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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF Co (II), Ni (II) AND Cu (II) WITH SCHIFF BASES DERIVED FROM SUBSTITUTED SALICYLALDEHYDE AND 1-AMINO -2-MERCAPTO -5-ALKANE -1,3,4-TRIAZOLES

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ABSTRACT

Complexes of Co (II), Ni (II) and Cu (II) with Schiff bases derived from condensation of substituted salicylaldehyde and 1-amino-2-mercapto-5-alkane-1,3,4-triazole, have been prepared. These complexes have been characterized by elemental analyses, conductance measurements, magnetic susceptibilities measurements, IR, NMR, electronic and ESR spectral data. On the basis of these studies, octahedral geometries have been assigned for these complexes.

Key words: Schiff base, Complexes, Triazoles, Magnetic susceptibility,

INTRODUCTION

Triazoles and their complexes have attracted immense attention in recent years, because of their manifold applications in technology and their use to impede the biological activity associated with the environment[1-2]. There is growing interest in the studies on the metal complexes of Schiff bases derived from triazoles, which are biologically important ligands[3-5]. Metal complexes of bis-(pyridyl) triazole have been reported and their absorption spectra, luminescence properties and electrochemical behavior have been studied[6,7]. Literature survey has revealed that no attempt has been made to study the bivalent cobalt, nickel and copper complexes with the Schiff bases. It was therefore, thought of interest to study the synthesis and characterization of some substituted salicylaldehydenamino-trizoles complexes of Co (II), Ni (II) and Cu (II) metal ions.

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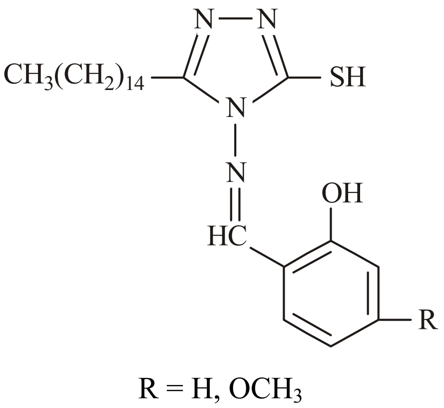

EXPERIMENTAL

All the chemicals and solvents used were of AR grade. Salicylaldehyde was obtained from Sisco-Chem. Industries. The metal salts were purchased from commercial sources. Metal contents were estimated using standard methods [8].

IR spectra of the compounds were recorded on a Beckman IR-20 spectrophotometer in the region 4000-250 cm^{-1} ^1H NMR spectra of ligands were recorded on a Perkin-Elmer 90 MHz spectrometer. The electronic spectra were recorded on an Elico SL 159 spectrophotometer in the 200-1000 nm ranges in DMF solution (10^{-3}). Elemental analyses were obtained HERAEUS C, H, N-O rapid analyzer. E.S.R measurements were carried out on a Varian E-109 GHz. The experiment was carried by taking DPPH as the reference with the field set at 3200 Gauss. Magnetic susceptibilities were determined by the Faraday method using a Model 300 Lewis coil force magnetometer of one Tesla field strength at room temperature. The instrument was calibrated with $Hg [Co (SCN)_4]$[9].

Reactions of Schiff bases with different metal ions viz., Co (II), Ni (II) and Cu (II) were carried out in hot ethanol solution of metal chlorides in 1 : 2 molar ratio. The solid products obtained were found to be stable in air and non-hygroscopic. The analytical data (Table 1) indicated complexes with general formula ML_2 in 1 : 2 molar ratios.

Preparation of ligands

Methyl palmatate, palmatic acid hydrazide and 1-amino-2-mercapto-5-alkane-1,3,4-triazoles were prepared by known method[10-14]. The substituted salicylaldehydeneamino-3-n-alkane-5-mercapto-1,3,4-triazoles were prepared by condensing substituted salicylaldehyde

(8.74 mL) and 4-amino-3-alkane-5-merapto-1,3,4-triazole (10 g) in hot 40 mL of ethanolic solution. Piperidine (1-2 mL) was also added to the reaction mixture. A light yellow solid started separating out after half an hour of refluxing. The product was filtered and washed with ethanol. The light yellow crystals were obtained on crystallization from ethanol[15].

