Synthesis, Characterization and Biological Activities of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) Complexes with Schiff Base Derived from 3-(4-Chlorophenoxymethyl)-4-amino-5-mercapto-1,2,4-triazole

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Abstract: Coordination complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) with Schiff bases derived from 3-(4-chlorophenoxymethyl)-4-amino-5-mercapto-1, 2, 4-triazole and substituted aldehydes have been synthesized. The complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility data, electronic, IR, ESR and ¹H NMR spectral data. On the basis spectroscopic studies, the Schiff base is monobasic bidentate ligand having the composition ML₂(2H₂O) Where M = Cu(II), Co(II), Ni(II), Mn(II), ML₂(H₂O)Cl Where M = Fe(III). Various physicochemical data suggest a six coordinated octahedral geometry for Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes. The antibacterial activities of ligand and its complexes were screened by cup plate method.

Keywords: Triazoles, Metal complexes, Spectral, Magnetic susceptibility and Antimicrobial activity

Introduction

Schiff bases are important class of ligands in coordination chemistry and their complexing ability containing different donor atom is widely reported. The chemistry of transition metal complexes containing heterocyclic donor continues to be of interest on account of their biological importance. There is a growing interest in the studies on the metal complexes of Schiff bases derived from triazoles and its derivatives which are biologically important ligands¹. Schiff base metal complexes have been widely studied because of their industrial

and biological applications, several derivatives of these have been used as drugs. The triazole Schiff bases constitute one of the most important classes of O, N, and S donor atoms. Triazoles and their derivatives have been proved effective bacteriocides², pesticides³, fungicides^{4,5} and insecticides^{6,7}. The Schiff base acts as a bidentate monobasic donor for Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) and prominent sites of coordination are nitrogen of the azomethine group and oxygen of the hydroxyl group. Thus the present study describes the synthetic and structural studies of bivalent transition metal Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes of Schiff base derived from 3-(4-Chlorophenoxy)methyl-4-amino-5-mercapto-1,2,4-triazole with salicylaldehyde. The survey of literature reveals that no work has been carried out on the synthesis of the ligand (CITHS) and its metal complexes.

Experimental

All the reagents /chemicals were of reagent grade. Solvents were dried and distilled before use according to standard procedures⁸. The precursor 3-(4-chlorophenoxy)methyl-4-amino-5-mercapto-1, 2, 4-triazole was prepared by literature method⁹. The metal chlorides / salts used were in their hydrated form.

Infrared spectra of the synthesized ligand and its metal complexes were recorded as on Perkin Elmer 1000 FT-IR spectrometer using KBr pellets. UV-Visible spectra were recorded on an Elico SL-164 DOUBLE BEAM UV-Vis. spectrophotometer in the range of 200-1200 nm. Magnetic susceptibilities were determined by the Faraday method using a model 300 Lewis coil Force Magnetometer of Tesla strength at room temperature. The instrument was calibrated¹⁰ using HgCo(NCS)₄. The molar conductance of the complexes were measured on ELICO CM-82 conductivity Bridge in DMF solution (1×10^{-3} M). ¹H NMR spectra were recorded on AMX-400 NMR spectrometer, using TMS as internal standard and DMSO as a solvent. ESR measurements were carried out on a BRUKER Biospin GmbH spectrometer working at a microwave frequency of 9.1 GHz. The experiment was carried out by using diphenylpicrylhydrazyl (DPPH) as reference with the field at 3200 Gauss. The CHN elemental analyses were determined using a Perkin-Elmer micro elemental analyzer. The metal chloride analysis was carried out by the following standard method. Sulphur¹¹ in the complexes estimated as BaSO₄.

Synthesis of ligand (CITHS)

A mixture of 3-(4-chlorophenoxy)methyl-4-amino-5-mercapto-1, 2, 4-triazole and salicylaldehyde in 1:1 molar proportions in alcoholic medium containing a few drops of concentrated hydrochloric acid, was refluxed for 4h on a steam bath. The reaction mixture was cooled to room temperature. The Schiff base 2-[(E)-({3-[(4-chlorophenoxy)methyl]-5-mercapto-4H-1,2,4-triazol-4-yl}imino)phenol(CITHS) separated was filtered, washed and recrystallized from alcohol.

