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Spectral studies on cobalt (II) and nickel (II) complexes of bis(1-phenyl tetrazoline)-5,5'-disulphide

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ABSTRACT

Bis(1-phenyl tetrazoline)-5,5'-disulphide forms stable complexes having general formula $[CoA_2(ligand)_2]X$ and $[Ni(H_2O)_4(ligand)_2]X$ (A = CH_3COO – and H_2O, X = ClO_4^-, NO_3^-, SO_4^{--}) at pH = 6. Cobalt (II) complexes are square planar having magnetic Bis (1-phenyl tetrazoline) –5,5'-disulphide forms stable complexes having general moment 2.74 – 2.76 BM. Sub-normal magnetic moment of octahedral Ni (II) complexes observed between 1.47 – 1.66 BM indicates square planar and octahedral equilibrium. The ligand field parameters $\nu_2/\nu_1 = 1.61$, B' = 764.9 cm^{-1}, 10 Dq = 9943.7 cm^{-1} and B = 0.96 cm^{-1} also supports octahedral structure. IR spectra suggest bonding through one of the disulphide sulphur of ligand.

Key words: Heterocyclic organic disulphide, spectral properties Ni(II) and Co(II) complexes.

INTRODUCTION

Organic disulphides are very important class of organic compounds of great biological significance[1]. They have unique and interesting insights into structure and bonding and used as ligands by several workers[2-6]. The present study describes the complexes of Co(II) and Ni(II) with heterocyclic organic disulphide, bis(1-phenyl-tetrazoline)-5,5'-disulphide (Fig I)

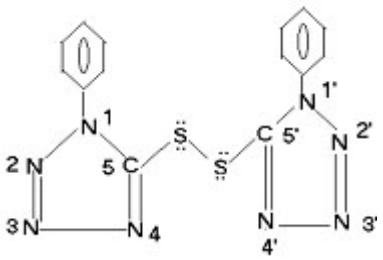

Fig. 1: DST

EXPERIMENTAL

All chemicals were chemically pure grade. The ligand was prepared by the method described earlier[7]. Complexes were prepared using a general method. Alcoholic solution of metal salt was mixed ligand solution in benzene using appropriate molar ratios. The reaction mixture was then refluxed on water-bath and the volume of solution mixture reduced to ca.40 mL by evaporation. The complexes formed were digested on water bath for half an hour, centrifuged, washed with ice-cold ethanol and dried at 110°C in an electric oven.

Electronic absorption spectra of the complexes were recorded with the help of Cary, Model 17D Spectrophotometer n nujol mull. The magnetic measurements on all solid complexes were made at room temperature (300K) on the gouy balance. Calibration was done using $Hg[Co(NCS)_4]$ as standard. The conductivity of complexes were

measured in DMF(10^{-3}M) solution with the help of a systronic conductometer. Carbon, hydrogen and nitrogen analysis and IR spectra were recorded at CDRI, Lucknow. Analytical and physical data of complexes are given in TABLE 1.

RESULTS AND DISCUSSION

Bis(1-phenyl tetrazoline)-5,5'-disulphide forms stable coloured solid having general formula $[CoA_2(DST)_2]X$ and $[Ni(H_2O)_4(DST)_2]X$ (A=$CH3COO^-$&H_2O, X=ClO_4^-,NO_3^-,SO_4^-) at PH=6. All complexes are insoluble in common organic solvents but fair solubility was attributed in DMF and solution of complexes in DMF (10^{-3}M) supports their formulation[8] (Table 1) . The magnetic moment of Co(II) complexes were found to be 2.74- 2.76 BM which corresponds square planar in structure[9]. A very intense absorption band at 27027 cm^{-1} in Co(II) complexes is assigned to charge transfer band either due to M→L or L→M. However, strong absorption bands at 16666 cm^{-1} and at 14285 – 14766 cm^{-1} indicate that these Co(II) complexes are square planar [10] and the bands are assigned due to $2A_1g \rightarrow B_1g$ and $2A_1g \rightarrow 2B_1g$ translations respectively.

