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Synthesis, spectroscopic characterization, electrochemical behaviour, reactivity and antibacterial activity of some transition metal complexes with 2-(*N*-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene

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Abstract

Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with a potentially tridentate Schiff base, formed by condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde were synthesized and characterized on the basis of elemental analyses, molar conductance values, magnetic susceptibility measurements, UV–vis, IR, EPR and NMR spectral data, wherever possible and applicable. Spectral studies reveal that the free ligand exists in a bifunctionally hydrogen bonded manner and coordinates to the metal ion in a tridentate fashion through the deprotonated phenolate oxygen, azomethine nitrogen and ester carbonyl group. On the basis of electronic spectral data and magnetic susceptibility measurements, suitable geometry has been proposed for each complex. The EPR spectral data of the Cu(II) complex showed that the metal–ligand bonds have considerable covalent character. The Ni(II) complex has undergone facile transesterification reaction when refluxed in methanol for a lengthy period. X-ray diffraction studies of Cu(II) complex showed that the complex has an orthorhombic crystal lattice. In view of the biological activity of thiophene derivatives, the ligand and the complexes were subjected to antibacterial screening. It has been observed that the antibacterial activity of the ligand increased on chelation with metal ion.

Keywords: Metal complexes; 2-(*N*-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene; EPR spectrum; Cyclic voltammetry; Reactivity; XRD; Antibacterial activity

1. Introduction

Schiff bases form an interesting class of chelating ligands that has enjoyed popular use in the coordination chemistry of transition, inner-transition and main group elements [1–5]. Among the prodigious number and variety of Schiff base complexes, those derived from salicylaldimines form the major part, mainly because of their synthetic proclivity and structural diversities. However, a deep survey of literature on salicylaldimine complexes reveal that metal chelates of salicylaldimines derived from heterocyclic systems particularly those from aminothiophenes have been largely ignored [6]. Most probably the instability of aminothiophenes is mainly responsible for this omission [7]. But in this investigation, 2-aminothiophene has been made stable by suitable substitution at the remaining positions of the thiophene ring by an ester group and two methyl groups [8]. The resulting compound, namely 2-amino-3-carboxyethyl-4,5-dimethylthiophene has been condensed with salicylaldehyde to form a potentially tridentate Schiff base, viz., 2-(*N*-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene (Hsat) containing an ONO donor sequence. Apart from providing stability to 2-aminothiophene, introduction of a carboxyethyl group at 3-position of the thiophene ring has provided further scope for reactivity and a new coordination site. In addition to this, highly substituted thiophenes have shown extensive potential in pharmaceutical industry. The Schiff base obtained has been versatile in forming a series of complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) ions under well defined conditions and these complexes have been investigated with particular reference to the structural aspects of the ligand moiety in the metal complexes. Besides the structural diversities and bonding interactions, bioisosteric relationship of thiophene to benzene has led to several structures of drug analogs in which benzene rings have been replaced by thiophene rings and the vivid applications of thiophene derivatives as important therapeutic agents have been well documented in literature [7]. It is

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expected that metal chelates containing thiophene ring system would carry bioisosteric relationship and therapeutic values, thus introducing another class of metal-based thiophene derivatives. In this investigation we report the synthesis, spectroscopic characterization, electrochemical behaviour, X-ray diffraction study, reactivity and antibacterial activity of some 3d metal complexes with a host of the title ligand.

2. Experimental

2.1. Materials and methods

All the chemicals used were of Analytical grade. Commercial solvents were distilled and used for synthesis. For physicochemical measurements, the solvents were purified by standard methods. Carbon, hydrogen, nitrogen and sulphur analyses were performed using Elementar Systeme, Vario EL III CHN analyser and the metal contents in the complexes were determined using a Nulab GBC 902 atomic absorption spectrophotometer in an acetylene/air flame. Molar conductance measurements were conducted using 10^{-3} M solutions of the complexes in appropriate solvents at room temperature with a Systronic model 304 digital conductivity meter. Infrared spectral studies were carried out using KBr discs on a Thermo-Nicolet Avatar 370 FT-IR spectrophotometer and electronic spectra were recorded on a Varian Cary 5000 UV–vis–NIR spectrophotometer. Far IR spectra were recorded on a polytec FIR 30 Fourier spectrometer using CsI discs. The proton NMR spectra of the ligand and the zinc(II) complex were recorded on a JEOL GSX 400 MHz FT NMR spectrometer employing TMS as internal reference and $CDCl_3$ as solvent. The EPR spectrum of the copper(II) complex was recorded using a Varian-112 EPR spectrometer employing DPPH as reference material. X-ray diffraction experiments were carried out on a Siemens D 5005 model spectrometer. Cyclic voltammetric study of copper(II) complex was performed with a BAS CV-50 analyser.

