Coordination Chemistry of Benzothiazole Derivatives. 2-Mercaptobenzothiazole and 2-(o-hydroxyphenyl)benzothiazole Complexes with Cu(II), Ni(II) and Co(II)

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The reaction of 2-mercaptobenzothiazole (MBTH) with Cu(II) ions resulted in a yellow diamagnetic Cu(II) complex, while the reaction with Co(II) produced a dimeric tetrahedral complex. The reaction of Ni(II) with MBTH gave a diamagnetic square planar complex. The yellow copper complex formed a blue five coordinate dimeric complex with pyridine. The isolated blue crystals were investigated by electron spin resonances. The reaction of the diamagnetic nickel complex with different bases yielded distorted octahedral dibase adducts. 2-(o-hydroxyphenyl)-benzothiazole gave a brown pseudo tetrahedral complex with Cu(II) and a distorted tetrahedral complex with Ni(II). The reaction with Co(II) produced a high spin five coordinate polymeric type compound. The solid spectra of the complexes as well as their base adducts were investigated.

Introduction

Coordination chemistry of metallo–sulfur compounds is a source of stimulation to many research workers, due to the fact that it possesses unique stereochemical, magnetic and spectral properties. Metal complexes of ligands containing sulfur as donor atoms were reviewed by Livingstone [1, 2]. The biological and carcinostatic activities of metallo–sulfur compounds have been surveyed for many years [3 4]. Foye and William [5] investigated the metal binding abilities of heterocyclic thiones as antibacterial agents. Kats [6] studied 2-(o-hydroxyphenyl)benzothiazole and its copper complexes as an antitubercular agent. Furthermore, the analytical and industrial applications of 2-mercaptobenzothiazole have been known for many years. Many research workers studied the chelation properties of benzothiazoles and its 2-mercapto derivatives [7, 8].

We report here a detailed preparation and characterization of 2-mercaptobenzothiazole metal complexes with Cu(II), Ni(II) and Co(II). The prepared solid complexes were investigated using the electronic absorption spectra together with infrared and magnetic measurements. The copper complexes were also investigated by electron spin resonance spectroscopy.

Experimental

Chemicals

2-mercaptobenzothiazole (MBTH) was purchased from Aldrich and was recrystallized from ethanol before use. 2-(o-hydroxyphenyl)benzothiazole (HPBT) was purchased from Eastman Kodak. Heterocyclic base amines (pyridine, 2-picoline, 3-picoline and 4-picoline) of high purity, were supplied by B.D.H.

Preparation of the Metal Complexes

Complexes of 2-mercaptobenzothiazole

Bis(2-mercaptobenzothiazolato)copper(II); Cu-(MBT)₂. A solution of $CuCl_2$ (0.2 mol) in 50 ml ethanol was added to a solution of MBTH (0.4 mol) in ethanol. A yellow compound was immediately precipitated, which was digested on a water bath for about an hour. Then, the solution was cooled, filtered and the resulting yellow compound was washed with hot ethanol and ether and dried *in vacuo*. The complex was soluble to some extent in acetonitrile, DMF and nitrobenzene. The analyses are given in Table I.

TABLE I. Analytical Results.

No.	Compound	Color	M% (Calcd)	C% (Calcd)	H% (Calcd)	N% (Calcd)
1.	$Cu(MBT)_2$	yellow	16.08 (16.0)	42.30 (42)	1.98 (2.0)	6.98 (7.0)
2.	$[Cu(MBT)_3 \cdot Py]_2$	blue	10.05 (10.0)	49.03 (49)	2.97 (3.0)	9.08 (9.0)
3.	$Cu(OPBT)_2$	brown	12.12 (12.0)	60.89 (61.0)	3.01 (3.0)	4.93 (5.0)
4.	$Ni(MBT)_2$	brown	15.02 (15.0)	43.05 (43.0)	2.12 (2.0)	6.91 (7.0)
5.	$Ni(MBT)_2 \cdot Py_2$	green	11.3 (11.0)	51.89 (52.0)	2.96 (3.0)	9.99 (10.0)
6.	$Ni(MBT)_2 \cdot (2\text{-Pic})_2$	green	10.20 (10.0)	53.85 (54.0)	3.89 (4.0)	9.58 (10.0)
7.	$Ni(MBT)_2 \cdot (3\text{-Pic})_2$	green	10.10 (10.0)	53.93 (54.0)	3.92 (4.0)	9.68 (10.0)
8.	$Ni(MBT)_2 \cdot (4\text{-Pic})_2$	green	10.08 (10.0)	54.21 (54.0)	3.87 (4.0)	10.20 (10.0)
9.	$Ni(MBT)_2 \cdot (n\text{-BuNH}_2)_2$	light green	11.30 (11.0)	51.08 (51.0)	5.88 (6.0)	10.86 (11.0)
10.	$Ni(OPBT)_2$	brown	11.13 (11.0)	56.86 (57.0)	3.96 (4.0)	4.90 (5.0)
11.	$[Co(MBT) \cdot Cl]_2$ [a]	dark green	23.40 (23.0)	32.07 (32.0)	2.10 (2.0)	4.89 (5.0)
12.	$Co(OPBT)_2$	green	12.30 (12.0)	61.05 (61.0)	2.94 (3.0)	4.87 (5.0)