The magnetic moment of Ni (II) complexes observed between 1.47-1.66 BM is intermediate between zero (square planar) and 2.83 BM (octahedral) probably due to square planar and octahedral equilibrium [11]. Similar observations have been reported by Saha etal [12] and Benzer and Co-workers [13]. If two water molecules associated with each Ni(II) ion revert to uncoordinated form to coordinated form and vice-versa then square planar and octahedral equilibrium is probable.

Electronic spectral bands and their assignment of Ni(II) complexes has been given in TABLE 2. All complexes display three major bands [14]of weak intensity. This is the characteristic of octahedral Ni(II) complexes. The ν_1/ν_2 value lies between 1.61-1.64 supports the octahedral geometry to complexes and suggest a strong configuration interaction between the high spin T_1g (P) and T_2g(F) excited state. The value of â in the range 0.84-.96 puts the ligand (DST) towards the strong end of the nephelauxetic series. Schaffer et al [15] and Jorgensen[16] have pointed out that ligands which coordinate through sulphur cause very pronounced nephelauxetic effects. Thus,

Table 1: : Analytical and physical data of complexes

Complexes/ (colour)	Magnetic Moment, BM	Molar Conductance (ohm^{-1} cm^2 mol^{-1})	%Analysis:Found/(calcd)			
			C	H	N	Metal
$[Co(ac)_2(DST)_2]$ (Blue)	2.75	9.8	43.5 (43.3)	3.0 (2.9)	25.4 (25.3)	7.1 (6.7)
$[Co(H2O)_2(DST)_2](NO_3)_2$ (Blue)	2.74	145	36.5 (36.3)	2.6 (2.5)	26.9 (27.1)	6.4 (6.3)
$[Co(H_2O)_2(DST)_2]SO_4$ (Pink)	2.78	142	36.8 (37.3)	3.0 (2.7)	25.0 (24.9)	6.7 (6.6)
$[Co(H_2O)_2(DST)_2](ClO_4)_2$ (Black)	2.73	144	33.6 (33.5)	2.2 (2.4)	22.8 (22.4)	6.1 (5.9)
$[Ni(H_2O)_4(DST)_2](ClO_4)_2$ (Greenish yellow)	1.47	139.3	32.2 (32.3)	3.0 (2.7)	21.4 (21.5)	5.8 (5.6)
$[Ni(H_2O)_4(DST)_2](NO_3)_2$ (Green)	1.56	176.6	35.0 (34.9)	3.0 (2.9)	26.2 (26.1)	6.0 (6.1)
$[Ni(H_2O)_4(DST)_2]SO_4$ (Light green)	1.67	141.3	35.8 (35.9)	3.0 (2.9)	24.0 (23.9)	6.5 (6.3)
$[NiCl_2(H_2O)_2(DST)_2]$ (Green)	1.66	10.2	38.2 (38.4)	2.7 (2.7)	25.5 (25.6)	7.0 (6.7)

coordination through sulphur may be suggested. It may be further noted that the ν_2 band is calculated to be equal to 12 D_q + 15 B', which is equal to 23405 cm^{-1} in the case of $[Ni(H_2O)_4(DST)_2]SO_4$. This is in good agreement with the observed band at 23239 cm^{-1}. The other ligand field parameters ν_2/ν_1=1.61, B'=764.9 cm^{-1}, 10 Dq = 9943.7 cm^{-1} and β = 0.96 of the complex also supports the octahedral structure [18].

