

Synthesis and Characterisation of Cu(II) Complexes with Schiff Base of Salicylidene-4-Tri-flouro-methyl Aniline and its Hydrogen Analogue

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Summary: Schiff base of 4-trifluoromethyl aniline and salicylaldehyde (4-CF₃ SAL) and its Cu complex was synthesized and characterized by using different spectroscopic techniques i.e NMR, UV, IR, and mass spectra. These were studied in comparison with its hydrogen analogue (salicylidene 4-methyl aniline) and corresponding Cu complex, with respect to its stability, peak shift and functional group effect on vibrational spectra.

Introduction

The compounds which are called "Schiff bases" include various types with C=N functional group¹, but this paper is concerned mainly with the synthesis and characterization of some novel Schiff bases derived from the condensation of salicylaldehyde with both fluoro-substituted aniline, its Cu complex in comparison with its non-fluoro hydrogen analogues and the corresponding Cu complex. The study of fluoro compounds are becoming more and more important because of their electronegative behavior and in relation with environment.

Imine formation is normally an acid catalyzed 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]. Aromatic aldehydes react readily under mild conditions and at relatively low temperatures with or, if liquid, without a suitable solvent. 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 [3]. Halogen substituents exert their expected effect in causing a withdrawal of electron density and hence in reducing the basic strength [4,5].

Salman and coworkers studied IR spectra of some salicylidene schiff bases and assigned the functional group peaks i. e. C=O, and C=N. Other absorptions were also assigned which helps in understanding the structure of the related compounds [6].

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 ¹H 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 [7]. B. Kamienski et al studied salicylidene Schiff bases with respect to their ¹⁵N and ¹³C NMR for assigning their O-H and N-H peaks [8]. Many studies of the electronic spectra of bidentate N,O Schiff bases derived from chiral primary amines have been reported [9]. NMR studies are mainly applied to elucidating the structural features of Schiff bases in solution. Several groups have determined the crystal structures of some salicylidene anilines. The most interesting feature of these structures is intramolecular hydrogen-bonding [10].

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 [11]. These complexes have a *trans* arrangement of ligands [12-13]. Cu(II) complexes of salicylideneimine and of its N-n-alkyl derivatives have essentially *trans*-planar structures in the solid state [14-15] Spectroscopic evidences [16-17] suggest that these complexes have

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the same structures in the solution as in the solid phase.

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. All chemicals were used as obtained from Aldrich.

General method of preparation of ligands:

To an ethanolic solution of salicylaldehyde (1 M, 25ml) a few drops of pH 5.0 solution (HCl + NaOH) were added to protonate the aldehyde. To it was added an ethanolic solution of the substituted aniline (1 M, 25ml) [calculated amounts are given in Table 2.1 for each ligand] in several small portions, in a 1:1 ratio. The reaction mixture was then stirred and refluxed for one hour, and allowed to cool slowly. The resulting precipitate was filtered off by suction washed by water, and dried using a vacuum desiccator. The dried precipitates were recrystallised from a CH₂Cl₂/n-hexane (1:10) mixture.

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 CHCl₃ as rhombic plates and dried in a desiccator under vacuum.

Table 1 Physical Characterization

Comps	M.P. °C	Colour/State	% Yield	λ_{max} /nm
SAL4(CF ₃)	104	Yellow/Flakes	54	350
SAL4(CH ₃)	92	Yellow/needles	78	322
Cu[SAL4(CH ₃) ₂]	120	Green/Powder	72	345
Cu[SAL4(CH ₃) ₂]	116	Brown/Powder	75	315

Salicylidene-4-trifluoro-Aniline = SAL4(CF₃), Salicylidene-4-methyl Aniline = SAL4(CH₃),

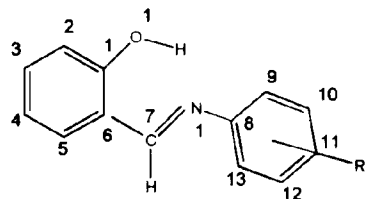


Table 2 ¹H NMR Peaks

Comps	Peaks Assigned	δ	Integral	Multiplicity
SAL4(CF ₃) ₂	Ar.H	6.79-7.56	8	m
	C ₇ H	8.47	1	s
	1-OH	12.69	1	s
SAL4(CH ₃) ₂	CH ₃	2.31	3	s
	Ar.H	6.79-7.33	8	m
	C ₇ H	8.76	1	s
	1-OH	13.33	1	s

Both compounds gave satisfactory ¹³C-DEPT NMR spectra. The peaks were in accordance to literature [18-20].

