.4,154.25,153.51, 152.85
$1CF_3AcAcF_5A$	C_5	19.7
	C_1F_3	178.2-179.5 (q, J- 123.39Hz)
	C_2	198.9
	C_3	92.8
	C_4	136.0
	C_6	145.6
	Ar. $C_{7\text{-}11}$	112.8,114.7,119.3,140.1,141.6

Compounds	Peaks Assigned	δ
AcAc2(OH)A	$C_{1,5}$ C_2 C_3 C_4 C_6 C_7 Ar. C_{8-11}	19.6,28.6 196.1 97.3 163.5 152.5 129.1 117.3,120.1,124.8,125.3,128.0,128.8
$1CF_3AcAc3,5(CF_3)_2$	C_1F_3 C_2 C_3 C_4 C_5 C_6 $2CF_3$ $C_{8,10}$ Ar. $C_{7,9,11}$	177.6-179.3 (q, J- 34.18Hz) 167.1 92.9 147.9 20.5 139.2 134.4-132.76 (q, J- 34.18Hz) 125.55,121.2 116.5,114.5,111.5
$AcAc3,5(CF_3)_2$	$C_{1,5}$ C_2 C_3 C_4 C_6 CF_3 CF_3 $C_{8,10}$ $C_{7,9,11}$	18.8,28.4 196.9 99.1 157.1 146.6 130.7-132.3 (q, J- 32.96Hz) 130.9-132.5 (q, J- 33.57Hz) 128.97-128.45,124.63-124.12,120.3-119.78,115.97-115.44 (dddd, J-32.35Hz) 122.5,117.3,117.2,113.1,110.4,110.3

^{13}C-DEPT. NMR DISCUSSION:-

All the compounds gave satisfactory ^{13}C-DEPT NMR spectra, peaks are assigined according to the regions given in literature[14-16]. Fluorine substituted carbons showed coupling to the fluorine, carbons bonded to a single fluorine gave a doublet and for the carbon of the CF_3 groups, a quartet.

Shifting of one of the two methylene protons to nitrogen is also verified by ^{13}C-DEPT NMR, as there is no peak for -CH_2 carbon expected to be in the region 0 to 50 ppm, instead there is a peak for -CH in the region 91.5-98.5 ppm with in the range 75 to 100 ppm expected for =CHR. Another important factor revealed in ^{13}C-DEPT NMR studies is that the majority of the fluorine-substituted ^{13}C atoms show splitting giving either quartet or doublet. No such splitting is observed in ^{19}F NMR, due to the fact that the vast majority of ^{19}F atoms are not attached to ^{13}C atoms. ^{13}C NMR spectrum of AcAc4FA is given in Figure 4.7.

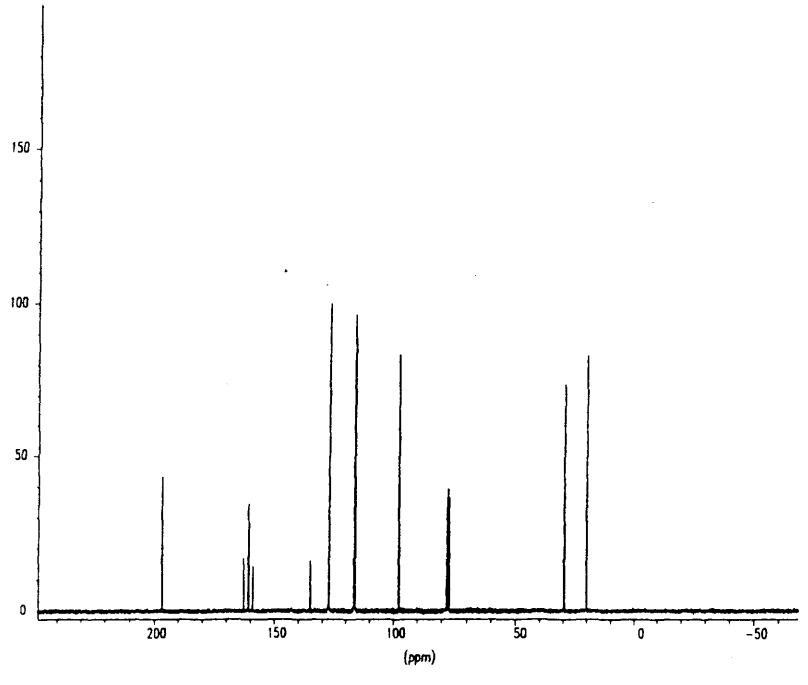
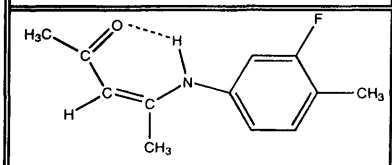
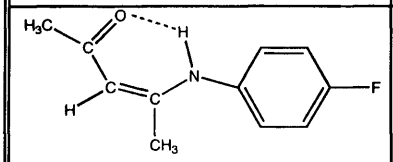
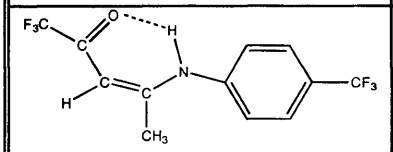
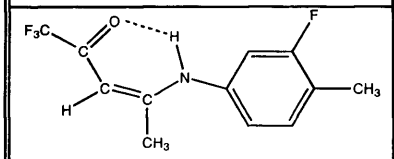
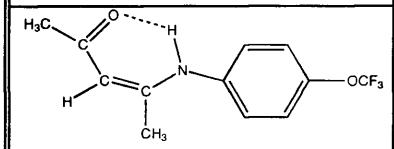
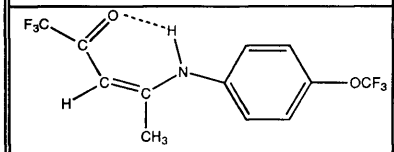
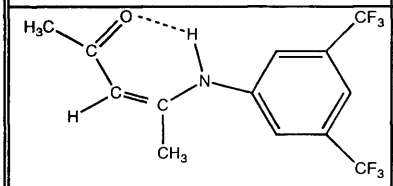


Figure 4.7 *^{13}C NMR Spectrum of AcAc4FA*

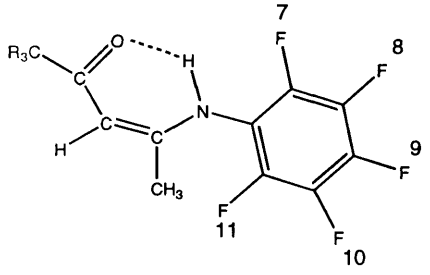
4.8.5 ^{19}F NMR DATA

TABLE 4.6

Compound	Peaks Assigned	δ	Multiplicity
	Coupled Decoupled	-115.86--115.95 -115.92	m s
	Coupled Decoupled	-127.42--127.53 -127.48	quintet J-6.79Hz s
	Coupled Decoupled	-62.95,77.31 -62.93,-77.32	s,s s,s
	Coupled F CF_3 Decoupled F CF_3	-114.66--114.74 -77.21 -114.7 -77.16	m s s s
	Coupled Decoupled	-58.54 -58.55	s s
	Coupled OCF_3,CF_3 Decoupled OCF_3,CF_3	 -58.51, -77.29 -58.52, -77.24	 s,s s,s
	Coupled $2CF_3$ Decoupled $2CF_3$	 -63.69,-63.82 -63.71 -63.85	 s,s s s

Compound	Peaks Assigned	δ	Multiplicity
	Coupled		
	C_1F_3	-77.65	s
	$2CF_3$	-63.77,-63.96	s,s
	Decoupled		
	C_1F_3	-77.65	s
	$2CF_3$	-63.78	s
		-63.96	s
	Coupled		
	$F_{8,10}$	-162.1--162.3	ddd, J- 6.62 Hz
	F_9	-156.5--156.7	t, J- 21.87 Hz
	$F_{7,11}$	-146.4--146.5	dd, J- 6.11 Hz
	Decoupled		
	$F_{8,10}$	-162.1--162.3	ddd, J- 6.77 Hz
	F_9	-156.5--156.7	t, J- 21.59 Hz
	$F_{7,11}$	-146.4--146.6	dd, J- 6.46 Hz
	Coupled CF_3	-77.65	s
	$F_{7,11}$	-145.43--145.54	dd, J- 4.7 Hz
	F_9	-153.52--153.70	t, J- 22.21 Hz
	$F_{8,10}$	-160.8--161.03	ddd, J- 5.7 Hz
	Decoupled CF_3	-77.52	s
	$F_{7,11}$	-145.43--145.54	dd, J- 4.58 Hz
	F_9	153.52--153.7	t, J- 21.36 Hz
	$F_{8,10}$	-160.8--161.03	ddd, J- 21.30 Hz

$CFCl_3$ was used as reference. The F atoms in the last two entries are numbered as follows



^{19}F NMR DISCUSSION:-

^{19}F NMR coupled and decoupled spectra were recorded for the fluoro-substituted ^{19}F molecules. All the peaks were in their expected region as given in literature[14-16]. Coupled ^{19}F NMR was done to study any possible interaction of fluorine with other atoms in the molecule, but no splitting and no significant shift in the chemical shifts of fluorine was observed, except in the case of AcAc3F,4(CH_3)A and 1CF3AcAc3F,4(CH_3)A there is a multiplet in the coupled spectra for fluorine substituted at C_8, this may be due to the interaction of fluorine with aromatic protons of $C_{7,9,11}$.

4.8.6 MASS SPECTROMETRY:-

All the diketoimines prepared were characterised by +FAB (Fast Atomic Bombardment) mass spectroscopy. All gave strong peaks corresponding to the molecular ion and a characteristic fragmentation was observed between the R group and the carbonyl group with all the compounds.

TABLE 4.7 MASS SPECTROSCOPIC DATA

Compounds	Calculated Mass	Ions observed
AcAcA	175	+FAB 175M^+, 160 (-15,-CH_3)
AcAc2(OH)A	192	+FAB, 192M^+, 176(-15,-CH_3)
AcAc3F,4(CH_3)A	207	+FAB, 207M^+, 192 (-15,-CH_3)
AcAc4(F)A	193	+FAB, 193M^+, 178 (-15,-CH_3)
AcAc4(CH_3)A	189	+FAB, 189M^+, 174 (-15,-CH_3)
1CF_3AcAc4(CF_3)A	297	+FAB, 297M^+, 228 (-69,-CF_3)
1CF_3AcAc3F,4(CH_3)A	261	+FAB, 261M^+, 192 (-69,-CF_3)
AcAcF_5A	265	+FAB, 265M^+,250(-15,-CH_3)
1CF_3AcAcF_5A	319	+FAB, 319M^+, 250 (-69,-CF_3)
AcAc4(OCF_3)A	259	+FAB, 259M^+, 244 (-15,-CH_3)
1CF_3AcAc4(OCF_3)A	313	+FAB, 313M^+, 244 (-69,-CF_3)
1CF_3AcAc3,5(CF_3)$_2$A	365	+FAB, 365M^+, 269 (-69,-CF_3)
AcAc3,5(CF_3)$_2$A	311	+FAB, 311M^+, 296 (-69,-CF_3)

In all the mass spectra for all the ligands there is a characteristic fragmentation, there is cleavage of either -CH_3 or CF_3 at position number one (Figure 4.2), no such fragmentation was mentioned in the literature for such compounds. No other fragmentation is observed.Mass spectra of AcAcA and AcAc4FA are given in Figures 4.8 and 4.9 respectively.

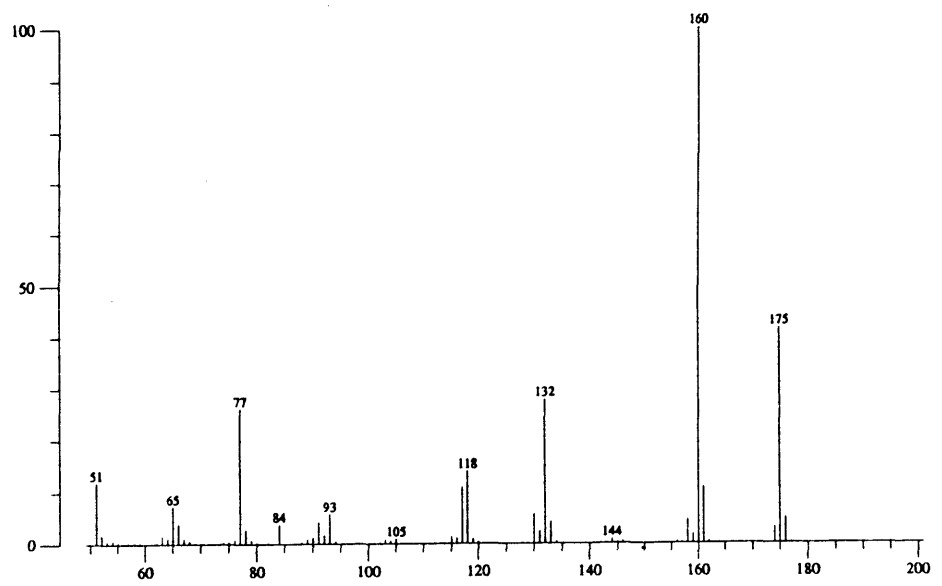


Figure 4.8 *Mass Spectrum of AcAcA*

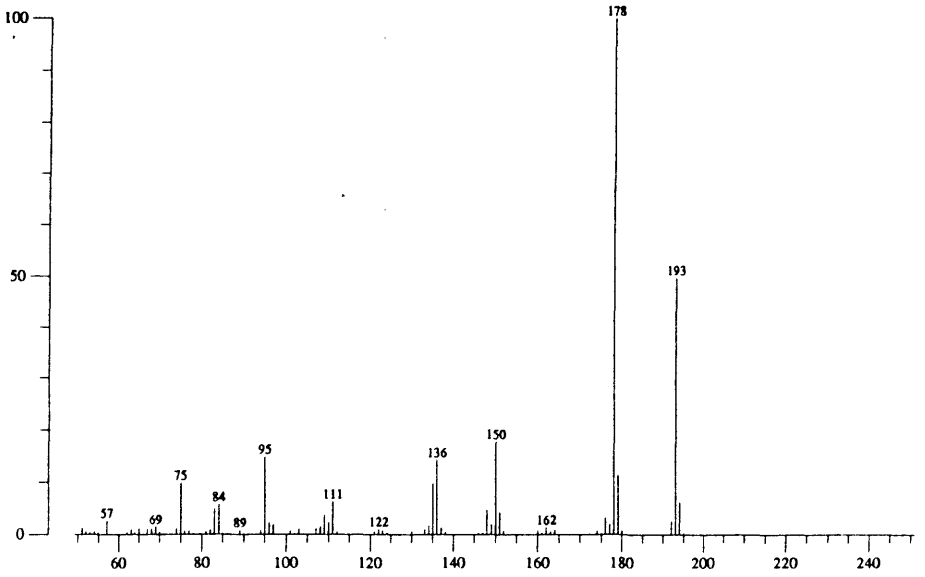


Figure 4.9 *Mass Spectrum of AcAc4FA*

4.8.7 I.R. DATA(Recorded as solutions in CH_2Cl_2)

TABLE 4.8

Compounds	Stretch+Bend	← Stretches →					Other
	C–H	C=C	C=O	N–H	C–N	C–F	Bands
AcAcA	3030,2980s,1350, 1370,1020,910s, 810,670,620m	1430s,1570m	_	_	1210,1180s, 1070,1020s		-
AcAc4(CH_3)A	3030,2970,2920s 1510,1370,910, 810,680,620s	1490m	1720w	_	990m,1010s, 1180,1300s, 1210m		-
AcAc4FA	3030,2970,1370s 910,840,820,640, 620s	1430s,1560w	1880w	3360w	1020,990s	1090,1150s	-
1CF_3AcAc4(OCF_3)A	3050,2980w,860, 810,770s,660,	1500,1430s	1770w	3380w	1380m,1350s	1025w,1010s 950m,920s	-

Compounds	Stretch+Bend	← Stretches →					Other
	C–H	C=C	C=O	N–H	C–N	C–F	Bands
	630m						
AcAc4(OCF_3)	3040,2965,2920m 1375m,915,850, 800,680,660s	1490,1435s	1770w,	-	1100,1020, 1010,990m	1350,1300m	3650w
1CF_3AcAc4(CF_3)A	3050s,2980,2920 w,860,780s	1520,1610s	1780w	3385w	1360,1300m	1010,1050m	3640w
AcAc3,5$(CF_3)_2$A	3080,3060,2980 2950,2920s,1430 1400m,860,840s, 680m	1570,1500, 1460s	1720w	3396,3220s	1070w,1020, 1000,960,940s	1360,1350, 1310s	3680,3480w
1CF_3AcAc3,5$(CF_3)_2$A	3060m,2990, 2920,1240w,890 880,840,780,680s	1520w,1460, 1430m	1695w	3395s	1010,985,940s	1380w	3480s

Compounds	Stretch+Bend	← Stretches →					Other
	C–H	C=C	C=O	N–H	C–N	C–F	Bands
$1CF_3AcAc3F4(CH_3)A$	3030,2980,2920m ,1410,920,900, 870,825730s,	1550,1465s, 1430m	1770w	-	1130w,1100, 950s	1350,1300s	
$AcAc3F4(CH_3)A$	3030,2970,2920, 1370m,910,800m, 880,780w	1430w	_	-	1020,1110s, 990m	1350,1300, 1180,1140s	3660m
$1CF_3AcAcF_5A$	3050,2980w, 1420s,985,890, 780,690s	1620,1580s	_	_	1330,1230m	1190,1140s, 1110,1030, 1010m	-
$AcAcF_5A$	3030,2970m, 1410s,980,870, 780,660s	1640,1550s	1740w	-	1290,1250m	1180,1135s, 1050,1020m	3680w
AcAc2(OH)A	3040,2990m,1350 1415,890,680w	1510,1500, 1490,1450m	1710,1680w	_	1130,1090, 1020w,		

I.R. DISCUSSION:-

All the ketoimines prepared were characterised by I.R. spectroscopy, all the spectra being recorded as solutions in CH_2Cl_2 against a CH_2Cl_2 blank. All the characteristic bonds(C=C, C=O, C-N, N-H, C-F and C-H) in the compounds gave bands in their expected region.

4-Anilino-penta-3en-2-ones have one phenyl ring in their structure; they gave stretching vibrations in the region 3100-2900 cm^{-1}, and their deformations are in the 1200-1450 cm^{-1} region. The out-of-plane bends are in the 980-650 cm^{-1} region. The majority of the compounds gave a strong to medium band for the N–H bond in the region of 3680-3360 cm^{-1}. The C=C, C=O, C–N, C–F bonds gave strong to medium bands in the region 1500-900 cm^{-1}. All the N-H peaks observed are either weak or medium in the IR spectra of all the compounds studied which predict the presence of strong hydrogen bond between N-H proton and keto oxygen, except AcAc3,5$(CF_3)_2$ and 1CF_3AcAc3,5$(CF_3)_2$. In the spectra of these two compounds strong N-H peaks were observed, which shows the absence of hydrogen-bonding. This behaviour is consistent with the X-ray and IR results for SAL3,5$(CF_3)_2$, that two -(CF_3) groups prohibit hydrogen-bonding; they cause the same effect in AcAcA molecules.

4.9 CONCLUSION:-

The preparation of these compounds was straightforward, but most were isolated in a very impure form. They were first purified by sublimation using the cold finger method described in the experimental section and then recrystallised from CH_2Cl_2.

According to ^1H and ^{13}C-DEPT NMR studies, one methylene proton is shifted to nitrogen. Fluorine-substituted ^{13}C atoms show peak splitting. In mass spectrometric studies only one characteristic fragmentation is observed with all the molecules. No evidence of such fragmentation was found in the literature, and no other characteristic fragmentation was observed.

They are air stable in the solid state but quite unstable in solution in organic solvents. They decompose in approximately an hour. No significant effect of the electron donating or electron withdrawing substituents was found on the spectroscopic behaviour of these ligands.

4.10 REFERENCES:-

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CHAPTER 5

STRUCTURE DETERMINATION OF SOME NOVEL 4-ANILINO-PENTA-3-EN-2-ONES

5.1 INTRODUCTION:-

This chapter describes the structures of some novel 4-anilino-penta-3-en-2-one derivatives [Acetyl Aceto Anilines(AcAcA)] (Figure 5.1) which were determined by single crystal X-ray diffraction and whose synthesis and characterisation have been given in Chapter 3. Information concerning bond lengths, bond angles and inter- and intra-molecular hydrogen-bonding has been gathered. No other crystal structure of 4-anilino-penta-3-en-2-one derivative has found in the literature.

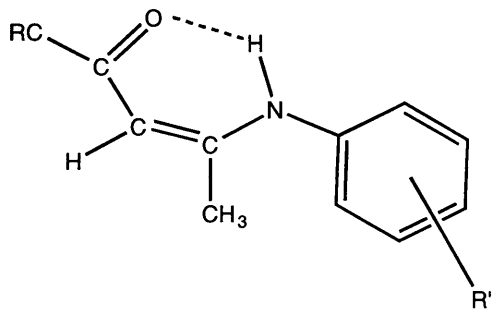


Figure 5.1 AcAcA

5.2 METHOD OF CRYSTALLISATION:-

In this work 4-anilino-penta-3-en-2-ones were first purified using the cold finger technique, as described in Chapter 3, as they had been isolated in very crude form. The purified sample was then recrystallised from ethanol by slow evaporation at low temperature, by placing the ethanolic solution in a sample tube with a perforated cover for several days in a refrigerator (0-5 °C). All of the six 4-anilino-penta-3-en-2-ones were crystallised as white transparent plates.

5.3 4-ANILINO-PENTA-3-EN-2-ONES

With all AcAcA (Figure 5.1) structures studied in this work by X-ray crystallography, it can be seen that the hydrogen of the CH_2 group is shifted onto the nitrogen in the solid form. It is also verified by ^1H and ^{13}C-DEPT NMR studies (Chapter 3) that they keep the keto form in solution as well. The structural formulae of the ligands investigated by X-ray crystallography in this work are shown below (Figures 5.2, 5.3, 5.4, 5.5, 5.6 and 5.7).

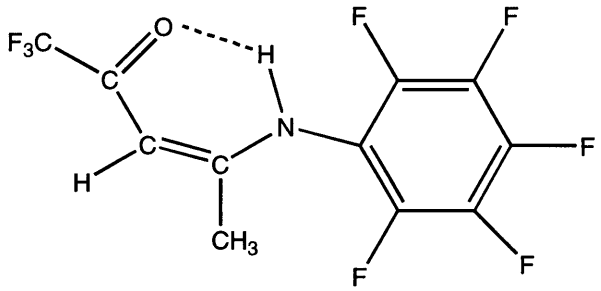


Figure 5.2 CF_3AcAcF_5A

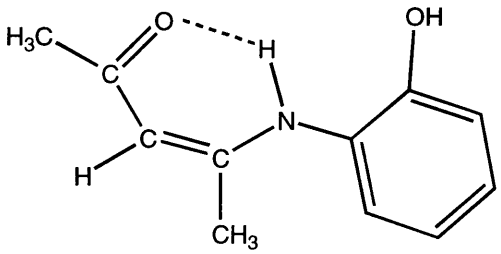


Figure 5.3 AcAc2(OH)A

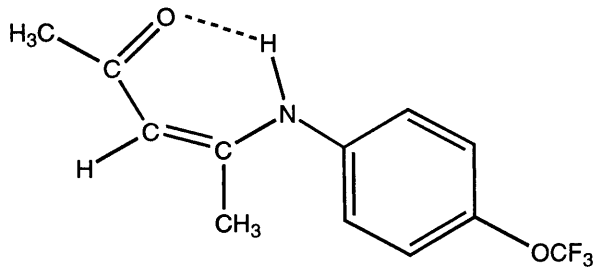


Figure 5.4 AcAc4(OCF$_3$)A

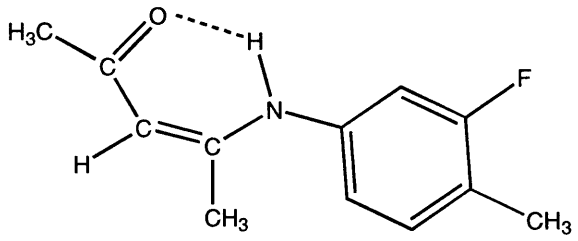


Figure 5.5 AcAc3F,4(CH$_3$)A

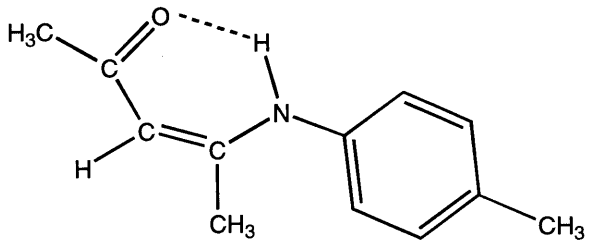


Figure 5.6 AcAc4(CH$_3$)A

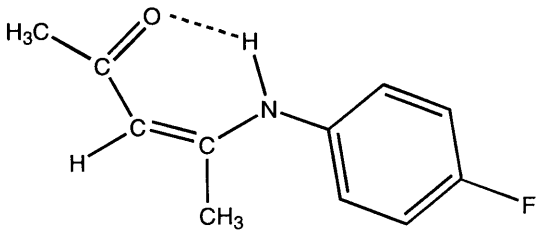


Figure 5.7 AcAc4FA

5.3.1 CF_3AcAcF_5A

CF_3AcAcF_5A (Figure 5.8) was first purified by sublimation and then recrystallised from CH_2Cl_2 by slow evaporation at low temperature (0-5^{0}C) giving white blocks. Its crystal system is monoclinic. The -C(8)H_3 group is found to be disordered. There is an intramolecular hydrogen-bond between the keto-oxygen and NH hydrogen having a bond length of 1.956(5) Å. The N(1)-H(1)...O(1) distance is 2.665(5)Å. There is intermolecular hydrogen-bond present, between the keto-oxygen of one molecule with the N-hydrogen of another having a bond length of 2.267(5) Å.. The intra and intermolecular hydrogen-bonds are shown in Figure 5.9 and its packing diagram in Figure 5.10. Selected bond lengths and bond angles are given in the Tables 5.1 and 5.2 respectively.

