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Synthesis and Characterization of metal Complexes of 2-(5-substituted-(Thiadiazolyl/Triazolyl)-2-thio) methylbenzimidazole

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Abstract

Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2-(4'-amino-5'-(nicotinyl)-1',2',4'-triazolyl-3'-thiomethylbenzimidazole(L_1), 2-(5'-(nicotinyl-4-phenyl-1',2',4'-triazolyl-3'-thio) methylbenzimidazole) (L_2),and 2-(5'-(nicotinyl)-1',3',4'-thiadiazolyl-2'-thio) methylbenzimidazole)(L_3) have been prepared and characterized.

Keywords- Methylbenzimidazole, dithiole, heterobimetallic, metalloproteins, electronic spectra.

Introduction

Several compounds of thiadiazoles and triazoles (Mishra, *et al.,* 1994, Ram, *et al.,* 1979 and Mishra, *et al.,* 1983) and the synthetic utility of benzimidazole derivatives containing the organic heterocycles as chemotheraputic agents are reported (Rastogi, *et al.,* 1983). Recently, the roles of dithioligands have been explored in the design of many electrically conducting molecular solids. The interest in this area stems from various reasons such as stabilization of transition metal ions in its unusual oxidation state, facile redox behaviour stablization of square planar geometry around transition metal ions, interesting spectral and magnetic properties (Singh, *et al.,* 2002). Imidazole, a five membered nitrogen heterocycle is an ubiquitous ligend in chemical and biological systems. Histidine plays an important role in stabilizing the active sites of a number of metalloproteins. In particular, copper protein such as azurin, plastocyanin, hemocyanin and tyrosinase are known to contain several imidazole molecules as ligands per copper centre (Jena, *et al.,* 1999). The antibacterial activities of the ligands and their cobalt and nickel complexes have been screened in vitro against the organisms *Staphylococus aureus* (S.C.), *Escherichia coli* (*E.* c*oli*), *Bacillus* (B) and *Pseudomonus aeruginoro* (P.S.) (Reddy, *et al.,* 1998). Synthesized and Characterized complexes of Mn(II), Fe(II), Co(II) and Zn(II) with N^2-ethoxythiocarbonylbenzoic acid hydrazide and N^2-ethoxycorbonyl pyridine carboxylic acid hydraizide have 1:2 and 1:1 stoichiometry (Singh, *et al.,* 1990).

Experimental

2-mercapto-5-(nicotinyl)-4-amino 1, 2, 4-triazole

It was prepared by using a mixture of KOH and carbon disulphide. Addition of dry diethyl ether, the crystalline solid obtained (Mishra, 1977) was filtered and washed with dry diethyl ether. 3-mercapto-4-

N^1-phenyl-5-(nicotinyl)1,2,4-triazole and 2-mercapto-5-(nicotinyl)-1,3,4-thiadiazole were prepared by literature procedure (Mishra, 1977 and Hughes, *et al.,* 1938).

2-(4′-amino-5′-(nicotinyl)-1′,2′,4′-triazolyl-3′-thiomethyl)benzimidazole (L_1)

3-mercapto-5-(nicotinyl)-4-amino-1,2,4-triazole (2.40 g, 0.01 mol) and 2-chloromethyl benzimidazole (1.70 g, 0.01 mol) were mixed together in 10 ml pyridine was gently heated on water bath for 5 hr (Hughes, *et al.,* 1938). The reaction mixture was cooled and then poured into 200 ml ice-cold water. The resulting product was solidified when whole content was kept in a refrigerator for 2 days. Solid product was crystallized in ethanol. m.p.170°C, Molecular formula $C_{16}H_{13}N_7S$.

Calcd: C = 57.31%, H = 3.88%, N = 29.25%, S = 9.55%
Found: C = 57.29%, H = 3.80%, N = 29.28%, S = 9.51%

2-(5′nicotinyl-4-phenyl-1′,2′4′-triazolyl-3′-thio)methylbenzimidazole(L_2)

A mixture of 3-mercapto-4-phenyl-5′-(nicotinyle)-1, 4-triazole (2.43 g 0.01 mol) and 2-chloromethylbenzimidazole (1.70 g, 0.01 mol) in 15 ml pyridine was gently heated on a water bath for 5 hr. The reaction mixture was cooled at room temperature and poured into 200 ml ice-cold water. Solid precipitated was filtered and washed several times with water and crystallized from ethanol. m.p.185°C, Molecular formula $C_{22}H_{16}N_6S$.