2.2. Synthesis of ligand

The starting material for the synthesis of the ligand, 2-amino-3-carboxyethyl-4,5-dimethylthiophene, was prepared by Gewald synthesis [8]. The ligand was prepared by condensing salicylaldehyde with an ethanolic solution of 2-amino-3-carboxyethyl-4,5-dimethylthiophene in 1:1 molar ratio (78% yield, m.p. 130 °C).

2.3. Preparation of metal complexes

The metal complexes were prepared by the following general procedure. To a hot magnetically stirred ethanolic solution (60 ml) of the ligand, added aqueous/ethanolic solution of metal(II) salts in appropriate ratios. The pH of the solution was adjusted to 6.5–7.0 and refluxed on a water-bath for 4–6 h. Then the volume of the solution was reduced to half the initial volume by evaporating on a water-bath. On cooling, the complex separated was filtered, dried and further purified by recrystallization from hot ethanol.

2.4. Antibacterial screening

Antibacterial activity of the ligand and the metal complexes were examined by agar diffusion method using streptomycin as standard [9].

The minimum inhibitory concentration of the ligand and complexes were ascertained using different bacteria. The concentration of the drug solution was maintained to be 200 μg/ml in DMSO. One day prior to the test, the bacteria was inoculated in a nutrient broth (inoculation medium) and kept in an incubator at 37 °C for 24 h. The hot nutrient agar solution (20 ml) was transferred into sterilized petri dishes and allowed to attain room temperature. The seed layer medium was melted and cooled to ∼45 °C with gentle shaking. The previously grown subculture was added to the seed layer medium aseptically and mixed well. It was immediately raked into the petri dishes and allowed to attain room temperature. Using a sterile cork borer, small wells were made in the agar medium. Then the drug solution (0.05 ml) was added and the petri dishes were allowed to cool in air to facilitate diffusion. The petri dishes were then kept in an incubator at 37 °C for about 48 h. On completion of the incubation period, the zones of inhibition around the wells were measured.

2.5. Transesterification

Transesterification was carried out using a reported method [10]. About 0.2 g of [Ni(sat)Cl] was dissolved in methanol (100 ml) and refluxed for 72 h on a water-bath. The resulting solution was evaporated to dryness and the solid product obtained was washed repeatedly with ether and dried over P_2O_5 in vacuum.

3. Results and discussion

Analytical data indicated that salicylaldehyde condensed with 2-amino-3-carboxyethyl-4,5-dimethylthiophene in 1:1 molar ratio and the product formed well defined complexes with the metal salts. Formation of the complexes can be symbolized as follows

$$MX_2 + Hsat \rightarrow [M(sat)X] + HX$$

M = Ni(II), Cu(II) or Zn(II); X = CI or NO_3.

$$MX_2 + 2Hsat \rightarrow [M(sat)_2] + 2HX$$

M = Mn(II), Fe(II) or Co(II); X = CI or NO_3; Hsat = 2-(*N*-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene.

Formulation of the complexes has been based on their elemental analytical data, molar conductance values and magnetic susceptibility data. Mn(II), Fe(II) and Co(II) complexes showed 1:2 metal–ligand stoichiometry while the other complexes exhibited 1:1 metal–ligand ratio (Table 1). All the complexes are non-hygroscopic, decomposed above 250 °C and possess good keeping qualities. The molar conductance values adequately support the non-electrolytic nature of the metal complexes [11].