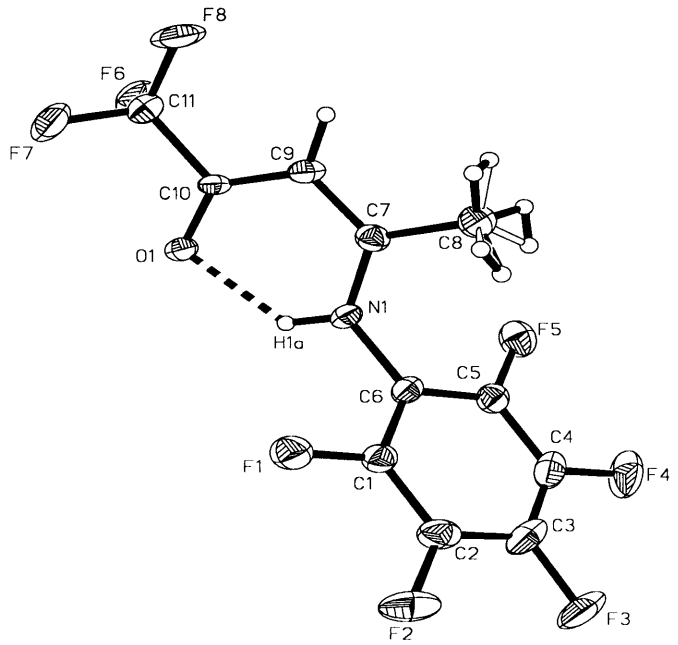


Figure 5.8 ***Molecular structure of CF_3AcAcF_5A***

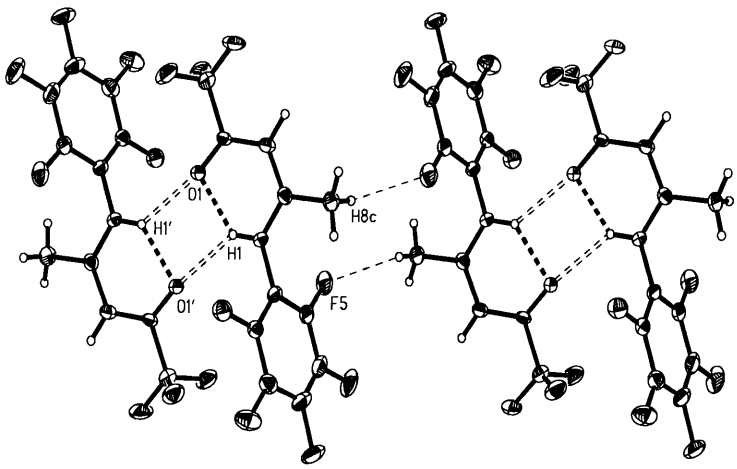


Figure 5.9 ***Inter- and Intramolecular Hydrogen-bonding in CF_3AcAcF_5A molecules***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(11)-C(10)	1.548(7)	C(11)-F(8)	1.314(4)
C(10)-O(1)	1.213(7)	C(10)-C(9)	1.394(9)
C(9)-C(7)	1.390(8)	C(7)-C(8)	1.503(8)
C(7)-N(1)	1.322(8)	N(1)-C(6)	1.423(7)
C(6)-C(5)	1.392(9)	C(6)-C(1)	1.372(9)
C(4)-C(3)	1.350(12)	C(3)-C(2)	1.387(11)
C(3)-F(3)	1.344(8)	N(1)-H(1)a	0.900

Table 5.1 *Selected Bond Lengths of CF_3AcAcF_5A*

	Angles[°]		Angles[°]
F(8)-C(11)-C(10)	113.7(4)	F(8)-C(11)-F(7)	108.2(4)
F(7)-C(11)-C(10)	110.3(4)	C(11)-C(10)-O(1)	114.6(8)
C(11)-C(10)-C(9)	118.0(5)	O(1)-C(10)-C(9)	127.4(5)
C(10)-C(9)-C(7)	122.2(5)	C(9)-C(7)-C(8)	120.3(5)
C(8)-C(7)-N(1)	118.6(8)	C(9)-C(7)-N(1)	121.0(5)
C(7)-N(1)-C(6)	126.3(5)	N(1)-C(6)-C(5)	120.6(6)
N(1)-C(6)-C(1)	121.3(5)	C(1)-C(6)-C(50	118.1(6)
C(4)-C(3)-C(2)	120.6(6)	C(4)-C(3)-F(3)	121.2(8)
C(2)-C(3)-F(3)	118.2(8)		

Table 5.2 *Selected Bond Angles of* CF_3AcAcF_5A

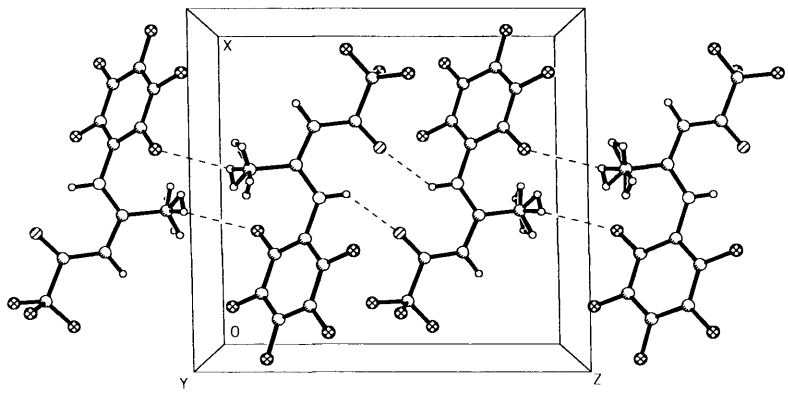


Figure 5.10 *Packing diagram of* CF_3AcAcF_5A

5.3.2 AcAc4(OCF_3)A

AcAc4(OCF_3)A (Figure 5.11) was crystallised from ethanol by slow evaporation at low temperature (0-5^{0}C), after purification by the cold finger sublimation method, giving white blocks. Its crystal system is monoclinic. There is a weak intramolecular hydrogen-bond between the keto-oxygen and the N-hydrogen having a bond length of 1.891(2) Å. The bond distance between the keto-oxygen and the nitrogen is 2.665(2) Å. The nearest intermolecular neighbouring atom to fluorine is a methyl hydrogen having a bond distance of 2.439(3) Å. The intramolecular hydrogen-bonding is shown in Figure 5.12 and its packing diagram in 5.13. Selected bond lengths and bond angles are given in Tables 5.3 and 5.4 respectively.

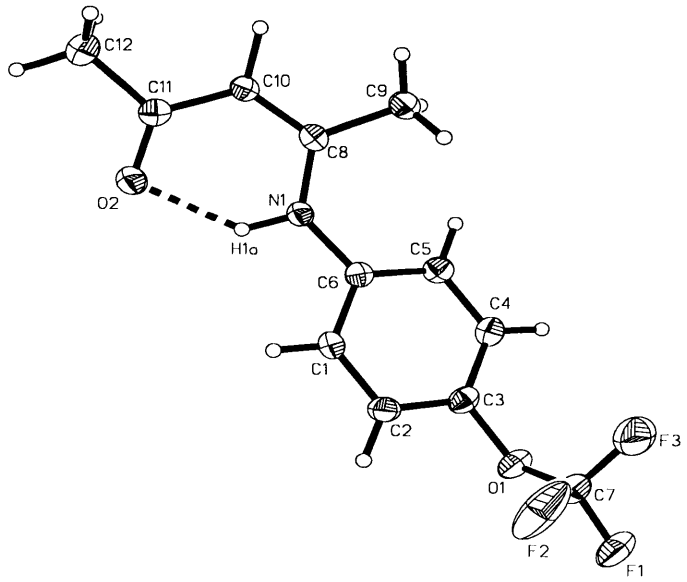


Figure 5.11 Molecular structure of AcAc4(OCF_3)A

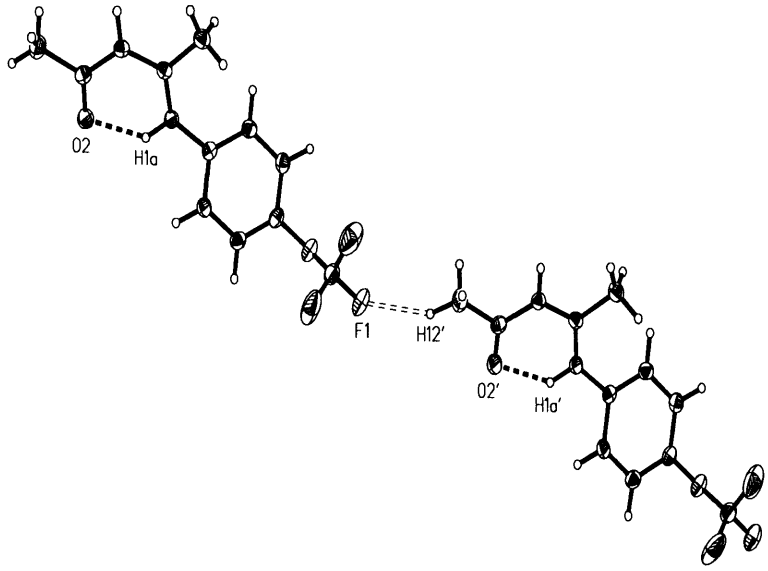


Figure 5.12 ***Inter- and Intramolecular hydrogen-bonding in AcAc4(OCF$_3$)A molecules***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(12)-C(11)	1.508(4)	C(11)-O(2)	1.250(3)
C(11)-C(10)	1.422(4)	C(10)-C(8)	1.370(30
C(8)-C(9)	1.492(4)	C(8)-N(1)	1.356(3)
N(1)-C(6)	1.411(3)	C(6)-C(5)	1.388(4)
C(6)-C(1)	1.390(4)	C(2)-C(3)	1.371(4)
C(3)-C(4)	1.369(4)	C(3)-O(1)	1.420(3)
O(1)-C(7)	1.323(3)	C(7)-F(1)	1.313(3)
F(3)-C(7)	1.307(4)	F(2)-C(7)	1.291(4)
N(1)-H(1)a	0.957(3)		

Table 5.3 *Selected Bond Lengths of **AcAc4(OCF$_3$)A***

Bonds	Angles[°]	Bonds	Angles[°]
C(12)-C(11)-O(2)	119.0(2)	C(12)-C(11)-C(10)	117.5(2)
C(10)-C(11)-O(2)	123.5(2)	C(11)-C(10)-C(8)	125.2(2)
C(10)-C(8)-N(1)	119.5(2)	C(10)-C(8)-C(9)	119.8(2)
C(9)-C(8)-N(1)	120.7(2)	C(8)-N(1)-C(6)	130.4(2)
N(1)-C(6)-C(1)	116.1(2)	N(1)-C(6)-C(5)	124.6(2)
C(1)-C(6)-C(5)	118.9(2)	C(2)-C(3)-C(4)	121.4(2)
C(2)-C(3)-O(1)	119.3(2)	O(1)-C(3)-C(4)	119.2(2)
C(3)-O(1)-C(7)	117.3(2)	O(1)-C(7)-F(1)	109.2(2)
N(1)-H(1)a-O(2)	136.2		

Table 5.4 *Selected Bond Angles of* ***AcAc4(OCF$_3$)A***

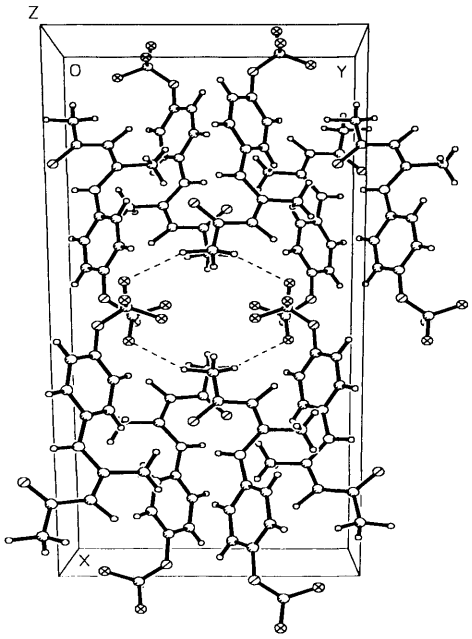


Figure 5.13 ***Packing diagram of AcAc4(OCF$_3$)A***

5.3.3 AcAc4(CH_3)A

AcAc4(CH_3)A (Figure 5.14) was first purified by sublimation and then recrystallised from ethanol by slow evaporation at low temperature (0-5 °C), giving white blocks. Its crystal structure is monoclinic. There is an intramolecular hydrogen-bond between the keto-oxygen and N-hydrogen having a bond length of 1.887(2) Å, the bond distance N...O(1) is 2.645(2) Å. Intermolecular hydrogen-bonding is also present between the keto-oxygen of one molecule and aryl hydrogen of another with a bond length of 2.497(3) Å. The intra- and intermolecular hydrogen-bonding and packing diagrams are shown in Figures 5.15 and 5.16. Selected bond lengths and bond angles are given in Tables 5.5 and 5.6 respectively.

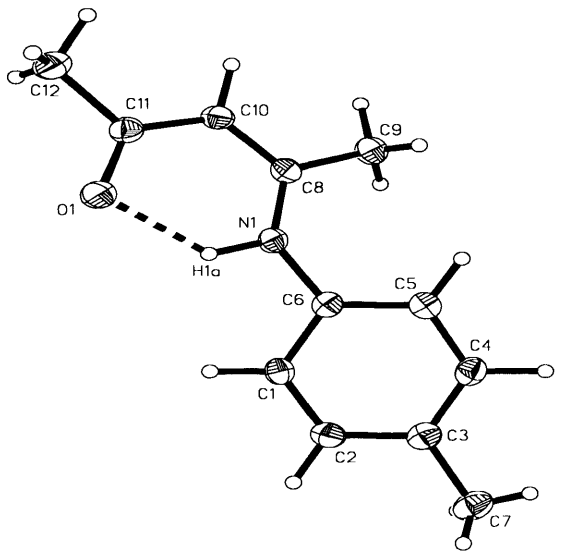


Figure 5.14 ***Molecular structure of AcAc4(CH_3)A***

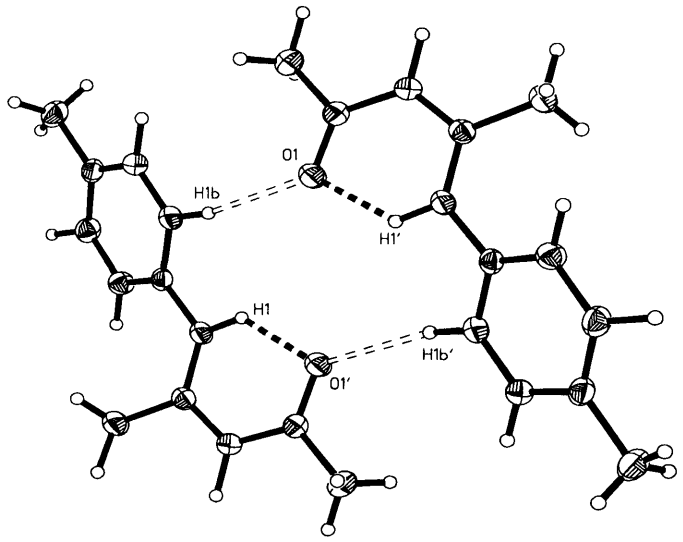


Figure 5.15 ***Inter- and intramolecular hydrogen-bonding in AcAc4(CH$_3$)A***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(7)-C(3)	1.518(3)	C(3)-C(4)	1.382(3)
C(3)-C(2)	1.387(3)	C(5)-C(6)	1.389(3)
C(1)-C(6)	1.393(3)	C(6)-N(1)	1.416(2)
N(1)-C(8)	1.352(3)	C(8)-C(9)	1.496(3)
C(8)-C(10)	1.373(3)	C(10)-C(11)	1.421(3)
C(11)-O(1)	1.252(2)	C(11)-C(12)	1.514(3)
N(1)-H(1)	0.977(2)		

Table 5.5 *Selected Bond Lengths of* ***AcAc4(CH$_3$)A***

	Angles[°]		Angles[°]
C(7)-C(3)-C(2)	120.4(2)	C(7)-C(3)-C(4)	122.2(2)
C(2)-C(3)-C(4)	117.4(2)	C(1)-C(6)-C(5)	118.7(2)
C(5)-C(6)-N(1)	124.5(2)	C(1)-C(6)-N(1)	116.7(2)
C(6)-N(1)-C(8)	130.6(2)	N(1)-C(8)-C(9)	120.7(2)
N(1)-C(8)-C(10)	119.7(2)	C(9)-C(8)-C(10)	119.6(2)
C(8)-C(10)-C(11)	124.6(2)	C(10)-C(11)-O(1)	123.3(2)
C(12)-C(11)-O(1)	118.5(2)	C(12)-C(11)-C(10)	118.2(2)
N(1)-H(1)a...O(1)	132.2(2)		

Table 5.6 *Selected Bond Angles of* ***AcAc4(CH$_3$)***

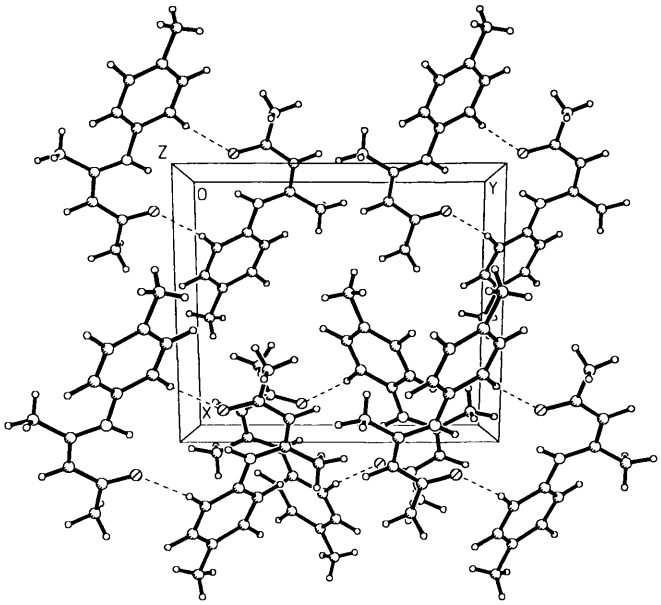


Figure 5.16 ***Packing diagram of AcAc4(CH$_3$)A***

5.3.4 AcAc4FA

AcAc4FA (Figure 5.17) was first purified by the cold finger sublimation method and then recrystallised from ethanol by slow evaporation at low temperature (0-5 °C) giving white blocks. Its crystal system is monoclinic. A strong intramolecular hydrogen-bond is present between the keto-oxygen and N-hydrogen having a bond length 1.911 Å. Intermolecular hydrogen-bonding is also present between the keto-oxygen of one molecule and aryl hydrogen of another having a bond length of 2.552 Å. The intra- and intermolecular hydrogen-bonding is shown in Figure 5.18 and its packing diagram in Figure 5.19. Selected bond lengths and bond angles are given in Tables 5.7 and 5.8 respectively.

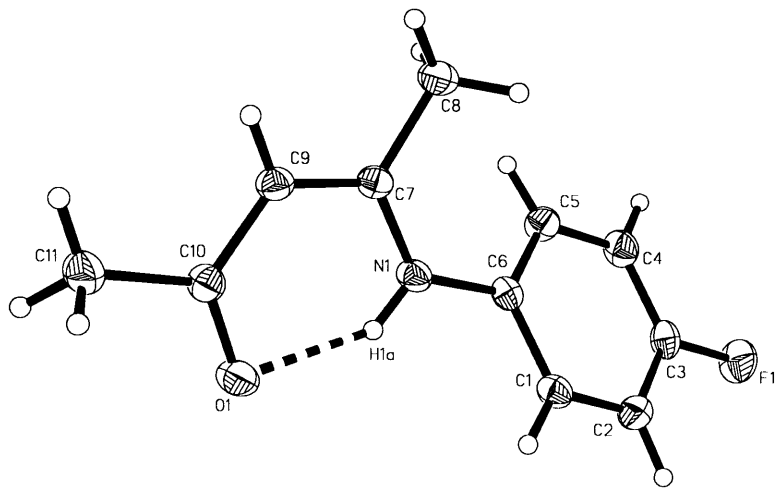


Figure 5.17 ***Molecular structure of AcAc4FA***

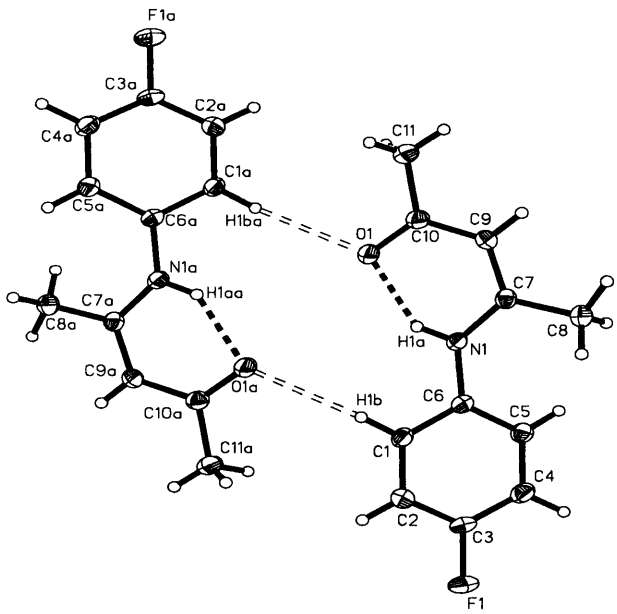


Figure 5.18 ***Inter- and Intramolecular hydrogen-bonding in AcAc4FA molecules***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
F(1)-C(3)	1.362(2)	C(3)-C(4)	1.371(2)
C(3)-C(2)	1.364(2)	C(1)-C(6)	1.387(2)
C(6)-C(5)	1.391(2)	C(6)-N(1)	1.415(2)
N(1)-C(7)	1.353(2)	C(7)-C(8)	1.491(2)
C(7)-C(9)	1.368(2)	C(9)-C(10)	1.422(2)
C(10)-O(1)	1.253(2)	C(10)-(11)	1.504(2)
N(1)-H(1)	0.921		

Table 5.7 *Selected Bond Lengths of **AcAc4F***

	Angles[°]		Angles[°]
F(1)-C(3)-C(2)	118.9(2)	F(1)-C(3)-C(4)	118.8(2)
C(2)-C(3)-C(4)	122.3(2)	C(1)-C(6)-C(5)	119.11(14)
C(1)-C(6)-N(1)	117.13(13)	C(5)-C(6)-N(1)	123.59(14)
C(6)-N(1)-C(7)	130.74(13)	N(1)-C(7)-C(8)	120.26(13)
N(1)-C(7)-C(9)	119.29(14)	C(8)-C(7)-C(9)	120.43(14)
C(7)-C(9)-C(10)	125.3(2)	C(9)-C(10)-O(1)	122.7(2)
O(1)-C(10)-C(11)	118.8(2)	C(9)-C(10)-C(11)	118.4(2)
N(1)-H(1)a...O(1)	143.0		

Table 5.8 *Selected Bond Angles of **AcAc4FA***

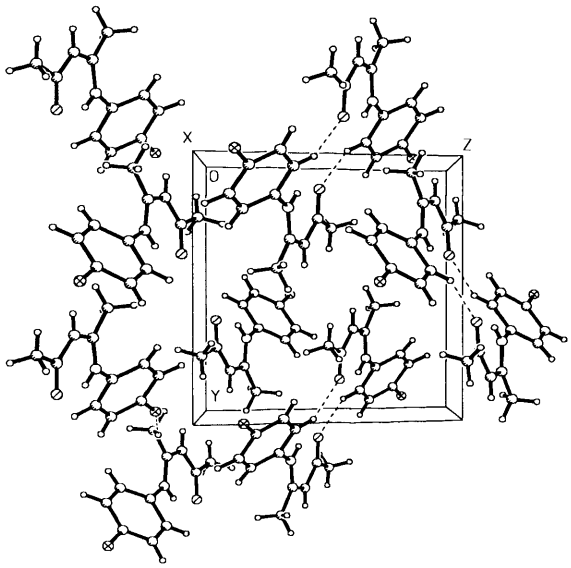


Figure 5.19 ***Packing diagram of AcAc4FA***

5.3.5 AcAc3F,4(CH_3)A

AcAc3F,4(CH_3)A (Figure 5.20) was first purified by sublimation and then recrystallised from ethanol by slow evaporation at low temperature (0-5 °C), giving white blocks. Its crystal system is monoclinic. There is an intramolecular hydrogen-bond present between the keto-oxygen and N-hydrogen having a bond length of 1.937 Å. The O(1)...N(1) bond distance is 2.646 Å. A weak intermolecular hydrogen-bond is also present between the keto-oxygen of one molecule and aryl hydrogen of another, having a bond length of 2.513 Å. The methyl group substituted in the aryl ring is disordered, due to rotation (it may be refined at low temperature). The intra- and intermolecular hydrogen-bonding is shown in Figure 5.21 and its packing diagram in Figure 5.22. Selected bond lengths and bond angles are given in Tables 5.9 and 5.10 respectively.