Infrared spectra of ligand (DST) and the complexes are similar from 3100cm^{-1} to 1600cm^{-1}. The medium band at 1595 cm^{-1}in the spectrum of the ligand assigned to νC = C + νC = N mode remains unchanged in position on complexation to metal ions indicating that C = C and C= N groups are not involved in coordination. The νC – S band of the ligands observed at 690 cm^{-1} split into two new bands on coordination.One band remains almost at the same position but other band is observed at 660-670 cm^{-1}. This indicates that out of the C–S-S-C moiety of the ligand , one of the two S-atoms has coordinated with divalent metal ion while the other sulpher atom remains uncoordinated. This generates two νC-S bands, νC-S-M. The bonding through one of the disulphide sulphur atoms is also indicated by red shift of νS-S bond of ligand[18] (500 cm^{-1}) by 25 cm^{-1} on coordination.

The absorption associated with anions in these complexes are identified at 1085 cm^{-1} and 620 cm^{-1} for perchlorate [19], 1104 and 610 cm^{-1} for

Table 2: Electronic Spectral bands (in cm^{-1}) and their Assignments

Complexes	Electronic Bands (cm^{-1})	Assignments
$[Co(ac)_2(DST)_2]$	27030	C T Band
	16670	$2A_1g \rightarrow 2B_1g$
	14285	$2A_1g \rightarrow 2Eg$
$[Co(H_2O)_2(DST)_2](NO_3)_2$	26670	C T Band
	16665	$2A_1g \rightarrow 2B_1g$
	14705	$2A_1g \rightarrow 2Eg$
$[Co(H_2O)_2(DST)_2]SO_4$	26680	C T Band
	16670	$2A_1g \rightarrow 2B_1g$
	14690	$2A_1g \rightarrow 2Eg$
$[Co(H_2O)_2(DST)_2](ClO_4)_2$	26770	C T Band
	16670	$2A_1g \rightarrow 2B_1g$
	14660	$2A_1g \rightarrow 2Eg$
$[Ni(H_2O)_4(DST)_2](NO_3)_2$	31260	C T Band
	21276	$3A_2g(F) \rightarrow 3T_1g(P)$ (ν_3)
	{16666 14492 13335}	$3A_2g(F) \rightarrow 3T_1g(F)$ (ν_2)
	9091	$3A_2g(F) \rightarrow 3T_2g(F)$ (ν_1)
$[Ni(H_2O)_4(DST)_2]SO_4$	34480	C T Band
	23239	$3A_2g(F) \rightarrow 3T_1g(P)$ (ν_3)
	14706	$3A_2g(F) \rightarrow 3T_1g(F)$ (ν_2)
	9095	$3A_2g(F) \rightarrow 3T_2g$ (ν_1)
$[Ni(H_2O)_4(DST)_2](ClO_4)_2$	34480	C T Band
	25000	$3A_2g(F) \rightarrow 3T_1g(F)$ (ν_3)
	{16950 14758 13333}	
	9091	$3A_2g(F) \rightarrow !3T_1g(F)$ (ν_2)
	$3A_2g$ (F)$\rightarrow 3T_2g(F)$ (ν_1)	
$[NiCl_2(H_2O)_2(DST)_2]$	3127029415	C T Band$3A_2g(F) \rightarrow 3T_1g(P)$ (ν_3)
	{16666 142851 3333}	$3A_2g(F) \rightarrow 3T_1g(F)$ (ν_2)
	9095	$3A_2g(F) \rightarrow 3T_2g(F)$ (ν_1)

sulphate[20] and 1360 and 810 cm^{-1} for nitrate[21] and all these correspond to their uncoordinated nature. However, in the acetato complexes (COO) and (COO) stretching vibrations occurs at 1560 and 1440 cm^{-1}respectively. The separation ($\Delta\nu$ - 120 cm^{-1}) of these two bands is diagnostic of unidentate carboxylate coordination [22] of acetato group through its C-O^{-} moiety.

Far IR spectra of complexes contains new bands at 380 and 385 cm^{-1} assigned to νNi – S [23] and one cobalt-sulphur stretching mode [24] at 360 cm^{-1} indicates two bulky heterocyclic disulphide ligands are at trans position in square planar structure probably due to steric repulsion.

Thus, on the basis of aforesaid observations square planar configuration for Co(II) and octahedral structure for Ni(II) complexes is tentatively assigned.

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