Table 1
Analytical data and other details of the metal complexes

Complex	Molecular mass	Yield (%)	Analytical data[a]					Molar conductance (Ω^{-1} cm^2 mol^{-1}) DMSO
			M	C	H	N	S	
[Mn(sat)$_2$]	659	74	8.5 (8.3)	58.1 (58.3)	4.8 (4.9)	4.3 (4.2)	9.8 (9.7)	9.8
[Fe(sat)$_2$]	660	70	8.7 (8.5)	58.4 (58.1)	4.9 (4.8)	4.4 (4.2)	9.8 (9.7)	9.6
[Co(sat)$_2$]	663	75	8.7 (8.9)	57.7 (57.9)	4.7 (4.8)	4.1 (4.2)	9.6 (9.7)	9.8
[Ni(sat)Cl]	396	72	14.7 (14.8)	48.6 (48.4)	4.1 (4.0)	3.6 (3.5)	8.2 (8.1)	8.6
[Cu(sat)Cl]	401	76	15.7 (15.8)	47.7 (47.9)	3.8 (3.9)	3.3 (3.5)	7.8 (7.9)	9.4
[Zn(sat)Cl]	403	73	16.0 (16.2)	47.5 (47.6)	4.0 (3.9)	3.7 (3.5)	7.9 (8.0)	8.8

[a] Calculated values are given in bracket.

3.1. Structure of the ligand

On the basis of UV, IR and proton NMR spectral studies, a phenolimine structure has been established for the ligand. Introduction of a hydroxy group at *ortho* position to the azomethine linkage raises the possibility of phenolimine–quinoneamine tautomerism. A bulk of information concerning this could be obtained from ultraviolet spectral studies, a method well suited for such investigation. It has been reported that the tautomeric equilibrium depends on the extent of conjugation, nature and position of the substituent, polarity of the solvent and this phenomenon has drawn considerable attention both from theoretical and experimental point of view [12]. Ultraviolet spectral studies on *N*-salicylidenebutylamine gave some important conclusion relating to this. Ultraviolet spectrum of the above compound in ethanol exhibited strong bands at 253 and 312 nm for the phenolimine form (assignable for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively) and much weaker bands at 278 and 401 nm for the quinoneamine form [13]. Spectra of compounds which cannot acquire the quinonoid form, for example, 3-hydroxybenzilidene bases lack the *ca*. 400 nm band altogether and systems which assume the quinonoid form show a prominent band at *ca*. 400 nm. Recently this phenomenon was examined in detail by Antonov et al., who explained this type of tautomerism exhibited by 2-hydroxy-1-naphthaldehyde Schiff base and arrived at the conclusion that the compound exists in the quinonoid form [12]. The ligand under investigation is also capable of exhibiting phenolimine–quinoneamine tautomerism (Fig. 1a and b). However, the ultraviolet spectrum of the ligand (recorded in ethanol) gave characteristic bands at 255 and 315 nm for the phenolimine form ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions). On the basis of the above spectral data, a phenolimine structural form of the ligand has been established (Fig. 1a). It has been reported that some amino acid Schiff bases derived from 2-hydroxy-1-naphthaldehyde exists predominantly in the quinoneamine form and the ligand is coordinated to the metal ion through the azomethine nitrogen, one of the carboxylate oxygen atoms and the quinone oxygen [14].

In agreement with UV spectral data, infrared spectrum of the ligand exhibited a broad band spreading well over the region 3300–3000 cm^{-1} and centred at 3200 cm^{-1}, which can be attributed to hydrogen bonded phenolic ν(O–H) and ν(C–O) has been observed at 1287 cm^{-1}. A strong band appearing at 1702 cm^{-1} is due to the ester carbonyl group and another medium intensity band appearing at 1630 cm^{-1} can be assignable to ν(C=N) of the azomethine group. However vibrations characteristic of the substituted thiophene ring have been observed at 1530, 1425 and 1360 cm^{-1} [15]. The ester carbonyl group is also involved in weak hydrogen bonding with the phenolic –OH of the salicylaldehyde moiety forming a sort of bifunctional hydrogen bonding [16]. However, in competition with azomethine group, for phenolic –OH, ester carbonyl can manage only a meagre share. This explains why the ester carbonyl frequency in the ligand is relatively higher than that in the free amine (1660 cm^{-1}). Above spectral data adequately support the formulation of the ligand as in Fig. 1a. The proton magnetic resonance spectral data of the ligand adequately support the facts drawn on the basis of UV and IR spectral data. The proton NMR spectrum of the ligand recorded in $CDCl_3$ (Fig. 2) exhibited a signal at 12.81δ. The downward shift of the proton is