[a]Cl: Found 14.2%; Calcd. 14.0%.

The pyridine adduct of Cu(MBT)₂. 2.0 gms of Cu-(MBT)₂ was dissolved in 50 ml pyridine and refluxed for about one hour. The color of the reaction mixture changed from yellow to dark green. The solution was left overnight at room temperature to form blue crystals which were not soluble in any common solvents. The analysis and the expected stoichiometric structure are given in Table I.

Bis(2-mercaptobenzothiazolato)Ni(II); Ni(MBT)₂. A solution of $NiCl_2$ (0.2 mol) in ethanol was mixed with MBTH (0.4 mol) in 50 ml ethanol. The solution was then neutralized with an NH_4OH solution. A brown compound was precipitated, then filtered, washed with ethanol and ether. The complex was dried *in vacuo.*

Adducts of Ni(MBT)₂. The adducts of Ni(MBT)₂ with Pyridine, 2-Picoline, 3-Picoline, 4-Picoline and n-butylamine were obtained as green crystals by dissolving 2 g of Ni(MBT)₂ in an excess of the amine. The diadducts were precipitated as a result of standing at room temperature, filtered and washed with ether and dried *in vacuo.*

2-mercaptobenzothiazolatochlorocobalt(II); [Co-(MBT)Cl]₂. A solution of $CoCl_2$ (0.2 mol) in ethanol was added to MBTH (0.4 mol) in ethanol.

The mixture was neutralized with NH_4OH solution to give a green complex which was then filtered and washed several times with ethanol and ether and dried *in vacuo* over P_2O_5. The complex was soluble in $CHCl_3$, CCl_4 and CH_3CN.

Metal complexes of 2-(o-hydroxyphenyl)benzothiazole

i) Bis(2-o-hydroxyphenylbenzothiazole)Cu(II); Cu-(OPBT)₂. Ethanolic solution of (0.2 mol) $CuCl_2$ was mixed with OHPBT (0.4 mol). The solution turned to a light brownish color. The mixture was refluxed for three h., dark brown crystals were then separated which were filtered off and washed with ethanol. The complex was soluble in DMF, acetonitrile and nitrobenzene but only slightly soluble in benzene and carbon tetrachloride.

Bis(2-o-hydroxyphenylbenzothiazole)Ni(II); Ni-(OPBT)₂·2H₂O. A hot solution of the ligand (0.4 mol) in alcohol was added to $NiCl_2$ (0.2 mol) in alcohol (50 ml). The mixture was refluxed for wto h. After being cooled a solution of acetate buffer was added. A yellow complex was precipitated and filtered off, washed with alcohol and ether and dried *in vacuo* over P_2O_5.

TABLE II. Major I.R. Bands and Their Assignments for 2-Mercaptobenzothiazole Metal Complexes.[a]

Ligand cm⁻¹	Cu(II)	Metal Complexes Ni(II)	Co(II)	Assignment
3100	–	–	–	ν_{N-H}
1600 s	–	–	–	Thioamide (I)
1505	1480	1450	1460	$\nu_{C\cdots N}$, $\nu_{C\cdots S}$
1465	1460	–	–	
1440 vs	1420	1405	1380	Thioamide (II)
1310	1300 w	–	1320 w	
1295	–	–	–	
1250	1230	1250	1240	$\nu_{C-S} + \delta_{NCS}$
1090 s	1090	1080	1090	Thioamide (III)

[a]vs = very strong; s = strong and w = weak.

iii) Bis (2-*o-hydroxyphenylbenzothiazole)Cobalt-(II)*; *Co(OPBT)₂*. A green solid complex was prepared by the same procedure as the Ni(II) complex described above using CoCl₂·6H₂O. The complex was insoluble in most of the common solvents.

