Asian Journal of Chemistry Vol. 6, No. 3 (1994), 468–471

Mixed Ligand Complexes of Bivalent Metal Ions with 4-Amino-5 Mercapto-3-Methyl-1, 2, 4-Triazole and gycine/Alanine

R.R. JHA*, D.K. SIRCAR, SADANAND and USHA JHA
Department of Chemistry, Co-operative College,
Jamshedpur-831 001, India

Mixed ligand complexes of the type [MLL′$(H_2O)_2$] where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, VO^{2+} and Zn^{2+} (HL = 4-amino-5-mercapto-3-methyl-1, 2, 4-triazole (HAMMT). L′ = glycine or alanine have been isolated from aqueous medium. The spectral data suggested coordination of the ligand through amino nitrogen and deprotonated thiol sulphur and the amino acids through nitrogen and oxygen. Octahedral geometry around the metal ions has been proposed from electronic spectral data, magnetic properties and thermal studies of the complexes.

INTRODUCTION

The role of mixed ligand complexes in biological process has been well documented[1, 2]. We report here the synthesis and characterisation of few mixed-ligand complexes of some bivalent metal ions and 4-amino-5-mercapto-3-methyl-1, 2, 4, triazole as primary ligand and glycine/alanine as secondary ligands.

EXPERIMENTAL

The ligand 4-amino-5-mercapto-3-methyl-1, 2, 4-triazole (HAMMT) was prepared by reported method[3, 4].

Synthesis of the complexes

A hot aqueous solution of the primary ligand (HAMMT) (1 mmol) was added to an aqueous solution of the metal acetate (1mmol) with constant stirring. The resulting mixture was treated with secondary ligand (1mmole) dropwise. After the addition the resulting solution was concentrated on a steam bath to half of its bulk when coloured preciptate appeared out slowly. The precipitate was filtered, washed several times with water and finally with ethanol and dried over fused calcium chloride.

RESULTS AND DISCUSSION

The analytical data (Table 1) of the complexes suggested the general composition of the complexes is [MLL′$(H_2O)_2$]. The complexes are insoluble in water and in comman organic solvents. The molar conductance values reveal the non-electrolytic nature of the complexes.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF THE METAL COMPLEXES

Compound/Colour	M.pt (°C)	% Found (Calc.)		
		M	N	S
$[\mathrm{Mn(AMMT)Gly(H_2O)_2}]$	>250°	18.75	23.89	10.55
Yellow		(18.69)	(23.81)	(10.89)
$[\mathrm{Mn(AMMT)(Ala)(H_2O)_2}]$	>250°	18.23	23.48	10.55
Yellow		(18.14)	(23.41)	(10.59)
$[\mathrm{Co(AMMT)(Gly)H_2O)_2}]$	>250°	19.85	23.89	10.91
Orange Yellow		(19.78)	(23.81)	(10.74)
$[\mathrm{Co(AMMT)(Ala)(H_2O_2}]$	>250°	18.56	23.12	10.31
Orange Yellow		(18.58)	(23.14)	(10.48)
$[\mathrm{Ni(AMMT)(Gly)H_2O)_2}]$	>250°	19.65	23.48	10.23
Green		(19.72)	(23.51)	(10.74)
$[\mathrm{Ni(AMMT)(Ala)(H_2O)_2}]$	>250°	18.51	23.04	10.44
Green		(18.58)	(23.14)	(10.58)
$[\mathrm{Cu(AMMT)(Gly)(H_2O)_2}]$	>250°	21.22	23.08	10.36
Bluish		(21.00)	(23.13)	(10.58)
$[\mathrm{Cu(AMMT)(Ala)(H_2O)_2}]$	>250°	18.65	22.96	10.34
Bluish		(18.75)	(22.98)	(10.38)
$[\mathrm{VO(AMMT)(Gly)(H_2O)_2}]$	>250°	16.57	22.82	10.39
Deep blue		(16.66)	(22.87)	(10.45)
$[\mathrm{VO(AMMT)(Ala)(H_2O_2)}]$	>250°	15.63	21.48	9.95
Deep blue		(15.88)	(21.81)	(9.99)

The primary ligand 4-amino-5-mercapto-3-methyl-1, 2, 4-triazole (HAMMT) in solution may exist either in the thione or thiol tautomeric forms. However, the IR spectra provide ample evidence in favour of the existence of the ligand HAMMT in the thione form at least in the solid state[5].