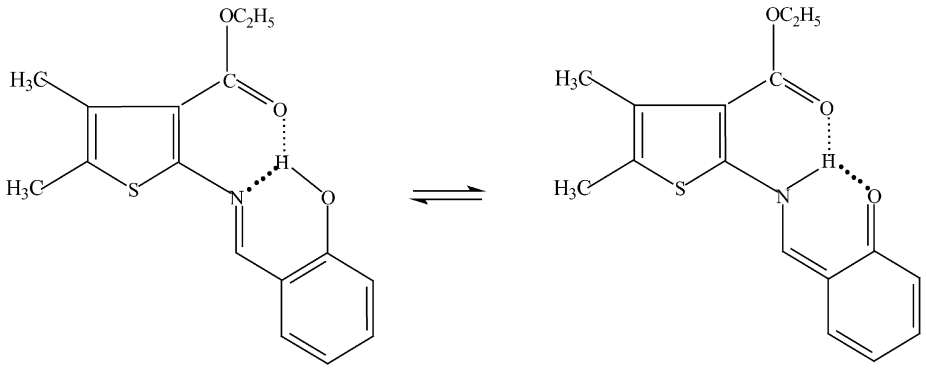

Fig. 1. (a and b) Tautomeric structures of the ligand.

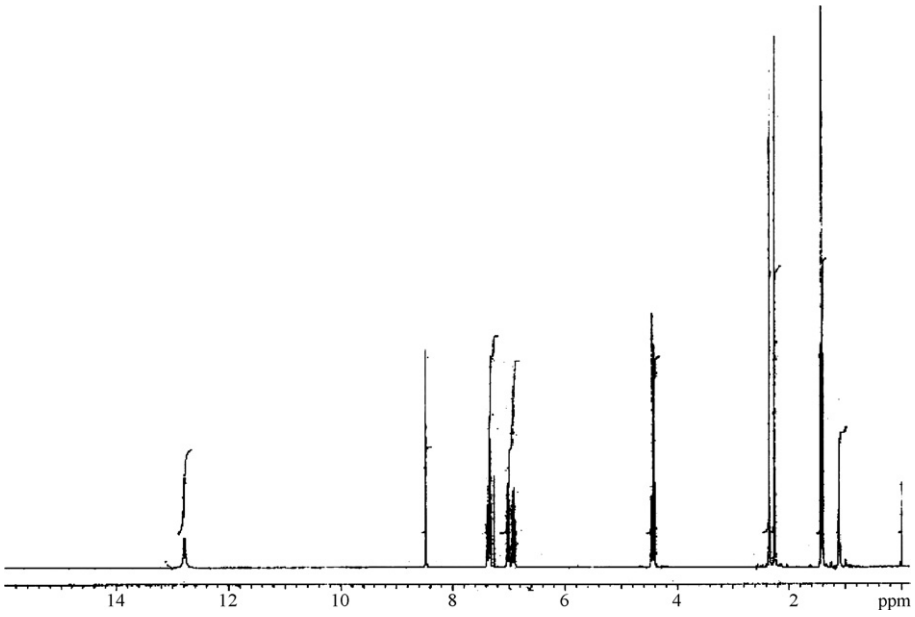

Fig. 2. NMR spectrum of the ligand.

presumably due to strong internal hydrogen bonding [17]. Signal for the hydrogen of the azomethine group has been observed at 8.89δ. Signals appearing at 1.50δ and 2.60δ can be attributed to methyl protons and methylene protons respectively of the ester group. On the basis of the spectral values, an internally hydrogen bonded phenolimine structure has been proposed for the ligand.

3.2. Structure of the metal complexes

The characteristic ultraviolet spectral bands for the phenolimine form of the ligand is only marginally red shifted in the relevant regions indicating that the phenolimine structural form of the ligand persists in the metal complexes also.