Physical Measurements

Electronic spectra were recorded with Unicam Sp 1800 and Sp 600 spectrophotometers. IR spectra were measured as KBr discs with a Unicam Sp 200 spectrophotometer. ESR data were obtained with an x-band (9 GHZ) using 1000 Hz field modulation at room temperature and liquid nitrogen temperature. DPPH (g = 2.0036) was used as internal standard. Conductometric measurements were carried out with an OK-10211 type conductivity meter. Magnetic measurements were carried out at room temperature using the Gouy method and the diamagnetic corrections were calculated by the use of Pascal's Constants [9].

Results and Discussion

2-Mercaptobenzothiazole (MBTH) is a thiocarbonyl derivative and can be represented by two tautomeric forms, *i.e.* thioketone (A) and thioenol (B)

(A)   (B)
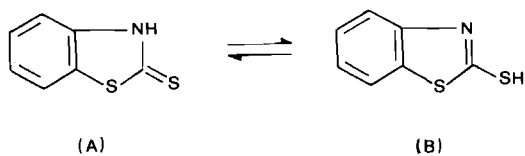
IR spectral studies showed that the –NH–C=S group exists. mainly in the solid form and the ligand exists mainly in the thioketo form (A) [10, 11]. The most characteristic bands of the ligand and its metal chelates are listed in Table II. The band at 3100

cm⁻¹ in the free ligand is due to ν(N–H) while the bands around 1600, 1505, 1465, 1440 and 1310 cm⁻¹ are due to the thioamide bands [12]. The bands at 1600–1505 cm⁻¹ are due to ν(N–C=S) which results from the coupling of (C–N) stretching and (N–H) deformation vibrations [13]. Therefore the MBTH contains three centers capable of chelation, either through the two sulfur atoms or through one of the sulfurs and the nitrogen atom. The latter case is the most likely since the heterosulfur atom present in the skeleton of the five membered ring has very weak coordination ability.

The spectra of the metal complex (Table II) exhibit to a similar extent the same pattern. The band due to ν_{N-H} and S_{N-H} are not present in the spectra of the complexes; besides, the bands at 1600 and 1310 cm⁻¹ of the free ligand are absent or decreased in intensity in all the complexes. There are pronounced shifts in the bands at 1505 and 1440 cm⁻¹. All the other bands are shifted to lower frequencies upon complexation and there is a decrease in their intensities. This may be due to the greater charge localization in sulfur atom upon complexation than in the case of the uncoordinated thioketo form. Consequently, the ligand coordinates through the thiol form. Wilson [7], Basson [14] and Dehad [15] have also observed that MBTH reacts with Pt(II) and Pd(II) by changing into thiol form. On the contrary, Busev *et al.* reported that MBTH reacts with Os(IV) and Ru(IV) through the keto form [16].

The i.r. spectra of 2(*o*-hydroxyphenyl)benzothiazole and its metal complexes are given in Table III. The spectra of the metal complexes showed pronounced shifts in the bands around 1640 and 1604 cm⁻¹ which are due to ν(C=N). All the bands shifted to lower frequencies and there is a decrease in their intensities. In the case of Ni(II) complex, a broad band due to $\nu_{(O-H)}$ is present at 3550 cm⁻¹ which is characteristic of coordinated water.

TABLE III. Major I.R. Bands (in cm^{-1}) and Their Assignment for 2-(o-Hydroxyphenyl)benzothiazole Metal Complexes.[a]

Ligand	Cu(II)	Metal Complexes Ni(II)	Co(II)	Assignment
–	–	3550 (b)	–	ν_{H_2O}
1640 m	1610 s	1590	1590	$\nu_{C=N}$
	1580 sh			
1605 s	1560	1540 m	1540 m	C=C arom.
1505 s	1505 s	1480 sh	1480 sh	C–O stretch
1460 m	1480	1460	1460	
	1440 m	1420 m	1420 m	
1315 s	1315 w	1300 m	1310	δ_{O-H}
1295 s	1300 w	1260 w	1260 m	ν_{C-O}