Synthesis of complexes

To the hot solutions of the ligand CITHS (0.01 mol) in ethanol (35 mL), a hot ethanolic solution of respective metal chlorides in ethanol (15 mL) was added and reaction mixture was then treated with sodium acetate (0.5 g) just to adjust the pH of the solution. The reaction mixture was further refluxed for 2 h. The resulting mixture decomposed by pouring into the 100 mL distilled water with stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccators. The yield was 70%.

Figure 1. 2-[(E)-({3-[(4-chlorophenoxy)methyl]-5-mercapto-4H-1,2,4-triazol-4-yl}imino)] phenol (CITHS).

Results and Discussion

The elemental analysis shown in Table 1 indicates that, all the metal complexes have 1:2 stoichiometry and are dark colored amorphous substances, soluble in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of $20\text{--}30\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded as non-electrolytes¹².

Magnetic susceptibility

The magnetic moment values for Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes of the ligand CITHS are shown in Table 1. The magnetic moment for Cu(II) complex is 1.94 BM. The reported values for the mononuclear Cu(II) complex having no major spin interactions ($1.75\text{--}2.20$ BM)^{13, 14}. Thus the present Cu(II) complex is devoid of any spin interaction with octahedral geometry. In octahedral Cu(II) complex the ground state is $^4T_{1g}$ and large orbital contribution to the magnetic moment is expected. The mixing of the singlet states lowers the magnetic moments of Co(II) complexes are in the range of $5.05\text{--}5.14$ BM indicating that the Co(II) complexes are typically high spin complexes and having octahedral structure¹⁵. For Ni(II) complex the observed magnetic moment value is 2.94 BM which is well within the expected range for Ni(II) complex with octahedral stereochemistry ($2.83\text{--}4.0\text{BM}$)^{16, 17}. The complexes of Mn(II) and Fe(III) values exhibited the magnetic moments of 5.70 BM and 5.86 BM respectively^{18, 19}, indicating it to be high-spin type paramagnetic, it lies within the octahedral range which very close to spin only value of 5.90 BM as the ground term is $^6A_{1g}$ and thus supports the octahedral stereochemistry²⁰.

Table 1. Physical, analytical, magnetic susceptibility and molar conductance data of the ligand CITHS and its complexes

Ligand / Complex	Empirical Formula	Mol. Wt.	M.P, °C	Yield %	M	C	H	N	S	Cl	μ_{ef} B.M.	Molar Conductance Λ_m Ohm ⁻¹ cm ² mol ⁻¹
CITHS	C ₁₆ H ₁₃ N ₄ O ₂ SCl	360.82	190	65	-	53.31 (53.26)	3.62 (3.63)	15.52 (15.53)	8.89 (8.85)	9.81 (9.83)	-	-
CuL ₂ (2H ₂ O)	C ₃₂ H ₂₈ Cl ₂ CuN ₈ O ₆ S ₂	819.2	297	60	7.71 (7.76)	46.95 (46.92)	3.41 (3.45)	13.70 (13.68)	7.84 (7.83)	8.65 (8.66)	1.94	17.15
CoL ₂ (2H ₂ O)	C ₃₂ H ₂₈ Cl ₂ CoN ₈ O ₆ S ₂	814.6	280	65	7.20 (7.23)	47.15 (47.18)	3.42 (3.46)	13.77 (13.76)	7.86 (7.87)	8.71 (8.70)	5.15	17.38
NiL ₂ (2H ₂ O)	C ₃₂ H ₂₈ Cl ₂ NiN ₈ O ₆ S ₂	814.3	275	64	7.22 (7.21)	47.17 (47.20)	3.45 (3.47)	13.75 (13.76)	7.81 (7.88)	8.69 (8.71)	2.94	19.89
MnL ₂ (2H ₂ O)	C ₃₂ H ₂₈ Cl ₂ MnN ₈ O ₆ S ₂	810.6	>300	60	6.75 (6.78)	47.43 (47.42)	3.47 (3.48)	13.80 (13.82)	7.95 (7.91)	8.73 (8.75)	5.70	15.13
FeL ₂ (H ₂ O)Cl	C ₃₂ H ₂₆ Cl ₃ FeN ₈ O ₅ S ₂	828.9	285	65	7.71 (6.74)	46.35 (46.37)	3.14 (3.16)	16.55 (16.52)	7.70 (7.74)	12.81 (12.8)	5.86	18.26