The diagnostic infrared spectral data of the complexes are presented in Table 2. The broad band due to internally hydrogen-bonded phenolic –OH group disappear from the region 3300–3000 cm^{-1} indicating deprotonation and formation of metal–oxygen bond. Consequently the band due to ν(C–O) is increased by *ca*. 35–40 cm^{-1} in the metal complexes and this adequately supported the bond formation by phenolate oxygen. The azomethine stretching frequency ν(C=N) is shifted to lower frequency by *ca*. 20–30 cm^{-1} that indicates the involvement of the azomethine nitrogen in coordination with metal ion. The decrease in ester carbonyl frequency ν(C=O) by *ca.* 40–45 cm^{-1} in the metal complexes give adequate evidence for chelation by the ester carbonyl group. This type of coordination by ester carbonyl group has been already reported by several investigators [18,19]. The vibrational characteristics of substituted thiophene ring of the ligand remains almost unaffected in the metal complexes. This observation rules out the possibility of coordination by the ring sulphur atom. Thus the ligand acted as monobasic tridentate, bonding to the metal ion through the phenolate oxygen, azomethine nitrogen and ester carbonyl group (Figs. 3 and 4). Apart from these bands, the non-ligand bands of low intensity appearing in the region 540–550, 440–450 and 350–360 cm^{-1} can be assigned to ν(M–O), ν(M–N) and ν(M–Cl) vibrations respectively [20,21]. Absence of ν(M–S) bands in the far IR spectra gives added evidence for non-participation of ring sulphur atom in bond formation. The above mode of bonding suggested by infrared spectral studies is reinforced by the proton NMR spectral study of the zinc(II) complex. In the spectrum of Zn(II) complex, the absence of –OH proton signal is a clear indication that phenolic oxygen is bonded to the metal ion after deprotonation. A careful comparison of the position of other

Table 2
Infrared and far infrared spectral data of the ligand and metal complexes

Hsat	[Mn(sat)$_2$]	[Fe(sat)$_2$]	[Co(sat)$_2$]	[Ni(sat)Cl]	[Cu(sat)Cl]	[Zn(sat)Cl]	Tentative assignments
3300–3000b	–	–	–	–	–	–	Hydrogen bonded ν(OH)
1702s	1662s	1660s	1658s	1660s	1657s	1659s	ν(C=O)
1630m	1606m	1608m	1610m	1605m	1607m	1608m	ν(C=N)
1530m	1532m	1528m	1530m	1532m	1531m	1529m	Substituted thiophene ring
1425m	1427m	1424m	1426m	1427m	1426m	1425m	Substituted thiophene ring
1360m	1362m	1361m	1358m	1362m	1359m	1361m	Substituted thiophene ring
1287s	1322s	1327s	1325s	1323s	1327s	1326s	ν(C–O)
–	542w	549w	548w	546w	547w	550w	ν(M–O)
–	448w	442w	449w	450w	446w	444w	ν(M–N)
–	–	–	–	351w	358w	360w	ν(M–Cl)

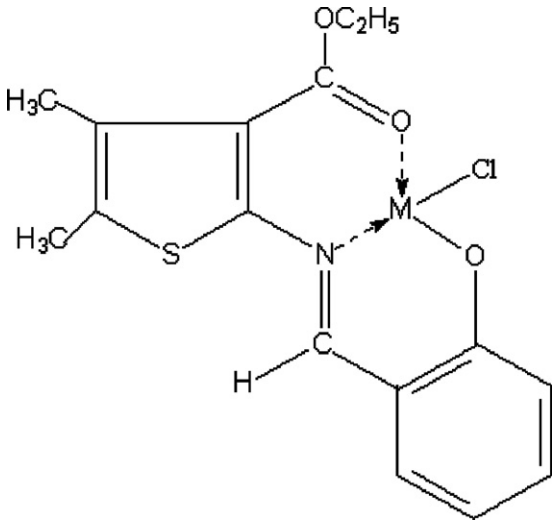

Fig. 3. Structure of the 1:1 metal complexes.

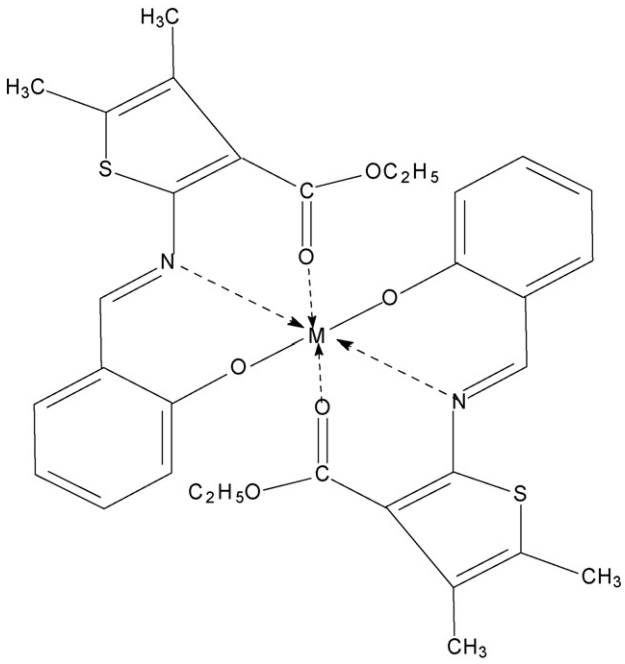

Fig. 4. Structure of the 1:2 metal complexes.