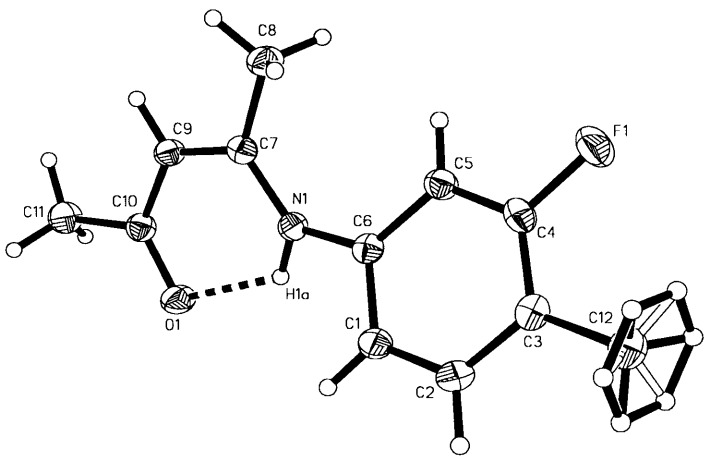


Figure 5.20 ***Molecular structure of AcAc3F,4(CH_3)A***

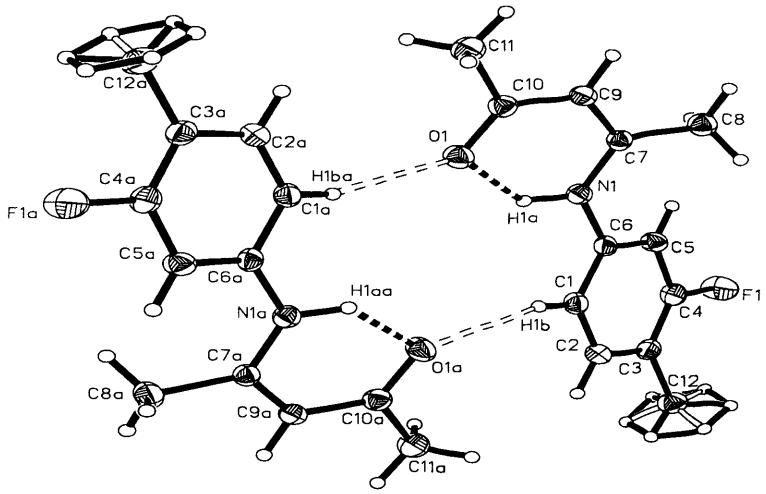


Figure 5.21 ***Inter- and Intramolecular hydrogen-bonding in AcAc3F,4(CH_3)A molecules***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(12)-C(3)	1.502(2)	C(3)-C(2)	1.389(2)
C(3)-C(4)	1.378(2)	C(4)-F(1)	1.365(2)
C(4)-C(5)	1.375(2)	C(6)-C(1)	1.394(2)
C(5)-C(6)	1.392(2)	C(6)-N(1)	1.410(2)
N(1)-C(7)	1.351(2)	C(7)-C(8)	1.495(2)
C(7)-C(9)	1.374(2)	C(9)-C(10)	1.421(2)
C(10)-C(11)	1.505(2)	N(1)-H(1)a	0.950

Table 5.9 *Selected Bond Lengths of* ***AcAc3F,4(CH_3)A***

	Angles[°]		Angles[°]
C(12)-C(3)-C(4)	122.7(2)	C(12)-C(3)-C(2)	122.5(2)
C(2)-C(3)-C(4)	114.8(2)	C(3)-C(4)-F(1)	117.5(2)
F(1)-C(4)-C(5)	117.3(2)	C(3)-C(4)-C(5)	125.1(2)
C(3)-C(2)-C(1)	122.7(2)	C(4)-C(5)-C(6)	118.5(2)
C(5)-C(6)-C(1)	118.6(2)	C(5)-C(6)-N(1)	124.5(2)
C(1)-C(6)-N(1)	116.9(2)	C(6)-N(1)-C(7)	131.33(14)
N(1)-C(7)-C(8)	120.9(2)	C(8)-C(7)-C(9)	119.6(2)
N(1)-C(7)-C(9)	119.4(2)	C(7)-C(9)-C(10)	125.0(2)
C(9)-C(10)-O(1)	122.9(2)	C(9)-C(10)-C(11)	118.2(2)
O(1)-C(10)-C(11)	118.9(2)	N(1)-H(1)A...O(1)	129.7

Table 5.10 *Selected Bond Angles of* ***AcAc3F,4(CH$_3$)A***

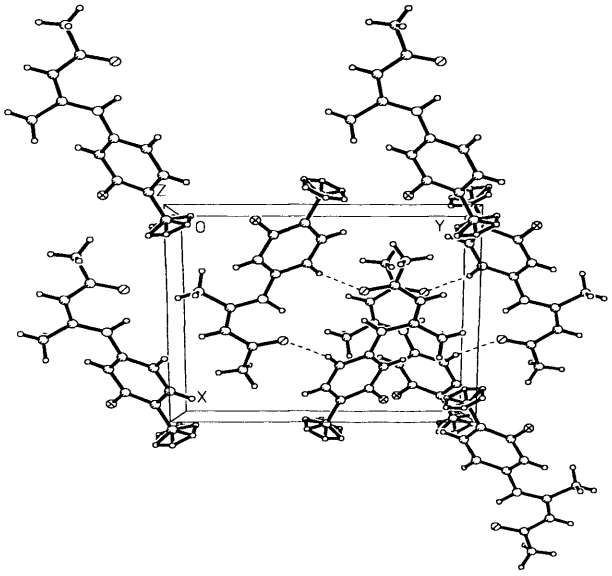


Figure 5.22 ***Packing diagram of AcAc3F,4(CH$_3$)A***

5.3.6 AcAc2(OH)A

AcAc2(OH)A (Figure 5.23) was first purified by cold finger sublimation and then recrystallised from ethanol by slow evaporation at low temperature (0-5 °C), giving white needles. Its crystal system is orthorhombic. The methyl group attached to the carbon bonded to the ketonic oxygen is disordered. An intramolecular hydrogen-bond is present between the keto-oxygen and N-hydrogen having a bond length of 1.891 Å. The N(1)...O(2) bond distance is 2.640 Å. Strong intermolecular hydrogen-bonding is present between the keto-oxygen of one molecule and hydroxyl-hydrogen of another having a bond length of 1.678 Å. The inter- and intramolecular hydrogen-bonding is given in Figure 5.24 and its packing diagram in Figure 5.25. Selected bond lengths and bond angles are given in Tables 5.11 and 5.12 respectively.

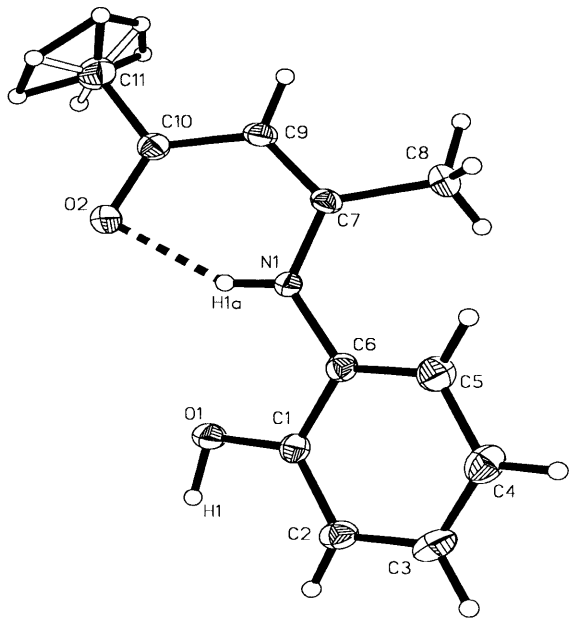


Figure 5.23 ***Molecular structure of AcAc2(OH)A***

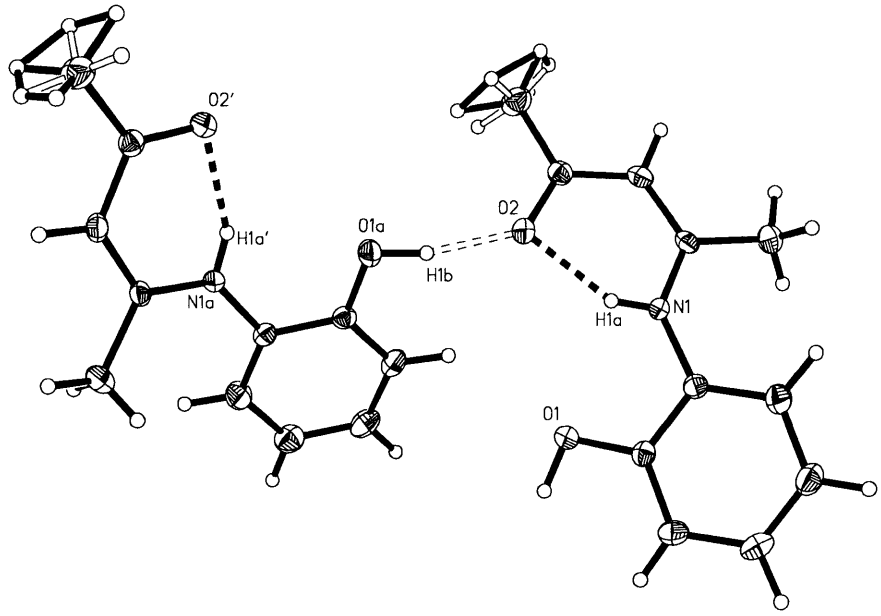


Figure 5.24 ***Inter- and Intra-molecular hydrogen-bonding in AcAc2(OH)A molecules***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
C(1)-O(1)	1.369(4)	C(1)-C(2)	1.381(5)
C(1)-C(6)	1.394(5)	C(5)-C(4)	1.380(5)
C(6)-C(5)	1.389(5)	C(6)-N(1)	1.418(4)
N(1)-C(7)	1.336(4)	C(7)-C(8)	1.502(5)
C(7)-C(9)	1.379(4)	C(9)-C(10)	1.418(5)
C(10)-C(11)	1.496(5)	C(10)-O(2)	1.264(4)
O(1)-H(1)	0.970	N(1)-H(1)A	0.823

Table 5.11 *Selected Bond Lengths of **AcAc2(OH)A***

	Angles[°]		Angles[°]
O(1)-C(1)-C(2)	122.8(3)	O(1)-C(1)-C(6)	116.8(3)
C(2)-C(1)-C(6)	120.3(3)	C(1)-C(6)-C(5)	119.2(3)
C(1)-C(6)-N(1)	116.3(3)	C(5)-C(6)-N(1)	124.3(3)
C(6)-C(5)-C(4)	120.1(4)	C(6)-N(1)-C(7)	131.0(3)
N(1)-C(7)-C(8)	120.5(3)	N(1)-C(7)-C(9)	120.8(3)
C(8)-C(7)-C(9)	118.6(3)	C(7)-C(9)-C(10)	124.5(3)
C(9)-C(10)-C(11)	119.1(3)	C(9)-C(10)-O(2)	121.8(3)
O(2)-C(10)-C(11)	119.1(3)	N(1)-H(1)A...O(2)	150.7

Table 5.12 *Selected Bond Angles of **AcAc2(OH)A***

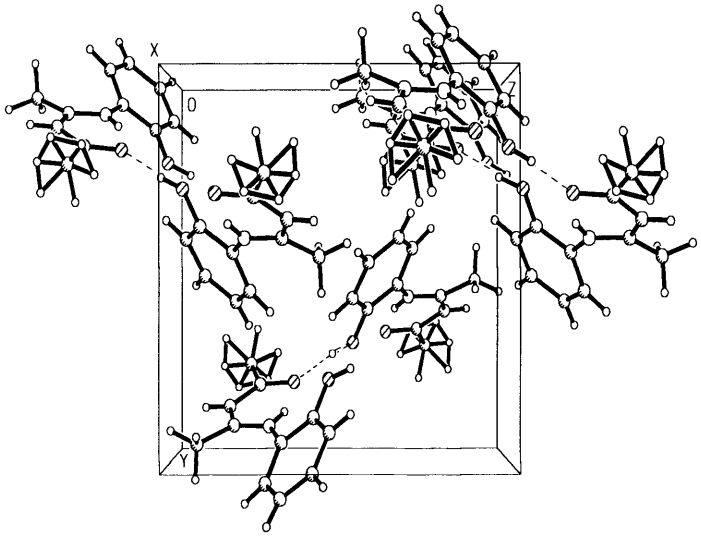


Figure 5.25 ***Packing diagram of AcAc2(OH)A***

5.4 DISCUSSION:-

All of the 4-aminophenyl-3-pentene-2-one structures show intra- and intermolecular hydrogen-bonding. In the case of intermolecular hydrogen-bonding the molecules form chains. In this type of ligand the fluorine substituted at the aniline ring also forms intermolecular hydrogen-bonds. One of the methylene hydrogens is shifted onto the nitrogen. This shift is also verified by ^{1}H and ^{13}C DEPT NMR studies (sections 3.7.3, 3.7.4), and their I.R. spectra (chapter 4). In these ligands there is also no significant substituent effect, all have similar bond lengths and bond angles irrespective of the substituent.

In this group of molecules there are two different types of hydrogen bonding present, inter- and intra-molecular. The intramolecular hydrogen-bond length(N-H...O) is ≈1.89Å and the N.....O bond distance is ≈2.65Å. The NO distance in these molecules is approximately the same as in the case of salicylideneanilines, but in salicylideneanilines the N...H hydrogen-bond has a short bond length(≈1.7Å) as compared to the O...H hydrogen-bond length in AcAcA molecules. Some important bond lengths and bond angles of all the solved AcAcA molecules are given in Table 5.13 and Table 5.14 respectively. The bond distances between N.....O in salicylideneanilines and in AcAcA are given in Table 5.15 for comparison.

The molecular structure of these compounds proved that amino β-diketones exists in ketoamine form instead of enolimine form in solids as was reported for such compounds in solution on the basis of IR[1-4] and NMR[5-7] studies.

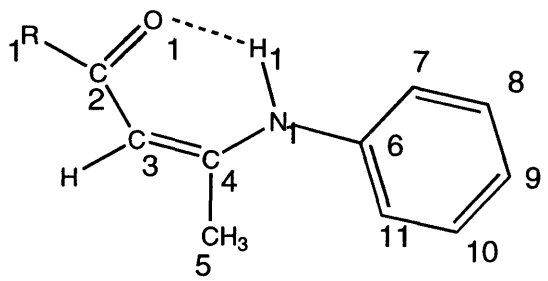
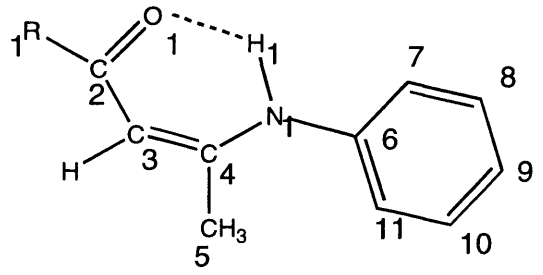


Figure 5.26 ***Numbering of atoms in AcAcA molecules***
R = -CH₃, -CF₃

BONDS	N(1)-C(6)	C(4)-N(1)	N(1)-H(1)	O(1)-H(1)
CF_3AcAcF_5A	1.423(7)	1.322(8)	0.900	1.956(5)
$AcAc4(OCF_3)A$	1.411(3)	1.356(3)	0.957(3)	1.891(2)
$AcAc4(CH_3)A$	1.416(2)	1.352(3)	0.977(2)	1.887(2)
AcAc4FA	1.415(2)	1.353(2)	0.921	1.911
$AcAc3F,4(CH_3)A$	1.41(2)	1.351(2)	0.95	1.937
AcAc2(OH)A	1.418(5)	1.336(4)	0.823	1.891

Table 5.13 *Selected Bond Lengths of CF_3AcAcF_5A, AcAc4FA, $AcAc4(OCF_3)A$, $AcAc4(CH_3)A$, $AcAc3F,4(CH_3)A$* and *AcAc2(OH)A.*



	C(6)-N(1)-C(4)	N(1)-C(4)-C(3)	N(1)-C(4)-C(5)	N(1)-H(1)...O(1)
CF_3AcAcF_5A	126.3(5)	121.0(5)	118.6(8)	134.4
$AcAc4(OCF_3)A$	130.4(2)	119.5(2)	120.7(2)	136.2
$AcAc4(CH_3)A$	130.6(2)	119.7(2)	120.7(2)	132.2
AcAc4FA	130.7(13)	119.2(14)	120.2(13)	143.0
$AcAc3F,4(CH_3)A$	131.3(14)	119.4(2)	120.9(2)	129.7
AcAc2(OH)A	131.0(3)	120.8(3)	120.5(3)	150.7

Table 5.14 *Selected Bond Angles of CF_3AcAcF_5A, $AcAc4(OCF_3)A$, $AcAc4(CH_3)A$, AcAc2(OH)A $AcAc3F,4(CH_3)A$, AcAc4FA.*

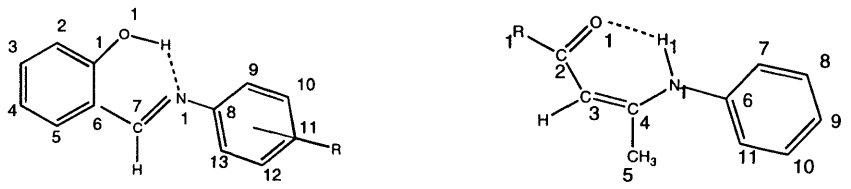


Figure 5.26 ***Molecular structures of AcAcA and SAL for comparasion***

COMPOUNDS	N.....O	COMPOUNDS	N.....O
SAL4(OCF3)A	2.603(6)	AcAc4(OCF3)A	2.665(2)
SAL4(CH3)A	2.597	AcAc4(CH3)A	1.887(7)
SAL4F	2.619(3)	AcAc4FA	1.911
SAL3F,4(CH3)A	2.600	AcAc3F,4(CH3)A	2.646
SALF5	2.616	CF3AcAcF5A	2.665
SAL3,5(CF3)2A	2.631(10)	AcAc2(OH)A	1.891

Table 5.15 *Comparison Of Bond Lengths of N.....O Between SAL and AcAc.*

5.5 REFERENCES:-

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(5) G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 2099, 1961.

(6) G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.,* **84**, 2691, 1962..

(7) G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, **86**, 4283, 1964.

CHAPTER 6

SYNTHESIS AND CHARACTERISATION OF SOME NOVEL SALICYLIDENEANILINE TRANSITION METAL COMPLEXES

6.1 INTRODUCTION:-

A new series of copper(II), nickel(II), cobalt(II) and cobalt(III) complexes derived from Schiff bases, SAL4F, SAL3,5$(CF_3)_2$, SAL4(CF_3), SAL3,5$(CH_3)_2$, and SAL3F,4(CH_3), has been synthesised and characterised by elemental analysis, infra red, UV, mass spectra and NMR data. These complexes were synthesised by following the methods present in the literature.[1-4] The general types of complexes are given in Figures 6.1 and 6.2, where R is an alkyl or aryl group.

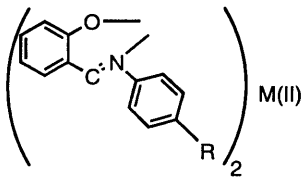


Figure 6.1

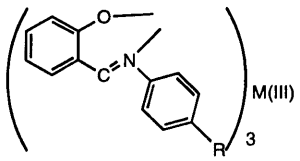


Figure 6.2

The coordination complexes formed between this type of ligand and divalent metal ions are of considerable interest as they vary in structure from planar to tetrahedral. This depends on the nature of the metal and on both the substituent on the nitrogen atom and the substituents, if any, on the aromatic ring of the salicylaldimine molecule[5]. These complexes have a trans arrangement of ligands[6-7]. Complexes of Ni(II) and Co(III) are diamagnetic in nature, some Ni(II) salicylideneimine complexes were found to be paramagnetic in solution.[8-10] Paramagnetism in four-coordinated Ni(II) complexes which would be expected to be diamagnetic, may be due to (a) the formation of six coordinate adducts with two molecules of polar solvents or (b) a planar-tetrahedral equilibrium in solutions in inert solvents.[11-13]

Diamagnetic and paramagnetic species of the complexes, dissolved in non-coordinating solvents have planar structures.[14-15] These complexes also develop paramagnetism when they are in the molten state[16-17] or even on heating.[18] Hence it was concluded by Yamada and Nishikawa[19] that bis[salicylideneimine]Ni(II) complexes showing paramagnetism are actually distorted from a planar configuration, which was later confirmed by X-ray studies[20].

Cu(II) complexes of salicylideneimine and of its N-n-alkyl derivatives have essentially trans-planar structures in the solid state.[21-22] Spectroscopic, i.e. IR[23] and UV[24], evidence suggests that these complexes have the same structures in the solution as in the solid phase.

The relationship between the basic strength and stability was first reported by Calvin[25]. The presence of an electron donating group would make the nitrogen atom more negative and increase the availability of the donor electrons for the M-N bond, whereas an electron withdrawing group would have the opposite effect.

Oxidation of bis-salicylaldimine complexes of Co(II) in solution and in the presence of an excess of the imine leads to the formation of tris-ligand complexes of Co(III), which have the general structure given in Figure 6.2. Co(III) shows a particular affinity for nitrogen donors. According to Sidgwick[26-27], in the case of a bidentate NO donor ligand, neutral nitrogen and negative oxygen may have approximately the same attraction for protons and, other things being equal, should attract metal ions to about the same extent.

In general these complexes were synthesised by a one-pot method, as suggested by Yamada[28]. For the preparation of N-n-alkyl salicylaldimine complexes, atmospheric oxidation suffices, but a stronger oxidising agent such as hydrogen peroxide is needed to produce the N-phenyl derivatives, which tend to be reduced again to the Co(II) complexes on heating in solution[29]. As one salicylaldimine molecule is unable to span opposite corners of the octahedron, only two geometric isomers of these tris Co(III) complexes are expected. These are the *fac* form, in which the nitrogen atoms occupy corners opposite to an oxygen atom, and the *mer* form in which one pair of nitrogen atoms occupy corners opposite to one another. Dipole moment[30], NMR[31] and steric considerations[29-30] predicts that *trans* forms, are most likely to form, but *cis* forms of tris Co(III) chelates with bidentate ligands[trifluoroacetylacetonate and benzoylacetylacetonate] were also reported by Fay and Piper[32-33] on the basis of NMR study.

6.2 GENERAL METHODS OF PREPARATION:-

All the solvents were standard reagent grade and were used without further purification. All other chemicals were from Aldrich and were used as received.

6.2.1 PREPARATION OF Cu^{II} COMPLEXES:-

A solution of copper acetate (1M, 10ml) in a 50% ethanol/water mixture was added to a hot solution of salicylaldehyde and the appropriate aniline (1M, 20ml)[calculated amounts are given in Table 6.1] in ethanol in 1:2 ratio. Precipitation occurred immediately. After the reaction mixture was cooled, the precipitates were filtered, washed with ethanol, recrystallised from $CHCl_3$ as rhombic plates and dried in a desiccator under vacuum.

6.2.2 PREPARATION OF Ni^{II} COMPLEXES:-

A nickel acetate (1M, 10ml) solution in 50% ethanol/water was added to a hot ethanolic solution of the respective ligand (1M, 20ml)[calculated amounts are given in Table 6.1] in 1:2 ratios, and on cooling a few drops of ethanolic NaOH solution were added. The precipitates were filtered, washed with a small amount of ethanol, and dried in a desiccator under vacuum.

6.2.3 PREPARATION OF Co^{II} COMPLEXES:-

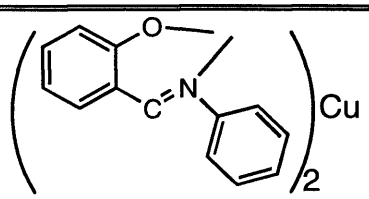
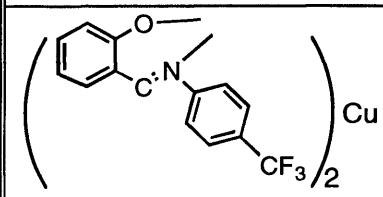
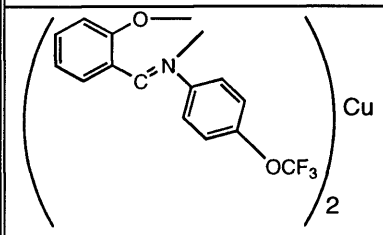
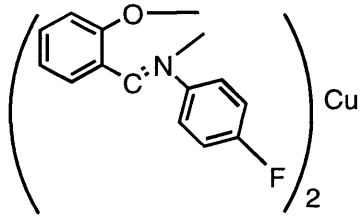
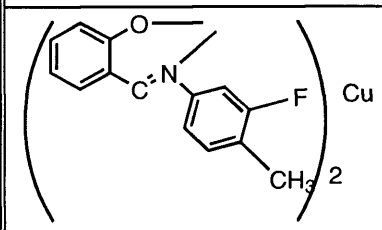
A cobalt acetate (1M, 10ml) solution in 50% ethanol/water mixture was added to an ethanolic solution of the respective ligand (1M, 20ml)[calculated amounts are given in Table 6.2] in 1:2 ratios, and refluxed for 3 to 4 hours. After the reaction mixture was cooled the precipitates were filtered, washed with a small amount of ethanol and dried in a desiccator under vacuum.

6.2.4 PREPARATION OF Co^{III} COMPLEXES:-

A cobalt acetate (1M, 5ml) solution in 50% ethanol/water mixture was added to an ethanolic solution of the respective ligand (1M, 15ml)[calculated amounts are given in Table 6.2] in 1:3 ratio, and refluxed for 3 to 4 hours. On cooling 0.1 ml of 0.1M H_2O_2 was added and the reaction mixture was left for 2 to 3 days. The precipitated solid was filtered and dried in a vacuum desiccator.

LIST OF $Cu[SAL]_2$ AND $Ni[SAL]_2$ COMPLEXES PREPARED

Table 6.1

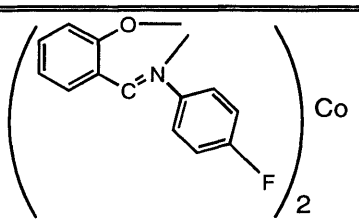
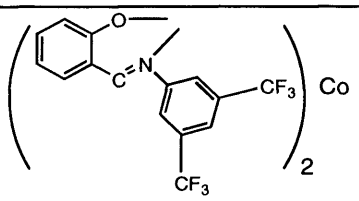
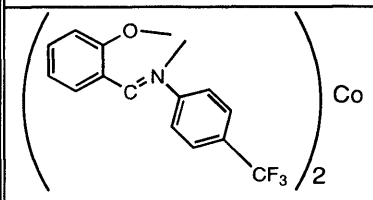
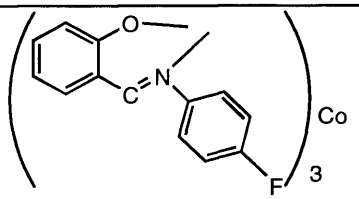
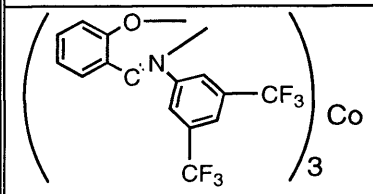
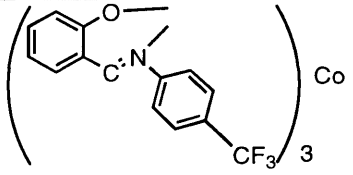
Complexes Formulae	Molecular Formulae	Abbreviation Used	Amounts Used gm
	$C_{26}H_{20}CuN_2O_2$	$Cu[SAL]_2$	Cu(ac) = 1.82 L = 3.96
	$C_{28}H_{18}CuF_6N_2O_2$	$Cu[SAL4(CF_3)]_2$	Cu(ac) = 1.82 L = 5.32
	$C_{28}H_{18}CuF_6N_2O_4$	$Cu[SAL4(OCF_3)]_2$	Cu(ac) = 1.82 L = 5.64
	$C_{26}H_{18}CuF_2N_2O_2$	$Cu[SAL4F]_2$	Cu(ac) = 1.82 L = 4.32
	$C_{28}H_{22}CuF_2N_2O_2$	Cu[SAL3F, $4(CH_3)]_2$	Cu(ac) = 1.82 L = 4.60

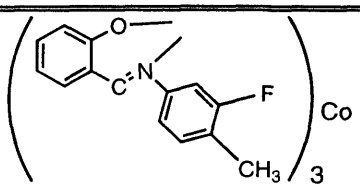
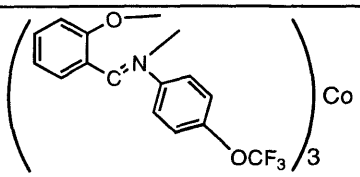
Complexes Formulae	**Molecular Formulae**	**Abbreviation Used**	**Amounts Used gm**
	$C_{30}H_{16}CuF_{12}N_2O_2$	Cu[SAL3,5 $(CF_3)]_2$	Cu(ac)[i] = 1.82 L[ii] = 6.68
	$C_{30}H_{28}CuN_2O_2$	Cu[SAL3,5 $(CH_3)]_2$	Cu(ac) = 1.82 L = 4.52
	$C_{26}H_{18}Cl_2CuN_2O_2$	Cu[SAL4Cl]$_2$	Cu(ac) = 1.82 L = 4.64
	$C_{26}H_{18}F_2NiN_2O_2$	Ni[SAL4F]2	Ni(ac)[iii] = 2.49 L = 4.32
	$C_{26}H_{22}F_2NiN_2O_2$	Ni[SAL3F, 4$(CH_3)]_2$	Ni(ac) = 2.49 L = 4.60

i Copperacetate, ii L = respective ligand, iii nickleacetate

LIST OF Co^{II} AND Co^{III} COMPLEXES

Table 6.2

Complexes Formulae	Molecular Formulae	Abbreviation Used	Amounts Used gm
	$C_{26}H_{18}CoF_2N_2O_2$	$Co[SAL4F]_2$	$Co(ac)^{i} = 2.49$ $L^{ii} = 4.32$
	$C_{30}H_{16}CoF_{12}$ N_2O_2	$Co[SAL3,5$ $(CF_3)_2]_2$	Co(ac) = 2.49 L = 6.68
	$C_{28}H_{18}CoF_6N_2O_2$	Co[SAL4 $(CF_3)]_2$	Co(ac) = 2.49 L = 5.32
	$C_{39}H_{27}CoF_3N_3O_3$	$Co[SAL4F]_3$	Co(ac) = 1.25 L = 3.24
	$C_{45}H_{24}CoF_{18}$ N_3O_3	$Co[SAL3,5$ $(CF_3)2]_3$	Co(ac) = 1.25 L = 5.01
	$C_{42}H_{27}CoF_9N_3O_3$	Co[SAL4 $(CF_3)]_3$	Co(ac) = 1.25 L = 3.39

Complexes Formulae	Molecular Formulae	Abbreviation Used	Amounts Used gm
	$C_{42}H_{33}CoF_3N_3O_3$	Co[SAL3F, 4(CH_3)]$_3$	Co(ac) = 1.25 L = 3.45
	$C_{42}H_{27}CoF_9N_3O_6$	Co[SAL4 (OCF_3)]$_3$	Co(ac) = 1.25 L = 4.23

i Cobaltacetate, ii respective ligand

6.3 EXPERIMENTAL:-

All the complexes were characterised by IR, UV, NMR and Mass spectra. Melting points were obtained using a Griffin apparatus. IR spectra were obtained as solutions in chloroform against a chloroform blank in the 4000 to 650 cm^{-1} region and in a Nujol mull from 650 to 200 cm^{-1}, on a Perkin Elmer 580B spectrophotometer. Electronic spectra were obtained on a Beckmann DU650 spectrometer. ^{1}H, ^{19}F and ^{13}C NMR were recorded on a Bruker AX250 MHz spectrometer. Fast atom bombardment (+FAB) mass spectra were obtained using a Kratos concept double-focussing mass spectrometer by Dr. G. Eaton, using a nitrobenzylamine matrix. C, H and N elemental analysis was performed by Butterworth Laboratories Ltd, Teddington.

