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Synthesis and characterization of Cu(II), Co(II), Ni(II) complexes with Schiff bases derived from 3-(4-chlorophenoxymethyl)-4-amino-5-mercapto-1,2,4-triazole

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ABSTRACT

A new bidentate Schiff base ligands derived from 3-(4-chlorophenoxymethyl)-4-amino-5-mercapto-1,2,4-triazole with substituted salicylaldehyde and its Cu(II), Co(II) and Ni(II) complexes have been synthesized and characterized by elemental analysis, IR, electronic, ^{1}HNMR and ESR spectra. The analytical data and spectral data reveals that the composition of the complexes to be $ML_2(H_2O)_2$ where M = Cu(II), Co(II), Ni(II) and are non-electrolytic in nature. It is found that these complexes exhibit octahedral geometry. The various spectral data shows the monobasic bidentate character of the ligand coordinating through 'N' of azomethine and 'O' of phenyl group.

Key words: Triazoles, metal complexes, spectral and magnetic susceptibility.

INTRODUCTION

Schiff bases of triazoles, their derivatives and their metal complexes have been found to have potential application in biology .The most important classes of O, N and S donor atoms.Triazoles and their derivatives have been proved effective bactericides[1], pesticides[2] and fungicides[3-4]. The triazole Schiff bases acts as monobasic bidentate donor for Cu(II), Co(II), and Ni(II) coordinating through nitrogen of azomethine group and oxygen of phenoxy group. In the present paper we report the synthesized and spectral studies of Cu(II), Co(II) and Ni(II) complexes of Schiff base derived from 3-(4-chlorophenoxymethyl)-4-amino-5-mercapto-1,2,4-triazole with substituted salicylaldehyde. The literature survey reveals that there is no work has been carried out on the $ClTCH_3S$ and ClTBrS and its metal complexes. Hence we have carried out studies on the synthesis and characterization of $ClTCH_3S$ and ClTBrS ligands and its metal complexes.

EXPERIMENTAL

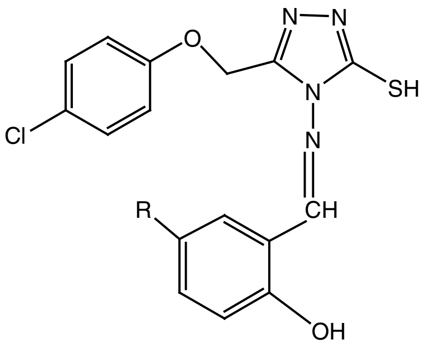
Material and Methods

All the reagents /chemicals are of reagent grade. Solvents were dried and distilled before use according to standard procedures[5]. The metal chlorides/ salts used were in their hydrated form.

Infrared spectral data of the synthesized ligands and its metal complexes were recorded as on Perkin Elmer 1000 FT-IR spectrometer using KBr pellets. Electronic spectra of complexes 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 calibrated using $HgCo(NCS)_4$[6]. The molar conductances of the complexes were measured on ELICO CM-82 conductivity Bridge in DMF solution (1×10^{-3}M). ^{1}H 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. Sulphur[7]in the complexes estimated as $BaSO_4$.

Synthesis of ligands

A equimolar mixture of 3-(4-Chlorophenoxymethyl)-4-amino-5-mercapto-1, 2, 4-triazole and 5- methyl/5-bromo salicyladehyde in alcoholic medium containing a few drops of concentrated hydrochloric acid , was refluxed for 4h on water bath. The reaction mixture was cooled to room temperature. The Schiff bases 2-[(E)-({3-[(4-chlorophenoxy) methyl]- 5 - mercapto - 4H - 1,2,4-triazol - 4 - yl} imino] - 5-methyl phenol ($ClTCH_3S$) and 2-[(E)- ({3- [(4- chlorophenoxy) methyl] -5-mercapto-4H -1,2,4-triazol-4-yl}imino]-5-bromophenol (ClTBrS) separated was filtered, washed and recrystellized from alcohol as shown below.



Where R= CH3,Br

Fig. Structure of ligands

Synthesis of Complexes

To the hot solutions of $ClTCH_3S$/ClTBrS ligands (0.01mol) was added hot ethanolic solution (10ml) of metal chlorides (0.01mol), the reaction mixture was refluxed on a water bath for 4h to get clear solution.1g of excess sodium acetate was added to the reaction mixture just to adjust the pH of the solution. The reaction mixture was further refluxed for 2h. The resulting mixture decomposed by pouring into the 100ml distilled water with stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and than with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a dessicator.