Preparation of complexes

A mixture of hot ethanol solution (50 mL) of the metal salt (0.002 mL) and the ethanol solution of H_2L^1/H_2L^2 (0.002 mol) was refluxed for 8 hours. The contents were cooled at room temperature for a day after reducing the volume of the solution to half, which leads to the precipitation of the complexes. The complexes were filtered, washed with hot ethanol and dried in vacuo. The yield of the complexes varied from 70-80%, the complexes obtained was solid and non-hygroscopic.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are given in Table 1. The results of elemental analyses of the complexes correspond to stoichiometry for metal : ligand in 1 : 2 molar ratios. Molar conductance measurements of these complexes in DMF correspond to non-electrolytes. IR spectra of ligand show a broad medium intensity band in the region 3450-3300 cm^{-1} due to phenolic-OH[16], in complexes. These bands disappear due to complexation through phenolic OH group via deprotonation. The band in the region 1640-1590 cm^{-1} was assigned to HC=N group indicating the condensation between amino group of triazole and substituted salicylaldehyde. In ligands, a medium intensity band was observed in the range of 2670-2620 cm^{-1} assigned to the $\nu_{(SH)}$ vibrations;[17] in complexes, these bands disappear due to complexation through phenolic -SH group via deprotonation. The band due to $\nu_{(C=N)}$ appears in the region of 1630-1590 cm^{-1} as a high intensity band in the complexes, indicating that the C=N group is involved in coordination of metal ions through nitrogen. In complexes, the bands due to C=N group are shifted to lower frequency by 30-20 cm^{-1}. The magnetic moment of the $Co(L^1)_2$, $Ni(L^1)_2$ and $Cu(L^1)_2$ are 4.82, 3.15 and 1.80 B.M, respectively. The μ_{eff} values are well within the range known for six coordinate octahedral geometry (Table 1). Similarly, magnetic moment for the $Co(L^2)_2$, $Ni(L^2)_2$ and $Cu(L^2)_2$ are 4.75 3.25 and 1.82 B.M., respectively[18]. The electronic spectra of the complexes recorded in DMF display three bands at 11760-15620 $cm^{-1}(\nu_1)$, 15600-19230 $cm^{-1}(\nu_2)$ and 20830-22720 $cm^{-1}(\nu_3)$ (Table 2). Six coordinate complexes with O_h symmetry show three spin allowed bands. These bands are due to ${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)(\nu_2)$ and

$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$ for cobalt complexes; $^3A_{2g}\rightarrow{}^3T_{2g}(\nu_1)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)(\nu_3)$ for nickel complexes and $^2B_{1g}\rightarrow{}^2A_{1g}(\nu_1)$, $^2B_{1g}\rightarrow{}^2B_{1g}(\nu_2)$ and $^2B_{1g}\rightarrow{}^2E_g(\nu_3)$ for copper complexes[19]. Various ligand field parameters have been evaluated for cobalt and nickel complexes (Table 2).

Table 1: Physical data, elemental analyses, magnetic measurements and molar conductance of metal complexes with ligands H_2L^1 and H_2L^2