6.4 RESULTS AND DISCUSSION:-

6.4.1 PHYSICAL PROPERTIES:-

Table 6.4 Cu(II) AND Ni(II) COMPLEXES

Complexes	M.P. °C	Colour	State	% Yield
$Cu[SAL]_2$	210	Brown	Crystals	75
$Cu[SAL4(CF_3)]_2$	290	Brown	Crystals	75
$CuSAL4(OCF_3)]_2$	205	Brown	Crystals	80
$Cu[SAL4F]_2$	220	Brown	Crystals	85
$Cu[SAL3F,4(CH_3)]_2$	225	Brown	Crystals	82
$Cu[SAL3,5(CF_3)]_2$	273	Brown	Crystal	78
$Cu[SAL3,5(CH_3)]_2$	228	Brown	Crystals	75
$Cu[SAL4Cl]_2$	240	Brown	Crystals	85
$Ni[SAL4F]_2$	85	Green	Powder	65
$Ni[SAL3F,4(CH_3)]_2$	105	Yellow	Powder	70

Table 6.4 Co(II) AND Co(III) COMPLEXES:-

Complexes	M.P. °C	Colour	State	% Yield
$Co[SAL4F]_2$	75	Dark Brown	Powder	70
$Co[SAL3,5(CF_3)]_2$	190	Green	Powder	45
$Co[SAL4(CF_3)]_2$	120	Red	Powder	43
$Co[SAL3,5(CF_3)_2]_3$	160	Dark Brown	Powder	45
$Co[SAL4F]_3$	100	Black	Powder	68
$Co[SAL4(CF_3)]_3$	95	Green	Powder	50
$Co[SAL3F,4(CH_3)]_3$	103	Red	Powder	60
$Co[SAL4(OCF_3)]_3$	58	Dark Green	Powder	52

6.4.2 ELEMENTAL ANALYSIS

Table 6.5

Compounds	% C		% H		% N	
	Cal.	Found	Cal.	Found	Cal.	Found
$Cu[SAL3,5(CF_3)_2]_2$	49.5	49.74	2.21	2.15	3.85	3.56
$Cu[SAL3F,4(CH_3)]_2$	64.6	64.29	4.20	4.18	5.40	5.02
$Cu[SAL4(OCF_3)]_2$	53.76	53.56	2.88	2.58	4.48	4.37

6.4.3 ^{1}H NMR DATA :-

Table 6.6 Co(III) AND Ni(II) COMPLEXES

Compounds	Peaks Assigned	δ	Integral	M[a]
$Co[SAL3,5(CF_3)_2]_3$	CH	8.65	1	s
	Ar[b] H	7.02-7.69	7	m
$Co[SAL4F]_3$	CH	8.59	1	s
	Ar H	6.64-7.67	8	m
$Co[SAL4(CF_3)]_3$	CH	8.62	1	s
	Ar H	6.97-7.70	8	m
$Co[SAL3F,4(CH_3)]_3$	CH_3	1.69	3	s
	CH	8.02	1	s
	Ar H	6.90-7.54	7	m
$Co[SAL4(OCF_3)]_3$	CH	8.13	1	s
	Ar H	6.57-7.03	8	m
$Ni[SAL4F]_2$	CH	7.70	1	s
	Ar H	6.47-7.69	8	m
$Ni[SAL3F,4(CH_3)]_2$	CH_3	1.7	3	s
	CH	8.04	1	s
	Ar H	6.60-7.22	7	m

a M = Multiplicity, b Ar = Aromatic

NMR DISCUSSION:-

^{1}H NMR spectra of Co(III) complexes gave unsplit peaks for -CH and -CH_3 protons, which shows that these complexes are *fac* forms. Similar unsplit spectra of *fac* forms of Co(III) chelates with trifluoroacetylacetonate[32] and benzoylacetonate[33] have been reported in the literature.

In Co(III) complexes there is no significant substituent effect on chemical shift observed in the case of Co[SAL3,5$(CF_3)_2$]$_3$, Co[SAL4F]$_3$ and Co[SAL4(CF_3)]$_3$, but for Co[SAL4(OCF_3)]$_3$ and Co[SAL3F,4(CH_3)]$_3$ a significant shift of 0.5 ppm in the peak for methylene -CH towards high field side is observed. A similar shift was observed in Ni(II) complexes. In Ni[SAL4F]$_2$ the chemical shift for the methylene -CH proton is ≈1 ppm and for Ni[SAL3F,4(CH_3)]$_2$ the shift for methylene -CH proton is ≈0.5 ppm towards the high field side.

^{1}H NMR chemical shifts of -CH, ArH and -CH_3 in the complexes are compared with those for the respective free ligands in Table 6.7. A significant shift in -CH is observed in Co(III) complexes, with -3F,4(CH_3) and -4(OCF_3) substituents, 0.5 ppm towards high field side, but no significant shift was observed for the -3,5$(CF_3)_2$, -4F and -4(CF_3) substituted complexes. Significant shifts were observed for the aromatic protons for complexes with -4F and -4(OCF_3) substituents. -CH_3 protons were significantly shifted on coordination.

In Ni(II) chelates a significant shift was observed in all the three types of protons i.e. -CH, ArH and -CH_3 with both substituents -4F and-3F,4(CH_3)

towards high field side, as compared to their respective free ligands. A comparison between the shifts in free ligands and their respective Co(III) and Ni(II) chelates is given in Table 6.7.

Most of the diamagnetic Ni(II) complexes become paramagnetic in solution and show broad ^{1}H NMR peaks. This behaviour is quite different from that of the Co(II) and Cu(II) complexes. The explanation for this change in magnetic properties of these Ni(II) chelates from diamagnetic to paramagnatic was given by Clark and Odell[12]. On the basis of their studies they concluded that in some solvents like pyridine nickel in Ni(II) chelates forms octahedral complexes by coordinating with two solvent molecules and becoming paramagnetic, these paramagnetic Ni(II) chelates gave slightly broad NMR peaks. The methylene -CH peak and ^{1}H NMR spectrum of $Co[SAL4F]_3$ is given in Figure 6.3 and 6.4 respectively.

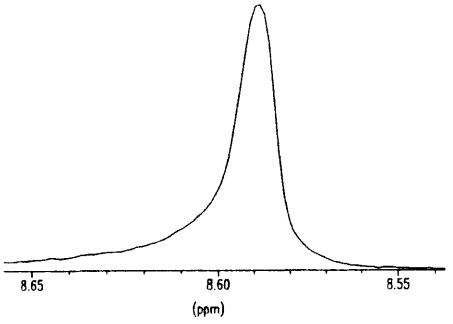


Figure 6.3 *-CH Peak of Co[SAL4F]$_3$ in ^{1}H NMR Spectrum*

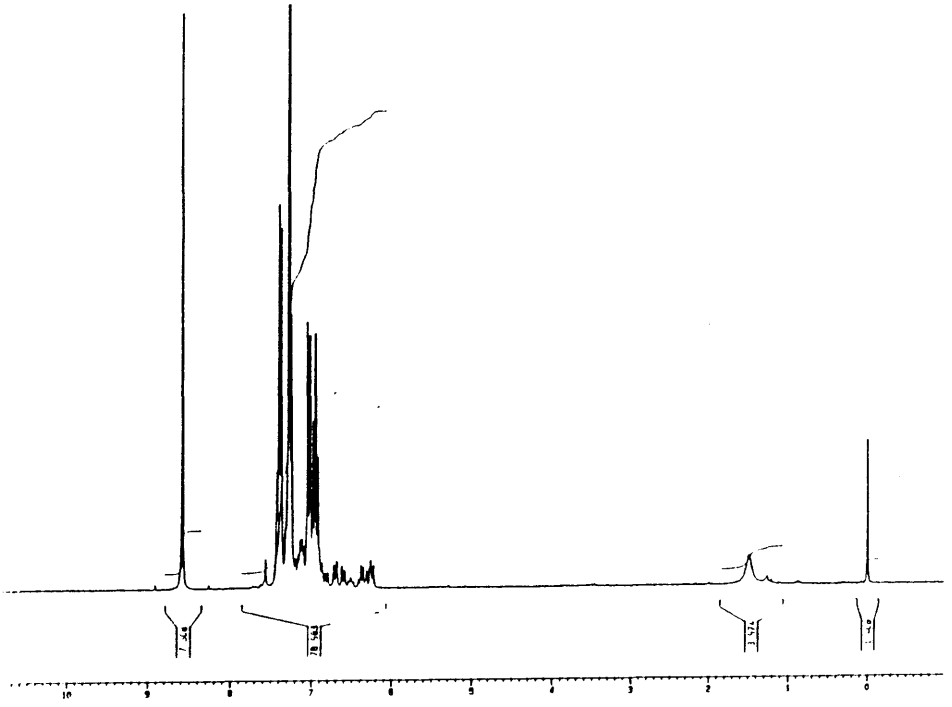


Figure 6.4 *^{1}H NMR Spectrum of Co[SAL4F]$_3$*

Table 6.7 *Comparison between shifts of C-H, ArH and -CH_3 of Co(III) and Ni(II) chelates and their free ligands.*

Substituted Groups	C-H δ ppm			ArH δ ppm			$-CH_3$ δ ppm		
	Lig[a]	Che[b]	Shift[c]	Lig*	Che[a]	Shift[c]	Lig*	Che[a]	Shift[c]
-3,5$(CF_3)_2$	8.58	8.65	(0.07)	6.88-7.7	7.02-7.69	(0.12)	-	-	-
-4F (Ligand)	8.77			7.1-7.6			-	-	-
Co(III)L_3		8.59	(0.18)		6.64-7.67	0.47			
Ni(II)L_2		7.7	1.07		7.1-7.6	0.63			
-3F,4(CH_3) (ligand)	8.59			6.9-7.41			2.3		
Co(III)L_3		8.02	0.57		6.9 - 7.54	(0.1)		1.69	0.6
Ni(II)L_2		8.04	0.5		6.60-7.22	0.3		1.7	0.6
-4(OCF_3)	8.69	8.13	0.56	7.0-7.5	6.5-7.03	0.5	-	-	-
-4(CF_3)	8.47	8.62	(0.15)	6.79-7.59	6.97-7.70	(0.1)	-	-	-

[a = Ligand, b = Chelates, c = High Field].

6.4.4 IR DATA :-

Table 6.8 Cu(II) AND Ni(II) COMPLEXES

Complexes	$\nu_{(C=N)}/cm^{-1}$	$\nu_{(C-N)}/cm^{-1}$	$\nu_{(C\_O)}/cm^{-1}$	$\nu_{(M\_N)}/cm^{-1}$	$\nu_{(M\_O)}/cm^{-1}$
$Cu[SAL]_2$	1590 (1611[23])	1370	1150	530 (529[23])	490 (495[23])
$Cu[SAL4(CF_3)]_2$	1580	1370	1110	550	470
$Cu[SAL4(OCF_3)]_2$	1530	1370	1150	535	415
$Cu[SAL4F]_2$	1580	1360	1140	520	450
$Cu[SAL3F,4(CH_3)]_2$	1580	1360	1140	520	435
$Cu[SAL3,5(CF_3)_2]_2$	1530	1380	1130	530	500
$Cu[SAL3,5(CH_3)_2]_2$	1530	1390	1140	555	410
$Cu[SAL4Cl]_2$	1580	1370	1200	525	425
$Ni[SAL4F]_2$	1550	1360	1140	540	430
$Ni[SAL3F,4(CH_3)_2]_2$	1570	1360	1140	520	415

Table 6.9 Co(II) AND Co(III) COMPLEXES

Complexes	$\nu_{(C=N)}/cm^{-1}$	$\nu_{(C\_O)}/cm^{-1}$	$\nu_{(C\text{-}N)}/cm^{-1}$	$\nu_{(M\_N)}/cm^{-1}$	$\nu_{(M\_O)}/cm^{-1}$
$Co[SAL]_2$	1600 (1607[23])	1210	1310	520 (519[23])	480 (494[23])
$Co[SAL4F]_2$	1530	1150	1330	510	460
$Co[SAL3,5(CF_3)_2]_2$	1530	1120	1320	520	470
$Co[SAL4(CF_3)]_2$	1520	1140	1340	560	470
$Co[SAL3,5(CF_3)_2]_3$	1520	1130	1320	540	490
$Co[SAL4F]_3$	1560	1100	1370	530	490
$Co[SAL4(CF_3)]_3$	1570	1170	1320	540	480
$Co[SAL3F,4(CH_3)]_3$	1580	1190	1360	570	500
$Co[SAL4(OCF_3)]_3$	1550	1110	1320	570	490

IR DISCUSSION:-

IR data for Cu(II), Ni(II), Co(II) and Co(III) chelates are given in Tables 6.8 and 6.9. In M(II) [Cu(II), Co(II) and Ni(II)] chelates the M-N bands are in the region 400-500 cm^{-1} and the M-O the bands are in the region 500-570cm^{-1}. This is consistent with the previous work described in the literature for M-N and M-O bonds for NO donor imine chelates[24]. No substituent effects on M-N and M-O bands are observed. Very small differences in ν values for Co-N bond were observed in the case of Co(III) as compared to Co(II), whereas significant differences had been expected.

The free ligands exhibit bands at 1600-1650 cm^{-1} and 1200-1250 cm^{-1} due to ν(HC=N) and ν(C-O) groups respectively, which in the complexes are shifted towards lower frequency, to 1500-1550 cm^{-1} and 1100-1150 cm^{-1} for ν(C=N) and ν(C-O) respectively. According to the X-ray studies the C-O bond length becomes shorter in chelates as compared to the free ligands. So its band was expected to appear at higher frequency. The observed lowering of frequency may be due to the replacement of the light hydrogen atom by a metal atom, in chelated form, which compels the C-O bond to vibrate slowly.

The disappearance of the band in the region 3600-4000 cm^{-1} due to the -OH group in the spectra of the chelates of Cu(II), Co(II), Co(III) and Ni(II) confirms the deprotonation of the -OH group on coordination to the metal through the oxygen atom. This is also supported by ^{1}H NMR spectra, which show no peak for -OH in the region of 9 - 11 ppm.

Comparison of ν_{C-N} cm^{-1} for free ligands with their respective chelates is given in Table 6.10. $\nu_{C=N}$, ν_{C-O}, ν_{M-N} and ν_{M-O} $cm^{-1}$for M(II) and M(III) chelates with -4F -4(CF_3) 3F,4(CH_3), and -4(OCF_3) substituents are compared in Table 6.11. ν_{M-N} and ν_{M-O} cm^{-1} for all of the chelates are compared in Tables 6.12 and 6.13 respectively.

Table 6.10 *Comparison of C-N stretch between free ligands and their Cu(II), Ni(II), Co(II) and Co(III) complexes*

	ν_{C-N} /cm^{-1}				
	Ligand	**Cu(II) Che[a]**	**Ni(II) Che[a]**	**Co(II) Che[a]**	**Co(III) Che[a]**
SAL	1380	1370	-	1310	-
SAL4F	1360	1360	1360	1360	1370
SAL4Cl	1380	1370	-	-	-
SAL4(CF3)	1370	1370	-	1340	1320
SAL4(OCF3)	1350	1370	-	-	1320
SAL3,5(CF_3)$_2$	1350	1380	-	1320	1320
SAL3,5(CH_3)$_2$	1350	1390	-	-	-
SAL3F,4(CH_3)	1360	1360	1360	-	1360

a = Chelates

Table 6.11 *Comparison of $\nu_{C=N}$, ν_{C-O}, ν_{M-N} and ν_{M-O} for M(II) and M(III) chelates with -4F and 3F,4(CH3) substituents.*

Ligands →	SAL3,5(CH_3)$_2$ *SAL3F,4(CH_3)* SAL4(CF_3) **SAL4F**			
Chelates ↓	**$\nu_{C=N}$ cm^{-1}**	**ν_{C-O} cm^{-1}**	**ν_{M-N} cm^{-1}**	**ν_{M-O} cm^{-1}**
Cu(II)	1530 *1580* 1580 **1580**	1130 *1140* 1110 **1140**	530 *520* 550 **520**	500 *435* 470 **450**
Ni(II)	- *1570* - **1550**	- *1140* - **1140**	- *520* - **540**	- *415* - **430**
Co(II)	1530 - 1520 **1530**	1320 - 1340 **1150**	520 - 560 **510**	470 - 470 **460**
Co(III)	1520 *1580* 1560 **1560**	1320 *1190* 1370 **1100**	540 *570* 530 **530**	490 *500* 490 **490**

Table 6.12 *Comparison of ν_{M-N} cm^{-1} of M(II) and M(III) chelates*

Ligands	ν_{M-N} cm^{-1}			
	Cu(II)	Ni(II)	Co(II)	Co(III)
SAL	530	-	520	-
SAL4F	520	540	510	530
SAL4(CF_3)	550	-	560	540
SAL4(OCF_3)	535	-	-	570
SAL3,5(CF_3)$_2$	530	-	520	540
SAL3F,4(CH_3)	520	520	-	570

Table 6.13 *Comparison of ν_{M-O} cm^{-1} for M(II) and M(III) chelates*

Ligands	ν_{M-O} cm^{-1}			
	Cu(II)	Ni(II)	Co(II)	Co(III)
SAL	490	-	494	-
SAL4F	450	430	460	490
SAL4(CF_3)	470	-	470	480
SAL3,5(CF_3)$_2$	500	-	470	480
SAL4(OCF_3)	415	-	-	490
SAL3,4(CH_3)	435	415	-	500

6.4.5 MASS SPECTROSCOPIC RESULTS:-

Table 6.14 Cu(II) AND Ni(II) COMPLEXES

Complexes	Calculated Mass	Ions Observed
$Cu[SAL]_2$	456	$^+$FAB 456CuL_2, 259CuL_1, 518Cu_2L_2, 716Cu_2L_3
$Cu[SAL4(OCF_3)]_2$	624	$^+$FAB 625CuL_2, 343CuL_1, 686Cu_2L_2, 968Cu_2L_3
$Cu[SAL3F,4(CH_3)]_2$	520	$^+$FAB 520CuL_2, 291CuL_1, 582Cu_2L_2, 812Cu_2L_3
$Cu[SAL4(CF_3)]_2$	593	$^+$FAB 592CuL_2, 328CuL_1
$Cu[SAL4F]_2$	493	$^+$FAB 492CuL_2, 277CuL_1, 554Cu_2L_2, 768Cu_2L_3
$Cu[SAL4Cl]_2$	525	$^+$FAB 526CuL_2, 293CuL_1, 588Cu_2L_2, 716Cu_2L_3
$Cu[SAL3,5(CF_3)_2]_2$	728	$^+$FAB 728CuL_2, 395CuL_1

Complexes	Calculated Mass	Ions Observed
$Cu[SAL3,5(CH_3)_2]_2$	512	$^+$FAB 513CuL_2, 287CuL_1, 574Cu_2L_2, 800Cu_2L_3
$Ni[SAL4F]_2$	487	$^+$FAB 486NiL_2, 273NiL_1, 572Ni_2L_2, 758Ni_2L_3
$Ni[SAL3F,4(CH_3)]_2$	515	$^+$FAB 514NiL_2, 287NiL_1, 572Ni_2L_2, 800Ni_2L_3

DISCUSSION:

All the chelates of M(II) and M(III) gave very significant peaks for ML_2 and ML_3 molecular ions respectively, and also gave significant peaks for ML_1, M_2L_2 and M_2L_3. M_2L_2 and M_2L_3 are thought to be formed in the gas phase at high temperature within the ionising tube. This difference between solution and gas phase may be because in solution of chelates different bonds break because of solvation and nucleophilic attack but in the gas phase the weakest bond breaks, due to high kinetic energy.

In the mass spectra of Co(II) complexes a peak for ML_1X where X = Ph(O)CH=N was also observed. Similarly, peaks for ML_1X and ML_2X were observed for Co(III) chelates, which is consistent with the behaviour of the Co(II) chelates. This fragmentation was observed for -3,5$(CF_3)_2$, -4(CF_3) and -4(OCF_3) substituents, but not for -4F and 3F,4(CH_3) substituents. No ML_nX peaks were observed in the mass spectra of any of the Cu(II) or Ni(II) chelates. This unusual behaviour of the Co(II) and Co(III) complexes, as compared to Ni(II) and Cu(II), is still not clear. It was thought that the =N-aryl bond weakens upon coordination with metals, which effect is more enhanced in Co(II) and Co(III) as compared to Cu(II) and Ni(II). This weakening of the =N-aryl bond was also noticed in IR studies; comparison of C-N stretches in free ligands with their respective Cu(II), Ni(II), Co(II) and Co(III) chelates is given in Table 6.10. Mass spectra of $Cu[SAL4F]_2$, $Ni[SAL4F]_2$, $Co[SAL4CF_3]_2$ and $Co[SAL4CF_3]_2$ are given in Figures 6.5, 6.6, 6.7 and 6.8 respectively.