RESULTS AND DISCUSSION

Nature and stiochiometry

The elemental analysis shown in table 1 indicates that, all the metal complexes have 1:2 stiochiometry 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 16-22 $ohm^{-1}mol^{-1}cm^2$. These values are too low to account for any dissociation of the complexes in DMF indicating their non-electrolytic nature[8].

Magnetic Susceptibility

The magnetic moment values for Cu(II), Co(II) and Ni(II) complexes are shown in table1. The magnetic moment for Cu(II) complexes is 1.94 -2.02 BM[9]. The reported values for the mononuclear Cu(II) complexes having no major spin interactions is 1.75-2.20 BM. Thus the present Cu(II) complexes is devoid of any spin interaction with octahedral geometry. The magnetic moments Co(II) complexes are in the range of 5.05-5.14 BM[10] indicating that the Co(II) complexes are typically high spin complexes and having octahedral structure. For Ni(II) complexes the observed magnetic moment value is 2.94 BM which is well within the expected range for Ni(II) complexes with octahedral stereochemistry (2.83- 4.0 BM)[11-12].

Electronic spectra

The electronic spectra of Cu(II), Co(II) and Ni(II) complexes of the ligands have been recorded in DMF as shown in table 2 . The light green colored Cu(II) complexes exhibit a broad asymmetric band in the region 12215-16255 cm^{-1} with maxima at 14265 cm^{-1} in an distorted octahedral geometry[13]. The broadness of the band may be due to dynamic Jahn-Teller distortion and is assigned to ${}^2T_{2g}\rightarrow{}^2E_g$ transitions. The electronic absorption bands of Co(II) complexes appears in the region 8728- 9975 cm^{-1}

Table 1 :Physical, Analytical, Magnetic Susceptibility and Molar Conductance data of the ligands and its complexes

Ligand/ complex	Empirical formula	Mol. wt	M.P. (°C)	Yield (%)	M	C	H	N	S	Cl	μ_{ef} B.M.	λ_m ohm^{-1} cm^{2}mol^{-1}
$ClTCH_3S$	$C_{17}H_{15}N_4O_2SCl$	374	190	77	-	54.47	4.03	14.95	8.55	9.46	–	–
						(53.26)	(3.63)	(15.53)	(8.85)	(9.83)		
$CuL_2(H_2O)_2$	$C_{34}H_{32}Cl_2CuN_8O_6S_2$	847.1	>300	62	7.50	42.20	3.81	13.23	7.57	8.37	1.94	19.00
					(7.76)	(46.92)	(3.45)	(13.68)	(7.83)	(8.66)		
$CoL_2(H_2O)_2$	$C_{34}H_{32}Cl_2CoN_8O_6S_2$	842.6	290	65	6.99	48.46	3.83	13.30	7.61	8.41	5.15	17.45
					(7.23)	(47.18)	(3.46)	(13.76)	(7.87)	(8.70)		
$NiL_2(H_2O)_2$	$C_{34}H_{32}Cl_2NiN_8O_6S_2$	842.4	270	64	6.97	48.48	3.83	13.30	7.61	8.42	2.94	20.24
					(7.21)	(47.20)	(3.47)	(13.76)	(7.88)	(8.71)		
ClTBrS	$C_{16}H_{12}BrN_4O_2SCl$	439.7	215	60	-	43.70	2.75	12.74	7.29	8.06	-	17.13
$CuL_2(H_2O)_2$	$C_{32}H_{26}Br_2Cl_2CuN_8O_6S_2$	977	280	66	6.50	39.34	2.68	11.47	6.56	7.26	1.98	16.26
$CoL_2(H_2O)_2$	$C_{32}H_{26}Br_2Cl_2CoN_8O_6S_2$	972	285	75	6.06	39.53	2.70	11.52	6.60	7.29	4.89	22.00
$NiL_2(H_2O)_2$	$C_{32}H_{26}Br_2Cl_2NiN_8O_6S_2$	965	275	60	6.04	39.54	2.70	11.53	6.60	7.29	2.86	18.50