Ligands/ Complexes	Colour M.P. (^{o}C)/ Yield (%)	Elemental analyses Found/(Calcd.)					μ_{eff} (B.M)	Molar Cond. mho cm^2 mol^{-1}
		M	C	H	N	S		
H_2L^1	Yellow	–	69.49	9.25	13.62	7.80	–	–
($C_{24}H_{38}N_4SO$)	128 (77)		(69.56)	(9.17)	(13.52)	(7.73)		
$Co(L^1)_2$	Brown	6.72	65.18	8.65	12.73	7.20	4.82	40.00
$Co(C_{24}H_{36}N_4SO)_2$	195 (65)	(6.67)	(65.13)	(8.60)	(12.68)	(7.24)		
$Ni(L^1)_2$	Pink	6.58	65.19	8.55	12.73	7.18	3.15	32.20
$Ni(C_{24}H_{36}N_4SO)_2$	198 (62)	(6.64)	(65.25)	(8.61)	(12.69)	(7.25)		
$Cu\ (L^1)_2$	Yellow	7.26	64.92	8.62	12.57	7.31	1.80	43.40
$Cu(C_{24}H_{36}N_4SO)$	205 (65)	(7.15)	(64.89)	(8.56)	(12.61)	(7.25)		
H_2L^2	Yellow	–	65.2	8.70	12.20	6.90	–	–
($C_{25}H_{40}N_4SO_2$)	137 (75)		(65.21)	(8.69)	(12.17)	(6.95)		
$Co\ (L^2)_2$	Brown	6.46	61.46	8.22	11.50	6.47	4.75	30.85
$Co(C_{25}H_{38}N_4SO_2)_2$	210 (68)	(6.41)	(61.41)	(8.18)	(11.46)	(6.55)		
$Ni(L^2)_2$	Brown	6.43	61.38	8.14	11.41	6.50	3.25	45.30
$Ni(C_{25}H_{38}N_4SO_2)_2$	220 (62)	(6.39)	(61.43)	(8.19)	(11.47)	(6.55)		
$Cu(L^2)_2$	Yellow	6.50	61.17	8.23	11.46	6.55	1.82	35.20
$Cu(C_{25}H_{38}N_4SO_2)_2$	228 (65)	(6.47)	(61.12)	(8.15)	(11.41)	(6.52)		

Table 2: Electronic spectra and ligand field parameters of complexes

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Dq (cm^{-1})	B\` (cm^{-1})	β	LFSE
$Co(L^1)_2$	12425	17650	21515	5223	1562.05	1.60	18.00
$Ni(L^1)_2$	11762	15875	22225	4112	1715.00	1.64	12.99
$Cu(L^1)_2$	12030	15622	22740	–	–	–	–
$Co(L^2)_2$	13510	19235	20836	5714	1520.10	1.59	15.40
$Ni(L^2)_2$	14715	16133	22720	1427	2310.75	2.23	5.85
$Cu(L^2)_2$	15622	17235	21745	–	–	–	–

The nephelauxetic parameter, β is readily obtained using the relation β = B (complex)/B (free ion), indicate that complex under study have appreciable covalent character. The value of Dq could be evaluated with the help of the curve transition energies versus Dq by Orgel using the energy level due to transitions $^4T_{1g}(F) \rightarrow {^4A_{2g}}(F)$ and $^3A_{2g} \rightarrow {^3T_{1g}}(P)$, respectively. The parameter B was evaluated by using the methods reported earlier.

The ESR spectra of the copper complexes as polycrystalline sample have been recorded at room temperature and ESR chart was calibrated with DPPH. The polycrystalline samples give one broad isotropic signal centered approximately at 2.023 and 2.040 for the complex $Cu(L^1)_2$. The observed g values of the $Cu(L^1)_2$ complex as follows $g_{||}$ =2.058, $g_{\perp}$ =2.014, g_{av} =2.028 and G = 4.19 while for $Cu(L^2)_2$, $g_{||}$ = 2.052 $g_{\perp}$ = 2.024 g_{av} = 2.030 and G = 4.22. The isotropic g values have been calculated Kneubuhl\`s methods[20] and methods reported earlier. G = $(g_{||}-2)/(g_{\perp}-2)$, which measures the exchange interaction between copper centers in a polycrystalline solid has been calculated. According the Hathaway[21], if the G value is greater than 4, the exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange in the solid complexes. G = 4.13 and G = 4.20 for $Cu(L_1)_2$ and $Cu(L_2)_2$, respectively, indicates the exchange interaction is negligible.

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