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Some Complexes of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) with Disubstituted Thiourea

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Some new mononuclear and heterodinuclear complexes of the type ML_2 and $[ZnL_2{\cdot}M'L_2]$ [where M = Co(II), Ni(II), Cu(II) and Zn(II); M′ = Co(II), Ni(II) and Cu(II) and HL = N-(2-thiophenol) N-phenylthiourea (MPT) and N-(2-thiophenol)-N-ethylthiourea (MET)] have been synthesized. Their tentative structures have been assigned on the bases of elemental analysis, molar conductance measurements, room temperature magnetic measurements, infrared and electronic spectral data. The ligands act as monobasic bidentates giving tetracoordinated species.

INTRODUCTION

Substituted thiourea and its mononuclear complexes with transition and non-transition metals have been studied extensively[1–3]. Homo, di- and polynuclear complexes of thiourea and substituted thiorea are also known. The latter type are mostly formed through chloride bridging[4, 5] and sometimes through bridging of chloride and thioketone (C═S) moiety[6]. In addition to their interesting ligational properties, disubstituted thioureas are also interesting from various biological points of view[7, 8]. Recently complexes of di-substituted thiourea have been reported as possible antitumour drugs with low toxicity[9, 10]. In view of the importance of such ligands and their complexes, and our interest in studying N,N′-di-substituted thioureas and their complexes with transition and non-transition metals[11–16], the author reports the formation and characterization of mono- and hetero-dinuclear complexes of two N,N′-disubstituted thioureas.

EXPERIMENTAL

IR spectra were recorded on a Unicam SP-2000 spectrophotometer as CsI pellets in the range 4000–200 cm^{-1}. Electronic spectra were recorded on a UV-visible spectrophotometer, model 160 of Shimadzu Kyoto (Japan) (range 200–1100 nm), using DMF as a solvent. Analyses of the compounds were carried out on a CHN analyser, type 1106 (Carlo Erba) and the metal analyses were done using Varian-40 atomic absorption spectrometer. Magnetic susceptibility measurements were made by the Faraday method at room temperature using Bruker BM6 instrument. Conductivity measurements were done for 10^{-3} M solution of the complexes in DMF at 20°C, using conductivity meter, model PCM3 (Jenway).

All the chemicals were of AnalaR grade used as such without further purification. Disubstituted thioureas were prepared by the reaction of 2-aminothiophenol with phenyl (or ethyl) isothiocyanate according to reported prodedure[17].

Preparation of Complexes

The mononuclear complexes of Co(II), Ni(II), Cu(II), and Zn(II) were prepared by refluxing a mixture of the metal chloride (2 mmol) and the disubstituted thiourea (4 mmol) in ethanol (75 cm^3) for *ca.* 2 h. The solution was filtered and reduced in volume to *ca.* 20 cm^3. The resulting precipitate was filtered off, washed with small portions of ethanol, acetone and then with petroleum spirit (40–60°C), and dried in *vacuo* for several hours.

The dinuclear complexes were prepared by the addition of ZnL_2 (1 mmol) dissolved in dichloromethane (15 cm^3) to a solution containing 1 mmol of anhydrous metal chloride in 15 cm^3 of methanol. The resulting mixture was stirred at ambient temperature for *ca.* 16 h. The product solution was filtered, and the filterate was added slowly to 50 cm^3 of 2-methylpentane. The precipitate formed was filtered off and dried in *vacuo* for several hours.

RESULTS AND DISCUSSION

The reaction of the N-(2-thiophenol)-N′-disubstituted thiourea MPT and MET ligands with metal(II) chlorides in a 2 : 1 ligand-to-metal molar ratio gave the neutral metal(II) chelates in which the mononegative anions of MPT and MET behave as monobasic bidentate ligand coordinated to the central metal ion through the deprotonated thiophenol sulphur and the thiocarbonyl sulphur atom. The reaction of the neutral four coordinated complexes, ZnL_2, with anhydrous metal(II) chlorides has resulted in the isolation of dinuclear metal(II) complexes of the type ZnL_2-$M'Cl_2$; the nucleophilicity of the thiolate sulphur atoms in the monomeric complexes is thought to be responsible for this type of adduct formation[18, 19].

The microanalytical data (Table-1) of the ligands and their complexes are in good agreement with the given formulation. Both mono- and dinuclear complexes are air stable but most of the dinuclear complexes decompose without melting above 160°C. The observed molar conductivities (Table-1) in DMF indicate the nonelectrolyte nature of the mono and dinuclear complexes.

Tentative assignments of selected IR bands are listed in Table-2. For the mononuclear complexes, ML_2, the weak band at 2550 cm^{-1} observed in the ligands assignable to ν(S—H)[20] disappeared in the complexes showing the coordination of ligands through deprotonated thiophenol. In all the mononuclear complexes studied there is a lowering by *ca.* 20 cm^{-1} of the ligand band at *ca.* 1350 cm^{-1} and much lowering of the band at *ca.* 770 cm^{-1}. As these two bands are assigned mainly to (C═S) vibrational modes, it is concluded therefore that chelation of the ligands has taken place through thiocarbonyl sulphur atom[13, 14, 21].