Electronic spectra

The electronic spectral data of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes of the ligand CITHS were recorded in DMF as shown in Table 2. The light green colored Cu(II) complex exhibit a broad asymmetric band in the region 12275-16262 cm^{-1} with maxima at 14265 cm^{-1} in an distorted octahedral geometry²¹. The broadness of the band may be due to dynamic Jahn-Teller distortion and is assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ transitions. In the electronic spectra of Co(II) complex the three absorption bands observed at 10055 cm^{-1} , 16005 cm^{-1} and 20345 cm^{-1} , due to ${}^4T_{2g}(F) \rightarrow {}^4A_{2g}(v_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v_2)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$ transitions respectively. These transition suggest octahedral geometry for Co(II) complex^{22,23}. These assignments are in good agreement with the reported value^{24,25}. The ligand field parameters such as Dq, B', β and $\beta\%$ have been calculated by using band-fitting equation given by Underhill and Billing²⁶. The crystal field splitting energy (Dq) value was found to be 846 cm^{-1} . These values are well within the range reported are most of the octahedral Co(II) complexes. The Co(II) complex under present investigation process interelectronic repulsion parameter (B') 917 cm^{-1} . The Racah parameter (B') is less than free ion value 971 suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the present Co(II) complex 0.94 which is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, $\beta\%$, LFSE, v_2 / v_1 (Table 2) suggest the octahedral geometry for Co(II) complex²⁷. Ni(II) complexes exhibit three bands at 10870 cm^{-1} , 15270 cm^{-1} and 25645 cm^{-1} are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(p)(v_3)$ transitions respectively are in confirmatory with the octahedral geometry for the Ni(II) ion. The Table 2 shows the ligand field parameter such as Dq, B', β , $\beta\%$ and LFSE have been calculated by using Band-fitting equation given by Underhill and Billing²⁶. Racah parameter B' is less than the free ion value of 1040 cm^{-1} indicating the covalent character of the complex. Moreover, the ratio v_2/v_1 was found to be 1.4046 which is well within the range (1.40 - 1.61) and is indicative of octahedral stereochemistry for this Ni(II) complex²⁸. The lowest band v_2 (10 Dq) was not observed due to limited range of the instrument used. However, it is calculated by using equation suggested by Billing and Underhill²⁶. The Racah parameter B' is 852 cm^{-1} , which is less than the free ion value of 1040 cm^{-1} indicating the covalent character of the Ni(II) complex. The ratio v_2/v_1 (1.4) and $\beta\%$ (17.98) supports the octahedral geometry around the Ni(II) ion²⁹. The Mn(II) complex observed bands at 12830-19275 cm^{-1} due to the transition ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ suggest the high spin octahedral geometry around the metal ion^{30,31}. The Fe(III) complex observed band at 17556-29590 cm^{-1} due to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ respectively suggest the high spin octahedral geometry around the metal ion^{32,33}.

Where M= Cu(II), Co(II), Ni(II) and Mn(II)

Figure 2. Probable structure of complexes of the ligand CITHS.

Where M=Fe(III)

Figure 3. Probable structure of Fe(III) complex of the ligand ClTHS.

Table 2. Electronic spectral data and ligand field parameters of Cu(II), Co(II), Ni(II) and Fe(III) complexes

Complexes	ν_1	ν_2	ν_3	Dq cm^{-1}	B^1	β	$\beta\%$	ν_2/ν_1	LFSE $kcal\ mol^{-1}$
CuL ₂ (2H ₂ O)	12275	16262	-	1426	-	-	-	1.3	24.44
CoL ₂ (2H ₂ O)	10055	16005	20345	847	917	0.94	5.60	1.5	14.50
NiL ₂ (2H ₂ O)	10870	15270	25645	937	852	0.82	17.9	1.4	32.13
MnL ₂ (2H ₂ O)	12005	17015	19000	896	790	0.74	25.09	1.4	15.36
FeL ₂ (H ₂ O)Cl	12910	15987	19635	838	854	0.80	19.05	1.2	14.36