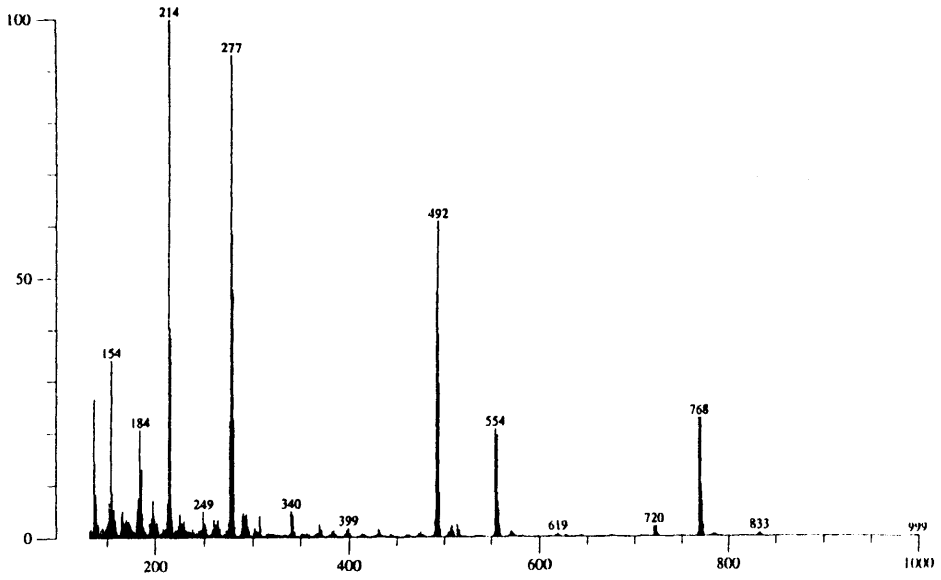


Figure 6.5 *Mass Spectrum of Cu[SAL4F]$_2$*

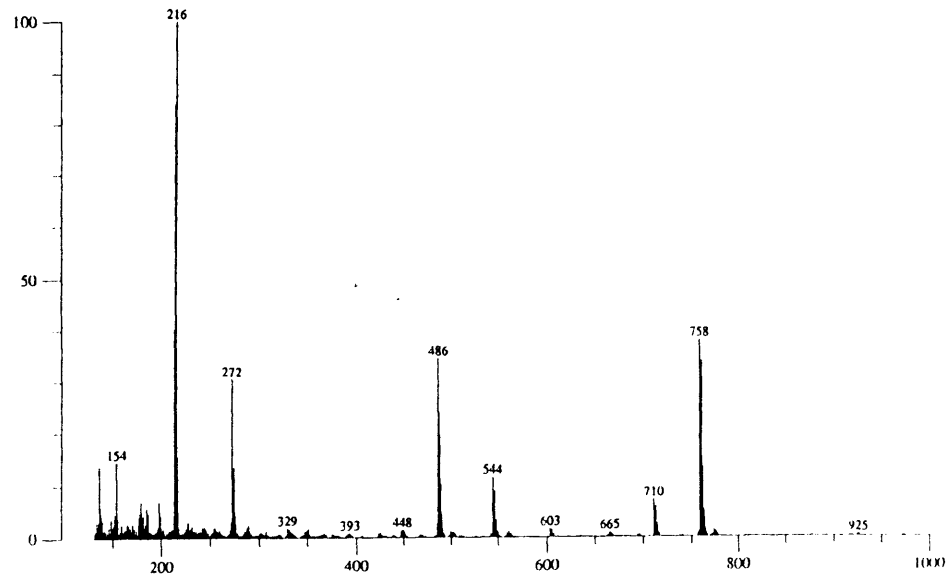


Figure 6.6 *Mass Spectrum of Ni[SAL4F]$_2$*

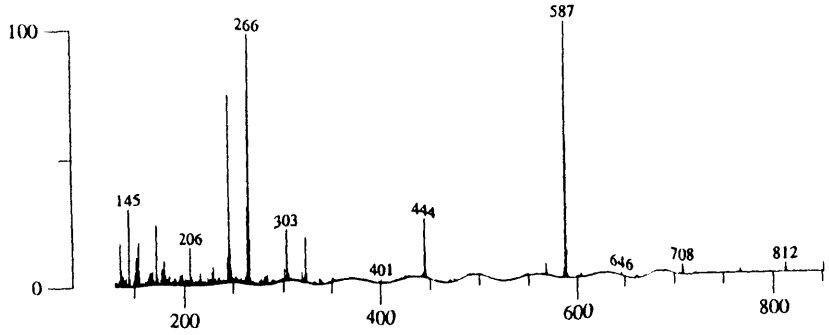


Figure 6.7 *Mass Spectrum of* $Co[SAL4(CF_3)]_2$

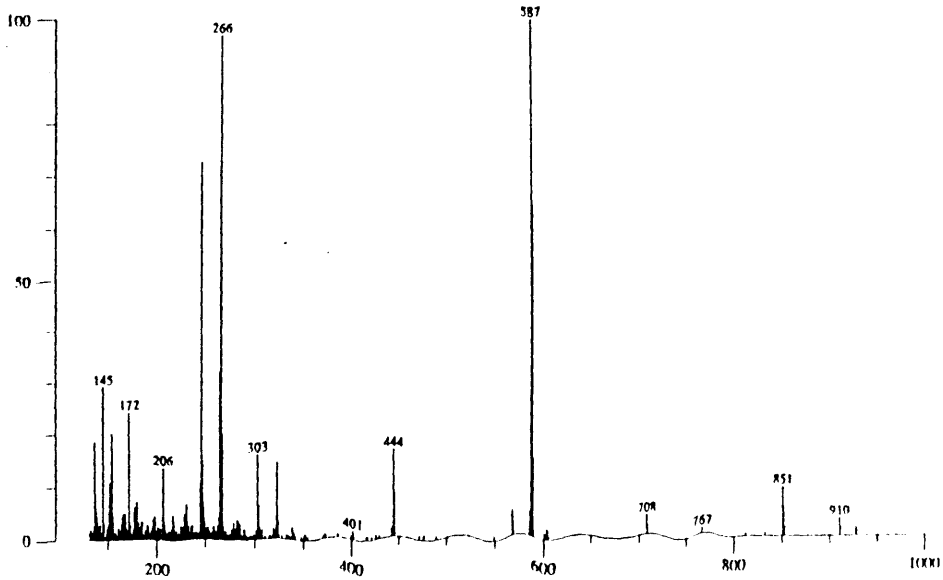


Figure 6.8 *Mass Spectrum of* $Co[SAL4(CF_3)]_3$

6.4.6 UV/VIS SPECTROSCOPY:-

All seven Cu(II) chelates gave bands in the visible region, in the range 650 to 670 nm. The parent complex, Cu[SAL] with no substituent, gave a peak at 667.5 nm, which is the highest value, and Cu[SAL4Cl] gave a peak at 650 nm which is the lowest value. All other chelates gave peaks in between 650 and 667 nm, the λ_{max}, ν, E(calc. from E = hν) and Hammett σ values are given in Table 6.13.

Table 6.13 *λmax, ν, E and Hammett σ values for Cu(II) complexes. σ and λmax values for $Cu[H_2O]_6$, $Cu[(NH_3)_4(H_2O)_2]$, $Cu[en]_2$, $Cu[acac]_2$ and $Cu[CH_3CHO]_2$ values are collected from literature*

Chelates	λ_{max}/nm	ν/s^{-1} $\times10^{14}$	$E/Jmol^{-1}$ $\times10^{10}$	σ^a
$Cu[SAL]_2$	667.5	3.40	23.21	0.0
$Cu[SAL4(CF_3)]_2$	655.0	3.50	23.21	0.53
$Cu[SAL4F]_2$	660.0	3.48	23.10	0.15
$Cu[SAL4Cl]_2$	650.0	3.53	23.40	0.24
$Cu[SAL4(OCF_3)]_2$	657.0	3.50	23.21	
$Cu[SAL3F,4(CH_3)]_2$	650.0	3.54	23.47	0.20^b
$Cu[SAL3,5(CF_3)_2]_2$	655.0	3.50	23.21	0.46
$Cu[H_2O]_6$[34]	800.0	2.90	19.23	
$Cu[(NH_3)_4(H_2O)_2]$[34]	600.0	3.83	25.39	
$Cu[en]_2$[35]	540.0	4.15	27.51	
$Cu[acac]_2$[36,37]	654.0	3.52	23.34	
$Cu[CH_3CHO]_2$[36]	660.0	3.48	23.1	

a = ref. 38 and 39, b = sum of +0.34 for p(-F) and -0.14 for m($-CH_3$)

Many other Cu(II) chelates with O and N donor ligands e.g NH_3, H_2O, ethylenediamine (en), acetylacetone (acac) and salicylaldehyde (SA), gave bands in the visible region approximately in the same region of 550 to 675 nm. A spectrochemical series was established with the energy ($E = h\nu$) values of these ligands, fitting them between the values for H_2O and en, considering H_2O as the weakest and en as the strongest ligand. The order of ligand strength is

H_2O < SAL < SA = SAL4F < SAL4(OCF_3) < SAL3,5(CF_3)$_2$ = SAL4(CF_3) < SAL3F,4(CH_3) = acac < NH_3 < en

As well as the d-d band in the visible region, there were two other peaks in the UV region, one at 250 to 300 nm, and other at 300 to 380 nm. There are many possibilities for these peaks to appear, they may be due to ligand transitions, π to π^* delocalised bond transitions, or may be due to charge transfer.

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CHAPTER 7

STRUCTURE DETERMINATION OF SOME NOVEL SUBSTITUTED SALICYLIDENEANILINE COPPER(II) COMPLEXES

7.1 INTRODUCTION:-

This chapter describes the structures of some novel copper(II) salicylaldimine complexes which were determined by single crystal X-ray diffraction. The synthesis and characterisation of these complexes have been given in chapter 6. Information concerning bond lengths and bond angles has been gathered here.

The 4-coordinate complexes formed with divalent metal ions are of considerable interest as they vary in structure from planar to tetrahedral, not only in dependence on the nature of the divalent metal involved, but also on the nature of the substituent on the nitrogen atom and the substituents, if any, on the aromatic ring of the salicylaldimine molecule. The complexes of salicylaldimine itself (R = H) with Ni(II), Cu(II) and Pd(II) are all planar and crystallise in isomorphous forms.

X-Ray diffraction studies show that an N-phenyl group causes considerable distortion from overall coplanarity in the molecule.[1-3] Distorted tetrahedral coordination occurs in some bis(salicylaldiminato) complexes, where R is bulky.

Stackelberg[4] confirmed the planar configuration for a number of copper chelates of the salicylaldehyde-imine type by means of X-ray crystal analysis[Figure 7.1]. For the anil chelates the benzene ring attached to the donor nitrogen is not coplanar with the rest of the molecule, but the four donor atoms are still coplanar with the central copper atom. In the

case of bis salicylaldehyde-anil Cu(II) the arrangement of the donors is trans, since the copper atom was shown to be the centre of symmetry.

The trans arrangement had already been demonstrated for a number of planar chelates of Cu, Ni, Pt and Pd by Cox *et al*[5,6]. Whereas all the bonds of the imine nitrogens lie in the plane of the metal chelate, phenyl groups attached to them are rotated out of the plane. Since there is no possibility of resonance interaction between the anil nitrogen and the phenyl group, as there are no free electron pairs in the nitrogen atom after chelation takes place, the N-phenyl bond is a purely single bond and the phenyl group would be free to rotate.

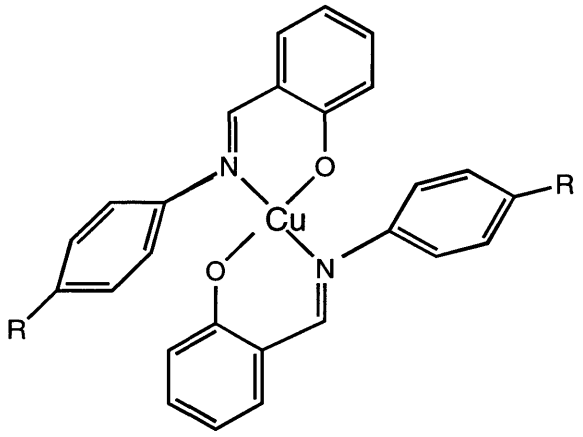

Figure 7.1 *General formula of bis[N-phenyl salicylaldimine]Cu(II) chelate.*

7.2 METHOD OF CRYSTALLISATION:-

To a concentrated solution of the copper salicylidimine complex in $CHCl_3$, petroleum ether(40-60 °C) was added down the side of the tube so that it formed a separate layer. The solution was left for a few days, during which the complex crystallised out as brown rhombic plates.

7.3 STRUCTURAL STUDY OF SALICYLIDENE ANILINE COPPER(II) COMPLEXES:-

All four of the complexes prepared for this work have been investigated using X-ray crystallography. Their formulae are shown in Figure 7.2, 7.3, 7.4, 7.5.

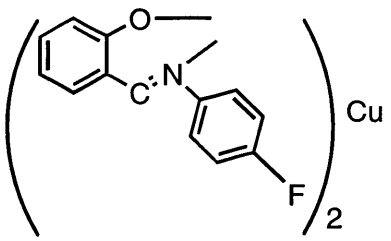

Figure 7.2 Cu[SAL4F]$_2$

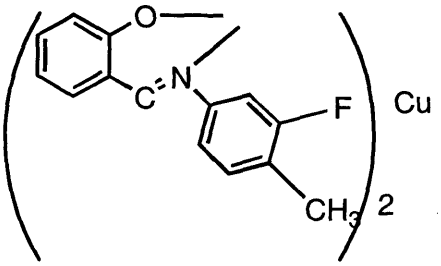

Figure 7.3 **Cu[SAL3F,4(CH_3)]$_2$**

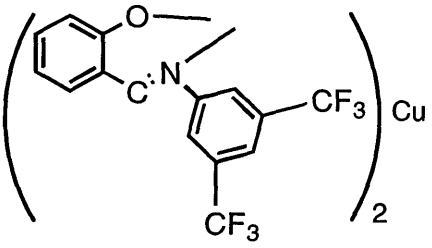

Figure 7.4 **Cu[SAL3,5(CF_3)$_2$]$_2$**

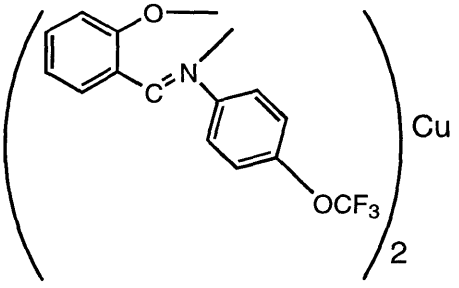

Figure 7.5 **Cu[SAL4(OCF_3)]$_2$**

7.3.1 Cu-Bis-SALICYLIDENE 4-FLUORO ANILINE:-

The $Cu[SAL4F]_2$ crystal system is triclinic with space group P-1. Its R value is 0.05. The N-phenyl group is rotated by an angle of 56.4° from the overall coplanarity of the CuN_2O_2 unit. Packing and 3D stereo pair diagrams are given in Figures 7.7 and 7.8. Selected bond lengths and bond angles are given in Tables 7.1 and 7.2 respectively.

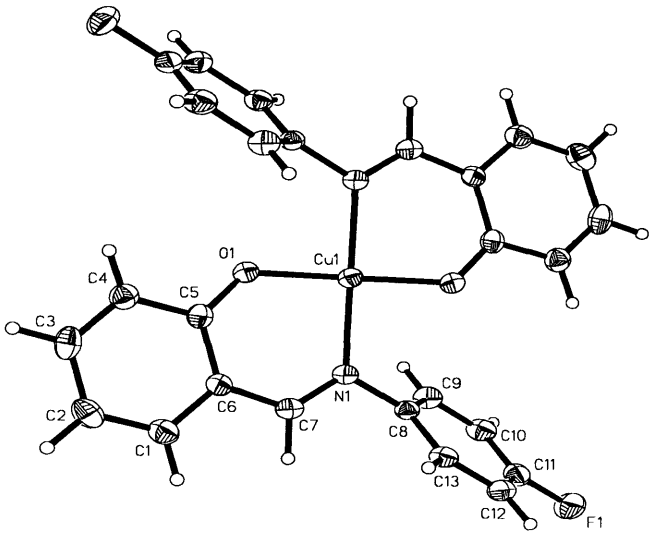

Figure 7.6 ***Cu[SAL4F]$_2$***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
N(1)-Cu(1)	2.007(4)	O(1)-Cu(1)	1.885(4)
C(7)-N(1)	1.285(6)	C(5)-O(1)	1.308(6)
C(8)-N(1)	1.440(7)	C(5)-C(6)	1.419(7)
C(9)-C(8)	1.389(7)	C(6)-C(7)	1.435(8)
C(8)C(13)	1.392(8)	C(11)-C(12)	1.368(9)
C(10)-C(11)	1.357(9)	C(11)-F(1)	1.369(7)

Table 7.1 *Selected Bond Lengths of Cu-bis-salicylidene-4-fluoro aniline.*

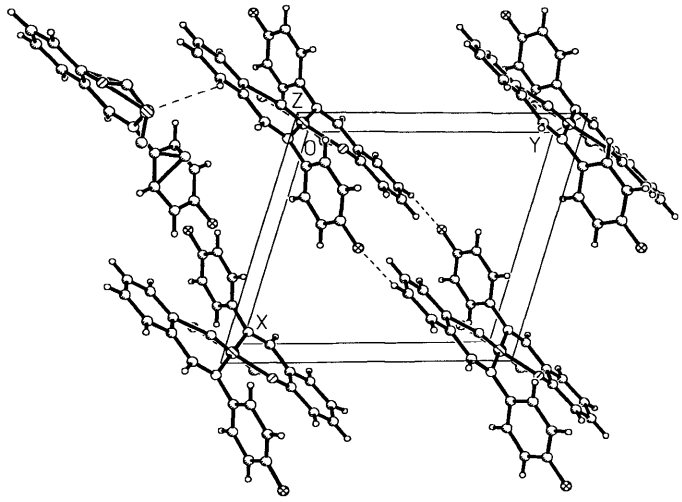

Figure 7.7 ***Packing Diagram of Cu[SAL4F]$_2$***

	Angles[°]		Angles[°]
O(1)-Cu(1)-N(1)	91.1(2)	C(5)-O(1)-Cu(1)	129.8(4)
C(7)-N(1)-Cu(1)	123.4(4)	C(5)-C(6)-C(7)	122.4(5)
C(7)-N(1)-C(8)	116.2(4)	C(9)-C(8)-C(13)	119.7(5)
O(1)-C(5)-C(6)	123.1(5)	N(1)-C(6)-C(7)	127.3(5)
C(10)-C(11)-C(12)	122.4(6)	C(12)-C(11)-F(1)	119.0(6)
C(10)-C(11)-F(1)	118.6(6)		

Table 7.2 *Selected Bond Angles of Cu bis-salicylidene-4-fluoro aniline.*

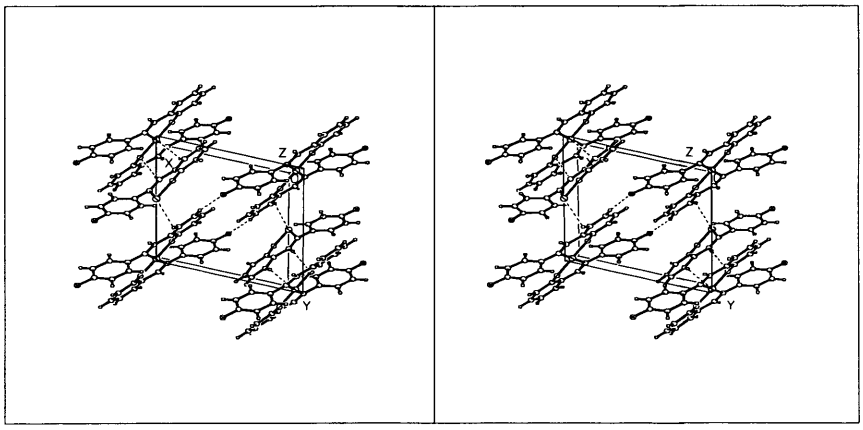

Figure 7.8 *3D Stereo pair of Cu-bis-salicylidene-4-fluoro aniline*

7.3.2 Cu-Bis-SALICYLIDENE 3-FLUORO 4-METHYL ANILINE

The $Cu[SAL3F,4(CH_3)]_2$ crystal system is orthorhombic with space group Pbca. Its R value is 0.044. The structure diagram is given in Figure 7.9. In this structure the substituted fluorine atom and the hydrogen atom on C(10) and C(12) are disordered with 50% probability at each site. The N-phenyl group is rotated by an angle of 137° from overall coplanarity of the CuN_2O_2 unit. Selected bond lengths and bond angles are given in Tables 7.3 and 7.4 respectively. Packing and 3D stereo pair diagrams are given in Figure 7.10 and 7.11 respectively.

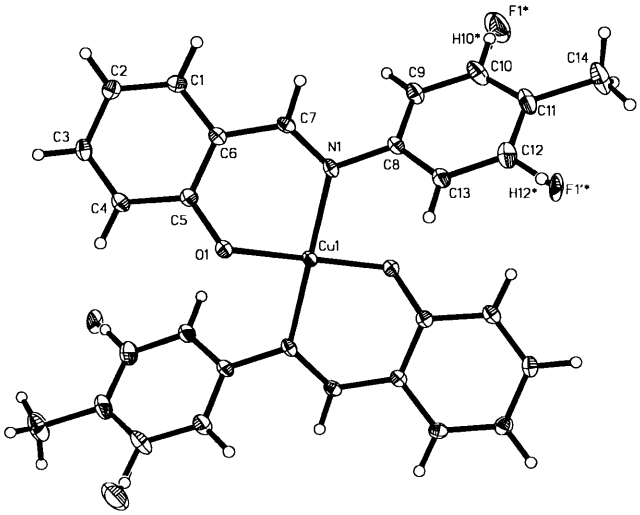

Figure 7.9 $Cu[SAL3F,4(CH_3)]_2$

Bonds	Lengths [Å]	Bonds	Lengths [Å]
N(1)-Cu(1)	2.018(3)	O(1)-Cu(1)	1.884(2)
C(7)-N(1)	1.295(4)	O(1)-C(5)	1.316(4)
N(1)-C(8)	1.444(4)	C(5)-C(6)	1.417(5)
C(7)-C(6)	1.434(5)	C(6)-C(1)	1.403(4)
C(8)-C(9)	1.384(5)	C(4)-C(5)	1.417(5)
C(8)-C(13)	1.381(5)	C(10)-C(11)	1.380(6)
C(11)-C(12)	1.381(6)	C(11)-C(14)	1.521(5)
C(10)-F(1)	1.304(6)	C(12)-F(1')	1.306(6)

Table 7.3 *Selected Bond Lengths of Cu-bis-salicylidene 3 fluoro,4-methyl aniline.*

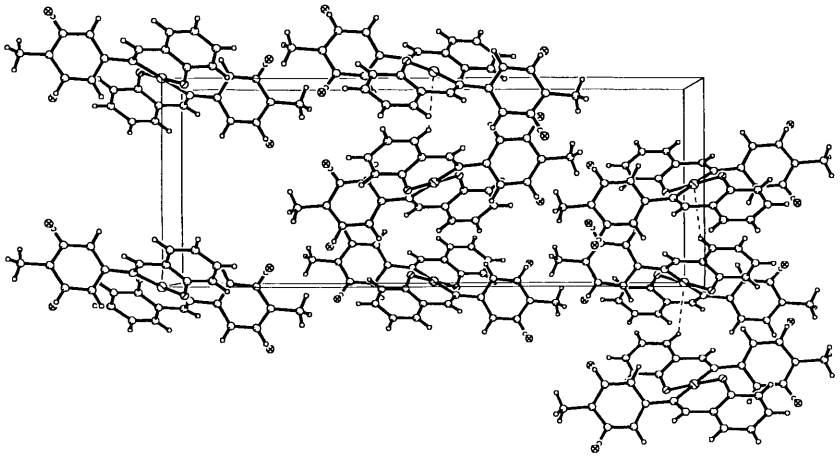

Figure 7.10 Packing Diagram Of Cu[SAL3F4Me]$_2$

	Angles[°]		Angles[°]
O(1)-Cu(1)-N(1)	91.05(11)	Cu(1)-N(1)-C(7)	121.6(2)
Cu(1)-O(1)-C(5)	123.9(2)	C(7)-N(1)- C(8)	116.1(3)
O(1)-C(5)-C(6)	123.2(3)	C(5)-C(6)-C(7)	122.4(3)
C(1)-C(6)-C(7)	117.8(3)	N(1)-C(8)-C(9)	121.5(3)
C(9)-C(10)-C(11)	123.5(4)	N(1)-C(8)-C(13)	118.5()3
C(13)-C(12)-C(11)	123.2(4)	N(1)-C(7)-C(6)	125.9(3)
F(1)-C(10)-C(11)	115.0(4)	F(1')-C(12)-C(11)	116.7(4)
C(12)-C(11)-C(10)	115.6(4)		

Table 7.4 *Selected Bond Angles of Cu-bis-salicylidene 3-fluoro, 4-methyl aniline.*

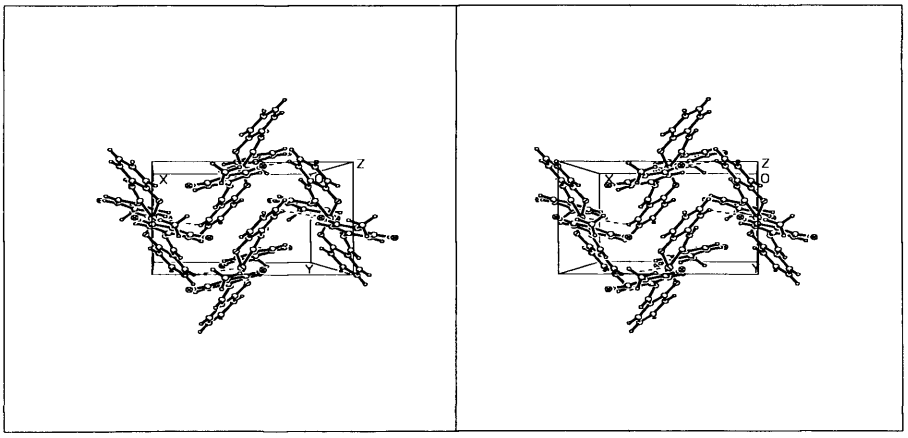

Figure 7.11 *3D Stereo pair of Cu-bis-salicylidene 3-F, 4-(CH_3) aniline.*

7.3.3 Cu-Bis-SALICYLIDENE 3,5 Di(TRIFLUORO METHYL) ANILINE

The $Cu[SAL3,5(CF_3)_2]_2$ crystal structure is monoclinic with space group C2/c. Its R value is 0.0395. In this structure both the trifluoro methyl groups is disordered. The structure diagram is given in Figure 7.12. The N-phenyl group is distorted by an angle 59.4° from the overall coplanarity in the molecule. Packing and 3D stereo pair diagrams are given in Figures 7.13 and 7.14 respectively. Selected bond lengths and bond angles are given in Tables 7.5 and 7.6 respectively.

