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Synthetic and spectral studies on complexes of some transition metals with 2,2'-imino bis-4,4'-diphenylthiazole

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Abstract: : The complexes of type M1, 2X2 where M=Co(II). Ni(II) and Cu(II), X=CI, Br, (NO3) and L=2,2'-imino bis-4,4-diphenylthiazole have been synthesized and characterized. The complexes are monomeric and nonelecrolytic in nature. IR reveal the coordination of the ligand and metal ion. The electronic spectral studies suggested octahedral geometry.

(Key words : 2,2'-imino bis-4,4' diphenylthiazole, 2,2'-imino bis thiazole)

Introduction

It is well known that the compounds containing sulphur and nitrogen atom can enhance antibacterial activities. It is reported that 2,2'-imino bis thiazole nucleus has physiological activity[1-2]. In the present work, an attempt has been made to synthesize and characterize the complexes of Co(II), Ni(II) and Cu(II) with 2,2'-imino bis-4.4'-diphenyl thiazole (IBPT)

Experimental

Organic reagent and solvent used in the present investigation were procured from B.d.H. and Bengal chemicals. Metal salts of NIckel, Cobalt and Copper used were procured from B.d.H. and Bengal chemicals. Metal salts of Nickel, Cobalt and Copper used were either B.D.H. or A.r. quality.

Preparation of ligand : A mixture of N'-(4-phenlthiazole-2-yl) thiourea (2.34g) and phenacylbromide (1.98g) in ethanol were refluxed for 0.5 h. It was cooled and neutralized with ammonium hydroxide solution. The resulting solid was washed and crystallized from ethanol: acetone (2:1) mixture to obtain pale yellow crystals (224^0C).

Preparation of metal complexes : Metal salts were dissolved in ethanol and the ligand in dry acetone and were mixed in 1:2 molar ratio and refluxed for 2-3 ih in perfectly dry condition. Coloured complexes were separated on standing. The separated on standing. The separated complexes were filtered, washed with alcohol and acetone mixture, then with petroleum ether and dried over fused calcium chloride under vacuo.

Elemental analysis were done[3-4] and tabulated (Table-) to ascertain their to molecular formulae. Molecular weight and molar conductance value were determined by standard method. Infrared spectrum of the complexes as well as the ligand were recorded in KBr disc.

Magnetic susceptibility of the complexes were measured by using Gouy's balance at room temperature. The effective magnetic moment (ueff) were calculated after diamagnetic correction using Pascal's constant and tabulated (Table-1)

Results and Discussion

The complexes were insoluble in water but readily soluble in organic solvent like DMF and dioxane. The stoichiometries of metal complexes were established on the basis of their elemental analysis. The stoichimetries of complexes were metal: ligand ratio as 1;2. The low molar conductance values of all complexes indicate their nonelectrolytic nature. The molecular weight values of complexes indicate monomeric nature.

The broad and strong band in the region 34-3050cm^{-1} represent a series of overlapping stretching vibrations of corresponding to NH group[5]. The The C-H stretching vibrations of aromatic ring seems to have been enveloped by H stretching vibrations. The bands observed in tehe spectra of the ligand are at 1600, 1595, 1500 and 1420 cm^{-1}. These bands arise due to v(NH), cyclic v(C-N) vibrations and v(C-S) vibrations[6-7]. Other bands observed are at 1330, 1260, 1140 and 1060 cm^{-1} which may be due to out of plane CH bending of substituted aromatic ring.

Table - 1

Compound (Colour)	ueff(BM)	**Analysis % Found (Calcd)**				
		M	C	H	N	S
IBPT			64.6	4.0	12.2	19.3
(Pale yellow)			(64.5)	(3.9)	(12.5)	(191)
$Co(IBPT)_2(NO_3)_2$	4.31	7.0	50.5	3.0	13.3	15.2
(Pale yellow)		(6.9)	(50.6)	(3.1)	(13.1)	(15.0)
$Co(IBPT)_2Cl_2$	4.25	7.5	53.9	32	10.6	16.1
(Orange)		(7.4)	(54.0)	(3.3)	(10.5)	(16.0)
Co(IBPT)2Br2	4.28	6.5	48.7	2.8	9.6	14.5
(Pale brown)		(6.6)	(48.6)	(2.9)	(9.5)	(14.5)
Ni(IBPT)2(NO3)	23.02	6.8	50.7	3.0	13.2	15.2
(Violet)		(6.9)	(50.6)	(3.1)	(13.1)	(15.0)
Ni(IBPT)2 Br2	2.91	6.5	48.5	2.8	9.6	14.3
(Violet)		(6.6)	(48.6)	(2.9)	(9.5)	(14.4)
Cu(IBPT)2(NO3)	21.90	7.3	50.3	3.1	13.2	14.8
(Green)		(7.4)	(50.4)	(3.0)	(13.1)	(14.9)
Cu(IBPT2)Cl2	1.86	7.8	53.9	3.3	10.5	16.0
(Green)		(7.9)	(53.7)	(3.2)	(10.4)	(15.9)
Cu(IBPT)2Br2	1.88	7.0	48.6	3.0	9.3	14.4
(Green)		(7.1)	(48.4)	(2.9)	(9.4)	(14.3)

In the spectra of metal complexes the twin bands at 1595 and 1500 cm^{-1} are disappeared and new sharp band is appeared t 1690 cm^{-1} indicating metal-ligand interaction[8]. The band at 840cm^{-1} due to v(C-S) of thiazole ring is shifted to lower frequency by 40-50 cm^{-1} indicating that sulphur atom of thiazole is involved in the bonding. The new bands at 460-420 cm^{-1} and 410-340 cm^{-1} of complexes are assigned to v(M-N)[10] respectively Bands at 1510, 1290 and 920 cm^{-1} suggest the presence of coordinated NO^{-}2 group[11.]

The magnetic moment values of Co(II), Ni(II) and Cu(II) complexes indicate[12.13] the presence of three, two and one unpaired electrons respectively.

The electronic spectra of Co(II) complexes show bands at 8950-9760 cm^{-1}, 18000 cm^{-1} and 20800-21590 cm^{-1} assignable to $^4T_1g(F)\rightarrow{}^4T_2g(F)(v_1)$, $^4T_1g(F)\rightarrow{}^4T_1g(F)'$ $\rightarrow{}^4A_2g(F)(v_2)$ and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ respectively. These transition suggest an octahedral geometry around metal ion[14.15]. Dq. B, B_2,B0 and v_2/v_1 values have been found to be 905-824, 796.7-687.3,0.82-71, 18-29 and 2-1.8 respectively, which agree with the values of octahedral Co(II) complexes[12]. The electronic spectra of Ni(II) complexes show bands

at 9810-10010 cm^{-1}. 16750-17100 cm^{-1} and 26120-26980 cm^{-1} which are assigned to $^3A2g\ (F)' \rightarrow$, $^3T2g\ (F)(v1)$, $^3T1g\ (F)(v2)' \rightarrow$, $^3T1g(P)(v3)$ transition respectively. Dq. B, B_2,B0 and v2/v1 values have been found to 1001-981, 878-809, 0.832-767, 16.7-23.29 and 1.67-1.71 respectively which agree with the values of octahedral Ni(II) complexes[16].

The electronic spectra of Cu(II) complexes show broad at 18800-14700cm^{-1}. and 27000cm^{-1}. assignable to $^2Eg \rightarrow {}^4T_1g$ and CT bands respectively[17] suggesting an octahedral geometry around the metal ion.

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