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Metal Chelates of α-Diimines Containing a Benzothiazole Moiety. II. Complexes of Cobalt(II), Nickel(II), and Copper(II) with 2-(6-Methyl-2-pyridyl)benzothiazole

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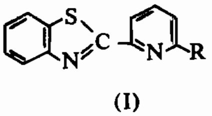
2-(6-methyl-2-pyridyl)benzothiazole (mpbt) acts as a bidentate ligand coordinating through both nitrogen atoms. Cobalt(II) forms the tetrahedral complexes CoX_2mpbt *(X=Cl, Br, I) and the polymeric five-coordinate complex* $Co(SCN)_2mpbt$*. Nickel(II) forms the tetragonal complexes* NiX_2mpbt *(X=Cl, Br, I) and the octahedral complex* $Ni(SCN)_2(mpbt)_2$*. The copper(II) complexes* CuX_2mpbt *(X=Cl, Br, SCN) are considered to be five- or six-coordinate in the solid state. The five-coordinate complexes* $[Cu(mpbt)_2ClO_4]ClO_4 . nH_2O$ *(n=0,2) and* $[Cu(mpbt)_2Cl]ClO_4$ *were also isolated. The complexes* $Co(SCN)_2mpbt$ *and* $Cu(SCN)_2mpbt$ *are antiferromagnetic. The steric effect of the methyl group of mpbt on the spectra of the complexes is discussed.*

Introduction

The complexes of iron(II), cobalt(II) and nickel(II) with α-diimines have been recently reviewed.[1] In Part I of this series[2] metal complexes formed by 2-(2-pyridyl)benzothiazole (pbt; I, R=H) with various transition metal ions were reported. The addition of a methyl group to the α-position of the pyridyl ring of pbt should result in an alteration of the steric requirements and the donor properties of the ligand. As part of a general study of the influence of steric and electronic effects upon the stereochemistry of some 3*d* metal ions, we now report the interaction of 2-(6-methyl-pyridyl)benzothiazole (mpbt; I, $R=CH_3$) with iron(II), cobalt(II), nickel(II), and copper(II).



(I)

Results and Discussion

The complexes of mpbt which have been isolated are listed in Table I, along with the conductivity and magnetic data. The complexes are stable in a dry atmosphere but slowly decompose on contact with water. They are sparingly soluble in polar organic solvents.

Table I. Conductivity and Magnetic Data on Metal Complexes of 2-(6-methyl-2-pyridyl)benzothiazole

Compound	Colour	Conductivity in $PhNO_2$ at 25°C[a] (ohm^{-1} cm^2 $mole^{-1}$)	Molar magnetic susceptibility $10^6\chi'_M$[b]	Magnetic moment μ (B.M.)
$CoCl_2mpbt$	green	0.2	8510	4.54
$CoBr_2mpbt$	green	0.3	8850	4.63
CoI_2mpbt	greenish yellow	0.8	9060	4.67
$Co(SCN)_2mpbt$	lilac	i.s.	7790	4.27
$NiCl_2mpbt$	yellow	i.s.	4270	3.22
$NiBr_2mpbt$	yellowish brown	[d]	4180	3.18
NiI_2mpbt	dark brown	2.6	4460	3.26
$Ni(SCN)_2(mpbt)_2$	green	i.s.	4200	3.19
$CuCl_2mpbt$	buff	1.1	1450	1.88
$CuBr_2mpbt$	yellowish green	2.8	1510	1.91
$Cu(SCN)_2mpbt$	brown	i.s.	1620	1.96
$Cu(mpbt)_2(ClO_4)_2 . 2H_2O$	yellowish green	36.3	1460	1.87
$Cu(mpbt)_2(ClO_4)_2$	brown	36.7	1550	1.92
$[Cu(mpbt)_2Cl]ClO_4$	green	26.4	[c]	[c]

[a] Concentration approx. 10^{-3} *M*. [b] Corrected for diamagnetism; i.s. insufficient solubility. [c] Not measured. [d] Decomposes in solution.

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(1) L. F. Lindoy and S. E. Livingstone, *Coordination Chem. Rev.*, 2, 173 (1967).