Calcd: C = 66.66%, H = 4.04%, N = 21.21%, S = 8.08%
Found: C = 66.68%, H = 4.04%, N = 21.19%, S = 8.10%

2-(5′-(nicotinyl)-1′,3′,4′-thiadiazolyl-2′-thio)methylbenzimidazole(L_3)

A mixture of 2-mercapto-5-(nicotinyl)-1,3,4-thiadiazole (2.93g, 0.01 mol) and 2-chloromethylbenzimidazole (1.70 g, 0.01 mol) in 15 ml pyridine was gently heated on a water bath for 4 hr. The reaction mixture was then poured into 250 ml ice-cold water. The solid precipitated was filtered, washed several times with water and crystallized in ethanol. m.p. 210 °C, Molecular formula $C_{16}H_{11}N_5S_2$.

Calcd : C = 56.97%, H = 3.26%, N = 20.77%, S = 18.99%
Found: C = 56.99%, H = 3.29%, N = 20.75%, S = 18.92%

Preparation of complexes: General procedure

A hot solution of metal chloride in 10 ml of ethanol was added to a hot solution of ligand in ethanol with stirring for 4 hr. The precipitate was filtered, washed and dried under vacuum.

The metals were estimated gravimetrically by standard procedure (Vogel, 1978) after decomposing with HNO_3 whereas chlorine and sulphur were estimated as silver chloride and barium sulphate respectively, after decomposing the complexes with fusion mixture and Na_2O_2 together in a nickel crucible. Carbon, hydrogen and nitrogen were determined microanalytically. Molar conductance was measured on Dist 1 HANNA digital conductivitymeter. The diamagnetic corrections were made using Pascal's constant (Levis, *et al.,* 1960). All complexes were found stable at room temperature and showed non-electrolytic behavior in solution. The empirical compositions of the complexes along with their physical and analytical data are represented in Table No 1.

Table No. 1 Physical and Analytical data of the Metal Complexes

Complexes	Color	Analyses Found (Calcd.)% M.P. (^{0}C)	C	H	N	M	S		μ_{eff} (B.M.)	Molar Conductance (ohm^{-1}cm^2 mol^{-1})
[Co(L_1)Cl_2]	Light blue	197	41.28	2.80	21.00	12.62	6.80	15.21	4.65	22.00
			(41.30)	(2.79)	(21.08)	(12.67)	(6.88)	(15.25)		
[Ni(L_1)Cl_2.2H_2O]	Light green	124d	38.30	2.51	19.60	11.69	6.35	14.10	3.08	10.50
			(38.35)	(2.59)	(19.57)	(11.72)	(6.39)	(14.16)		
[Cu(L_1)$_{1/2}$$Cl_2$.2$H_2$O]	Deep green	209d	56.79	3.80	28.92	18.75	9.43	20.91	1.65	12.00
			(56.81)	(3.84)	(28.99)	(18.80)	(9.46)	(20.98)		
[Zn(L_1)Cl_2]	Colorless 240±2	40.71	2.78	20.75	13.82	6.82	15.00	dia	5.01	
			(40.74)	(2.75)	(20.79)	(13.87)	(6.79)	(15.04)		
[Co(L_2)Cl_2]	Light blue	160d	50.25	3.07	15.91	11.15	6.10	13.42	4.92	8.10
			(50.20)	(3.04)	(15.97)	(11.20)	(6.08)	(13.48)		
[Ni(L_2)$_{1/2}$$Cl_2$.2$H_2$O]	Yellowish green	250	72.56	4.43	23.05	16.10	8.72	19.41	2.50	9.09
			(72.60)	(4.40)	(23.10)	(16.14)	(8.80)	(19.49)		
[Cu(L_2)$_{1/2}$$Cl_2$.2$H_2$O]	green	221d	71.61	4.39	22.81	17.19	8.62	19.29	1.75	22.61
			(71.65)	(4.34)	(22.79)	(17.24)	(8.68)	(19.24)		
[Zn(L_2)Cl_2]	Colorless	224d	49.50	3.09	15.75	12.21	6.07	13.36	dia	20.82
			(49.59)	(3.00)	(15.78)	(12.28)	(6.01)	(13.32)		
[Co(L_3)Cl_2]	Light blue	300	41.09	2.30	14.91	12.67	13.75	15.21	4.75	13.52
			(41.12)	(2.35)	(14.99)	(12.62)	(13.70)	(15.18)		
[Ni(L_3)$_{1/2}$$Cl_2$.2$H_2$O]	Yellowish green	250	57.40	3.22	20.99	17.51	19.12	21.19	2.58	9.10
			(57.46)	(3.29)	(20.95)	(17.57)	(19.15)	(21.22)		
[Cu(L_3)$_{1/2}$$Cl_2$.2$H_2$O]	Deep green	220d	56.61	3.29	20.60	18.79	18.81	20.45	1.75	22.62
		(56.64)	(3.24)	(20.65)	(18.74)	(18.88)	(20.91)			
[Zn(L_3)Cl_2]	Colorless	225d	40.51	2.37	14.71	13.75	13.45	14.92	dia	20.86
			(40.56)	(2.32)	(14.79)	(13.81)	(13.52)	(14.98)		