The formation of dinuclear complexes from the monomeric ZnL_2 complexes results in large shift of phenolic (C—S) to higher region (30–35 cm^{-1}) indicating that thiophenolic sulphur becomes tricoordinated[19]. The observed new bands located at *ca.* 350–260 cm^{-1} (Table-2) assigned to both M—S and M—Cl,[22] is another evidence for the bridging dinuclear structure of the adducts (Fig. 1).

TABLE-1
PHYSICAL AND ANALYTICAL DATA FOR THE LIGANDS AND THEIR COMPLEXES

Compounds (Colour)	% Analysis : Found (calcd)					Λ (cm^2 mole^{-1})
	C	H	N	M	M′	
MPT	59.71	4.59	10.74			
(Pale yellow)	(60.00)	(4.61)	(10.77)			
MET	50.71	5.62	13.06			
(Pale yellow)	(50.94)	(5.66)	(13.20)			
Co(MPT)$_2$	53.62	3.76	9.59	10.09		12.3
(Brown)	(53.66)	(3.81)	(9.70)	(10.21)		
Co(MET)$_2$	44.66	4.51	10.96	12.10		13.7
(Brown)	(44.91)	(4.57)	(11.64)	(12.25)		
Ni(MPT)$_2$	53.10	3.82	9.70	10.01		10.5
(Bright red)	(53.90)	(3.80)	(9.67)	(10.17)		
Ni(MET)$_2$	52.97	3.68	9.49	11.98		8.9
(Bright red)	(53.29)	(3.76)	(9.49)	(12.21)		
Cu(MPT)$_2$	53.20	3.69	9.58	10.40		10.1
(Greenish brown)	(53.65)	(3.78)	(9.58)	(10.92)		
Cu(MET)$_2$	44.30	2.19	11.58	13.06		8.2
(Brown)	(44.49)	(2.26)	(11.53)	(13.08)		
Zn(MPT)$_2$	48.90	3.43	8.80	10.99		9.7
(Pale yellow)	(49.22)	(3.48)	(8.85)	(10.99)		
Zn(MET)$_2$	44.64	4.52	11.61	12.98		7.6
(Pale yellow)	(44.72)	(4.56)	(11.60)	(13.42)		
Zn(MPT)$_2$·CoCl$_2$	43.68	2.98	7.79	8.90	7.94	18.2
(Bluish green)	(43.74)	(3.08)	(7.84)	(9.16)	(8.25)	
Zn(MET)$_2$·CoCl$_2$	34.83	3.49	9.00	10.40	9.40	16.8
(Bluish green)	(34.99)	(3.56)	(9.06)	(10.58)	(9.53)	
Zn(MPT)$_2$·NiCl$_2$	43.68	3.03	7.78	9.00	7.96	14.7
(Red)	(43.75)	(3.08)	(7.85)	(9.16)	(8.22)	
Zn(MET)$_2$·NiCl$_2$	43.84	3.52	9.05	10.32	9.34	17.8
(Red)	(45.01)	(3.56)	(9.07)	(10.32)	(9.50)	
Zn(MPT)$_2$·CuCl$_2$	43.50	3.02	7.72	8.89	8.52	20.1
(Brown)	(43.43)	(3.06)	(7.79)	(9.10)	(8.84)	
Zn(MET)$_2$·CuCl$_2$	34.69	3.48	8.90	10.43	10.01	18.3
(Brown)	(34.74)	(3.53)	(8.99)	(10.43)	(10.20)	

Complexes of Zn(II) are diamagnetic and do not display d-d absorption band in their electronic spectra; it is therefore expected that magnetic moment values and electronic spectral activities observed in the dinuclear complexes, [ZnL$_2$-M′Cl$_2$] are essentially those of the M$'_2$Cl$_2$ portion.

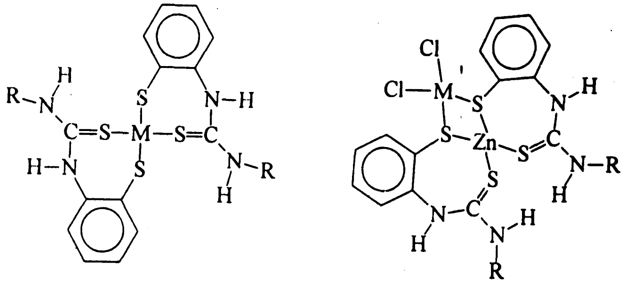

Fig. 1. Proposed structures for the mono-and dinuclear complexes

TABLE-2
INFRARED SPECTRAL BANDS (cm^{-1}), ELECTRONIC SPECTRAL AND MAGNETIC MOMENTS (B.M.)