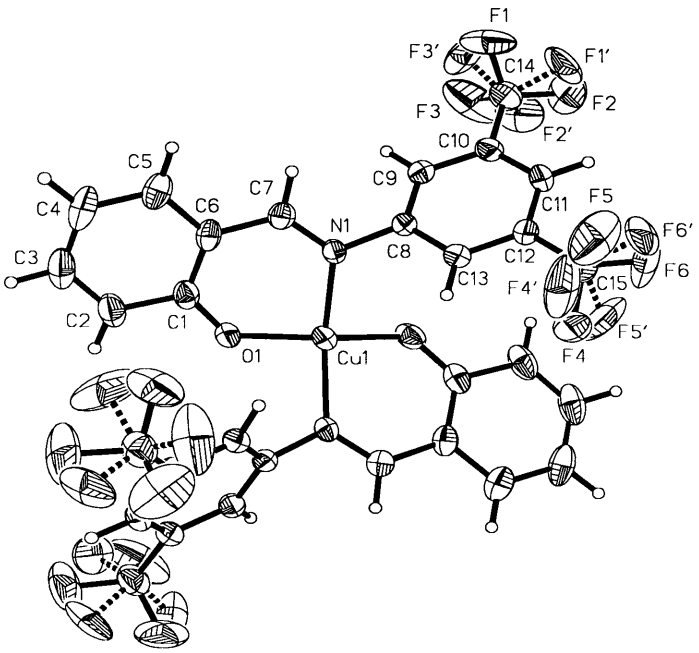

Figure 7.12 ***$Cu[SAL3,5(CF_3)_2]_2$***

Bond	Lengths[Å]	Bonds	Lengths[Å]
Cu(1)-N(1)	1.969(2)	Cu(1)-O(1)	1.869(2)
N(1)-C(7)	1.295(3)	O(1)-C(5)	1.300(4)
N(1)-C(8)	1.435(3)	C(5)-C(6)	1.408(4)
C(8)-C(9)	1.370(4)	C(6)-C(7)	1.431(4)
C(8)-C(13)	1.386(4)	C(6)-C(1)	1.413(4)
C(9)-C(10)	1.392(4)	C(13)-C(12)	1.374(3)
C(10)-C(14)	1.509(4)	C(10)-C(11)	1.374(4)
C(12)-C(15)	1.496(4)	C(12)-C(11)	1.383(4)
C(15)-F(5')	1.298(13)	C(14)-F(1)	1.279(10)
C(14)-F(1')	1.381(14)	C(15)-F(5)	1.302(8)

Table 7.5 *Selected Bond Lengths of Cu-bis-salicylidene-3,5 di(trifluoro methyl) aniline.*

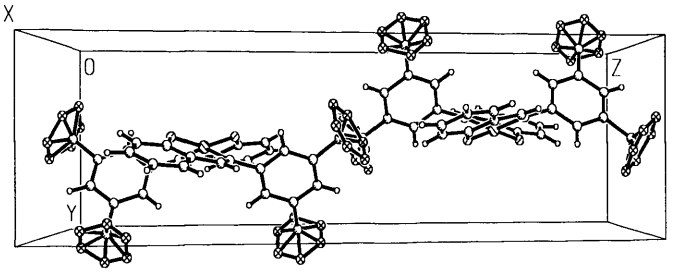

Figure 7.13 ***Packing Diagram Of Cu[SAL3,5(CF$_3$)$_2$]$_2$***

	Angles[°]		Angles[°]
O(1)-Cu(1)-N(1)	93.47(8)	C(7)-N(1)-Cu(1)	123.9(2)
C(5)-O(1)-Cu(1)	127.6(2)	Cu(1)-N(1)-C(8)	118.3(2)
O(1)-C(5)-C(6)	124.1(2)	N(1)-C(8)-C(9)	122.1(2)
C(5)-C(6)-C(7)	122.9(3)	N(1)-C(8)-C(13)	117.6(2)
C(6)-C(7)-N(1)	125.9(3)	C(9)-C(8)-C(13)	120.2(3)
C(5)-C(6)-C(7)	122.9(3)	C(8)-C(9)-C(10)	119.0(3)
C(2)-C(5)-C(6)	117.4(3)	C(8)-C(13)-C(12)	120.2(2)
C(10)-C(11)-C(12)	119.1(2)	C(14)-C(10)-C(11)	120.1(3)
C(11)-C(12)-C(15)	120.2(3)		

Table 7.6 *Selected Bond Angles of Cu-bis-salicylidene-3,5 di(tri fluoromethyl)aniline.*

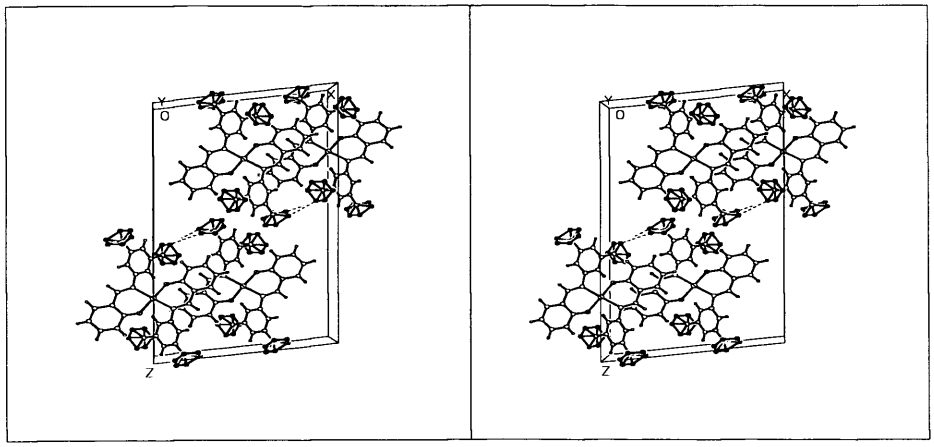

Figure 7.14 *3D Stereo pair of Cu-bis-salicylidene-3,5(CF_3)$_2$ aniline.*

7.3.4 Cu-Bis SALICYLIDENE 4-TRIFLUOROMETHOXY ANILINE

The $Cu[SAL4(OCF_3)]_2$ crystal structure is monoclinic with space group $P2_1/c$. Its R value is 0.0496. The structure diagram is given in Figure 7.15. In this structure the trifluoro methoxy group is found to be disordered. The N-phenyl group is rotated by an angle 129.3° from the overall coplanarity of the CuN_2O_2 unit. Packing and 3D stereo pair diagrams are given in Figures 7.16 and 7.17 respectively. Selected bond lengths and bond angles are given in Tables 7.7 and 7.8 respectively.

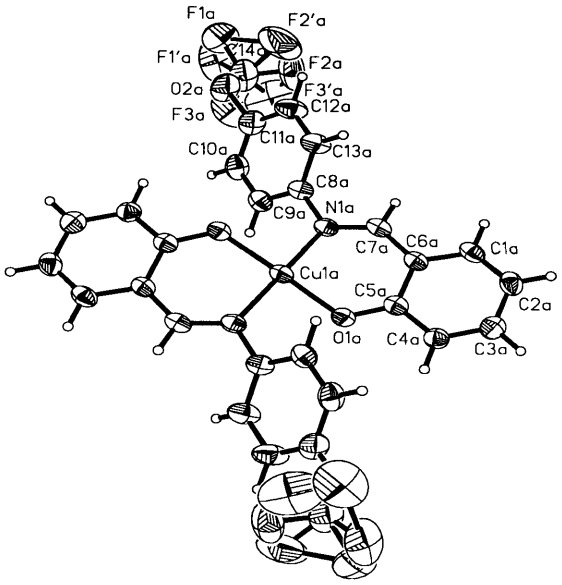

Figure 7.15 ***$Cu[SAL4(OCF_3)]_2$***

Bonds	Lengths[Å]	Bonds	Lengths[Å]
Cu(1)-O(1)	1.877(2)	Cu(1)-N(1)	2.018(2)
O(1)-C(5)	1.309(4)	N(1)-C(7)	1.291(4)
C(5)-C(4)	1.409(5)	N(1)-C(8)	1.434(4)
C(5)-C(6)	1.414(4)	C(8)-C(9)	1.384(5)
C(6)-C(7)	1.431(5)	C(5)-C(6)	1.414(4)
C(10)-C(11)	1.364(6)	C(8)-C(13)	1.375(5)
C(11)-O(2)	1.430(5)	O(2)-C(14)	1.281(7)_
C(14)-F(1)	1.381(14)	C(14)-F(1')	1.25(2)
C(12)-C(11)	1.376(6)		

Table 7.7 *Selected Bond Lengths of Cu-bis salicylidene-4 trifluoromethoxy aniline.*

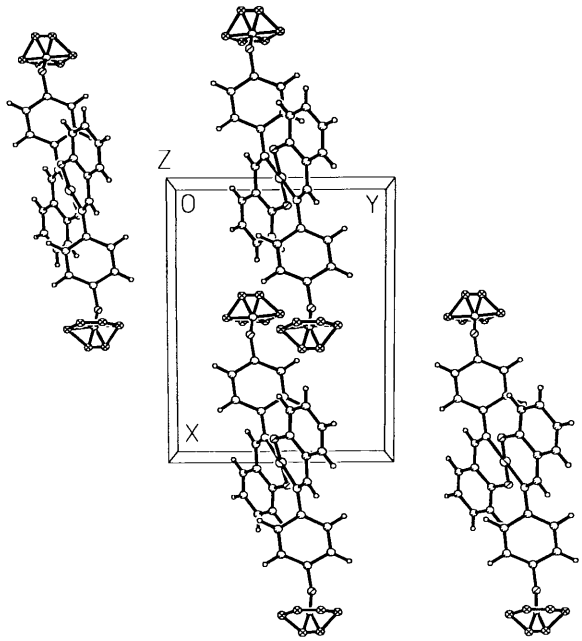

Figure 7.16 ***Packing Diagram Of Cu[SAL4OCF$_3$]$_2$***

	Angles[°]		Angles[°]
N(1)-Cu(1)-O(1)	90.72	Cu(1)-O(1)-C(5)	126.8(2)
Cu(1)-N(1)-C(7)	122.2(2)	O(1)-C(5)-C(4)	119.5(3)
Cu(1)-N(1)-C(8)	121.6(2)	O(1)-C(5)-C(6)	123.1(3)
N(1)-C(7)-C(6)	127.0(3)	C(7)-N(1)-C(8)	116.0(3)
C(5)-C(6)-C(1)	119.1(3)	C(5)-C(6)-C(7)	127.9(3)
N(1)-C(8)-C(9)	119.7(3)	N(1)-C(8)-C(13)	120.8(3)
C(10)-C(11)-C(12)	120.8(4)	C(10)-C(11)-O(2)	119.8(4)
C(12)-C(11)-O(2)	118.0(4)	C(11)-O(2)-C(14)	119.9(5)

Table 7.8 *Selected Bond Angles of Cu-bis-salicylidene 4-trifluoro methoxy aniline.*

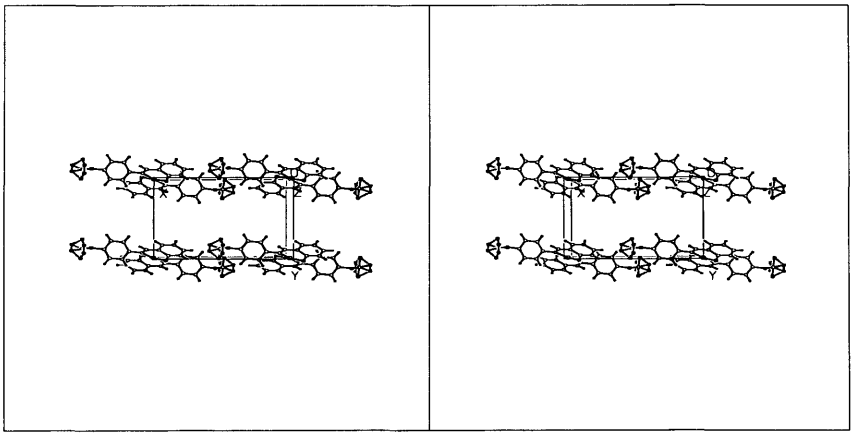

Figure 7.17 *3D Stereo pair of Cu-bis-salicylidene-4 -(trifluoro methoxy) aniline.*

7.4 DISCUSSION:-

In the structures solved during this work no significant differences in the Cu-O and Cu-N bond lengths of bis[SAL4F]$_2$Cu(II), bis[SAL3F,4(CH$_3$)]$_2$Cu(II) and bis[SAL4(OCF$_3$)]$_2$Cu(II) were observed. However, the Cu-O and Cu-N bond lengths for bis[SAL3,5(CF$_3$)$_2$]$_2$Cu(II) are significantly shorter than those in the other complexes. Bond distances in the complexes are compared in Table 7.9.

There is a significant change in the bond length of O-C(5) after chelation as compared to the free ligands. There is no significant change observed in the bond length N-C(7) before and after chelation of Cu[SAL4F]$_2$ and Cu[SAL4(OCF$_3$)]$_2$. But a significant change[0.021(5)] was observed in the case of Cu[SAL3F,4(CH$_3$)]$_2$. A significant change in N-C(8) bond length was noticed in Cu[SAL4F]$_2$, Cu[SAL3F,4(CH$_3$)]$_2$ and Cu[SAL4(OCF$_3$)]$_2$ before and after chelation, the increases in the respective bond lengths were 0.031(7), 0.035(5) and 0.019(5) respectively. The e.s.d. values for the bond lengths of O-C(5)[1.413(13)], N-C(7)[1.254(13)] and N-C(8)[1.374(12)] of SAL3,5(CF$_3$)$_2$ are high in ligands, but reasonably low when coordinated, 1.300(4), 1.295(3) and 1.435(3) respectively. Comparison of changes in bond lengths upon coordination is given in Table 7.10; Figure 7.18 represents the numbering of carbon atoms.

Burgess and coworkers[7] studied VO[SAL4(OCF$_3$)]$_2$. According to their studies there was no significant change in N-C(7)[1.295(4)] bond

length. But a significant change was noticed in N-C(8)[1.440(4)] and O-C(5)[1.317(4) Å] bond lengths. The increase in the bond length of N-C(8) upon coordination was 0.035(5) Å, and the decrease in the bond length of O-C(5) upon coordination was 0.033(5) Å.

It is interesting to compare the Cu-O and Cu-N bond lengths in complexes with ligands containing both N and O donor atoms with such bonds in complexes with only O,O or N,N donor sets.

For example, Cu(II) complexes with ligands acetylacetonate[8] and oxalate[9], both having a oxygen pair donor set, the Cu-O bond lengths in both cases are approximately the same i.e. 1.91-1.93 Å. For complexes with ligands having a pair of nitrogen donor atoms, for example, bis[H-pyrrole-2-aldimine]Cu(II)[10], the average Cu-N bond length is 1.95 Å. In the bis[N-methylsalicylaldiminato]Cu(II)[11] complex , the Cu-O bond length is 1.90 Å which is slightly shorter than in the O,O chelates and the Cu-N bond length is 1.99 Å, slightly longer than the Cu-N bond length in N,N Cu(II) chelates. This effect is enhanced in the case of the structure solved during this work [average Cu-O = 1.877, st. dev. = 0.005 and Cu-N 2.004 st. dev. = 0.02]. This may be the effect of fluorine substitution in the N-phenyl ring.

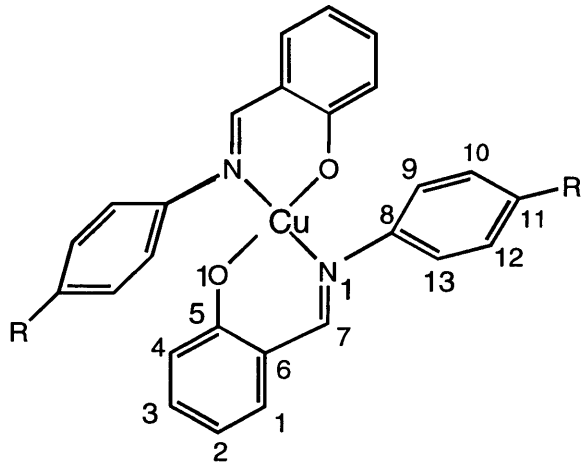

Figure 7.18 *Numbering of carbon, nitrogen and oxygen atoms in Cu(II) complexes*

BONDS	Cu[SAL3,5 $(CF_3)_2]_2$ [Å]	Cu[SAL4F]$_2$ [Å]	Cu[SAL3F,4 $(CH_3)]_2$ [Å]	Cu[SAL4 $(OCF_3)]_2$ [Å]
Cu-O(1)	1.869(2)	1.879(4)	1.884(2)	1.877(2)
Cu-N(1)	1.969(2)	2.009(4)	2.018(3)	2.018(2)
N(1)-C(7)	1.295(3)	1.298(7)	1.295(4)	1.291(4)
N(1)-C(8)	1.435(3)	1.443(7)	1.444(4)	1.434(4)
O(1)-C(5)	1.300(4)	1.301(7)	1.316(4)	1.309(4)
C(6)-C(7)	1.431(4)	1.427(8)	1.434(5)	1.431(5)
C(8)-C(9)	1.370(4)	1.395(8)	1.384(5)	1.384(5)
C(8)-C(13)	1.386(4)	1.379(7)	1.381(5)	1.375(5)
C(1)-C(6)	1.413(7)	1.396(8)	1.403(5)	1.408(5)
C(5)-C(6)	1.408(4)	1.419(7)	1.417(5)	1.414(4)

Table 7.9 *Selected bond lengths of Cu[SAL3,5$(CF_3)_2]_2$, Cu[SAL4F]$_2$, Cu[SAL3F,4$(CH_3)]_2$ and Cu[SAL4$(OCF_3)]_2$.*

Bonds	Lengths Å		Difference
	Ligands	Chelates	Che[a]-Lig[b]
	SAL4F	**Cu[SAL4F]$_2$**	
N-C(7)	1.273(2)	1.285(6)	(ns)
N-C(8)	1.419(2)	1.440(7)	0.031(7) (s)
O-C(5)	1.354(2)	1.308(6)	-0.046(6) (s)
	SAL3F4(CH$_3$)	**Cu[SAL3F4(CH$_3$)]$_2$**	
N-C(7)	1.274(4)	1.295(4)	0.021(5) (s)
N-C(8)	1.419(4)	1.444(4)	0.035(5) (s)
O-C(5)	1.354(4)	1.316(4)	-0.038(5) (s)
	SAL3,5(CF$_3$)$_2$	**Cu[SAL3,5(CF$_3$)$_2$]$_2$**	
N-C(7)	1.254(13)	1.295(3)	0.041(13)
N-C(8)	1.374(12)	1.435(3)	0.061(12)
O-C(5)	1.413(13)	1.300(4)	-0.113(13)
	SAL4(OCF$_3$)	**Cu[SAL4(OCF$_3$)]$_2$**	
		VO[SAL4(OCF$_3$)]$_2$	
N-C(7)	1.289(7)	1.291(4)	(ns)
		1.295(4)	*(ns)*
N-C(8)	1.415(4)	1.434(40	0.019(5) (s)
		1.440(4)	*0.035(5) (s)*
O-C(5)	1.350(8)	1.309(4)	-0.041(9) (s)
		1.317(4)	*-0.033(5) (s)*

Table 7.10 *Comparison of selected bond lengths with their respective ligands.* [a = chelate, b = free ligand]

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CHAPTER 8

STRUCTURE DETERMINATION OF ANHYDROUS BIS[ACETYL ACETONATO]Co(II)

8.1 INTRODUCTION:-

This chapter describes the structure and bonding of anhydrous bis(acetylacetonato)Co(II), $Co(acac)_2$ [acacH is acetylacetone = 2,4-pentanedione]. Its bonding pattern, bond lengths and bond angles are compared with other bis(acetylacetonato)M(II) complexes [M = Cr, Zn, Cd, Cu and Ni] and with other forms of Co(II) complexes i.e. $Co(acac)_2.H_2O$, $Co(acac)_2.2H_2O$ and polynuclear forms.

The anhydrous bis(acetylacetonato)Co(II) complex was a by-product of attempts to synthesise complexes of Co(II) with substituted acetylacetonatoimine ligands. Due to the instability of these ligands, as described earlier in Chapter 4, their complexes could not be synthesised. During one of these unsuccessful attempts a few green plate-like crystals were obtained, and were at first thought to be the crystals of the desired complex. However they proved to be crystals of novel anhydrous bis(acetylacetonato)Co(II) complex.

The bonding pattern and square-planar geometry were found to be interesting and the related information along with the comparison with other bis(acetylacetonato)M(II) complexes and $Co(acac)_2.H_2O$, $Co(acac)_2.2H_2O$ and polynuclear Co(II) complexes, have been gathered in this chapter.

8.2 EXPERIMENTAL:-

The crystal under discussion was obtained during a template reaction. In this reaction an ethanolic solution of metal acetate (5ml, 2 millimols) had been added to an ethanolic solution of acetylacetone (5ml, 4millimols) and stirred for a while, followed by addition of an ethanolic solution of 4-fluoro aniline (5ml, 4millimols). The reaction mixture was then stirred and refluxed for an hour. After cooling, the reaction mixture was a clear green solution. It was left in a sample tube; after two days a few green crystals had settled at the bottom. They were taken out and the structure of one was determined.

The X-ray structure determination was carried out on a X-ray Siemens P4 diffractometer by Dr. J. Fawcett.

8.3 STRUCTURE:-

The structure of bis[acetylacetonato]Co(II) is given in Figure 8.1. Its crystal system is monoclinic with space group $P2_1/n$; its R value is 0.0528. It is an anhydrous monomer stacked in columns, having a square-planar structure. The mean deviation from the plane is 0.0367 Å. There is negligible interaction between the molecules. The nearest atom to Co in an adjacent molecule is H(5a) at 2.93 Å [the sum of the van der Waals[1] radii of Co and H is 3.17 Å] There is also no significant interaction between the nearest oxygen above and below which are at 4.078Å [the sum of the van der Waals radii of Co and O is 3.57 Å]. Bis[acetylacetonato]Co(II) is isomorphous with bis[acetylacetonato]Cu(II) and bis[acetylacetonato]Cr(II). Selected bond lengths and bond angles are given in Tables 8.1 and 8.2 respectively. Packing, end-on view, and 3D stereo pair diagrams are given in Figures 8.2, 8.3 and 8.4 respectively.

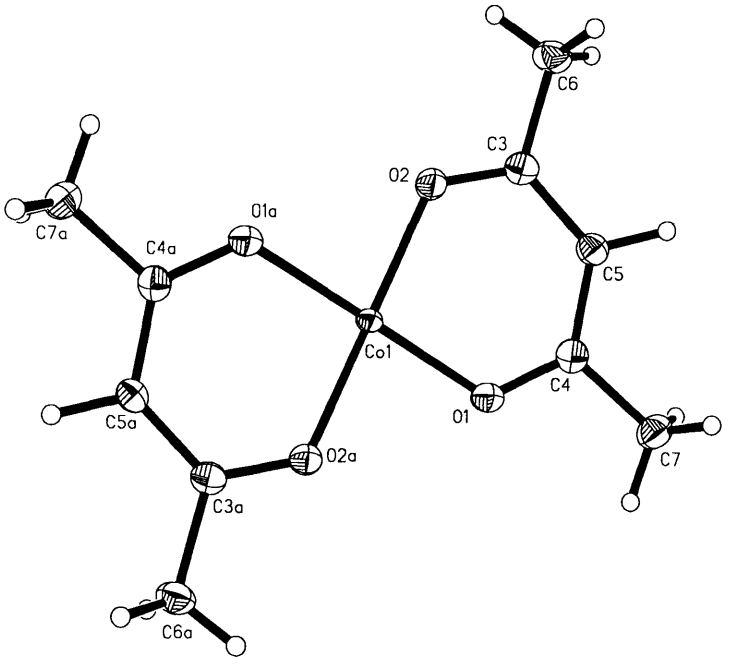

Figure 8.1 Anhydrous Bis[acetylacetonato]Co

Bond	Lengths[Å]	Bond	Lengths[Å]
O_2-Co_1	1.917(3)	O_1-Co_1	1.920(3)
C_3-O_2	1.268(5)	C_4-O_1	1.275(5)
C_3-C_6	1.492(6)	C_4-C_7	1.504(6)
C_3-C_5	1.405(6)	C_4-C_5	1.380(6)

Table 8.1 Selected Bond Lengths of Bis[acetyl acetonato]Co(II)

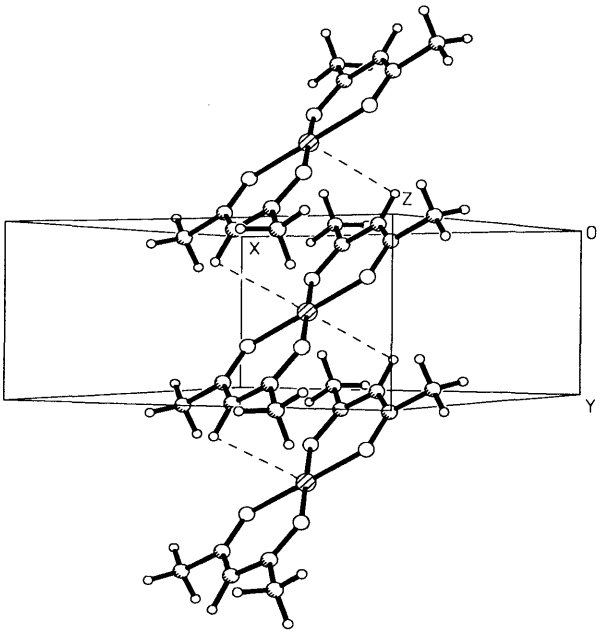

Figure 8.2 Packing Diagram of Bis[acetylacetonato]Co(II)

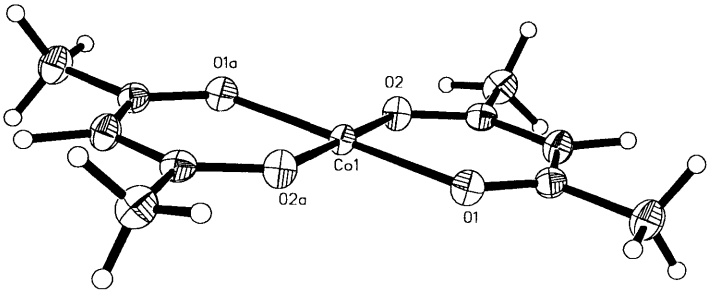

Figure 8.3 ***Structure showing the planarity of the molecule***

	Angles[°]		Angles[°]
O_2-Co_1-O_1	93.37(11)	O_2-Co_1-O_{2a}	180.0
O_2-Co_1-O_{1a}	86.63(11)	O_1-Co_1-O_{2a}	86.63(11)
O_{2a}-Co_1-O_{1a}	93.37(11)	O_1-Co_1-O_{1a}	180.0
Co_1-O_2-C_3	126.0(3)	Co_1-O_1-C_4	125.2(3)
C_3-C_5-C_4	124.5(4)	O_2-C_3-C_6	11 5.7(4)
O_1-C_4-C_7	115.2(4)		

Table 8.2 Selected Bond Angles of Bis[acetylacetato]Co(II)

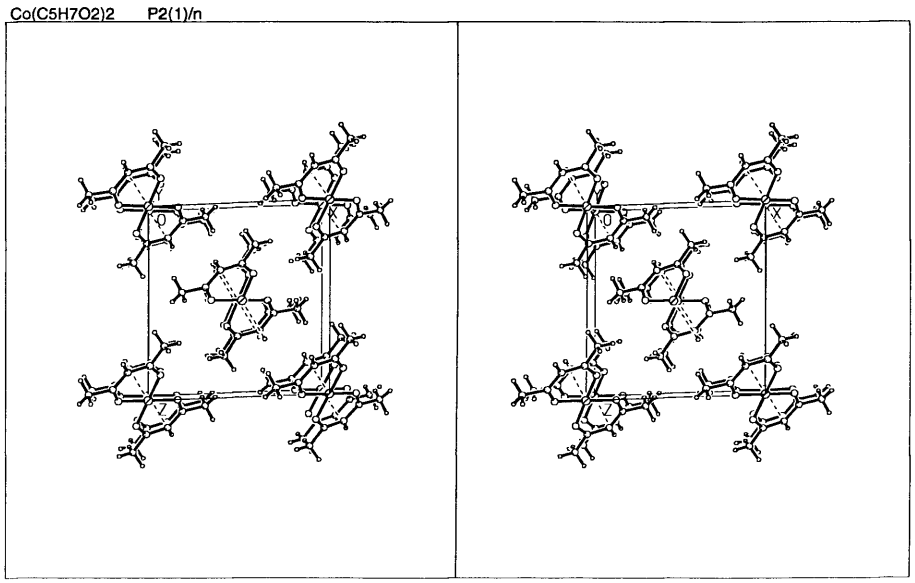

Figure 8.4 3D Stereo Pair of Bis[acetylacetonato]Co(II)

8.4 DISCUSSION:-

The crystal structures of bis[acetylacetonato]M(II) complexes of first row transition metals have been studied extensively. Some of them were isolated as trimeric[2] or tetrameric[3-5] complexes, whereas some were isolated as monomers, either anhydrous, or mono or diaqua solvates. Here monomers, trimers and tetramer will be discussed and compared, with respect to their geometry, bond lengths and bond angles, with anhydrous bis[acetylacetonato]Co(II) complex obtained during this work.

It is surprising that bis(acetylacetonato)Co(II) has square-planar geometry instead of tetrahedral, tetragonal or octahedral, which are expected in Co(II) complexes. There is very little direct evidence in the form of X-ray structural determinations for the existence of planar quadricoordinate Co(II) complexes of either the high spin or low spin type. There is no evidence of any sort for high spin complexes of this type and the only low spin complex which has been examined is planar bis-(salicylal)ethylenediimineCo(II)[6]. Arrangement of bis-salicylaldehyde ethylenediimine-Co(II) molecules in unit cell is given in Figure 8.4.