(2) L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 2, 119 (1968).

Table II. Absorption Bands of Complexes of 2-(6-Methyl-2-pyridyl)benzothiazole

	λ_{max} (mμ); (cm^{-1}) in parentheses
$CoCl_2mpbt$	480 sh (20830), 575 (17380), 650 (15380), 1020 b (9800), 1330 b (7520), 1710 (5845)
$CoBr_2mpbt$	600 (16670), 660 (15150), 1060 b (9430), 1400 b (7140), 1700 b (5880)
CoI_2mpbt	690 (14490), 1090 b (9170), 1470 b (6800), 1700 sh (5880)
$Co(SCN)_2mpbt$	560 (17870), 600 (16670), 750 b (13350), 1730 vb (5780)
$NiCl_2mpbt$	430 (23250), 510 sh (19610), 730 (13710), 940 (10640), 1060 (9430), 1420 (7040)
$NiBr_2mpbt$	440 (22750), 530 sh (18890), 720 (13900), 950 (10530), 1160 b (8630), 1435 (6970)
NiI_2mpbt	490 (20450), 660 sh (15160), 970 sh (10320), 1060 (9430)
$Ni(SCN)_2(mpbt)_2$	630 (15880), 1020 (9800)
$CuCl_2mpbt$	845 b (11850)
$CuBr_2mpbt$	490 sh (20410), 870 b (11500)
$Cu(SCN)_2mpbt$	490 sh (20410), 860 b (11630)
$[Cu(mpbt)_2ClO_4]ClO_4$	1010 b (9900)
$[Cu(mpbt)_2ClO_4]ClO_4 . 2H_2O$	1010 b (9900)
$[Cu(mpbt)_2Cl]ClO_4$	830 (12050), 950 sh (10530)

sh, shoulder; b, broad; vb, very broad.

Interaction with Iron(II). The addition of the benzothiazole mpbt to a solution of iron(II) perchlorate in alcohol gives rise to a faint pink coloration, whereas with pbt a bright red colour is produced, although no complex could be isolated.[2] These results indicate that the benzothiazole mpbt shows little tendency to form a tris-complex with iron(II).

Cobalt Complexes. The complexes CoX_2mpbt (X=Cl, Br, I) are green and their diffuse reflectance spectra (Figure 1) show an intense band near 15000 cm^{-1} and a system of three strong peaks in the region 10000-5500 cm^{-1}; the frequencies are listed in Table II.

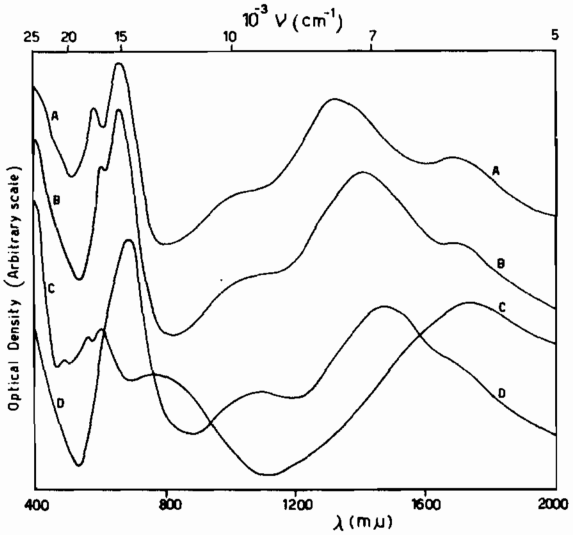

Figure 1. Electronic spectra: (A), $CoCl_2mpbt$; (B), $CoBr_2mpbt$; (C), $Co(SCN)_2mpbt$; (D), CoI_2mpbt.

The spectra are very similar to those exhibited by CoX_2L_2 (X=Cl, Br, I; L=2-chloropyridine, 2-bromopyridine)[3] and those exhibited by other tetrahedral cobalt(II) complexes.[4-7] Other workers have shown that the ν_2 absorption in the region 5500-10000 cm^{-1} can be resolved into three bands[5-8] and it has been suggested that the large degree of splitting is caused by distortion from ideal tetrahedral symmetry.[5,9,10] This type of splitting of the ν_2 band occurs in the spectra of the complexes CoX_2mpbt.

