Transition Metal Complexes of 6-Methyl-2-Amino Benzothiazole—Part III

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Abstract. Complexes of the type ML_2X_2 and ML_4X_2 (where M = *Cu*(II), *Ni*(II), *Co*(II), *Mn*(II), *Zn*(II), *Hg*(II) and *Cd*(II); L=6-methyl-2-aminobenzothiazole; X= —I, —*NCS* and —*OAC*) have been isolated and characterised on the basis of analytical, magnetic moment, molar conductance, electronic and i.r. spectral data. The antifungal screening of *Cu*(II) and *Hg*(II) complexes is also reported.

1. Introduction

A survey of literature reveals that substituted benzothiazoles have analytical[1–2] and biological[3–5] importance. It was, therefore, thought worthwhile to investigate the metal complexes of 6-methly-2-aminobenzothiazole.

The activities of many enzymes depend upon the interaction of thiozole group with a transition metal ion[6]. It was, therefore, interesting to know the coordinating behaviour of the ligand containing these groups. It had been found that the substituents in 2, 4, 5 and 6 positions modify the stoichiometries and stereochemistries of the complexes formed[6]. The i.r. data show that the coordination in these complexes is through NH_2 of the thiozole group.

The *Cu*(II) and *Hg*(II) complexes were screened for antifungal activity on *Aspergillus niger*, *Alternaria alternata*, *Curvularia plunata* and *Penicillium fumculorus* by the Potato dextrose agar method at two dilutions.

2. Experimental

All the chemicals used in this study were of BDH make. 6-Methyl-2-aminobenzothiazole was prepared by the method of Hugershoff[7].

Preparation of ML_2X_2 and ML_4X_2 type of complexes

The above referred complexes were prepared by mixing together hot ethanolic solution of metal iodide, thiocyanate, acetate and 6-methyl-2-aminobenzothiazole in 1:2 and 1 : 4 (metal : ligand) molar ratio except cadmium and mercury complexes which were prepared by mixing the solution in acetone of cadmium or mercuric iodide and the ligand. The reaction mixtures were refluxed for 3 to 4 hours. The solutions were evaporated to dryness. The resulting coloured solids were washed with distilled water and 10 per cent alcohol and dried in vacuo over anhydrous calcium chloride.

Physical Measurements

Molar conductance of the complexes in methanol, chloroform and acetone (M/1000) was measured in WTW conductivity meter. Magnetic susceptibility measurements were carried out at room temperature on Cahn-Faraday (model-7550) electrobalance using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections were applied by a method outlined by Figgis and Lewis[8]. The values of electromagnetic moments (μ_{eff}) and molar conductance of the complexes are included in Table 1.

Table 1. Analytical Data and General Behaviour of the Complexes

Complexes	M.P. (°C)	Analysis						Molar conductance at 10^{-3}M ($\mho cm^2$)	μ_{eff} (B.M.)	Stereo-chemistry
		M.		N.		S.				
		Found	Calcd.	Found	Calcd.	Found	Calcd.			
CuL_2I_2	137	9.83	9.85	8.87	8.67	9.77	9.92	0.05	1.84	$D_{4}h$
NiL_2I_2	60	9.36	9.16	8.91	8.74	9.72	9.92	20.92	dia.	,,
CoL_2I_2	97	9.49	9.19	8.92	8.73	9.82	9.98	0.00	4.44	Td
$CoL_2(NCS)_2$	60	11.99	11.72	16.72	16.70	25.75	25.45	0.00	4.40	,,
MnL_2I_2	108	8.82	8.62	8.52	8.79	10.45	10.05	0.03	5.90	,,
ZnL_2I_2	151	10.40	10.10	8.51	8.65	9.90	9.88	0.01	dia.	,,
CdL_2I_2	125	16.42	16.12	8.29	8.06	9.48	9.21	7.37	,,	,,
CuL_4I_2	99	6.79	6.66	11.96	11.75	13.67	13.42	0.09	1.92	Oh
NiL_4I_2	60	6.09	6.05	11.69	11.56	13.56	13.21	18.26	3.20	,,
CoL_4I_2	143	7.60	6.08	11.59	11.56	13.42	13.20	0·00	4.70	,,
$CoL_4(OAC)_2$	69	7.27	7.08	13.76	13.45	15.46	15.36	0.00	4.58	,,
MnL_4I_2	85	5.89	5.69	11.31	11.61	13.56	13.26	0.04	6.10	,,
ZnL_4I_2	113	6.41	6.10	11.59	11.48	13.32	13.12	0.01	dia.	,,
CdL_4I_2	110	10.92	10.99	10.89	10.95	12.99	12.52	6.39	,,	,,
HgL_4I_2	87	18.96	18.86	10.81	10.08	11.59	11.52	0.00		,,