In the IR spectrum of the ligand (HAMMT), two bands at *ca.* 3250 and 3050 cm^{-1} are observed which can be assigned to νNH_2 and νNH respectively. But a broad band is observed in the spectra of the complexes in the region 3400-3200 cm^{-1} which is centered around *ca.* 3350 cm^{-1}. This band may be due to νOH of coordinated water and νNH_2. Again the broadness of the band possibly due to the overlaping of these bands and also due to the intramolecular hydrogen bonding[6].

The weak band located in the spectrum of the ligand *ca.* 2500 cm^{-1} has been attributed to ν(S-H) vibration. This band is absent in the spectra of the metal complexes establishing the deprotonation and coordination of thiol sulphur of the ligand (HAMMT) to metal ion.

Bands around *ca.* 1570 and 1040 cm^{-1} in the spectrum of the ligand (HAMMT) correspond to $\nu(C=N)$ and $\nu(N-N)$ respectively. These bands remained unaltered in the spectra of the complexes suggesting non-participation of ring nitrogen in coordination. The next structurally important band of the ligand is 745 cm^{-1} which may be assigned to $\nu(C=S)$. This band is found absent in the spectra of the complexes indicating thereby that $C=S$ undergoes thio enolisation. In the presence of a metal the proton is abstracted and the ligand satisfies one valance on the metal ion. This observation is supplimented by the appearance of a new band in the complexes at *ca.* 660 cm^{-1} characteristic of $\nu(\mathrm{C}\overset{-}{\cdots}\mathrm{S})$. Thus the ligand 4-amino-5-mercapto-3-methyl-1, 2, 4-triazole (HAMMT) behaves as an uninegative bidentate ligand.

In the IR spectra of the secondary ligands *i.e.* amino acids complexes of glycine and alanine the band observed *ca.* 1605 cm^{-1} in the spectra of the complexes suggest the unidentate nature of the carboxylate group.

The lower frequency region of the spectra of the complexes furnished vital information regarding the mode of coordination of the ligands. The presence of ν(M-N), ν(M-O) and ν(M-S) bands is evident from (M-N), (M-O) and (M-S) linkages appearing at *ca.* 470, 410 and 440 cm^{-1} respectively[7].

The above IR spectral data logically let us to suggest that the ligand (HAMMT) is coordinated through its nitrogen and sulphur atoms and amino acids through nitrogen and carboxylic oxygen. Coordination of water molecules to metal ion is further confirmed by the thermogravimetric analysis.

Electronic spectra and magnetic properties

In the present study the electronic spectra of copper(II) complexes show a broad asymmertic ligand field-band in the region 14000--17500 cm^{-1} with maxima at *ca.* 1500 cm^{-1}corresponding to $^2E_g \rightarrow {}^2T_{2g}$ transition in a nearly octahedral arrangement around the metal ion. The width and symmetry of the band suggest tetragonal distortion and Jahn-Tellor effect. Another band *ca.* 25,000 cm^{-1} are also noticed in the spectra may be due to charge transition. All the complexes possess normal magnetic moment around 2.00 B.M. at room temperature which is in agreement with the previously reported value for octahedral complexes.

The electronic spectra of Ni(II) complexes show bands around *ca.* 9000 cm^{-1}, 16,500 cm^{-1} and 26,500 cm^{-1} which are due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transition respectively[8] in an octahedral field. The magnetic moment value (2.90 B.M.) also confirm the octahedral stereochemistry around Ni(II) ion. The nephelauxetic ratio (β) calculated for Ni(II) complexes are 0.86 indicating partial covalency in the metal-ligand bond.