Infrared spectra

The important infrared frequencies exhibited by the ligand ClTHS and its complexes are given in Table 3. The ligand does exhibit tautomerism³⁴ and one can expect both ν_{S-H} and $\nu_{C=S}$. A medium intensity band around $2523\ cm^{-1}$ due to ν_{S-H} indicates the thiol form of the ligand. The band due to $\nu_{C=S}$ in the $780-740\ cm^{-1}$ of the ligands has remained unperturbed in these complexes indicating that N or S of the thiamide group is not involved in the bond formation³⁵. These observations suggest the non-involvement of sulfur atom in coordination. The infrared spectra of ligands exhibits high intensity band around $1617\ cm^{-1}$ is due to $\nu_{C=N}$. In the complexes, this band shifted to lower frequency ($15-20\ cm^{-1}$) around $1602\ cm^{-1}$ is suggestive of coordination through nitrogen of the azomethine group³⁶⁻³⁸ to the metal(II) chlorides. The band observed in the region $1284\ cm^{-1}$ for ν_{C-O} stretching vibrations undergoes shift to higher wave number at 1310 to $1377\ cm^{-1}$ compared with free ligand band. The band around $3332\ cm^{-1}$ due to phenolic OH, which is observed in ligand, disappears in complexes, this indicates the ligand co-ordinate to the metal ion through phenolic oxygen atom³⁹ of OH group via deprotonation. A broad band appeared in the region $3443-3523\ cm^{-1}$ in all complexes indicates the presence of coordinated water or lattice water⁴⁰. The participation of oxygen and nitrogen in coordination with the metal ion is further supported by the new band appearance of ν_{M-N} and ν_{M-O} at $550-520\ cm^{-1}$ and $380-420\ cm^{-1}$, respectively in the far infrared region⁴¹⁻⁴⁴. The bands in the region $320-325\ cm^{-1}$ have been assigned to ν_{M-Cl} bands in all the complexes⁴⁵. The presence of chlorine atoms in all the complexes is further confirmed by quantitative chloride estimation.

Table 3. Characteristic IR frequencies (cm^{-1}) of the ligand CITHS and its complexes

Ligand/ complexes	$\nu_{\text{H}_2\text{O}}$	ν_{OH}	ν_{SH}	$\nu_{\text{C=S}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
CITHS	-	3332	2523	780	1617	1289	-	-	-
$\text{CuL}_2(2\text{H}_2\text{O})$	3420	-	2523	778	1596	1353	412	520	-
$\text{CoL}_2(2\text{H}_2\text{O})$	3451	-	2523	772	1603	1355	380	526	-
$\text{NiL}_2(2\text{H}_2\text{O})$	3470	-	2523	776	1602	1362	405	532	-
$\text{MnL}_2(2\text{H}_2\text{O})$	3495	-	2523	779	1603	1310	420	546	-
$\text{FeL}_2(\text{H}_2\text{O})\text{Cl}$	3433	-	2523	770	1598	1377	415	550	320

¹H NMR Spectra of ligand CITHS

The ^1H NMR spectra of ligand CITHS shows multiplets were observed around $\delta 6.9$ - 8.62 (m, 8H, Ar-H) are due to phenyl protons. A proton due to -OH group at 2-position of salicylaldehyde ring has resonated as a singlet at $\delta 12.00$ (S, 1H, OH) and a signal at $\delta 3.32$ due to (ArO-CH₂) protons, signal due to (S, 1H, HC=N) resonated at $\delta 8.4$. Signals in the range of $\delta 9.6$ - 10 (S 1H, SH) are due to SH protons⁴⁶. This shows that the ligand exists in thiol form rather than in thione⁴⁷ form, which supports IR observation.

¹H NMR Spectra of Zn(II) complex

In its ^1H NMR spectrum, the sixteen aromatic protons have resonated in the region $\delta 7.2$ - 8.42 (m, 16, 16 X H) as a multiplet. The signal due to OH at $\delta 12.00$ in ligand, disappears in case of complexes indicating the involvement of OH in the complexes formation via deprotonation. The HC=N, proton signal appears at $\delta 8.8$ the downfield shift in the complex indicate that the deshielding due to coordination of C=N group through nitrogen. The signal due to SH proton appears unperturbed in the complexes indicates the non-involvement of sulfur atom of SH group.