Electronic spectra were recorded on Cary-14 and VSU-2Ph spectrophotometers. The i.r spectra were obtained in the 4000-200 cm^{-1} range in *KBr* and Nujol Mulls on Perkin-Elmer spectrophotometer (model-621 and 720). The spectral data are given in Table 2.

Table 2 Ligand Field Parameters of the Complexes

Complexes	10Dq (cm^{-1})	B′ (cm^{-1})	β	β° (%)	ν_2/ν_1	λ′ (cm^{-1})	ζ3d (cm^{-1})	LFSE (K.J./mole
CuL_2I_2	17123	—		—	—	—494.8	494.8	122.8
CoL_2I_2	3440	703.09	0.72	27.52	1.55	—119.6	358.8	49.35
$CoL_2(NCS)_2$	3483.1	704.60	0.71	27.36	1.55	—116.7	350.1	49.97
CuL_4I_2	14451	—	—	—	—	—793.6	793.6	103.65
NiL_4I_2	8211	1154.6	1.12	12.10	1.87	—355.4	710.8	117.80
CoL_4I_2	10413.95	968.13	0.99	0.41	1.90	—		99.59
$CoL_4(OAC)_2$	10472.95	1034.73	1.07	6.67	1.89	—		100.16

3. Results and Discussion

The complexes are soluble in methanol, dioxan and acetone. The low molar conductivities of 10^{-3}M solutions demonstrate that the complexes are non-electrolytes[9].

Magnetic Moments

The magnetic moments (Table 1) are all normal and indicate that CuL_2I_2 and NiL_2I_2 are square planar. The magnetic moments of CoL_2I_2 and $CoL_2(NCS)_2$ (4.44 and 4.40 B.M.) in the range 4.4 to 4.8 B.M., normally observed for the tetrahedral *Co*(II) complexes[10] confirm tetrahedral geometries. The complexes of *Cu*(II), *Ni*(II), *Co*(II), *Zn*(II), *Cd*(II) and *Hg*(II) in 1 : 4 molar ratio show octahedral geometry. The diamagnetic ZnL_2I_2 and CdL_2I_2 show sp3 type of hybridization.

Electronic Spectra

Ni(II) complexes : The intraligand bands occur in the Nujol spectra of NiL_2I_2 and NiL_4I_2 in the regions 19942-46468 cm^{-1} and 15342-26611 cm^{-1} respectively. The spectrum of NiL_2I_2 assumes D_4h symmetry[11]. The bands can be assigned to the transitions 15949 $^1A_{1g} \rightarrow {}^1A_{2g}(\nu_1)$, 19942 $^1A_{1g} \rightarrow {}^1E_g(\nu_2)$, 23469 $^1A_{1g} \rightarrow {}^1B_{1g}(\nu_3)$.

The electronic spectrum of NiL_4I_2 is in accordance with the octahedral *Ni*(II) environment[12] with the ligand field; $\nu_1 = 8211$, $\nu_2 = 15342$, $\nu_3 = 26611$ cm^{-1} which can be assigned to $^3A_{2g}(F)$, $\rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$, $^3T_{1g}(P)$ transitions.