signals in this complex with those of the ligand indicates a downward shift of the other protons by about 0.10–0.25δ in the metal complexes. Thus the azomethine proton signal observed at 8.89δ in the free ligand is shifted down field by 0.23δ. The positions of the other proton signals have been also observed in the expected regions and have been shifted only slightly as a result of metallation.

3.3. Electronic spectra

Visible spectral data along with magnetic susceptibility measurements gave adequate support in establishing the geometry of the metal complexes. These data along with the tentative assignments are presented in Table 3. Electronic spectrum of manganese(II) complex exhibited three peaks in the visible region. These data along with the magnetic moment values are compatible with an octahedral geometry around the metal ion [22]. However, spectrum of the iron(II) complex showed an absorption band at 11,050 cm^{-1} characteristic of $^5T_{2g} \rightarrow {}^5E_g$ transition in an octahedral environment [23]. Cobalt(II) complex exhibited two low energy bands at 7350 and 17,200 cm^{-1} and a high energy band at 20,500 cm^{-1}. These observations together with the magnetic moment value of the cobalt(II) complex give adequate support to an octahedral environment around the Co(II) ion [24]. The nickel(II) and zinc(II) complexes were found to be diamagnetic. The electronic spectral data of the nickel(II) complex are consistent with a square planar geometry around the metal ion [25]. However, for the zinc(II) complex an tetrahedral geometry has been presumed. It has been reported that for a tetracoordinated zinc(II) complexes, tetrahedral geometry is the most preferred one [26]. The copper(II) complex having a magnetic moment value of 1.88 BM, a broad d–d band centred at 13,850 cm^{-1}, which supports a distorted square planar geometry around the metal ion [27].

3.4. EPR spectral study

The X-band EPR spectrum of copper(II) complex has been recorded in the solid state at room temperature and also in DMSO at 77 K using DPPH as the 'g' marker (Fig. 5). The solution spectrum of the complex possessed well-resolved $g_{||}$

Table 3
Electronic spectral data and magnetic moment values of the metal complexes

Complex	Absorption bands (cm^{-1})	Tentative assignments	Magnetic moment (BM)
[Mn(sat)$_2$]	14,000	$^6A_{1g} \rightarrow {}^4T_{1g}$	5.94
	16,500	$^6A_{1g} \rightarrow {}^4T_{2g}$	
	19,500	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$	
[Fe(sat)$_2$]	11,050	$^5T_{2g} \rightarrow {}^5E_g$	5.20
[Co(sat)$_2$]	7,350	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.84
	17,200	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	20,500	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
[Ni(sat)Cl]	13,500	$^1A_{1g} \rightarrow {}^1A_{2g}$	D
	18,800	$^1A_{1g} \rightarrow {}^1B_{1g}$	
[Cu(sat)Cl]	13,850	$^2B_{1g} \rightarrow {}^2A_{1g}$	1.88

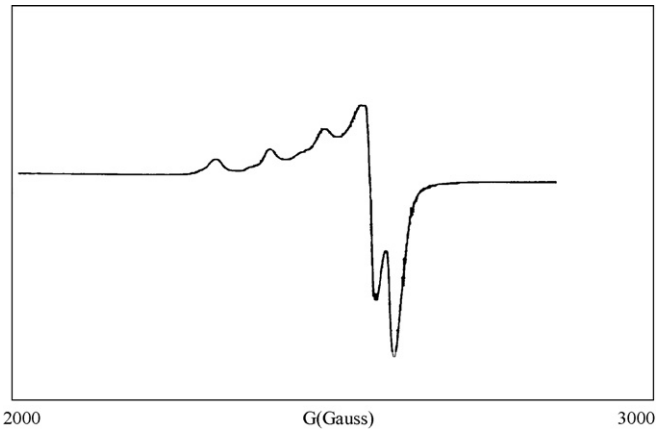

Fig. 5. EPR spectrum of [Cu(sat)Cl].