[a]s = strong; m = medium; w = weak; b = broad and sh = shoulder.
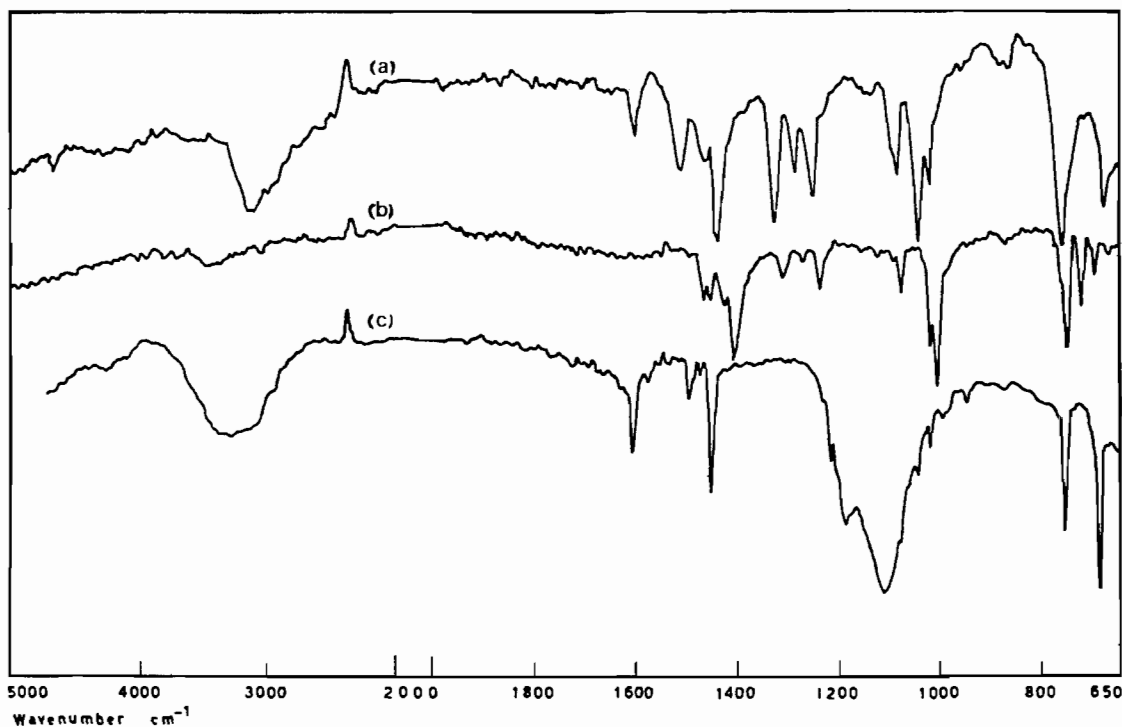
Figure 1. Infrared spectra of (a) 2-mercaptobenzathiazole; (b) bis(2-mercaptobenzothiazolato)Cu(II) and (c) pyridine adduct of [Cu-(MBT)$_2$].

Electronic Spectra and the Structure of the Complexes

Copper(II) complexes

The reaction of 2-mercaptobenzothiazole with copper(II) salts gave a yellow complex. The stoichiometric analysis showed that the complex is Cu(MBT)$_2$, in which the copper is present in a (+2) oxidation state. The effective magnetic moment at room temperature produced $\mu_{eff} = 0$.

The anomalously low effective magnetic moments observed for many copper(II) complexes [21] were attributed to strong spin–spin interaction between two cupric ions [21, 22]. In general, the decrease in the magnetic moment below the spin only value (1.73 BM) was attributed to molecular associations forming bi- or polynuclear molecules [21, 23, 24].

The esr measurements at room temperature as well as at liquid nitrogen temperature showed a very weak and broad signal which may be due to the polymeric nature of the complex.

The Nujol mull spectrum of the yellow Cu(MBT)$_2$ complex (Fig. 2-a) exhibits only one band at 21,505 cm^{-1} with a shoulder around 23,809 cm^{-1} and no
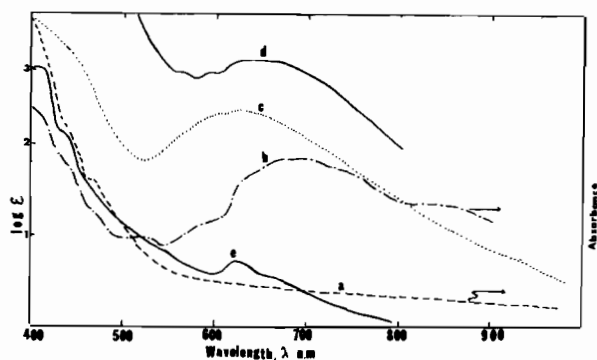
Figure 2. Electronic spectra of (a) the yellow Cu(MBT)$_2$ (nujol mull); (b) [Cu(MBT)$_3$Py] (mull); (c) and (d) Cu-(MBT)$_2$ in n-butylamine and 4-picoline, respectively.
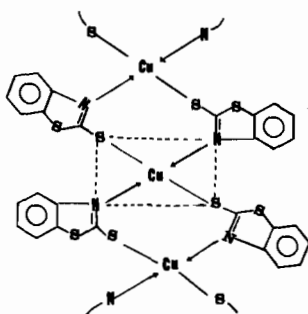
Figure 3. The structure of Cu(MBT)$_2$.