The Co(II) complex possesses magnetic monent 4.85 B.M. The electronic spectrum of the complexes show band at *ca.* 15,000 cm^{-1}, 17,500 cm^{-1} and 24,500 cm^{-1}. The band at 15,000 cm^{-1} is attributed to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition. The band at *ca.* 17,500 cm^{-1} can be unambiguously interpretated to arise due to ligand field transition of the octahedral component of the Co(II) complexes and may be assigned to transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ in an approximately octahedral field[9]. The band at *ca.* 24,500 cm^{-1} may be attributed to charge transfer.

The magnetic moment of the Mn(II) complexes are *ca.* 5.92 B.M. Its electronic spectrum show band at *ca.* 18,000 cm^{-1}, 24,5000 cm^{-1} and 2 7,000 cm^{-1} suggesting an octahedral geometry around the central metal ion and may be attributed to transition $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4E_g + {}^4A_{1g}(G)$ and

$^6A_{1g}(S) \rightarrow {}^4E_{2g}(D)$ respectively. This is in accordance with the earlier reported values for Mn(II) ion[10].

The room temperature magnetic moment value of the VO(II) complexes (*ca.* 0.513 B.M.) are abnormally lower then spin-only value (1.73 B.M.) which may be due to the presence of exchange coupled antiferromagnetism. The VO(II) complexes exhibit three band at *ca.* 12,5000 cm^{-1}, 16,000 cm^{-1} and 22,000 cm^{-1} which may be assigned to $e_g \rightarrow b_{2g}$, $e_g \rightarrow a_{1g}$ and $e_g \rightarrow b_{1g}$ transition respectively. The transitions are based on octahedral symmetry with teragonal distortion, the elongation being on Z-axis[11, 12].

Thermal analysis

The thermogram of the metal complexes follow similar pattern. The Mn(II) complexes starts losing water around 175°C with a weight-loss of 12.19% at 190°C corresponding to the loss of two water molecules (12.25% theor) in one step and supported by an endothermic peak in DTA curve. This suggests that the two water molecules are coordinated to the metal ion in a similar chemical environment[13]. The decomposition proceeds slowly about 215°C and the final weight loss becomes 26.08% at about 760°C which corresponds to the formation of metalic oxide [Mn_3O_4] (25.79%). The thermal behaviour corresponds to the stoichiometry suggested for the complexes. The complexes of Co^{2+} Ni^{2+} and Cu^{2+} show the same trend. The thermal stability of the complexes is in the order Ni > Mn > Co > Cu.

REFERENCES

1. G.J. Horsfall, Principles of Fungicidal Action, Chronica Botanica Co., Wallhan, (1956).
2. D.P. Meller and L. Maley, *Nature (London)*, **161**, 486 (1948).
3. L.F. Audrieth, E.S. Scott and P.S. Kipper, *J. Org. Chem.*, **19**, 733 (1954).
4. K.S. Dhaka, Jagmohan, V.K. Chadha and H.K. Pujari, *Indian J. Chem.*, **12**, 288 (1974).
5. R.V. Gadag and M.R. Gajendragad., *Indian J. Chem.* **16A,** 703 (1978).
6. C.N.R. Rao, Chemical Applications of Inferared Spectroscopy, Academic Press, New York (1963).
7. K.C. Satpathy, R. Mishra and B.B. Jal, *Indian J. Chem.*, **22A**, 340 (1983).
8. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elevier Publishing Co., Amsterdam (1968).
9. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 12 (1954).
10. V. Banerjee and A.K. Day, *J. Indian Chem. Soc.*, **59**, 991, (1982).
11. V.V. Zelentov, *Russ. J. Chem.*, **7**, 680 (1967).
12. M.S. Patil, H.C. Deeve and M.M. Kulkarni, *J. Indian Chem. Soc.*, **60**, 817 (1983).
13. B. Singh, P.L. Maurya, B.V. Agarwal and A.K. Dey, *J. Indian Chem. Soc.*, **59**, 29 (1982).

(*Received:* 8 September 1992, *Accepted:* 30 August 1993) AJC–678.