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Spectral and Magnetic Studies of Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Silver(I) Complexes with 4-(2-Thiazolyl) Thiosemicarbazide

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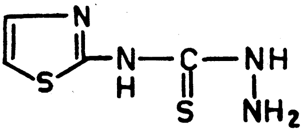
Paramagnetic cobalt(II), nickel(II), copper(II) and diamagnetic zinc(II) and Ag(I) complexes of 4-(2-thiazolyl) thiosemicarbazide (L) of the compositions $MLCl_2$ [M = Co(II), Ni(II) and Cu(II)], ZnL_2Cl_2 and $AgLNO_3$ have been prepared and characterized by spectral (ir, ^{14}N nmr and esr for $CuLCl_2$ only) and magnetic studies as well as by elemental analyses. All of the complexes except Ag(I) have octahedral coordination whereas Ag(I) has tetrahedral arrangement of ligand around it.

INTRODUCTION

Many enzymatic activities of thiazoles are dependent upon their metal ion[1–3], besides their being good coordinating ligands because of the presence of potential exocyclic and endocyclic coordinating sites in them. In this connection Craig *et al.*[4] in their recent report have also pointed out significant influence on the properties of metal chelates which the substituents on the thiazole ring have. It has therefore been thought that it would be worthwhile to investigate the coordinating behaviour of analogous thiazole (L) towards the biologically active trace metal ions as a follow-up to our recent spectral studies on similar ligand framework.[5]



(L)

Fig. 1

EXPERIMENTAL

All the reagents used were of chemically pure grade. The ligand was synthesized by the method reported earlier[6]. The complexes were prepared by adding 10 ml of an ethanolic solution of respective metal chlorides (*ca.* 1 mmole) to that of ligand (*ca.* 1.1 mmol) in about 10 cm^3

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ethanol and by digesting the resulting solution on a water bath for 10–15 minutes, followed by cooling in ice bath at 10°C for half an hour. The crystalline material thus formed was separated by filtration and washed successively by 5 cm^3 water, EtOH (5 cm^3) and dried in open air. Elemental analyses for C, H, N, S, Cl and other physico-chemical measurements (IR electronic, ^{1}H, ^{14}N, epr, magnetic and molar conductance were carried out as described earlier[7,8]. The diamagnetic corrections by the use of Pascal's constants[9]. Metals were estimated by the literature procedures[10]. The empirical formulations of the complexes and the results of other physicochemical methods are given in Table 1. Obviously the nonconducting behaviour of the solutions of the complexes in DMF suggests their nonionic nature.

TABLE 1

PHYSICAL DATA OF METAL COMPLEXES

Complexes (Colour)	M.pt. (°C)	C(%)	H(%)	N(%)	S(%)	Cl (%)	Metal (%)	Molar conductance ohm^{-1} cm^2/ mole (DMSO)	Magnetic moment μ_{eff} (B.M.)
Cu(L)Cl$_2$ (Dark green)	>350	16.2 (15.5)	1.34 (1.94)	17.9 (18.1)	21.1 (20.7)	23.2 (23.0)	20.1 (20.6)	0.57	1.8
Ni(L)Ci$_2$ (Yellowish green)	>350	16.3 (15.8)	2.1 (1.9)	18.5 (18.4)	21.4 (21.1)	22.9 (23.4)	20.2 (19.3)	1.01	3.4
Zn(L$_2$)Cl$_2$ (White)	240 (decomposed)	20.2 (19.8)	1.1 (1.2)	22.8 (23.1)	13.8 (13.2)	13.9 (14.6)	13.6 (13.4)	3.73	diamag.
Co(L)Cl$_2$ (Pink)	>300	16.2 (15.8)	2.2 (1.9)	18.9 (18.4)	21.4 (21.1)	23.1 (23.3)	19.7 (19.4)	1.47	4.8
Ag(L)NO$_3$ (Black)	170 (decomposed)	14.1 (13.9)	1.3 (1.7)	15.8 (16.2)	18.9 (18.6)	—	30.9 (31.3)	2.03	diamag.