Co(II) Complexes : CoL_2I_2 and $CoL_2(NCS)_2$ may be proposed to have tetrahedral structures[13] as the electronic spectra of the complexes resemble those of *Co*(2-aminothiazole)$_2I_2$ and *Co*(2-bromo thiazole)$_2Cl_2$. The complexes show absorptions at 15523, 15610 $cm^{-1}(\nu_3)$ and 5343, 5410 $cm^{-1}(\nu_2)$ attributed to the transitions $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$ and are characteristics of *Co*(II) ion in the tetrahedral environment having C_2v symmetry.

Using the values of ν_2 and ν_3, 10Dq and B′ were calculated by the equation for *Co*(II) *T.J.* given by Drago[14]. Two bands, observed at 7946 and 20000 cm^{-1} in CoL_4I_2 and at 8002 and 21052 cm^{-1} in $CoL_4(OAC)_2$, are typical of Co(II) complexes in octahedral[15] environment and may be assigned to the transitions $4_{T_{1g}}(F) \rightarrow 4_{T_{2g}}(F)(\nu_1)$ and $4_{T_{1g}}$ (P) (ν_3) respectively.

Cu(II) *complexes*: CuL_2I_2 yields one broad band at 17123 cm^{-1} which is supposed to be a composite envelope of three transitions[16] $2_{B_{1g}} \rightarrow 2_{A_{1g}}, 2_{B_{2g}}, 2_{E_{1g}}$.

14451 cm^{-1} band in the spectrum of CuL_4I_2 may be due to $2_{T_g} \rightarrow 2_{T_{2g}}$ transition[12]. The ratio $\nu Cu/\nu Ni$ comes out to be 1.76 indicating considerable distortion[17] in the octahedral geometry of the complexes.

The electronic spectra of Mn(II) complexes in Nujol do not show any d-d transition bands in the visible region.

Using the above assignments, the values of 10Dq, Racah Parameter (B'), Nephelauxetic ratio (β), percentage lowering of the energy of 3*p* state in the complexes compared to the energy of 3*p* in the free gaseous ion(β°), ligand field stabilization energy (LFSE), spin-orbit coupling constant(λ') and spin-orbit coupling constant per electron (ζ3d) have also been calculated by the method of Lever[18].

The i.r spectrum of the ligand shows $\nu as(NH)$, $\nu s(NH)$[19], $\nu(C = N)$, $\delta(NH)$, $\rho r(NH_2)$, $\rho w(NH_2)$ and $\nu(C - S - C)$ at 3425, 3315, 1550, 1650, 1120, 760 and 815cm^{-1} respectively[20]. The complexes show considerable change in $\nu as(NH)$, (3300-3410-cm^{-1}), $\nu s(NH)$ (3200-3310 cm^{-1}), δNH (1615-1640 cm^{-1}) $\rho r(NH_2)$ (1100-1115 cm^{-1}) and $\rho w(NH_2)$ (715–725 cm^{-1}) indicating the coordination through NH_2 group. The $\nu(C\text{–}S\text{–}C)$ and $\nu C = N$ remain unchanged showing the absence of coordination through cyclic sulpher and $C = N$ groups.

Using i.r. spectra of the metal complexes containing coordinated thiocyanate groups, certain correlations between νCN and νCS modes and the type of thiocyanate bonding, have been made[21–23]. For *M–NCS* bonding, νCN and νCS appear to fall in the range 2080-2040 cm^{-1} and 860-780 cm^{-1} respectively. The corresponding ranges for *M–SCN* bonding are 2120-2080 cm^{-1} and 720-680 cm^{-1}. For bridging thiocyanate groups *M–SCN–M*, νCN fall in a broader and generally in higher range than *M–NCS* while νCS usually occurs at intermediate frequencies. In the ionic thiocyanate, νCN occurs at 1963 cm^{-1} and νCS at 963 cm^{-1}. Moreover, the mode of thiocyanate bonding may also be characterised by examining the doubly degenerate δNCS frequency[24].