Compounds	ν(C=S)	ν(C—S)	ν(M—S) and ν(M—Cl)	Electronic spectra (cm^{-1})	μ_{eff}
MPT	1300, 770	670			
MET	1305. 772	675			
$Co(MPT)_2$	1275, 705	645	330, 335	10150, 15280, 25800, 27000	2.62
$Co(MET)_2$	1278, 710	648	332, 335	10210, 15300, 26300, 28500	2.54
$Ni(MPT)_2$	1280, 695	650	328, 330	16200, 22020, 27000, 28500	Dia.
$Ni(MET)_2$	1275, 705	658	330, 337	16190, 22000, 26800, 30000	Dia.
$Cu(MPT)_2$	1278, 698	655	320, 325	18220(br), 24050, 27050,	1.94
$Cu(MET)_2$	1278, 695	658	318, 327	18200(br), 26000, 28500	2.00
$Zn(MPT)_2$	1275, 705	655	305, 312		
$Zn(MET)_2$	1275, 690	660	298, 307		
$Zn(MPT)_2{\cdot}CoCl_2$	1280, 708	685	290, 310 340, 348	14680, 15620, 16340, 27800, 30000	4.46
$Zn(MET)_2{\cdot}CoCl_2$	1278, 698	693	292, 312 340, 345	14720, 15870, 16390, 26400, 28500	4.42
$Zn(MPT)_2{\cdot}NiCl_2$	1278, 710	689	260, 308 330, 335	16500, 23010, 25020, 30000	0.78
$Zn(MET)_2{\cdot}NiCl_2$	1280, 698	695	265, 308, 338	16450, 22980, 27020, 29000	Dia.
$Zn(MPT)_2{\cdot}CuCl_2$	1278, 708	690	278, 305 320, 328	16050, 18600, 20100, 24900, 27000	1.98
$Zn(MET)_2{\cdot}CuCl_2$	1278, 695	692	270, 308, 325	15980, 18600, 20050, 26000, 29200	2.06

The magnetic moment values of CuL_2 and $[ZnL_2\text{-}CuCl_2]$, complexes (1.94–2.06 B.M.) are within the observed range corresponding to one unpaired electron[23]. Tetrahedral Cu(II) complexes are expected to give single broad band in the near infrared region and no absorption between 20000–10000 cm^{-1} while in the case of square planar geometry the bands are expected in the range 18000–14000 cm^{-1}.[24–26] For CuL_2 complexes the observed band at *ca.* 18200 cm^{-1} may be assigned as combination of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ corresponds to square planar Cu(II)[26]. The two ZnL_2-CuL_2 complexes show bands at *ca.* 16000, 18600 and 20000 cm^{-1}. The positions of these bands are in favour of distorted square planar configuration[19, 26].

The two NiL_2 complexes are diamagnetic, therefore these complexes must have a square planar geometry around Ni(II)[23]; this is further supported by their electronic spectra which exhibit a broad band at *ca.* 22000 cm^{-1} and a shoulder at *ca.* 16200 cm^{-1}. These two bands assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transition respectively, in a square planar field[23, 26]. The $[Zn(MET)_2$-$NiCl_2]$ complex possesses a magnetic moment of 0.78 B.M. As this value is much lower than the spin only value, a planar structure may be proposed for this complex. The magentic moment value of 0.78 B.M. is close to the range observed for some square planar Ni(II) complexes in which the partial paramagnetism (0.94–1.24 B.M.) considered to be caused by spin crossover from singlet to triplet state[27]. The electronic spectra of the two complexes show bands at *ca.* 16500 and 23000 cm^{-1} confirming the square planar structure for Ni(II) complexes and have their usual assignment of $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transition respectively. The electronic spectra of CoL_2 complexes exhibited bands at *ca.* 10200 and 15300 cm^{-1}. The second band was assigned to $^2A_{1g} \rightarrow {}^2E_g$ and the first to $d_{xy} - d_{yz}$ spin allowed transition in a square planar field[26]. This is supported by the magnetic moment values of 2.62 and 2.54 B.M. which are typical of square planar Co(II) complexes[23]. The electronic spectra of the dinuclear ZnL_2-$CoCl_2$ complexes show strong bands in the visible region at (16390–14680) cm^{-1} corresponding to $^4A_2(F) \rightarrow {}^3T_1(P)(\nu_3)$ in a distorted tetrahedral field and are similar to other tetrahedral Cu(II) complexes with $[CoS_2Cl_2]$ ~~chromophores~~[21, 28]. Other d-d transitions (mainly ν_1 and ν_2), normally occurring in the region 7000–3000 cm^{-1}, are beyond the range of the instrument used. The room temperature magnetic moment value of *ca.* 4.4 B.M. is also in favour of tetrahedral Co(II) complexes[23, 28]. Besides the discussed ligand field bands for $M'L_2$ and ZnL_2-$M'Cl_2$ complexes, additional charge transfer transitions were observed (Table-2). These may be due to ligand-to-metal charge transfer from both the sulphur and the chloride atoms to the metal vacant d-orbitals[21, 28].

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