Figure 4. Proposed structure of the pyridine adduct of Cu(MBT)$_2$.
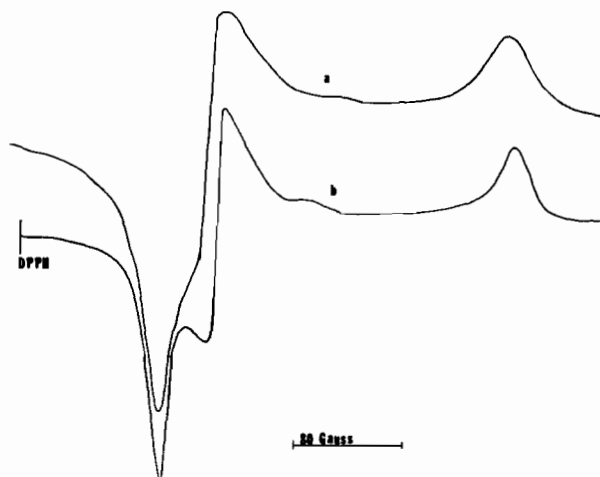
Figure 5. ESR spectra of the pyridine adduct at (a) room temperature; (b) liquid nitrogen temperature.

intense bands are located in the lower energy side of the visible region. The spectrum feature is in agreement with the reported diamagnetic copper(II) complexes [19, 20].

The reported ir spectrum for Cu(I) complex with mercaptobenzothiazole [7] showed a strong band at 1600 cm^{-1} which is different from the observed spectrum shown in Fig. 1, thus ruling out the formation of a Cu(I) complex. Consequently, due to the insolublity of the yellow complex in most organic solvents, the stoichiometric analysis and visible, ir and esr spectral data, the yellow complex may be assigned as a square polymeric structure. Fig. 3. Therefore, the yellow Cu(MBT)$_2$ represents one of the few copper(II) complexes in which the paramagnetism is almost completely quenched at room temperature [25–27].

It is well known that four coordinate copper(II) complexes may act as Lewis acids. They react with Lewis bases, such as pyridine, to expand their coordination number to form either five or six coordinate adducts. The electronic spectra of the yellow Cu(MBT)$_2$ in different amines were measured. The results are given in Table V. It is apparent that the spectra of the adducts are completely different from the yellow complex (Fig. 2-a), which indicates strong interaction with the amines and consequently support
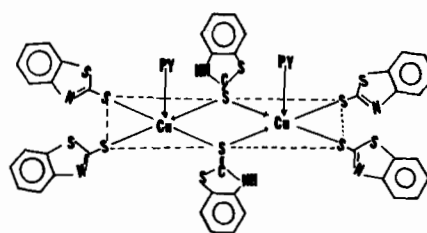
the proposed structure of the diamagnetic copper(II) complex.

When the yellow Cu(MBT)$_2$ was refluxed with excess pyridine, the colour of the solution changed to dark green, which, having stood overnight, formed blue crystals with a stoichiometric formula of [Cu-(MBT)$_3$Py]. The effective magnetic moment at room temperature was found to be μ = 2.07 BM. The nujol spectrum of the blue complex (Fig. 2-b) exhibits intense bands at 12,658 and 14,925 cm^{-1}, with two shoulders at 12,658 and 17,241 cm^{-1} respectively. The band around 20,408 cm^{-1} is a charge transfer. The position of these bands is in agreement with that reported for distorted square-based pyramidal structure [28–30].

The ir spectrum of the blue pyridinate complex (Fig. 1-c) shows a band for ν_{N-H} at 3300 cm^{-1} and a sharp band at 1600 cm^{-1} due to $\nu_{NH, C=S}$. These bands are absent in the spectrum of the yellow complex. All the other bands showed a decrease in their intensities and shifted to lower frequencies. Therefore, these results suggest that one molecule of the ligand in the Cu(MBT)$_3$Py exists in the thioketo form and a polymeric structure (Fig. 4) may be tentatively assigned to the blue pyridinate complex in which the thioketo sulfur atom acts as a bridge between two copper centers. Villa and Hatfield [31]

TABLE IV. Magnetic Properties and Electronic Spectra of Copper Complexes.