In the i.r. spectrum of $CoL_2(NCS)_2$, the νCN occurs at 2075 cm^{-1} indicative of $M-NCS$ bonding[22].

$CoL_4(OAC)_2$ shows additional bands at 1570 and 1395 cm^{-1} which are assignable to $\nu as\left(C\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right)$ and $\nu s\left(C\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right)$ vibrations[22].

The CuL_2I_2, CuL_4I_2, HgL_2I_2 and HgL_4I_2 were screened for anti fungal activity on *Aspergillus niger, Alternaria alternata, Curvularia plunata* and *Penicillium fumculorus* by employing *Potato dextrose agar method* at two dilutions (1:2143 and 1:5000).

The results indicate that the activity of Cu(II) and Hg(II) complexes against *Alternaria alternata* is of very high order (100%) whereas that of *Aspergillus niger* is only 91 per cent. CuL_4I_2 inhibits 100 per cent spore germination of *Penicillium fumculorus* and 85 per cent of *Culvularia Plunta.*

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References

1. Kawa, K. Y. & Shinra, K., *J. Chem. Soc.*, **75** (1954) .
2. Tyozo Uno, Terada, K. & Bunseki Kagaku., *Akihama Sumiyaki*, **10** (1961), 1117.
3. Edelson, E. & Haskim, A. H., *Dermatol and Syphilal*, **66** (1952), 244.
4. Rabit, H. G., *J. Am. Med. Assoc.*, **148** (1952), 1005.
5. Christison, I, B. *et al.* "Therapy of Fungus Diseases" (Little Brown & Co, Boston, Mass), 1955, p. 268.
6. Campbell, M. J. M. & Card, D. W., *J. Chem. Soc.* (A) (1970), 672.
7. Hughershoff, A., *Ber.*, **36** (1903), 3134.
8. Figgis, B. N. & Lewis, J., "In Modern Coordination Chemistry" (Ed. J. Lewis and R. G. Wilkings, Interscience, N. Y.), (1960), 403.
9 Geary, W. J., *Coord. Chem. Rev.*, (1964), 3119.
10. Duff, E. J., Hughes, M. N., & Rutt, K. J., *J. Chem. Soc.*, (A) (1968), 2499.
11. Goodgame, M. L. & Goodgame, M., *J. Chem.Soc.*, (1963), 207.
12. Lever, A. P. B., "Inorganic Electronic Spectroscopy" (Elsevier, Amsterdam), 1968.
13· Duff, E. J., Hughes, M. N. & Rutt, K. J., *J. Inorg. Chim. Acta*, **6** (1972), 408.
14. Drago, R. S., "Physical Methods in Inorganic Chemistry" (An East-West Edition) p, 411.
15. Mathews, R. W. & Walton, R. A., *Inorg Chem.*, **10** (1971), 1433.
16. Sacconi, L. & Ciampolini, M., *J. Chem. Soc.*, (1964), 276.
17. Agrawal, R. C. & Rao, T. R., *Transition Metal Chemistry*, **2** (1977), 21.
18. Lever, A. P. B., *J. Chem. Educ.*, **45** (1968), 711.
19. Ahuja, I. S. and Singh, R., *J. Inorg. Nucl. Chem.* **35** (1973), 302.
20. Mishra, R. P., Mahapatra, B. B. & Guru, S., *J. Indian. Chem. Soc.*, **56** (1979), 832.
21. Burmeister, J. L., *Co-ord. Chem. Rev.*, **1** (1966), 205; **3** (1968), 225.
22. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds" (John Wiley, N. Y.), 1970.
23. Ahuja, I. S. and Garg, A., *J. Inorg Nucl. Chem.*, **34** (1972), 1929.
24. Mishra, B. & Rao, D. V., *J. Indian Chem. Soc.*, **51** (1979), 439.