d = decomposed

Results and Discussion

The IR spectra of ligands (L_1, L_2 and L_3) were compared with the IR spectra of their metal complexes. Ligands showed peaks at ~3150-3060 cm^{-1} which were assigned as ν(NH) (Lane, *et al.,* 1962). The IR spectra of the complexes synthesized have been interpreted in the light of earlier investigation (Reddy, *et al.,* 2005, Nike, *et al.,* 2002, Halli, *et al.,* 2001, Sandhya, *et al.,* 1999, Gupta, *et al.,* 2003 and Venkataeswar, *et al.,* 2003) with transition metal complexes of nitrogen donor. IR spectra of their nickel(II) and copper(II) complexes showed broad peaks in the region 3250-3500 cm^{-1} which may be due to vibration of -OH of H_2O. The free ligand peak due to ν(NH) at ~3100 cm^{-1} remains constant in the spectra of all complexes which suggest non coordination behavior of NH group.

Ligands peak observed in the range of ~1630-1600 cm^{-1} due to ν(C=N). Lowered down in the position and in the intensity both show its co-ordination with metal ions. Furthermore, ν(C-N) vibrations due to heterocyclic ring observed at ~1080-1040 and ~1200 cm^{-1} in the IR spectra of ligands have shown significant change in the position of all the metal complexes. This strongly supports that rings are involved in the co-ordination with the metal ions and the most probable coordinating site on both rings is C=N group.

In the lower region of the IR spectra of the complexes with ($L_1$and L_3) show bands due to ν(M-N) at ~480 cm^{-1} and ~400 cm^{-1} respectively. The distinction between two ν(M-N) bands arising due to coordination of C=N group of either triazole ring system or thiadiazole ring system could not made due to poor resolution of the spectra in this region. In addition to this, weaker peaks observed at ~280-270 cm^{-1} in all metal complexes were assigned to ν(M-Cl) vibrations.

The magnetic moment values calculated for the metal complexes, suggested the octahedral co-ordination for nickel(II), copper(II) and tetrahedral for cobalt(II) and zinc(II) complexes respectively. Zinc(II) complexes were found to be diamagnetic. The electronic absorption bands observed for ligands at ~33500-43300 cm^{-1} were assigned to intra-ligand transitions. The bands observed for the metal complexes at ~25000 - 29000 cm^{-1}, have been assigned to $M\rightarrow L(\pi^*)$ transitions. The electronic spectra of nickel(II) complexes with ligands (L_1, L_2 and L_3) showed the peaks at ~8300, 15380, ~20800 cm^{-1}, ~9600, ~16000 and ~23000 cm^{-1}; and ~12300, ~17800, ~23700 cm^{-1} respectively. The peak position and nature of bands corresponded to six coordinated high-spin nickel(II) complexes based on the earlier reports (Venkataeswar, *et al.,* 2003).

The ESR spectra of copper(II) complexes, Fig 1(a-c) with L_1, L_2 and L_3 ligands was recorded in both solid as well as in solution state. The ESR spectrum of $[Cu(L_1)Cl_2.2H_2O]$ complexes showed only a broad signal which gave only g-isotropic value (g_{iso} = 2.10). In the ESR spectrum of $[Cu(L_2)Cl_2.2H_2O]$ complex, the g_{II}, $g_\perp$, A_{II} and $A_\perp$ values were calculated and found to be g_{II} = 1.963, $g_\perp$ = 2.040, A_{II} = 50 and $A_\perp$ = 17 Gauss. It is thus observed that $g_{II} < g_\perp$, which indicated that the unpaired electron is lying in the d_z^2 orbital. The ESR spectra of $[Cu(L_1)_{1/2}Cl_2.2H_2O]$ complex showed g_{II} = 2.3024 Gauss and A_{II}= 175 Gauss, but due to poor resolution in perpendicular region, we could not calculated the $g_\perp$ and $A_\perp$values for the same complex. A half field signal was observed for the same complex which suggested its dimeric structures. The half field signal disappeared in solution (DMSO) may be due to dissociation of complex.