Compound	μ, B.M. (293 °K)	E.S.R. Data			State	$\nu_{max} \times 10^3$ cm^{-1}
[Cu(MBT)$_2$]	0	—	—	—	solid	21.05; 23.809(sh)
[Cu(MBT)$_3$Py]$_2$	2.07	g_1 2.06	g_2 2.08	g_3 2.21	solid	12.658; 14.925; (sh) 17.241; 20.408 (sh)
[Cu(OPBT)$_2$]	2.02	$g_\perp$ 2.07	$g_\parallel$ 2.25		solid	14.285; 18.519; 23.809
		$K_\perp^b$	$K_\parallel^b$		CHCl$_3$	12.346; 13.889; 15.625; 16.667; 19.607
		0.84	0.73		Py	14.286; 20.000 (broad)

[a] Solid = diffuse reflectance spectra; Py = pyridine.   [b] K = the orbital reduction factor.

TABLE V. Electronic Spectra of Cu(MBT)$_2$.

Base	$\nu_{max} \times 10^3$ cm^{-1} (ϵ mol^{-1} lit^{-1} cm^{-1})		
	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	C.T.[a]
Pyridine	13.699 (2.63)	15.625; 16.949; 18.868 (3.63) (6.32) (sh)	23.809 (527)
2-Picoline	13.514 (11.22)	16.393; 17.544; 18.860 (20.09) (21.66) (sh)	23.809 (659)
3-Picoline		15.152; 16.949; 17.544 (164) (152) (sh)	22.988 (659)
n-butylamine		15.873; 16.949 (150) (135)	
DMF		15.873	22.727

[a] C.T. = charge transfer band; sh = shoulder.

proposed a similar structure for tetrabis(N,N'-diethyl-dithiocarbamato)dicopper(II). Recently, the reaction between ruthenium salts and 2-mercaptobenzothiazole was investigated by Wilkinson et al. [32]. They reported the formation of [Ru(MBT)$_3$]$_2$, which is dimeric in chloroform. They proposed that dimerization takes place through the thiol sulfur atom.

The esr spectra of the polycrystalline blue pyridinate Cu(II) adduct are shown in Fig. 5. The spectrum is anisotropic with g-values of g_1 = 2.06, g_2 = 2.08 and g_3 = 2.21. The average g-value in an anisotropic system can be calculated using the relation

$$g_{av} = \sqrt{g_\parallel^{2/3} + 2g_\perp^{2/3}}$$

where $g_\parallel$ = g_z = 2.06 and $g_\perp$ = $(g_x + g_y)/2$ = 2.15.

In the present case, the value of g_{av} = 2.06 can be obtained. Therefore, the esr data is consistent with distorted square-based pyramidal stereochemistry [29].

Bis[2-(o-hydroxyphenyl)benzothiazolato] Cu(II); OPBT)$_2$Cu

The mull spectrum of the Cu(HPBT)$_2$ exhibits three bands in the regions 14,285, 18.519 and 23,809 cm^{-1}, while the absorption spectrum in chloroform (Table IV) showed bands at 12,346, 13,889, 15,625, 16.667 and 19,607 cm^{-1}. The shape as well as the position of these bands could not be taken for a square planar structure which usually shows a broad band around 14,000–16,000 cm^{-1} [35]. The spectra

TABLE VI. Magnetic Properties and Electronic Spectra of Cobalt(II) and Nickel(II) Complexes.

Compound	μ, B.M. (296 °K)	State	$\nu_{max} \times 10^3$ cm^{-1}
[Ni(MBT)$_2$]	0	solid	16.260; 18.860(sh); 22.727;
		CHCl$_3$	11.100(sh); 16.390; 22.700
[Ni(OPBT)$_2$]	3.10	solid	14.000; 14.492; 13.300(sh);
			19.608
[Co(MBT)·Cl]$_2$	4.40	solid	13.888(sh); 16.393; 17.291
[Co(OPBT)$_2$]	4.36	solid	10.869; 17.241
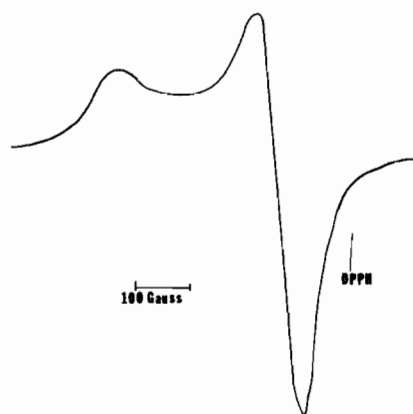
Figure 6. ESR spectrum of Cu(HPBT)$_2$ at room temperature.