and 19730 -19800cm^{-1} due to $^4T_{1g}$ (F) $\rightarrow ^4A_{2g}$ (ν_1) and $^4T_{1g}$ (F)$\rightarrow$ $^4T_{1g}$ (P) (ν_3) transitions respectively, in an octahedral environment. The bands due to the $^4T_{1g}$ (F) $\rightarrow ^4A_{2g}$ (F)(ν_2) transition could not observed because of its very low intensity. However the position of the n_2 band has been computed (14995-16005cm^{-1}) by the equation. $\nu_2 = \nu_1 + 10Dq$. The ligand field parameter such as Dq, B', β and β% have been calculated by using band-fitting equation given by Underhill and Billing[15]. The crystal field splitting energy (Dq) value was found to be 803-853 cm^{-1}. These values are well within the range reported for most of the octahedral Co(II) complexes. The Co(II) complex under present investigation process interelectronic repulsion parameter (B') 896-922 cm^{-1}. The Racha 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) complexes 0.94-0.92 which is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, β%, LFSE, ν_2/ν_1 (Table 2) suggest the octahedral geometry for Co(II) complexes[14]. Ni(II)complexes exhibit three bands at 9900-10000 cm^{-1},15580-15600 cm^{-1} and 25650-25700 cm^{-1} are assigned to $^3A_{2g}(F)\rightarrow ^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F)\rightarrow ^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F)\rightarrow ^3T_{1g}(p)(\nu_3)$ 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, β% and LFSE have been calculated by using Band-fitting equation given by Underhill and Billing[15]. Racah parameter B' is less than the free ion value of 1041 cm^{-1} indicating the covalent character of the complexes. Moreover, the ratio ν_2/ν_1 was found to be 1.56 -1.6 indicative of octahedral stereochemistry for this Ni(II) complex[16]. The Racha parameter B^1 is 816-819 cm^{-1}, which is less than the free ion value of 1041 cm^{-1} indicating the covalent character of the Ni(II) complexes.

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

Complexes	ν_1	ν_2	ν_3	Dq (cm^{-1})	B^1	β	β%	ν_2/ν_1	LFSE (kcalmol^{-1})
ClTCH3S	12215	-	16255	-	-	-	-	-	
$CuL_2(H_20)_2$				1423					24.40
$CoL_2(H_20)_2$	9975	14995	19730	803	922	0.94	5.04	1.50	13.76
$NiL_2(H_20)_2$	9900	15580	25650	965	816	0.78	21.98	1.59	28.00
ClTBrS									
$CuL_2(H_20)_2$	12300	16315	-	1430	-	-	-	1.32	24.52
$CoL_2(H_20)_2$	8728	16005	19800	855	896	0.92	7.70	1.9	14.65
$NiL_2(H_20)_2$	10000	15600	25700	967	819	0.8	21.25	1.56	33.12

IR Spectra

The infrared frequencies exhibited by the ligands and its complexes are given in table 3. The ligands do exhibit tautomerism[17] and one can expect both ν_{S-H} and $\nu_{C=S}$. A medium intensity band around 2540-2560cm^{-1} due to ν_{S-H} indicates the thiole form of the ligand. The band due to $\nu_{C=S}$ in the 754-759 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 formation[18] These observations suggest the non-involvement of sulfur atom in coordination. The infrared spectra of ligands exhibits high intensity band around 1620cm^{-1} is due to $\nu_{C=N}$. In the complexes, this band shifted to lower frequency (15-20cm^{-1}) around 1600-1558 cm^{-1} is suggestive of coordination through nitrogen of the azomethine group[19-21] to the metal(II) chlorides. The band observed in the region 1284 - 1290cm^{-1} for ν_{C-O} stretching vibrations undergoes shift to higher wave number at 1310 to 1377cm^{-1} compared with free ligand band. The band around 3200-3400 cm^{-1} due to phenolic OH, which is observed in ligands, disappears in complexes indicating complex formation via deprotonation[22]. A broad band appeared in the region 3420-3500 cm^{-1} in all complexes indicates the presence of