ESR spectra

The ESR spectra of the polycrystalline sample of the complexes were recorded at room temperature Table 4. The observed value for the Cu(II) complex for the ligand. The anisotropic G values have been calculated by Kneubuhl's method⁴⁸. $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$ which measures the exchange interaction between copper(II) centers. According to Hathaway⁴⁹ if the G value is greater than 4, the exchange interaction is negligible, while a value of less than 4 indicates a considerable exchange interaction in the complexes. One unpaired electron in Cu(II) complex with $^2\text{B}_{1g}$ as ground state lies in $d_{x^2-y^2}$ spectrum of Cu(II) complex of ligand orbital and follows the trend $g_{\parallel} > g_{\perp} > g_e$ ($g_e = 2.0036$ free ion value). The observed $g_{\parallel} = 2.257$ and $g_{\perp} = 2.059$ values of the Cu(II) complex under present study followed the same trend $g_{\parallel} > g_{\perp} > g_e$ which suggest that the presence of unpaired electron $d_{x^2-y^2}$ orbital giving octahedral geometry⁵⁰. The observed $G = 4.4$ for the complex under present study evidenced the monomeric nature of the complex⁵¹ and indicates that there is no spin exchange interaction in the copper complexes and hence distorted octahedral geometry proposed for the Cu(II) complex.

Table 4. ESR data of the Cu(II) complex of the ligand CITHS

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	g_{iso}	G
$\text{CuL}_2(2\text{H}_2\text{O})$	2.257	2.059	2.12	2.20	4.4

Antimicrobial activity

The synthesized CITHS ligand and its complexes were screened for their antibacterial activity⁵² against *E. coli* and *S. aurious* and antifungal activity against⁵³ *A. niger* and *A. flavous* at 100 µg/0.1 cm³ concentration. The standard drugs streptomycin and clotrimazole were also tested for their antibacterial and antifungal activity at the same concentration under the conditions similar to that of the test compounds concentration. The zones of inhibitions of the antimicrobial activity have been presented in Table 5. The results of antibacterial activity of ligands and its complexes Cu(II), Co(II) and Ni(II) shows weak activity against *E. coli* and *S. aurious* when compared with standard Streptomycin. The antifungal activity results revealed that the ligands and its Cu(II), Co(II) and Ni(II), complexes have exhibited weak to good activity against *A. niger* and *A. flavous*. The ligand and its Cu(II) and Co(II) complexes shows weak activity when compared to the standard drug clotrimazole.

Table 5. Antimicrobial activity of the ligands CITHS and its complexes

Compound	Antibacterial Activity of zone of inhibition (in mm)		Antifungal Activity of zone of inhibition, mm	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. falvours</i>
Ligand CITHS	13	13	11	13
CuL ₂ (2H ₂ O)	16	15	14	17
CoL ₂ (2H ₂ O)	15	18	14	15
NiL ₂ (2H ₂ O)	16	14	18	17
MnL ₂ (2H ₂ O)	15	15	13	16
FeL ₂ (H ₂ O)Cl	17	16	16	14
Streptomycin	24	21	24	23
Clotrimazole	-	-	-	-
DMF (Control)	0	0	0	0
Bore size	08	08	08	0

Conclusions

The ligand 2-[(E)-({3-[(4-chlorophenoxy) methyl]-5-mercapto-4H-1, 2, 4-triazol-4-yl} imino) phenol behaved as a monobasic bidentate coordinating through 'N' and 'O' of OH group. Analytical data, electronic spectra, magnetic susceptibility, IR, ¹HNMR, ESR spectral data reveal octahedral geometry for all the complexes. The low conductance values show non-electrolytic behavior of the complexes. The ligand [CITHS] and its all complexes were tested for antimicrobial activity. The complexes are shows moderate to good antibacterial and antifungal activity compared to its ligand. On the basis of spectral evidence, the following probable structures have been assigned for synthesized compounds.

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