of the complex in both the solid and chloroform are similar to that reported for pseudotetrahedral complexes [36]. Also the effective magnetic moment of the compound is 2.20 B.M., which is in agreement with those reported for pseudo-tetrahedral. In neat pyridine, the spectrum exhibits a broad band at 14,286 cm^{-1} and a charge transfer one at 20.000 cm^{-1}, which indicates the formation of a distorted octahedral dipyridinate adduct.

The esr spectrum as polycrystalline is shown in Fig. 6. The spectrum is similar to those reported for axial symmetry (29.30), with $g_\perp = 2.07$ and $g_\parallel = 2.25$. This result is in very good agreement with those reported by Wasson *et al.* [37] during the course of these investigations. In the axial symmetry the g-values are related by the expression (33) G = $g_\parallel - 2/g_\perp - 2$, which gave a value of 3.75 indicating the presence of exchange coupling [29]. Recently Wasson *et al.* [38] showed that, based on the magnetic susceptibility behavior of Cu(OPBT)$_2$ over the temperature range 2–77 °K, exchange coupling is less than -1 cm^{-1} and is due to an out-of-plane copper–oxygen interaction. The value of the orbital reduction of $K_\perp$ and $K_\parallel$ have been calculated from the expression [34]

$$g_\perp = 2 - 2K_\perp^2\lambda/E(E^2g \leftarrow {}^2B_{1g})$$

and

$$g_\parallel = 2 - 8K_\parallel^2\lambda/E({}^2B_{2g} \leftarrow {}^2B_{1g})$$

where K is the orbital reduction factor and λ is the spin–orbit coupling constant, by using the observed g-values, $\lambda = -829$ cm^{-1} and the energies of the transitions ${}^2E \leftarrow {}^2B_{1g}$ and ${}^2B_{2g} \leftarrow {}^2B_{1g}$. The calculated values are shown in Table IV.

Nickel(II) Chelates

2-Mercaptobenzothiazolato complexes. The magnetic and electronic spectral data for [Ni(MBT)$_2$] are reported in Table VI. The general features of the spectra in the mull as well as in chloroform are consistent with a singlet (${}^1A_g$) ground state ($\mu = 0$).

It has been found that the liability of the geometry of many metal chelates with amines gives rise to molecular configurations in solutions together with complexes which differ from the parent solid complexes [39]. The reaction of [Ni(MBT)$_2$] with some base adducts such as butylamine, pyridine, 2-, 3- and 4-picoline gave bluish–green crystals of the general formula [Ni(MBT)$_2$X$_2$], where X = amine. The value of the effective magnetic moments at room temperature for the adducts falls in the range 3.30–3.60 B.M. and is consistent with octahedral complexes [35, 39].

The solution spectra in the neat amine, as well as the mull for the solid complexes (Table XII) showed four major bands of relatively low intensities around 10,000–10,525 (ν_1); 11,040–12,800; 15,000–16,500 (ν_2) and 18,000–20,000 cm^{-1}(ν_3). The positions of these bands and their intensities are consistent with tetragonal distortion in octahedral Ni(II) complexes [35, 39]. The ligand field parameters were calculated according to the method given by Lever [40]. The results are given in Table VII. For tetragonal Nickel-(II) complexes, values of ν_2/ν_1 are found to be greater than the usual theoretical value of 1.80 for octahedral symmetry. The interaction between high

TABLE VII. Electronic Spectra (cm^{-1}) and Ligand Field Parameters of the [Ni(MBT)$_2$] Adducts.