The electronic spectra of cobalt(II) complexes exhibited three bands at ~9000, ~16000 and 18000 cm^{-1}, which may be due to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$, $^4T_{2g}(F)\rightarrow{}^4A_{2g}(F)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transitions respectively. The electronic spectral bands of copper(II) complexes are very similar to those reported by our group for other six coordinated copper(II) system. The crystal field parameters for nickel(II), cobalt(II) and copper(II) complexes calculated by the reported method (Lever, 1968) are in good agreement with those reported for tetrahedral cobalt(II), zinc(II), octahedral nickel(II) and copper(II) complexes Fig 2.

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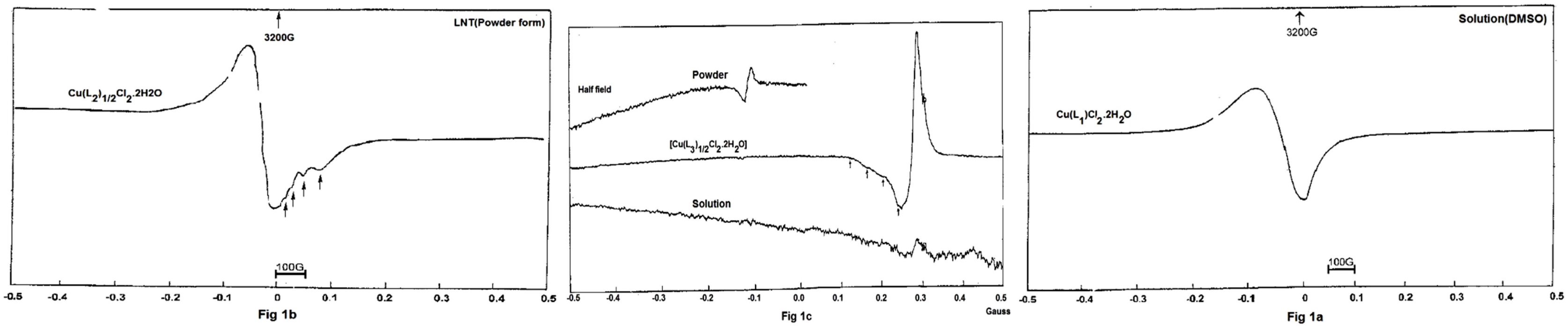

Fig 1b

Fig 1c

Fig 1a

Fig. 1 ESR spectra of the complexes.

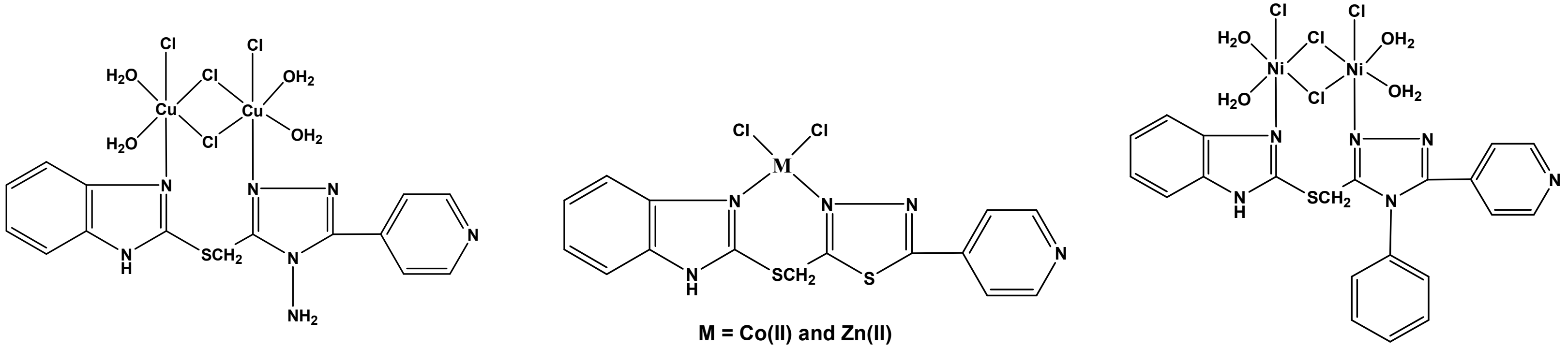

Fig. 2 Suggested structures for the complexes.

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