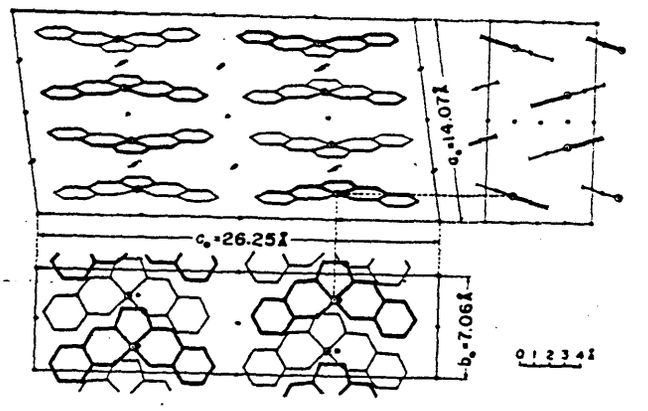

Figure 8.4 *Arrangement of bis-salicylaldehyde ethlenediimine-Co(II) molecules in unit cell.*

Consider the position of the oxygen-bearing ligands in the spectrochemical series $I^- < Cl^- < OH^- < NO_3^- < F^- < C_2O_4^{2-} \leq H_2O < py \leq NCS^- < NH_3 < en \approx NO_2^- < phen \leq bipy << CN^-$, where the ligands are arranged in increasing ligand field strength, orbital contributions in the values of magnetic moment for the tetrahedral Co(II) complexes decrease as the ligands vary from I^- to CN^-. In terms of ligand field theory[6] the size of the orbital contribution in the magnetic moment values for $Co\text{-}O_4$ complexes is too large to be compatible equally with both planar and tetrahedral conformations and is strongly against the later.

Bullen[7] has reported the crystal structure of diaaquabis[acetyl acetonato]Co(II) $\{Co(C_5H_7O_2)_2.2H_2O\}$. Its crystal system is monoclinic, space group $P2_1/c$. The cobalt atom, lying on a centre of symmetry, is

oxygens of the acetylacetonate ligand are significantly shorter than the bond lengths of Co with water oxygen, the difference between the two being 0.18(1) Å, and are significantly longer than the bond lengths of Co(II) with the coordinating oxygens in anhydrous bis[acetylacetonato]Co(II) solved in this work, the difference between the two being here 0.14(3) Å.

Montgomery and Lingafelter[10] have reported the crystal structure of diaquabis[acetylacetonato]Ni(II). They reported the same structure as of diaquabis[acetylacetonato]Co(II), the only significant difference being in its bond lengths of Ni-O, which are 2.01 and 2.02 Å, and Ni-OH_2 both 2.14 Å.

Lippert and Truter[11] reported the structure of monoaquabis[acetyl acetonato]Zn, which was later redetermined by Montgomery and Lingafelter[12]. The five oxygen atoms coordinated to the zinc ion are at the same distance 2.02 ± 0.02 Å. The arrangement of the oxygen atoms is intermediate between tetragonal pyramidal and trigonal bipyramidal, although somewhat nearer to the former.

Bis[acetylacetonato]Cu(II) has been widely studied[13-15]. Starikova and Shugam[16] reported bis[acetylacetonato]Cu(II) as having planar coordination, the Cu-O bond lengths are 1.91-1.93 Å, but because of the weak interactions(3.01 Å) of Cu with carbons of the neighbouring molecules [sum of van der waals radii of Cu and C is 3.65 Å] its structure becomes elongated tetragonal bipyramid.

Cotton et al[17] reported an anhydrous monomer of bis[acetylacetonato]Cr(II). Its crystal system was monoclinic with space group $P2_1/n$. The chromium atom in anhydrous bis[acetylacetonato]Cr(II) lies on an inversion centre and has planar coordination, with four oxygen atoms at a mean Cr-O distance of 1.984 Å. There are weak interactions (3.05 Å)with carbon atoms of the ligands in the adjacent molecules to give a tetragonally distorted octahedral coordination sphere about chromium. Bis[acetylacetonato]Cr(II) complex is isomorphous with bis[acetylacetonato]Cu(II). Anhydrous bis(acac)Co(II) complex is isomorphous with anhydrous bis(acac)Cr(II) and anhydrous bis(acac)Cu(II).

Some polymeric i.e. trimeric and tetrameric, bis[acetylacetonato]M(II) complexes have also been isolated and structurally characterised. Cotton and Elder[3,5] reported the structure of tetrameric bis[acetylacetonato]Co(II). The triclinic unit cell with space group P1 contains one centrosymmetric tetramer. Octahedral [Figure 8.5] coordination is achieved by sharing one oxygen atom between cobalt atoms. There are three distinct type of rings: those with both oxygen atoms bonded to only one terminal cobalt atom with average bond length 2.23 Å, those with one oxygen atom serving as a bridge between two cobalt atoms with average bond length 2.05 Å and those with both oxygen atoms serving as bridges between three cobalt atoms with average bond length 2.24 Å. The bridge bonds in the centre of the tetramer are approximately coplanar with the chelate ring.

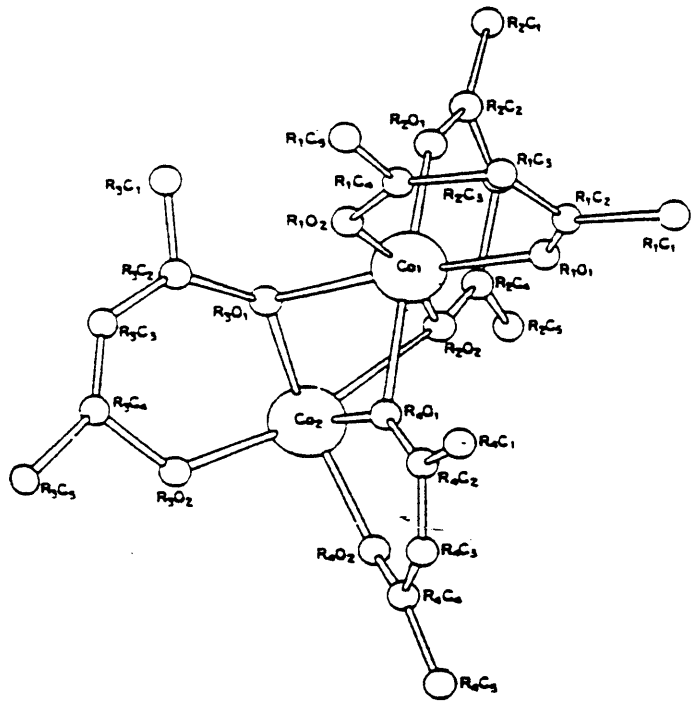

Figure 8.5 *The asymmetric unit of tetrameric bis(acetylacetonato)Co(II)*

The trimer[2], $[Zn(acac)_2]_3$ with space group: C2 contains a central octahedrally coordinated zinc atom, lying on the crystallographic twofold axis, and two terminal pentacoordinated zinc atoms. The coordination geometry about the terminal zinc atoms is closer to a trigonal bipyramidal than to a square pyramidal arrangement. Both the octahedron and the trigonal bipyramids show considerable distortions from their ideal geometries. Each terminal zinc atom is connected to the central one by two shared oxygen atoms, one at an axial and the other at an equatorial position of the trigonal bipyramid. Two types of Zn-O bond length were observed, bonds from zinc atoms to bridging oxygen atoms average 2.00 Å and the bonds from zinc atoms to non-bridging oxygen atoms average 2.10 Å. The

former value is in agreement with the average value of 2.01 ±0.02 Å for the Zn-O bond lengths in $Zn[acac]_2H_2O$. Both the terminal five-coordinate zinc atom and the central six-coordinate zinc atom have considerable angular distortion observed in the other polymeric acetylacetonato complexes and is probably due to intramolecular crowding and to restrictions imposed by the internal geometry of the ligand, since intermolecular crystal packing forces would not be expected to have such large effects on the inner coordination sphere. Trimeric nickel acetylacetonate achieves six coordination through sharing of oxygen atoms between adjacent metal atoms. In $[Ni(acac)_2]_3$, trimerisation occurs by sharing of faces of octahedra.[18-20] The average bond length between nickel and terminal oxygen is 2.06 Å and average bond length between nickel and bridging oxygen is 2.12 Å.

Selected bond lengths and bond angles of diaquabis[acetylacetonato]Ni(II), diaquabis[acetylacetonato]Co(II), monoaquabis[acetylacetonato]Zn(II), anhydrous bis[acetylacetonato]Cr(II) anhydrous bis[acetylacetonato]Cu(II) and anhydrous bis[acetylacetonato]Co(II) are given in Tables 8.3 and 8.4 respectively.

Table 8.3 Selected Bond Lengths[Å] of Diaquabis[AcAc]Co(II), Diaquabis[AcAc]Ni(II), Monoaquabis[AcAc]Zn(II), anhydrous Bis[AcAc]Cr(II), anhydrous Bis[AcAc]Cu(II) and anhydrous Bis[AcAc]Co(II).

Compounds	**M*-O(1)**	**M*-(O2)**	**M*-OH_2**
$Co(C_5H_7O_2)_2.2H_2O$	2.05(1)	2.06(1)	2.23(1)
$Ni(C_5H_7O_2)_2.2H_2O$	2.021(1)	2.014(1)	2.139(1)
$Zn(C_5H_7O_2)_2.H_2O$	1.999(2)	2.026(2)	2.038(2)
$Cr(C_5H_7O_2)_2$	1.984(3)	1.979(3)	-
$Cu(C_5H_7O_2)_2$	1.91	1.93	-
$Co(C_5H_7O_2)_2$	1.917(3)	1.92(3)	-

* M = Co, Zn, Cr, Ni and Cu.

Table 8.4 Selected Bond Angles[°] of diaquabis[acac]Co(II), diaquabis[acac]Ni(II), monoaquabis[acac]Zn(II), anhydrous bis[acac]Cr(II), anhydrous bis[acac]Cu(II) and anhydrous bis[acac]Co(II).

Compounds	**O(1)-M*-O(2)**	**O(1)-M*-OH_2**	**O(2)-M*-OH_2**
$Co(C_5H_7O_2)_2.2H_2O$	92.0(4)	91.6(4)	87.1(4)
$Ni(C_5H_7O_2)_2.2H_2O$	92.4(4)	90.9(4)	88.6(4)
$Zn(C_5H_7O_2)2.H_2O$	88.5(8)	104.9(8)	97.5(8)
$Cr(C_5H_7O_2)_2$	90.3(1)	-	-
$Cu(C_5H_7O_2)_2$	95.0	-	-
$Co(C_5H_7O_2)_2$	93.37(11)	-	-

*M = Co, Ni, Zn, Cr and Cu.

8.5 REFERENCES:-

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APPENDIX

SAL3,5(CF_3)$_2$

Table 1 Crystal data and Structure refinement for 1

Identification code	RZ3S	
Emperical formula	$C_{15}H_9F_6NO$	
Formula weight	333.2	
Temperature	293 °K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.0310(10) Å	α = 90 °
	b = 26.708(8) Å	β = 117.510(10) °
	c = 7.6090(10) Å	γ = 90 °
Volume	1447.6(5) Å	
Z	4	
Density	1.529 Mg/m^3	
Absorption coefficient	0.149 mm^{-1}	
F(000)	672	
Crystal size	0.7 × 0.41 × 0.39 mm	
θ range for data collection	3.5 to 22.5 °	
Index ranges	$-8 \leq h \leq 8$, $-28 \leq k \leq 1$	
Reflections collected	2405	
Independent reflections	1798 (R_{int} = 2.05%)	
Refinement method	Full matrix least squares on F	
Data / restraints / parameters	1798 / 0 / 160	
Goodness of fit on F^2	3.34	
Final R indices [I > 2 ≈ (I)]	R_1 = 0.129, wR_2 = 0.188	
R indices (all data)	R_1 = 0.169, wR_2 = 0.199	
Extinction coefficient	Not applied	
Largest diff. peak and hole	0.58 and -0.43 $eÅ^{-3}$	

Table 1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$)

	x	y	z	U(eq)
N(1)	6071(12)	7973(3)	4751(13)	63(4)
O(1)	6410(11)	6995(3)	5174(12)	88(4)
C(1)	1893(15)	7347(5)	935(19)	79(6)
C(2)	1127(19)	6871(6)	248(22)	100(7)
C(3)	2140(22)	6454(6)	1223(25)	98(8)
C(4)	3907(21)	6476(5)	2846(21)	92(8)
C(5)	4588(19)	6956(4)	3564(19)	75(7)
C(6)	3709(16)	7390(5)	2633(16)	74(6)
C(7)	4490(18)	7889(4)	3316(19)	69(6)
C(8)	6781(13)	8447(4)	5307(14)	59(3)
C(9)	6317(13)	8852(3)	3978(16)	65(3)
C(10)	7048(14)	9299(4)	4627(16)	69(3)
C(11)	8275(13)	9393(4)	6618(15)	68(3)
C(12)	8737(13)	9000(4)	7897(15)	64(3)
C(13)	8059(12)	8533(4)	7306(14)	57(3)
C(14)	6591(10)	9741(2)	3183(9)	94(7)
F(1)	5809	9585	1360	202(8)
F(2)	5409	10026	3257	241(11)
F(3)	7907	9988	3311	213(8)
C(15)	10093(11)	9076(3)	9967(9)	96(7)
F(4)	11070	8730	10938	247(8)
F(5)	9306	9155	11052	272(12)
F(6)	11185	9426	10467	312(11)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

SAL3F,4(CH_3)

Table 1. Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{14}H_{12}FNO$
Formula weight	229.25
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 19.347(6) Å α = 90°
	b = 4.743(2) Å β = 101.31°
	c = 12.314(2) Å γ = 90°
Volume	1108.0(6) $Å^3$
Z	4
Density (calculated)	1.374 Mg/m^3
Absorption coefficient	0.098 mm^{-1}
F(000)	480
Crystal size	0.69 x 0.13 x 0.12 mm
θ range for data collection	3.22 to 22.47°
Index ranges	$-20 \le h \le 20$, $-5 \le k \le 1$, $-1 \le \ell \le 12$
Reflections collected	1945
Independent reflections	1288 (R_{int} = 0.0362)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1288 / 0 / 149
Goodness-of-fit on F^2	1.022 4.88%
Final R indices [$I>2\sigma(I)$]	R1 = 0.0488, wR2 = 0.1187
R indices (all data)	R1 = 0.0696, wR2 = 0.1331
Largest diff. peak and hole	0.232 and -0.224 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	4357(1)	-1739(6)	10376(2)	47(1)
O(1)	1985(1)	7415(5)	10574(2)	47(1)
N(1)	2510(1)	4635(5)	9105(2)	28(1)
C(1)	1173(1)	9595(6)	7768(3)	32(1)
C(2)	697(2)	11543(7)	7974(3)	37(1)
C(3)	647(2)	12067(7)	9069(3)	41(1)
C(4)	1076(2)	10688(7)	9932(3)	41(1)
C(5)	1563(2)	8719(7)	9712(3)	31(1)
C(6)	1613(1)	8121(6)	8614(2)	26(1)
C(7)	2108(1)	6048(6)	8355(3)	28(1)
C(8)	2988(1)	2603(6)	8839(2)	26(1)
C(9)	3017(2)	1688(7)	7771(3)	32(1)
C(10)	3511(2)	-277(7)	7621(3)	33(1)
F(1A)	3537(4)	-1218(16)	6681(6)	50(3)
C(11)	3989(1)	-1479(7)	8479(3)	29(1)
C(12)	3927(2)	-577(7)	9525(3)	32(1)
C(13)	3443(1)	1391(7)	9722(2)	32(1)
C(14)	4533(2)	-3606(7)	8305(3)	38(1)

SAL4(OCF_3)

Table 1 Crystal data and Structure refinement for 1

Identification code	RZ2S
Emperical formula	$C_{14}H_{10}F_3NO_2$
Formula weight	281.2
Temperature	293 °K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1c$
Unit cell dimensions	a = 5.6470(10) Å α = 90 °
	b = 7.977(2) Å β = 90.630(0) °
	c = 29.197(4) Å γ = 90 °
Volume	1315.1(4) Å
Z	4
Density	1.420 Mg/m^3
Absorption coefficient	0.124 mm^{-1}
F(000)	576
Crystal size	0.38 × 0.38 × 0.22 mm
θ range for data collection	2.5 to 24.0 °
Index ranges	-1 ≤ h 6, -1 ≤ k 9
Reflections collected	3203
Independent reflections	2071 (R_{int} = 2.67%)
Refinement method	Full matrix least squares on F
Data / restraints / parameters	2071 / 0 / 181
Goodness of fit on F^2	0.81
Final R indices [I > 2 ≈ (I)]	R_1 = 0.0902, wR_2 = 0.145
R indices (all data)	R_1 = 0.142, wR_2 = 0.238
Extinction coefficient	Not applied
Largest diff. peak and hole	0.44 -0.42 eÄ$^{-3}$

Table 1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
N(1)	12637(9)	5799(6)	2679(2)	54(2)
O(1)	16312(9)	4795(6)	2224(2)	78(2)
O(2)	8735(10)	6288(7)	4414(2)	95(2)
F(1)	8319(14)	7340(8)	5088(2)	161(3)
F(2)	9339(20)	8933(8)	4545(2)	194(5)
F(3)	11717(18)	7306(13)	4818(2)	203(5)
C(1)	12186(13)	7093(9)	1484(2)	68(3)
C(2)	13319(14)	6952(10)	1071(2)	75(3)
C(3)	15356(15)	6067(9)	1049(2)	74(3)
C(4)	16352(13)	5331(9)	1431(2)	69(3)
C(5)	15275(11)	5474(7)	1849(2)	56(2)
C(6)	13133(10)	6352(7)	1886(2)	50(2)
C(7)	11894(10)	6537(7)	2312(2)	52(2)
C(8)	11536(11)	6012(7)	3108(2)	51(2)
C(9)	9450(12)	6844(9)	3183(2)	64(2)
C(10)	8571(12)	6999(9)	3624(3)	70(3)
C(11)	9758(13)	6256(9)	3972(2)	67(2)
C(12)	11854(14)	5411(9)	3913(2)	71(3)
C(13)	12700(12)	5280(8)	3479(2)	60(2)
C(14)	9411(27)	7468(13)	4703(3)	111(5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

SAL4F

Table 1. **Crystal data and structure refinement for 1.**

Identification code	p21c
Empirical formula	$C_{13}H_{10}FNO$
Formula weight	215.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.8200(10) Å α = 90°
	b = 5.7870(10) Å β = 107.93(2)°
	c = 14.817(2) Å γ = 90°
Volume	1045.9(2) $Å^3$
Z	4
Density (calculated)	1.367 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	448
Crystal size	0.48 x 0.45 x 0.26 mm
θ range for data collection	2.86 to 23.99°
Index ranges	$-1 \le h \le 14$, $-1 \le k \le 6$, $-16 \le \ell \le 16$
Reflections collected	2299
Independent reflections	1642 (R_{int} = 0.0202)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1642 / 0 / 150
Goodness-of-fit on F^2	1.038
Final R indices [$I>2\sigma(I)$]	R1 = 0.0388, wR2 = 0.1006
R indices (all data)	R1 = 0.0564, wR2 = 0.1138
Extinction coefficient	0.014(2)
Largest diff. peak and hole	0.194 and -0.135 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	4655(1)	289(3)	3380(1)	79(1)
N(1)	317(1)	-937(3)	1290(1)	44(1)
O(1)	-1095(1)	-3620(2)	91(1)	59(1)
C(1)	-1854(1)	-1999(3)	96(1)	44(1)
C(2)	-2939(2)	-2404(4)	-425(1)	52(1)
C(3)	-3730(2)	-783(4)	-446(1)	54(1)
C(4)	-3460(2)	1280(4)	52(1)	54(1)
C(5)	-2385(2)	1685(3)	570(1)	48(1)
C(6)	-1564(1)	69(3)	610(1)	41(1)
C(7)	-446(1)	545(3)	1178(1)	43(1)
C(8)	1414(1)	-513(3)	1854(1)	40(1)
C(9)	2169(2)	-2188(3)	1831(1)	47(1)
C(10)	3265(2)	-1940(4)	2345(1)	54(1)
C(11)	3578(2)	16(4)	2876(1)	51(1)
C(12)	2855(2)	1707(4)	2926(1)	53(1)
C(13)	1766(2)	1446(3)	2413(1)	50(1)

SAL4(CH_3)

Table 1 Crystal data and Structure refinement for 1

Identification code	RZ1S
Emperical formula	$C_{14}H_{13}NO$
Formula weight	211.3
Temperature	293 °K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 19.314(4) Å α = 90 °
	b = 4.7670(10) Å β = 102.11(0) °
	c = 12.225(4) Å γ = 90 °
Volume	1100.5(5) $Å^3$
Z	4
Density	1.275 Mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	448
Crystal size	0.60 × 0.57 × 0.06 mm
θ range for data collection	3.5 to 22.5 °
Index ranges	$-20 \leq h \leq 21$, $-5 \leq k \leq 1$
Reflections collected	2002
Independent reflections	1344 (R_{int} = 2.28%)
Refinement method	Full matrix least squares on F
Data / restraints / parameters	1344 / 0 / 145
Goodness of fit on F^2	0.83
Final R indices [I > 2 ≈ (I)]	R_1 = 0.0486, wR_2 = 0.0437
R indices (all data)	R_1 = 0.0749, wR_2 = 0.0581
Extinction coefficient	Not applied
Largest diff. peak and hole	0.16 and -0.20 $eÅ^{-3}$

Table 1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
O(1)	7032(2)	7305(7)	5652(2)	64(1)
N(1)	7545(2)	4525(7)	4176(3)	37(1)
C(1)	6191(2)	9420(8)	2820(3)	44(2)
C(2)	5710(2)	11381(9)	3031(4)	53(2)
C(3)	5674(2)	11898(10)	4132(4)	59(2)
C(4)	6114(2)	10554(10)	5001(4)	59(2)
C(5)	6599(2)	8580(9)	4785(3)	46(2)
C(6)	6640(2)	7990(8)	3685(3)	37(1)
C(7)	7134(2)	5949(8)	3417(3)	38(1)
C(8)	8023(2)	2505(8)	3905(3)	37(1)
C(9)	8497(2)	1337(9)	4794(3)	46(2)
C(10)	8990(2)	-626(9)	4609(3)	48(2)
C(11)	9017(2)	-1497(8)	3539(3)	40(1)
C(12)	8526(2)	-376(9)	2666(3)	46(2)
C(13)	8037(2)	1605(9)	2827(3)	45(2)
C(14)	9552(2)	-3651(9)	3343(3)	54(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

$SALF_5$

Table 1. Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{13}H_6F_5NO$
Formula weight	287.19
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 12.038(3) Å α = 90°
	b = 7.2890(10) Å β = 95.63°
	c = 12.821(3) Å γ = 90°
Volume	1119.6(4) $Å^3$
Z	4
Density (calculated)	1.704 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	576
Crystal size	0.80 x 0.36 x 0.22 mm
θ range for data collection	3.19 to 23.00°
Index ranges	$-1 \le h \le 13$, $-1 \le k \le 8$, $-14 \le \ell \le 14$
Reflections collected	2129
Independent reflections	1548 (R_{int} = 0.0336)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1548 / 0 / 182
Goodness-of-fit on F^2	1.077
Final R indices [$I>2\sigma(I)$]	R1 = 0.0341, wR2 = 0.0942
R indices (all data)	R1 = 0.0414, wR2 = 0.1012
Extinction coefficient	0.030(3)
Largest diff. peak and hole	0.215 and -0.176 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	6937(1)	5146(2)	-3336(1)	36(1)
F(2)	9129(1)	5005(2)	-2718(1)	44(1)
F(3)	9866(1)	3624(2)	-812(1)	50(1)
F(4)	8387(1)	2471(2)	511(1)	46(1)
F(5)	6167(1)	2543(2)	-119(1)	39(1)
N(1)	5327(1)	3908(2)	-1996(1)	28(1)
O(1)	3322(1)	4632(2)	-1483(1)	38(1)
C(1)	3269(2)	3207(3)	-4233(2)	31(1)
C(2)	2138(2)	3273(3)	-4530(2)	36(1)
C(3)	1424(2)	3797(3)	-3800(2)	38(1)
C(4)	1823(2)	4264(3)	-2788(2)	35(1)
C(5)	2961(2)	4189(3)	-2483(2)	30(1)
C(6)	3703(2)	3656(3)	-3210(1)	26(1)
C(7)	4888(2)	3522(3)	-2924(1)	27(1)
C(8)	6490(2)	3790(3)	-1751(1)	26(1)
C(9)	7273(2)	4412(3)	-2393(1)	28(1)
C(10)	8395(2)	4372(3)	-2081(2)	32(1)
C(11)	8766(2)	3708(3)	-1106(2)	34(1)
C(12)	8017(2)	3109(3)	-440(2)	33(1)
C(13)	6896(2)	3157(3)	-766(1)	29(1)

5ClSAL4Cl

Table 1. Crystal data and structure refinement for 1.

Identification code	9603
Empirical formula	$C_{13}H_9Cl_2NO$
Formula weight	266.11
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 27.419(7) Å α = 90°
	b = 6.901(2) Å β = 95.57(2)°
	c = 6.137(1) Å γ = 90°
Volume	1155.8(5) Å^3
Z	4
Density (calculated)	1.529 Mg/m^3
Absorption coefficient	0.541 mm^{-1}
F(000)	544
Crystal size	0.69 x 0.62 x 0.26 mm
θ range for data collection	2.99 to 22.49°
Index ranges	$-29 \le h \le 29$, $-7 \le k \le 1$, $-1 \le \ell \le 6$
Reflections collected	2378
Independent reflections	1507 (R_{int} = 0.0274)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1506 / 0 / 144
Goodness-of-fit on F^2	1.135
Final R indices [$I>2\sigma(I)$]	R1 = 0.0346, wR2 = 0.0924
R indices (all data)	R1 = 0.0403, wR2 = 0.1080
Largest diff. peak and hole	0.217 and -0.247 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4582(1)	-737(1)	1687(1)	41(1)
Cl(2)	381(1)	423(1)	-2701(1)	46(1)
O(1)	2819(1)	707(3)	6114(3)	32(1)
N(1)	2305(1)	-256(3)	2505(3)	23(1)
C(1)	3606(1)	-704(3)	1895(4)	23(1)
C(2)	4054(1)	-349(3)	2996(4)	25(1)
C(3)	4097(1)	380(4)	5117(4)	28(1)
C(4)	3681(1)	722(3)	6131(4)	26(1)
C(5)	3220(1)	362(3)	5055(4)	23(1)
C(6)	3178(1)	-343(3)	2887(4)	21(1)
C(7)	2705(1)	-556(3)	1642(4)	23(1)
C(8)	1852(1)	-175(3)	1177(4)	21(1)
C(9)	1815(1)	625(3)	-907(4)	24(1)
C(10)	1362(1)	805(3)	-2095(4)	26(1)
C(11)	948(1)	183(4)	-1186(4)	26(1)
C(12)	977(1)	-609(3)	888(4)	28(1)
C(13)	1430(1)	-772(3)	2068(4)	25(1)

CF_3AcAcF_5A

Table 1. Crystal data and structure refinement for 1.