| Compound	μ (2.95 °K)	Band Maxima	ν_2/ν_1	Dq (cm^{-1})	B(cm^{-1})	$\beta*$
[Ni(MBT)$_2$Py$_2$]	3.25	10,416; 16,129; 16,660; 20,000	1.51	1042	128.6	0.707
[Ni(MBT)$_2$(2-Pic)$_2$]	3.30	10,258; 11,709; 15,152; 16,393; 18,182	1.54	1026	653.5	0.634
[Ni(MBT)$_2$(3-Pic)$_2$]	3.40	10,526; 12,048; 15,873; 17,241; 19,609	1.61	1031	859.1	0.834
[Ni(MBT)$_2$(4-Pic)$_2$]	3.40	10,204; 12,364; 16,393; 18,867	1.60	1020	803.1	0.771
[Ni(MBT)$_2$(n-but NH$_2$)$_2$]	2.96	10,593; 12,919; 16,393; 16,950	1.57	1059	740.5	0.718

spin $^3T_{1g}$(P) and $^3T_{1g}$(F) states gradually lowers the ratio ν_2/ν_1 from the theoretical value of 1.8 to *ca.* 1.50–1.70, and values of about 1.60–1.70 are common for octahedral Nickel(II) complexes [41]. In the present case the ν_2/ν_1 ratios are 1.54–1.60 as expected for D$_{4h}$ symmetry.

The values of the Racah parameter B found in the complexes are always less than the value of 1041 cm^{-1} found in the free ion. The size of the reduction is considered to be an indication of the amount of covalent character in the complex. The calculated values of B and β are given in Table VII. The value of Dg obtained in Table VII is referred to as the mean crystal field strength. The axial (Dg$_z$) and equatorial ligand field strength (Dg$_{xy}$) can be derived according to the "average environment rule" [38, 40]. The calculation was carried out for two adducts, [Ni-(MBT)Py$_2$] and [Ni(MBT)$_2$(DMF)$_2$]. Employing the data for [Ni(Py)$_6$]$^{2+}$ [41] and [Ni(DMF)$_6$]$^{2+}$ [35], values for Dg$_{xy}$ of 1070, 1090 cm^{-1} and 986, 850 cm^{-1} for Dg$_z$ were obtained for the pyridinate and DMF adducts respectively.

[Ni(OPBT)$_2$]·2H$_2$O. The reflectance spectrum of the complex displays a split band around 14,000–14,492 cm^{-1} and a shoulder at 13,300 cm^{-1} beside a band at 19.608 cm^{-1} (Table VI). According to the observed magnetic moment, μ_{eff} = 3.10 B.M. (296 °K), a distorted tetrahedron may be tentatively assigned for the compound.

Cobalt(II) Complexes

[Co(MBT)Cl]$_2$. The green cobalt (II) complex with MBTH showed a magnetic moment of 4.40 B.M. which indicates a high-spin type complex. The nujol reflectance as well as the chloroform solution spectra exhibited a split band in the range 17,291–16,393 cm^{-1}, and in addition there is a shoulder at 13,880 cm^{-1}. The split band is a typical tetrahedral spectral type and can be assigned as $^4A_2 \rightarrow {}^4T_1$(P) [44,45]. The
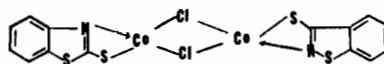
Figure 7. The tetrahedral structure of [Co(MBT)Cl]$_2$.
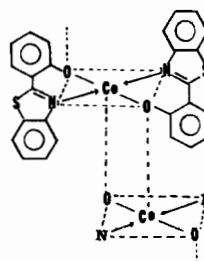
Figure 8. Proposed structure of the polymeric Co(HPBT)$_2$.

green color as well as the magnetic moment indicate a tetrahedral geometry. These results are consistent with those reported for the Cobalt(II) complexes with thiazolidine-2-thione [46] and pyridine-2-thione [18]. The molar conductance showed that the complex is non-electrolyte (<15 ohm^{-1} cm^2 at 25 °C). Therefore, it may be possible to tentatively assign dimeric tetrahedral structure (Fig. 7) based on the stoichiometric analysis and lower solubility. These results are consistent with those of Khullar and Agarwala [8].

[2-(o-hydroxyphenyl)benzothiazole] Co(II); (OP-BT)$_2$Co(II). The nujol mull spectrum of (OPBT)$_2$-Co showed two bands, a strong one around 17,241 cm^{-1} and a weak one at 10,869 cm^{-1}. The magnetic moment at room temperature is equal to 4.36 B.M. which may indicate a tetrahedral configuration around the metal ion. However, its spectrum differs considerably from high spin tetrahedral Cobalt(II) complexes [44, 45]. The complex is insoluble in most of the common solvents and this can be attributed to its polymeric nature. Therefore, we can tentatively assign a polymeric five coordinate structu-

re, Fig. 8, similar to the one reported for the Cobalt-(II) complexes with N-aryl salicylaldimine [47, 48].

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