RESULTS AND DISCUSSION

In order to identify the mode of binding in the complexes, IR spectra of the ligand and the complexes were compared. Bands due to ν(NH) and ν(NH$_2$) in the ligand spectrum were observed at 3140 and *ca.* 3280 cm^{-1} respectively and the 3280 cm^{-1} band showed a negative shift by 20–30 cm^{-1} in the spectra of all metal complexes, ν_{asym} (C=N) of the ligand observed at *ca.* 1630 cm^{-1} also shifted towards lower region in the metal complexes except in Zn(II) and Ag(I) complexes, where it remained constant. In Co(II), Ni(II) and Cu(II) complexes, δ(N—H) band of the ligand overlaps with the ν(C=C) of thiazole ring observed at *ca.* 1560 cm^{-1}. The slightly broad band at *ca.* 1105 cm^{-1}, the ligand has been assigned to thiomide band (II) having major contribution from ν(C=N). In the spectra of the complexes the band showed an upward shift by about 20 cm^{-1} due to the electronic shift as shown in Fig. 2. This electronic shift further causes to move ligand peak at *ca.* 680 cm^{-1} due to ν(C—S) of thiazole ring towards higher region and overlaps with the ligand peak at *ca.* 720 cm^{-1}. In addition to these observations, the medium peaks of ligand lying between 1080–1060 and at *ca.* 840 cm^{-1} due to mixed vibrations of $(\mathrm{NH{-}\overset{\overset{S}{\|}}{C}{-}NH{-}})$ group and ν(C=S) (thiomide bands III and IV) showed negative shift by 100 and 70 cm^{-1} respectively. This suggested coordination of C=S group of exocyclic part of thiazole ring. In lower region of i.r. spectra of the complexes, weak bands observed at *ca.* 400, *ca.* 370 and *ca.* 320 cm^{-1} could be assigned as ν(M—N=C—), ν(M—NH_2) and ν(M—S=C—) respectively.

In addition to these peaks, IR spectra of Ag(I) complex showed peaks at 1470 and 1300 cm^{-1} due to bidentate coordinated nitrate group[13] which is also supported by the presence of two ν(M—O) bands observed at *ca.* 390 and *ca.* 380 cm^{-1} [13]. Thus decrease towards lower wavenumber in δ(NH), ν(NH_2) and ν(C=S) band position increase in the ν(C=N) and ν(C—S) thiazole ring band positions are in keeping with the following bonding scheme in Co(II), Ni(II) and Cu(II) complexes constancy in the thiomide band positions observed for Zn(II) complex made it to behave as bidentate ligand.

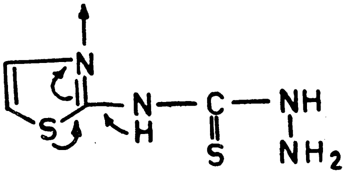

Fig. 2

Electronic spectra of ligand and metal complexes showed intraligand bands lying in the region of 29,800–30,700 cm^{-1}, in addition to charge transfer bands observed between 23,000–22,000 cm^{-1} in metal complexes only. Ligand field bands for Co(II), Ni(II) and Cu(II) complexes were also observed at 8,900, 17,300; 8,700, 16,700 and 15400 cm^{-1} respectively and were found to lie in the range of high spin octahedral/distorted octahedral complexes[9]. Ligand field parameters for these complexes were calculated using the literature procedure[9] and their respective values were found to be 10 Dq = 10405, 8695 and 15400 cm^{-1} as well as B′ = 1083.9 and 887.2 cm^{-1} (for Co(II) and Ni(II) complexes) showing 96% and 85% reduction of β values in comparison to their free ion B values.

^{14}N nmr spectra of ligand and complexes were recorded in DMSO using 5 mm tubes and chemical shifts are referenced to pure NH_4NO_3 at −356.62 ppm.

Nmr signals are quite broad, and ligand showed signal at −235.6 ppm whereas its Cu(II), Ni(II), Co(II) and Ag(I) complexes showed broad signals lying between −(253.6–380.5), −(225.2–437.4), −(489.9–575.2) and − (546.7–634.2) ppm respectively. This shift in higher region showed coordination of nitrogen atom with the metal but due to broadening of the peaks, it is difficult to assign specifically whether nitrogen of C=N, NH_2 or NH groups are involved in coordination. But this observation combined with IR and ESR (Cu(II) complex only) could certainly identify the mode of nitrogen coordination.

ESR spectrum of Cu(II) complex in DMSO was studied and g_{11}, g_1 and g_{iso} were calculated to be 2.1176, 2.0287 and 2.0583 respectively indicating that $g_{11} > g_1$. Thus a possible orthorhombic geometry could be assigned to this complex[11]. Copper hyperfine splitting is very clear but nitrogen hyperfine splitting is not seen as yet in parallel region whereas in perpendicular region one could easily see seven small peaks. Thus it shows probably two nitrogen atoms around Cu(II) ion in the complex.

Magnetic moments for Co(II) and Ni(II) complexes were found to be 4.8 B.M. and 3.4 B.M. respectively and for Cu(II) complex, it was found to be 1.8 B.M. which is in the normal range[10].

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