Identification code	9621
Empirical formula	$C_{11}H_5F_8NO$
Formula weight	319.16
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.183(3) Å α = 90°
	b = 9.028(4) Å β = 90.99(3)°
	c = 11.605(4) Å γ = 90°
Volume	1171.5(7) $Å^3$
Z	4
Density (calculated)	1.810 Mg/m^3
Absorption coefficient	0.203 mm^{-1}
F(000)	632
Crystal size	0.32 x 0.22 x 0.09 mm
θ range for data collection	2.86 to 23.99°
Index ranges	$-1 \le h \le 12$, $-1 \le k \le 10$, $-13 \le \ell \le 13$
Reflections collected	2415
Independent reflections	1799 (R_{int} = 0.0430)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1799 / 6 / 190
Goodness-of-fit on F^2	1.044
Final R indices [$I>2\sigma(I)$]	R1 = 0.0713, wR2 = 0.2047
R indices (all data)	R1 = 0.1238, wR2 = 0.2778
Largest diff. peak and hole	0.554 and -0.528 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	3716(4)	4892(5)	5257(3)	41(1)
N(1)	5219(4)	3986(6)	6922(4)	33(1)
F(1)	6713(3)	1893(5)	5984(3)	51(1)
F(2)	9025(4)	1581(5)	6673(4)	72(2)
F(3)	9927(3)	3315(6)	8379(4)	77(2)
F(4)	8513(4)	5390(6)	9395(4)	80(2)
F(5)	6225(4)	5694(5)	8691(3)	55(1)
C(1)	7154(5)	2755(7)	6820(5)	37(2)
C(2)	8329(6)	2590(8)	7175(6)	48(2)
C(3)	8775(6)	3478(9)	8057(7)	54(2)
C(4)	8076(7)	4509(9)	8551(6)	51(2)
C(5)	6900(6)	4674(8)	8188(5)	39(2)
C(6)	6422(5)	3786(7)	7314(5)	33(1)
C(7)	4245(5)	3727(7)	7519(5)	34(2)
C(8)	4381(6)	3086(9)	8709(5)	48(2)
C(9)	3115(5)	3966(7)	7038(5)	37(2)
C(10)	2950(5)	4511(7)	5923(5)	32(1)
C(11)	1655(4)	4632(5)	5441(4)	47(2)
F(6)	1374(4)	6040(4)	5241(3)	65(1)
F(7)	1557(3)	3941(5)	4440(3)	71(2)
F(8)	846(3)	4090(6)	6132(3)	94(2)

AcAc4(OCF_3)A

Table 1. Crystal data and structure refinement for 1.

Identification code	9618
Empirical formula	$C_{12}H_{12}F_3NO_2$
Formula weight	259.23
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 24.425(4) Å α = 90°
	b = 10.691(2) Å β = 105.44°
	c = 9.485(2) Å γ = 90°
Volume	2387.4(8) Å^3
Z	8
Density (calculated)	1.442 Mg/m^3
Absorption coefficient	0.129 mm^{-1}
F(000)	1072
Crystal size	0.57 x 0.52 x 0.15 mm
θ range for data collection	2.88 to 23.46°
Index ranges	$-26 \le h \le 25$, $-10 \le k \le 10$, $-1 \le \ell \le 10$
Reflections collected	3473
Independent reflections	1596 (R_{int} = 0.0262)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1596 / 0 / 175
Goodness-of-fit on F^2	1.049
Final R indices [$I>2\sigma(I)$]	R1 = 0.0415, wR2 = 0.1043
R indices (all data)	R1 = 0.0560, wR2 = 0.1159
Largest diff. peak and hole	0.318 and -0.251 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	2609(1)	8986(2)	-3505(2)	34(1)
O(1)	4744(1)	8540(2)	475(2)	48(1)
O(2)	2041(1)	10526(2)	-5591(2)	44(1)
F(1)	5564(1)	7714(2)	1379(2)	69(1)
F(2)	5209(1)	7605(3)	-902(2)	122(1)
F(3)	4874(1)	6517(2)	479(3)	108(1)
C(1)	3607(1)	9341(2)	-2793(3)	39(1)
C(2)	4142(1)	9247(2)	-1830(3)	43(1)
C(3)	4203(1)	8589(2)	-556(3)	38(1)
C(4)	3747(1)	8046(3)	-214(3)	39(1)
C(5)	3210(1)	8165(3)	-1158(3)	38(1)
C(6)	3138(1)	8796(2)	-2474(3)	32(1)
C(7)	5087(1)	7617(3)	342(3)	49(1)
C(8)	2146(1)	8235(2)	-3898(3)	33(1)
C(9)	2129(1)	7018(3)	-3140(3)	43(1)
C(10)	1695(1)	8584(2)	-5031(3)	33(1)
C(11)	1663(1)	9705(2)	-5856(3)	37(1)
C(12)	1147(1)	9888(3)	-7130(3)	55(1)

AcAc4(CH_3)A

Identification code	9617
Empirical formula	$C_{12}H_{15}NO$
Formula weight	189.25
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.2380(10) Å α = 90° b = 11.138(2) Å β = 109.00° c = 9.802(2) Å γ = 90°
Volume	1056.8(3) Å^3
Z	4
Density (calculated)	1.189 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	408
Crystal size	0.76 x 0.55 x 0.38 mm
θ range for data collection	2.79 to 23.99°
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 1$, $-1 \le \ell \le 11$
Reflections collected	2209
Independent reflections	1664 (R_{int} = 0.0201)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1664 / 0 / 142
Goodness-of-fit on F^2	1.043
Final R indices [$I>2\sigma(I)$]	R1 = 0.0455, wR2 = 0.1272
R indices (all data)	R1 = 0.0566, wR2 = 0.1391
Largest diff. peak and hole	0.211 and -0.197 eÅ^{-3}

Table 2. **Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.**

	x	y	z	U(eq)
N(1)	9246(2)	7922(1)	1656(2)	35(1)
O(1)	11162(2)	8672(1)	581(2)	47(1)
C(1)	7432(2)	9356(2)	1332(2)	38(1)
C(2)	6306(2)	9811(2)	1649(2)	41(1)
C(3)	5782(2)	9252(2)	2625(2)	40(1)
C(4)	6459(2)	8237(2)	3315(2)	44(1)
C(5)	7599(2)	7770(2)	3029(2)	41(1)
C(6)	8080(2)	8313(2)	2008(2)	33(1)
C(7)	4514(2)	9752(3)	2907(3)	55(1)
C(8)	9713(2)	6802(2)	1547(2)	35(1)
C(9)	9035(2)	5728(2)	1944(3)	45(1)
C(10)	10810(2)	6646(2)	1050(2)	37(1)
C(11)	11497(2)	7591(2)	584(2)	38(1)
C(12)	12675(2)	7269(2)	38(3)	50(1)

AcAc4FA

Table 1. Crystal data and structure refinement for 1.

Identification code	9649
Empirical formula	$C_{11}H_{12}FNO$
Formula weight	193.22
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.284(2) Å α = 90°
	b = 10.858(1) Å β = 106.93(1)°
	c = 10.177(1) Å γ = 90°
Volume	981.4(2) Å^3
Z	4
Density (calculated)	1.308 Mg/m^3
Absorption coefficient	0.097 mm^{-1}
F(000)	408
Crystal size	0.51 x 0.33 x 0.27 mm
θ range for data collection	2.81 to 23.50°
Index ranges	$-1 \le h \le 10$, $-1 \le k \le 12$, $-11 \le \ell \le 11$
Reflections collected	1961
Independent reflections	1448 (R_{int} = 0.0161)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1447 / 0 / 127
Goodness-of-fit on F^2	1.073
Final R indices [$I>2\sigma(I)$]	R1 = 0.0371, wR2 = 0.0950
R indices (all data)	R1 = 0.0458, wR2 = 0.1020
Largest diff. peak and hole	0.182 and -0.270 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	5514(1)	229(1)	1669(1)	57(1)
O(1)	-1217(1)	1271(1)	4556(1)	43(1)
N(1)	834(2)	2054(1)	3417(1)	31(1)
C(1)	2862(2)	643(1)	3614(2)	33(1)
C(2)	4027(2)	164(2)	3180(2)	38(1)
C(3)	4375(2)	707(2)	2103(2)	37(1)
C(4)	3596(2)	1704(2)	1423(2)	40(1)
C(5)	2418(2)	2171(2)	1843(2)	35(1)
C(6)	2059(2)	1658(1)	2960(2)	29(1)
C(7)	270(2)	3194(1)	3478(2)	30(1)
C(8)	966(2)	4287(2)	3016(2)	40(1)
C(9)	-923(2)	3337(1)	3998(2)	33(1)
C(10)	-1643(2)	2370(2)	4509(2)	34(1)
C(11)	-2954(2)	2685(2)	5032(2)	46(1)

AcAc3F,4(CH_3)A

Table 1. Crystal data and structure refinement for 1.

Identification code	9631
Empirical formula	$C_{12}H_{14}FNO$
Formula weight	207.24
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.3090(10) Å α = 90°
	b = 11.552(2) Å β = 107.95°
	c = 9.3070(10) Å γ = 90°
Volume	1054.4(2) Å^3
Z	4
Density (calculated)	1.305 Mg/m^3
Absorption coefficient	0.095 mm^{-1}
F(000)	440
Crystal size	0.54 x 0.51 x 0.30 mm
θ range for data collection	2.72 to 24.00°
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 1$, $-1 \le \ell \le 10$
Reflections collected	2214
Independent reflections	1658 (R_{int} = 0.0208)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1658 / 0 / 140
Goodness-of-fit on F^2	0.994
Final R indices [$I>2\sigma(I)$]	R1 = 0.0378, wR2 = 0.1022
R indices (all data)	R1 = 0.0461, wR2 = 0.1089
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.274 and -0.167 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	9333(1)	7192(1)	911(1)	57(1)
O(1)	3791(1)	6379(1)	4326(2)	44(1)
N(1)	5785(1)	7042(1)	3277(2)	33(1)
C(1)	7468(2)	5557(1)	3627(2)	35(1)
C(2)	8607(2)	5079(2)	3374(2)	37(1)
C(3)	9290(2)	5612(2)	2479(2)	35(1)
C(4)	8722(2)	6639(2)	1828(2)	36(1)
C(5)	7582(2)	7148(2)	2020(2)	35(1)
C(6)	6951(2)	6612(1)	2967(2)	31(1)
C(7)	5377(2)	8136(1)	3418(2)	31(1)
C(8)	6128(2)	9150(2)	3065(2)	43(1)
C(9)	4273(2)	8318(2)	3923(2)	33(1)
C(10)	3516(2)	7432(2)	4362(2)	35(1)
C(11)	2340(2)	7782(2)	4903(2)	46(1)
C(12)	10546(2)	5102(2)	2237(2)	45(1)

AcAc2(OH)A

Table 1. Crystal data and structure refinement for .

Identification code	9616
Empirical formula	$C_{11}H_{13}NO_2$
Formula weight	191.22
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.7870(10) Å $\alpha = 90^\circ$
	b = 10.4180(10) Å $\beta = 90^\circ$
	c = 11.177(5) Å $\gamma = 90^\circ$
Volume	1023.2(5) $Å^3$
Z	4
Density (calculated)	1.241 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	408
Crystal size	0.57 x 0.32 x 0.21 mm
θ range for data collection	2.67 to 23.97°
Index ranges	$-1 \le h \le 10$, $-1 \le k \le 11$, $-1 \le \ell \le 12$
Reflections collected	1145
Independent reflections	1068 (R_{int} = 0.0560)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1068 / 0 / 127
Goodness-of-fit on F^2	1.066
Final R indices [$I>2\sigma(I)$]	R1 = 0.0471, wR2 = 0.1186
R indices (all data)	R1 = 0.0546, wR2 = 0.1258
Absolute structure parameter	1(3)
Largest diff. peak and hole	0.142 and -0.169 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	1982(3)	785(3)	7797(2)	27(1)
O(1)	830(2)	2074(2)	9618(2)	36(1)
O(2)	4550(2)	1860(2)	8502(2)	37(1)
C(1)	-65(3)	1113(3)	9168(3)	28(1)
C(2)	-1467(3)	802(3)	9645(3)	36(1)
C(3)	-2314(4)	-184(3)	9146(4)	42(1)
C(4)	-1745(4)	-869(4)	8192(4)	44(1)
C(5)	-332(4)	-580(3)	7726(3)	39(1)
C(6)	505(3)	436(3)	8190(3)	28(1)
C(7)	2604(3)	779(3)	6706(3)	27(1)
C(8)	1710(4)	317(4)	5644(3)	44(1)
C(9)	4064(4)	1226(3)	6525(3)	31(1)
C(10)	4991(4)	1777(3)	7428(3)	30(1)
C(11)	6520(4)	2298(4)	7096(4)	46(1)

$Cu[SAL3F,4(CH_3)]_2$

Table 1. Crystal data and structure refinement for 1.

Identification code	9675
Empirical formula	$C_{28}H_{22}CuF_2N_2O_2$
Formula weight	520.02
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 10.752(1) Å α = 90°
	b = 7.893(1) Å β = 90°
	c = 27.391(3) Å γ = 90°
Volume	2324.6(4) Å^3
Z	4
Density (calculated)	1.486 Mg/m^3
Absorption coefficient	0.985 mm^{-1}
F(000)	1068
Crystal size	0.58 x 0.43 x 0.34 mm
θ range for data collection	2.97 to 25.00°
Index ranges	$-1 \le h \le 12$, $-1 \le k \le 9$, $-32 \le \ell \le 1$
Reflections collected	2677
Independent reflections	2026 (R_{int} = 0.0348)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2025 / 0 / 169
Goodness-of-fit on F^2	1.054
Final R indices [$I>2\sigma(I)$]	R1 = 0.0441, wR2 = 0.1097
R indices (all data)	R1 = 0.0700, wR2 = 0.1265
Largest diff. peak and hole	0.616 and -0.504 eÅ^{-3}

* The F atom and H atom on C10 and C12 are disordered 50% prob at each site.

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	0	0	20(1)
F(1)	-3053(6)	-1888(9)	1943(2)	71(2)
F(1')	932(4)	48(6)	1974(1)	38(1)
O(1)	376(2)	-1658(3)	-472(1)	26(1)
N(1)	-711(3)	-1776(4)	450(1)	21(1)
C(1)	-1806(3)	-5189(4)	-339(1)	24(1)
C(2)	-1805(3)	-5837(5)	-804(1)	26(1)
C(3)	-1069(3)	-5046(5)	-1157(1)	26(1)
C(4)	-347(3)	-3662(5)	-1045(1)	24(1)
C(5)	-338(3)	-2972(4)	-567(1)	22(1)
C(6)	-1110(3)	-3750(4)	-213(1)	20(1)
C(7)	-1145(3)	-3196(5)	286(1)	21(1)
C(8)	-858(3)	-1485(4)	968(1)	23(1)
C(9)	-1959(4)	-1861(5)	1206(1)	30(1)
C(10)	-2033(4)	-1589(6)	1701(1)	42(1)
C(11)	-1063(4)	-961(6)	1976(1)	40(1)
C(12)	13(4)	-592(6)	1722(1)	37(1)
C(13)	135(3)	-830(5)	1226(1)	27(1)
C(14)	-1174(5)	-647(7)	2522(2)	58(1)

$Cu[SAL3,5(CF_3)_2]_2$

Table 1. Crystal data and structure refinement for 1.

Identification code	9666
Empirical formula	$C_{15}H_8Cu_{0.50}F_6NO$ * ..... $C_{30}H_{16}F_{12}N_2O_2$
Formula weight	363.99 ..... 727.98
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 14.607(2) Å α = 90°
	b = 7.423(1) Å β = 98.07(1)°
	c = 27.109(2) Å γ = 90°
Volume	2910.3(6) Å^3
Z	8 4
Density (calculated)	1.662 Mg/m^3
Absorption coefficient	0.860 mm^{-1}
F(000)	1452
Crystal size	0.47 x 0.36 x 0.33 mm
θ range for data collection	2.82 to 25.00°
Index ranges	$-1 \le h \le 17$, $-1 \le k \le 8$, $-32 \le \ell \le 31$
Reflections collected	3160
Independent reflections	2566 (R_{int} = 0.0173)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2566 / 0 / 267
Goodness-of-fit on F^2	1.062
Final R indices [$I>2\sigma(I)$]	R1 = 0.0395, wR2 = 0.0887
R indices (all data)	R1 = 0.0583, wR2 = 0.0983
Largest diff. peak and hole	0.179 and -0.305 eÅ^{-3}

* in asymmetric unit with Cu on 0, y, 1/4 position of space group C2/c

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	452(1)	2500	49(1)
O(1)	716(1)	-100(3)	2000(1)	64(1)
N(1)	1081(1)	1119(3)	2984(1)	43(1)
F(1)	2457(6)	474(15)	4946(4)	141(5)
F(2)	1174(7)	80(20)	5179(3)	166(5)
F(3)	1669(11)	-1715(11)	4693(3)	173(4)
F(1')	1639(14)	1062(22)	5225(4)	121(6)
F(2')	1168(11)	-1327(28)	4889(7)	125(6)
F(3')	2421(11)	-362(43)	4795(8)	135(10)
F(4)	-1142(9)	5083(19)	3700(4)	135(5)
F(5)	-81(6)	6370(12)	4170(8)	158(4)
F(6)	-965(11)	4628(22)	4451(5)	155(5)
F(4')	-426(20)	6204(24)	3778(9)	163(8)
F(5')	-1384(8)	4396(36)	3943(12)	182(9)
F(6')	-521(15)	5481(27)	4493(4)	124(6)
C(1)	1571(2)	342(4)	1983(1)	56(1)
C(2)	1915(3)	219(5)	1518(1)	77(1)
C(3)	2806(3)	656(6)	1477(2)	87(1)
C(4)	3414(3)	1228(5)	1883(2)	84(1)
C(5)	3112(2)	1354(4)	2341(1)	68(1)
C(6)	2189(2)	931(4)	2397(1)	53(1)
C(7)	1915(2)	1230(4)	2877(1)	49(1)
C(8)	936(2)	1554(4)	3483(1)	42(1)
C(9)	1367(2)	632(4)	3888(1)	49(1)
C(10)	1171(2)	1088(4)	4360(1)	55(1)
C(11)	559(2)	2442(5)	4426(1)	59(1)
C(12)	128(2)	3356(4)	4013(1)	51(1)
C(13)	300(2)	2892(4)	3544(1)	46(1)
C(14)	1618(3)	15(7)	4802(1)	83(1)
C(15)	-527(3)	4863(6)	4074(1)	77(1)

$Cu[SAL4(OCF_3)]_2$

Table 1. Crystal data and structure refinement for 1.

Identification code	9680
Empirical formula	$C_{14}H_9Cu_{0.50}F_3NO_2$
Formula weight	311.99
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.768(1) Å α = 90°
	b = 10.663(1) Å β = 95.87(1)°
	c = 8.320(1) Å γ = 90°
Volume	1303.3(2) Å^3
Z	4
Density (calculated)	1.590 Mg/m^3
Absorption coefficient	0.919 mm^{-1}
F(000)	630
Crystal size	0.69 x 0.55 x 0.22 mm
θ range for data collection	2.77 to 26.50°
Index ranges	$-18 \le h \le 18$, $-13 \le k \le 1$, $-1 \le \ell \le 10$
Reflections collected	3579
Independent reflections	2684 (R_{int} = 0.0307)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2683 / 0 / 214
Goodness-of-fit on F^2	1.033
Final R indices [$I>2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1235
R indices (all data)	R1 = 0.0783, wR2 = 0.1432
Largest diff. peak and hole	0.428 and -0.273 eÅ^{-3}

TORSION ∡ C7 N1 C8 C13 51.3°

" ∡ Cu1 N1 C8 C9 55.7°

Cu1 N1 O1 (N1 O1') planar by space group symmetry

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	5000	0	50(1)
O(1)	-905(2)	4715(2)	1386(3)	61(1)
O(2)	4547(2)	6337(4)	1210(4)	104(1)
N(1)	840(2)	5702(2)	1848(3)	48(1)
C(1)	-597(3)	6745(3)	4935(4)	58(1)
C(2)	-1451(3)	6743(3)	5396(5)	64(1)
C(3)	-2130(3)	6063(3)	4498(4)	63(1)
C(4)	-1939(2)	5398(3)	3164(4)	57(1)
C(5)	-1059(2)	5383(3)	2649(4)	50(1)
C(6)	-377(2)	6093(3)	3555(4)	47(1)
C(7)	541(2)	6128(3)	3148(4)	51(1)
C(8)	1794(2)	5868(3)	1727(4)	53(1)
C(9)	2316(3)	4858(3)	1331(4)	61(1)
C(10)	3230(3)	4991(4)	1221(5)	71(1)
C(11)	3612(2)	6149(5)	1459(5)	76(1)
C(12)	3113(3)	7177(4)	1841(6)	87(1)
C(13)	2194(2)	7026(4)	1968(6)	73(1)
F(1)	5929(7)	6708(10)	1967(19)	143(4)
F(2)	5000(6)	6715(19)	3717(14)	169(7)
F(3)	5275(10)	5015(14)	2735(19)	188(6)
C(14)	5165(4)	6233(10)	2400(10)	120(2)
F(3')	5020(19)	5688(41)	3590(46)	221(19)
F(2')	5138(18)	7434(33)	3037(47)	276(23)
F(1')	5958(15)	5927(30)	2168(36)	188(16)

$Cu[SAL4F]_2$

Table 1. Crystal data and structure refinement for 1.

Identification code	9671
Empirical formula	$C_{26}H_{18}CuF_2N_2O_2$
Formula weight	491.96
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.009(2) Å α = 95.08(1)°
	b = 10.4780(1) Å β = 92.44(1)°
	c = 10.560(2) Å γ = 105.42(2)°
Volume	1060.9(3) Å^3
Z	2
Density (calculated)	1.540 Mg/m^3
Absorption coefficient	1.074 mm^{-1}
F(000)	502
Crystal size	0.48 x 0.36 x 0.22 mm
θ range for data collection	2.50 to 29.06°
Index ranges	$-1 \le h \le 11$, $-12 \le k \le 12$, $-12 \le \ell \le 12$
Reflections collected	4238
Independent reflections	3330 (R_{int} = 0.0217)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3309 / 0 / 301
Goodness-of-fit on F^2	1.165
Final R indices [$I>2\sigma(I)$]	R1 = 0.0505, wR2 = 0.1108
R indices (all data)	R1 = 0.0768, wR2 = 0.1415
Largest diff. peak and hole	0.327 and -0.381 eÅ^{-3}

Table [illegible] Atomic coordinates [illegible] equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	0	5000	35(1)
F(1)	5402(4)	3447(4)	9128(4)	67(1)
O(1)	-1125(4)	-1763(4)	4797(3)	43(1)
N(1)	796(5)	-260(4)	6707(4)	33(1)
C(1)	-1581(7)	-3161(6)	7836(6)	47(2)
C(2)	-2666(7)	-4268(7)	7504(6)	53(2)
C(3)	-3257(6)	-4511(6)	6246(6)	49(2)
C(4)	-2720(6)	-3671(6)	5358(6)	44(2)
C(5)	-1605(6)	-2522(5)	5677(5)	38(1)
C(6)	-1030(6)	-2278(5)	6956(5)	34(1)
C(7)	161(6)	-1200(6)	7365(5)	37(1)
C(8)	1987(6)	716(5)	7346(5)	33(1)
C(9)	3251(6)	970(6)	6775(6)	45(2)
C(10)	4402(7)	1886(6)	7383(6)	49(2)
C(11)	4272(6)	2539(6)	8530(6)	46(2)
C(12)	3046(7)	2311(6)	9105(5)	45(2)
C(13)	1883(6)	1381(6)	8508(5)	40(1)
Cu(2)	0	5000	10000	35(1)
F(1A)	4343(4)	7889(4)	5703(4)	71(1)
O(1A)	-1103(5)	3269(4)	10171(3)	46(1)
N(1A)	465(5)	4417(4)	8250(4)	33(1)
C(1A)	-1976(6)	1183(6)	7127(5)	41(1)
C(2A)	-2965(6)	136(6)	7461(6)	46(2)
C(3A)	-3328(7)	147(6)	8729(6)	49(2)
C(4A)	-2708(7)	1196(6)	9614(6)	47(2)
C(5A)	-1683(6)	2292(5)	9294(5)	36(1)
C(6A)	-1301(6)	2285(5)	8015(5)	33(1)
C(7A)	-216(6)	3326(5)	7599(5)	34(1)
C(8A)	1482(6)	5317(5)	7592(5)	35(1)
C(9A)	1071(6)	5797(5)	6498(5)	36(1)
C(10A)	2041(7)	6662(6)	5872(5)	44(2)
C(11A)	3388(7)	7034(6)	6338(6)	47(2)
C(12A)	3824(7)	6576(6)	7413(6)	51(2)
C(13A)	2872(6)	5714(6)	8045(5)	43(2)

Anhydrous Bis[acetylacetonato]Co

Table 1. **Crystal data and structure refinement for 1.**

Identification code	9661
Empirical formula	$C_{10}H_{14}CoO_4$
Formula weight	257.14
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.276(2) Å α = 90°
	b = 4.677(1) Å β = 92.22(2o
	c = 11.296(2) Å γ = 90°
Volume	542.5(2) Å^3
Z	2
Density (calculated)	1.574 Mg/m^3
Absorption coefficient	1.572 mm^{-1}
F(000)	266
Crystal size	0.48 x 0.21 x 0.09 mm
θ range for data collection	2.63 to 25.00°
Index ranges	$-1 \le h \le 12$, $-1 \le k \le 5$, $-13 \le \ell \le 13$
Reflections collected	1420
Independent reflections	961 (R_{int} = 0.0289)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	961 / 0 / 70
Goodness-of-fit on F^2	1.136
Final R indices [$I>2\sigma(I)$]	R1 = 0.0528, wR2 = 0.1339
R indices (all data)	R1 = 0.0638, wR2 = 0.1432
Largest diff. peak and hole	0.984 and -1.201 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Co(1)	0	0	0	22(1)
O(1)	655(3)	1985(6)	-1341(2)	33(1)
O(2)	-1620(3)	2038(6)	-67(2)	32(1)
C(3)	-1897(4)	4163(10)	-727(4)	29(1)
C(4)	105(4)	4111(10)	-1860(4)	30(1)
C(5)	-1084(4)	5260(9)	-1589(4)	33(1)
C(6)	-3175(4)	5562(11)	-526(4)	40(1)
C(7)	859(5)	5438(10)	-2833(4)	41(1)