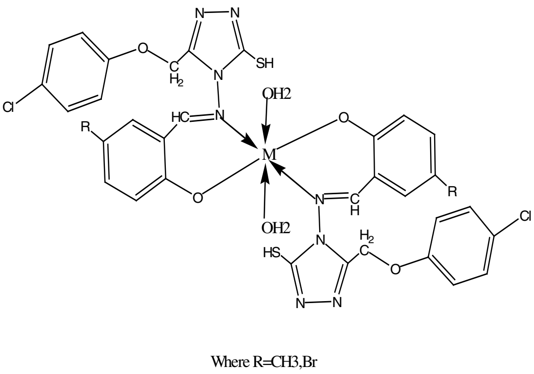
Table 3 : Characteristic IR frequencies (cm^{-1}) of the ligands $ClTCH_3S$ /ClTBrS and its metal complexes

Ligand/ complexes	ν_{H2O}	ν_{OH}	ν_{SH}	$\nu_{C=S}$	$\nu_{C=N}$	ν_{C-O}	ν_{M-O}	n_{M-N}
$ClTCH_3S$	-	3232	2545	758	1617	1289	-	-
$CuL_2(H_20)_2$	3420	-	2552	759	1609	1355	364	506
$CoL_2(H_20)_2$	3421	-	2545	756	1603	1360	364	507
$NiL_2(H_20)_2$	3420	-	2545	756	1602	1310	387	507
ClTBrS	-	3234	2560	756	1603	1280	-	-
$CuL_2(H_20)_2$	3421	-	2555	752	1598	1338	362	507
$CoL_2(H_20)_2$	3421	-	2545	754	1580	1340	380	508
$NiL_2(H_20)_2$	3421	-	2540	755	1585	1377	420	507

coordinated water or lattice water[23]. 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 506-508 cm^{-1} and 380-420 cm^{-1}, respectively in the far infrared region[24-27]. The presence of chlorine atoms in all the complexes is further confirmed by quantitative chloride estimation.

^1H NMR Spectra

The ^1H NMR spectrum of the ligands displays a sharp singlet which corresponds to the methyl proton in the region δ2.18-2.77. The aromatic rings give a group of multisignals at δ6.80-7.70. The CH=N hydrogen resonates at δ9.6- 9.8 as a sharp singlet. The ligands shows a peak at δ 12.0-12.2 characteristic of OH proton and it also shows a sharp singlet at δ9.5-10 due to SH protons[28]. On analyzing the spectrum of the Cd(II) complex there is no signal in the region δ12.0-12.2, thus it can be concluded that the –OH group coordinates to the metal via deprotonation and the signal at δ9.5-10 due to SH proton unperturbed in the complexes indicates the non-involvement of sulfur atom of SH group



Where R=CH3,Br

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

ESR Spectra

The ESR spectra of the Cu(II) complexes of the ligands ClTCH3S/ClTBrS were recorded in polycrystalline form at room temperature. The anisotropic G values have been calculated by Kneubuhl's method[29] $G = (g_{||}-2)/(g_{4(-)}-2)$ which measures the exchange interaction between Cu(II) centers. According to Hathaway[30] 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) complexes with $^2B_{1g}$ as ground state lies in d_{x2-y2} orbital and follows the trend $g_{||} > g_{\perp} > g_e$ ($g_e = 2.0036$ free ion value). The observed ESR parameters of Cu(II) complexes of the ligands ClTCH3S/ClTBrS were found to be $g_{||} = 2.248$ and $g_{\perp} = 2.058$ and $g_{||} = 2.276$ and $g_{\perp} = 2.059$ follows the same trend $g_{||} > g_{\perp} > g_e$ which suggest that the presence of unpaired electron in d_{x2-y2} orbital giving octahedral geometry[31]. The observed G values are G = 4.2 and 4.5 for the Cu(II)complexes under present study evidenced the monomeric nature of the complexes[32] and indicates that there is no spin exchange interaction in the Cu(II) complexes and hence distorted octahedral geometry proposed for the Cu(II) complexes.

CONCLUSIONS

The ligands ClTCH3S/ClTBrS behaved as a monobasic bidentate coordinating through 'N' of azomethine and 'O' of phenyl group. Analytical data, electronic spectra, magnetic susceptibility, IR, ^{1}HNMR, ESR spectral data reveal octahedral geometry for all the complexes. The low conductance values show non-electrolytic behavior of the complexes. On the basis of spectral evidence, the following probable structures have been assigned for synthesized complexes.

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