and a broad $g_\perp$ regions. The various Hamiltonian parameters have been calculated for this complex ($g_{||} = 2.2350$, $g_\perp = 2.1140$, $A_{||} = 170$). It has been reported that $g_{||}$ value of copper(II) complex can be used as a measure of the covalent character of the metal–ligand bond. If the value is more than 2.3, the metal–ligand bond is essentially ionic and the value less than 2.3 is indicative of covalent character [28]. Apart from this, the covalency parameter (α^2) has been calculated using Kivelson and Neiman equation [29]. The covalency parameter ($\alpha^2 = 0.79$) indicates considerable covalent character for the metal–ligand bond [30]. Also the trend $g_{||} > g_\perp > g_e$ observed for this complex indicated that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital. The empirical ratio $g_{||}/A_{||}$ is frequently used to evaluate distortions in tetracoordinated copper(II) complexes [31]. The ratio close to 100, indicates a roughly square planar structure around the copper(II) ion and the values from 170 to 250 are indicative of a distorted tetrahedral geometry. The four peaks in the spectrum are evidently due to the coupling of the electron spin of the ^{63}Cu nucleus ($I = 3/2$). The peaks are broad and have the appearance of ill-resolved triplets. The breadth and triplet appearance can be attributed to hyperfine splitting by the nitrogen atom ($I = 1$) of the ligand. The triplet appearance is adduced as an evidence for nitrogen coordination. Based on this observation, a distorted square planar geometry is proposed for the complex. The EPR study of the copper(II) complex has provided supportive evidence to the conclusion obtained on the basis of electronic spectrum and magnetic moment value.

3.5. X-ray diffraction

X-ray diffraction study on [Cu(sat)Cl] has been carried out and the data obtained are presented in Table 4. The X-ray diffraction pattern of the complex indicates high crystallinity of the complex. The diffraction study recorded 15 reflections between 2θ ranging from 15° to 60° with maxima at $2\theta = 16.1535$ which corresponds to interplanar distance $d = 5.4824$ Å. The main peaks have been indexed and the $\sin^2\theta$ and 2θ values obtained have been compared with calculated values [32,33]. A comparison of these values revealed good agreement between calculated and observed values of $\sin^2\theta$ and 2θ. The complex was successfully indexed to orthorhombic crystal systems with the lattice constants; $a = 10.3461$ Å, $b = 6.9821$ Å, $c = 4.2850$ Å and unit cell volume 309.5377 Å^3. Although single crystal X-ray crystallographic investigation is the most precise source of information regarding the structure of a complex, the difficulty of obtaining crystalline complexes in proper symmetric form has rendered this method unsuitable for such a study. However, a variety of other spectroscopic techniques could be used with good effect for characterizing the metal complexes.

3.6. Cyclic voltammetry

The copper(II) complex, [Cu(sat)Cl] has been subjected to cyclic voltammetric studies with a view to examine its electrochemical behaviour. A glassy carbon was used as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. All the measurements were carried out using a 2 mM solution at room temperature in the potential range −1.5 to +1.5 V with a scan rate 80 mV s^{-1}. The solution was degassed with argon and kept under argon atmosphere throughout the experiment.

Table 4
X-ray diffraction of [Cu(sat)Cl]

Peak no.	d (Å)	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	$h\,k\,l$	Observed 2θ	Calculated 2θ
1	5.4824	0.0197	0.0177	1 1 0	16.1535	15.2968
2	5.0430	0.0233	0.0221	2 0 0	17.5715	17.1266
3	4.3111	0.0319	0.0343	2 1 0	20.5848	21.3594
4	3.9253	0.0385	0.0378	1 0 1	22.6336	22.4387
5	3.7687	0.0417	0.0444	0 1 1	23.5871	24.3516
6	3.5481	0.0471	0.0486	0 2 0	25.0766	25.4937
7	3.2689	0.0552	0.0544	2 0 1	27.2581	26.9970
8	3.0391	0.0642	0.0620	3 1 0	29.3635	28.8502
9	2.8310	0.0740	0.0809	0 2 1	31.5765	33.0698
10	2.5878	0.0885	0.0886	4 0 0	34.6330	34.6516
11	2.3472	0.1076	0.1095	0 3 0	38.3149	38.6549
12	2.2635	0.1157	0.1150	1 3 0	39.7893	39.6608
13	2.2270	0.1196	0.1210	4 0 1	40.4698	40.7119
14	2.0012	0.1481	0.1473	1 3 1	45.2759	45.1534
15	1.6184	0.2265	0.2270	0 4 1	56.8415	56.9136