Table 3: ¹³C NMR Peaks Assignments

Compounds	Peaks Assigned	δ Values
SAL4(CF ₃) ₂	C ₇	164.5
	CF ₃	127.9, 128.4, 129.0
	C ₁	151.6
	C ₈	161.2
	C ₁₁	122.0
	C ₆	118.9
	ArC _{9-10,12-13}	117.4, 119.4, 121.5, 126.7, 130.6, 133.9
	SAL4(CH ₃) ₂	CH ₃
SAL4(CH ₃) ₂	C ₇	161.7
	C ₈	161.1
	C ₁₁	119.3
	C ₁	136.9
	ArC _{9-10,11-12}	117.2, 119.0, 121.0, 132.1, 132.9

Table 4 ¹⁹F NMR

Compound	Reference	δ	M*
SAL4(CF ₃)	Coupled	-62.587	s
	Decoupled	-62.332	s

* Multiplicity

Mass Spectrometry:

All the prepared compounds were characterized by a variety of mass spectroscopic techniques including +FAB, EI or Electron Spray as required by the nature of the compound. All gave strong peaks corresponding to the molecular ions. No significant fragmentation was observed, because the expected fragments were too small for the mass spectrum detection.

Table 5 Mass Spectroscopic Data

Compounds	Calc. Mass	Ions Observed
SAL4(CF ₃)	265.117	E Spray MH+ 266 Polar
SAL4(CH ₃)	211.0	EIM+211(Nonpolar, Volatile, Stable)
Cu[SAL4(CF ₃) ₂]	593	+FAB 592 CuL ₂ , 328CuL ₁
Cu[SAL4(CH ₃) ₂]	485	+FAB 485 CuL ₂ , CuL ₁ 274

IR DATA

All the salicylideneanilines were characterised by I.R. spectroscopy. The I.R. spectra were recorded as solutions in CH₂Cl₂ against a CH₂Cl₂ blank. All

the characteristic bands 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.

The M-N bands in complexes are in the region 400-500 cm^{-1} and the M-O the bands are in the region 500-570 cm^{-1} . This is consistent with the previous work described in the literature for M-N and M-O bonds for NO donor imine chelates²⁴. No substituent effects on M-N and M-O bands are observed.

Table-6: IR Data of Ligands recorded in solutions in CH_2Cl_2

Compound	C-H(S & B)*	C=N(S)	O-H(S)	N-C	C-F
SAL4(CF ₃)	3035 2970s, 870,980	1590s	4000, 3740m	1370m	1060, 1200s
SAL4(CH ₃)	3060,2970, 780,840s	1610s	4000 .3660m	1360m	-

Table 7 IR Data of complexes recorded in solutions in CH_2Cl_2

Complexes	C=N	C-N	C-O	M-N	M-O
Cu[SAL4(CF ₃) ₂]	1580	1370	1110	550	470
Cu[SAL4(CH ₃) ₂]	1590	1385	1140	580	490

UV Scans

U.V. scans of the solutions of the ligands as well as their complexes 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. The λ_{max} of Cu[SAL4(CF₃)₂] was 655nm. Thus it was concluded that the compounds were stable in solution.

Conclusions

The preparation of these ligands and their complexes was straightforward. The ligands were isolated as crystals, and were easily recrystallised for purification. The complexes were obtained as powder and was purified using by recrystallization method.

They are air and hydrolytically stable in solid and solution forms. No significant effect of electron

donating or electron withdrawing substituent groups on the properties of the ligands was found.

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