The CV profile displayed two waves at E_{pc} values −0.11 and +0.13 V corresponding to the reversible reduction of the metal complex and irreversible reduction of the ligand respectively. Also the copper(II) complex has undergone oxidation process at $E_{pa} = -0.18$ V. The separation between the peak potential (ΔE_p) is nearly close to 70 mV indicate one electron transfer in the electrode reaction and the observed reaction voltage of the complex is lower than that of the ligand and the ratio of the anodic to cathodic peak current (ip_a/ip_c) nearly equal to one. From these observations it is concluded that the redox process is diffusion controlled and demetallation of copper(II) complex on the electrode is not involved [34].

3.7. Transesterification

Transesterification reaction effect interchange of ester fragment on the substituent group attached to the coordinated azomethine group. There are several reports that metal chelates of carboxylic esters undergo facile transesterification on refluxing with alcohol for lengthy periods. Two types of transesterification reactions are reported; those in which the ester group is coordinated to the metal ion and the other type involves interexchange reactions of non-coordinated ester group. The complex [Ni(sat)Cl] has been subjected to transesterification reaction in methanol medium using a reported method [10]. The crystallinity, appearance and the solubility behaviour of the product obtained after transesterification have been distinctly different from those of [Ni(sat)Cl]. Apart from these observations, the ester carbonyl stretching frequency observed for the methyl derivative at 1652 cm^{-1} is a direct indication for the occurrence of transesterification. Substitution of ethyl group by methyl group is further confirmed by proton NMR spectrum of the nickel(II) complex. Several mechanisms have been proposed for transesterification reactions. However it appears that increased nucleophilicity of the acyl carbon atom induced by the azomethine group is of prime importance. It has been also reported that alkoxycarbonyl group immediately attached the α-carbon atom can be transesterified easily [10]. In view of the difficulty in preparing metal chelates of esters, this general method of synthesis by transesterification should prove beneficial.

3.8. Antibacterial activity

Biological significance of thiophene derivatives has been well documented in literature [7]. Allured by these observations, biological experiments for evaluating antibacterial activity of the ligand and the metal complexes have been performed using a reported method [9]. The screening data obtained for two pathogenic bacteria (*Staphylococcus aureus* and Alpha-haemolytic streptococci) are presented in Table 5. It has been observed that the ligand has been physiologically active and chelation enhanced its activity.

A possible mode of toxicity can be speculated in the light of chelation theory [35]. Chelation reduces the polarity of the metal ion to a considerable extent due to the partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Lipids and polysaccharides are some important constituents of cell walls and membranes, which are preferred for metal ion interaction. Reduction in polarity in turn increases the lipophilic character of the chelate and the interaction between the metal ion and the lipid is favoured. This may result in breaking down of the permeability barrier of the cell and interference with the normal cell processes [36]. If the geometry and charge distribution around the molecule are incompatible with those around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot takes place and this in turn prevent the toxic reaction within the pores [36]. The presence of co-ligand also plays a decisive role in determining the antibacterial property of metal complexes [37]. Nature of the metal ion, nature of the ligand, coordinating sites, geometry of the complex, hydrophilicity, lipophilicity, presence of co-ligand, pharmacokinetic factors etc also play decisive roles in determining the antibacterial activity of Schiff bases and their metal complexes. The mode of action of the complexes also indulge in the formation of hydrogen bonded interaction through the coordinated anion, azomethine group etc with the active centers of the cell constituents resulting in interference with the normal cell processes [20].

Table 5
Antibacterial study of the ligand and metal complexes

Compound	Zone of inhibition (mm)	
	S. aureus	Alpha-*H. S. cocci*
Hsat	14	12
$[Mn(sat)_2]$	21	20
$[Fe(sat)_2]$	23	22
$[Co(sat)_2]$	22	19
[Ni(sat)Cl]	25	21
[Cu(sat)Cl]	27	23
[Zn(sat)Cl]	24	24
Standard	30	27

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