The magnetic moments of these compounds lie well within the range (4.4-4.8 B.M.) generally found for tetrahedral cobalt(II) compounds.[3,10,11] The complexes behave as non-electrolytes in nitrobenzene. They are assigned tetrahedral structures in which the benzothiazole coordinates through both nitrogen atoms.

The spectrum of the thiocyanato complex $Co(SCN)_2mpbt$ (Figure 1) is different from those of the halide complexes and also from those of octahedral cobalt(II) complexes.[3] The spectrum is similar to those of the complexes $Co(SCN)_2MeS.C_6H_4.CH=NCH_2CH_2NEt_2$ and $CoX_2MeN(CH_2CH_2NMe_2)_2$ (X=Cl, Br, I), which have been assigned five-coordinate structures.[10,12] The five-coordinate structure of $CoCl_2MeN(CH_2CH_2NMe_2)_2$ has been confirmed by X-ray crystal analysis.[13] Accordingly the complex $Co(SCN)_2mpbt$ is considered to contain five-coordinate cobalt.

The X-ray powder-diffraction patterns of the complexes CoX_2mpbt (X=Cl, Br, I) show that these compounds are isostructural. On the other hand, the diffraction pattern of $Co(SCN)_2mpbt$ does not resemble in any way those of the halide complexes; this suggests that the thiocyanato complex has a different stereochemistry.

Three five-coordinate structures are possible for $Co(SCN)_2mpbt$: (i) the dimeric structure (II) with two bridging and two terminal thiocyanato groups per

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(3) D. G. Billing and A. E. Underhill, *J. Chem. Soc. (A)*, 29 (1968).

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(5) J. Ferguson, *J. Chem. Phys.*, *32*, 528 (1960).

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(7) D. P. Graddon and G. M. Mockler, *Austral. J. Chem.*, *21*, 1775 (1968).

(8) D. P. Graddon and G. M. Mockler, private communication.

(9) J. Ferguson, *J. Chem. Phys.*, *39*, 116 (1963).

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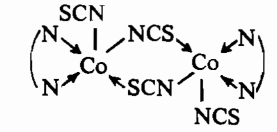
(11) B. N. Figgis and J. Lewis, «Progress in Inorganic Chemistry», Wiley Interscience, New York, *6*, 37 (1964).

(12) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, *5*, 45 (1966).

(13) M. di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

dimer; (ii) the polymeric structure (III) with one bridging and one terminal thiocyanato group per cobalt atom; (iii) a polymeric structure (IV) in which the dimers of (II) are linked by Co---Co interaction.



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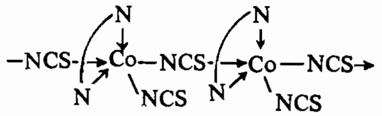

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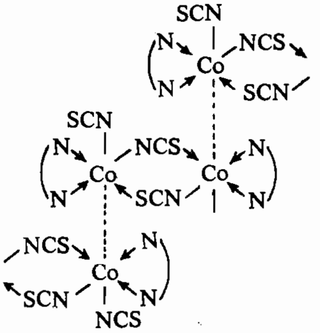

(IV)

The infrared spectrum in the C≡N stretching region exhibits two strong bands at 2075 and 2135 cm^{-1}, which are assigned as due to terminal and bridging thiocyanato groups on the basis of published data.[14]

The magnetic moment of Co(SCN)$_2$mpbt at room temperature is 4.3 B.M.; this value is within the range found for five-coordinate cobalt(II) complexes.[10,12,15] The magnetic susceptibility of Co(SCN)$_2$mpbt was measured over the range 87-393°K. The susceptibility is independent of field strength and the compound obeys the Curie-Weiss Law — $\chi_M = \frac{C}{T-\theta}$ with a large value (−75°) for θ (see Table III). Such a large value for θ indicates that the compound is not a simple paramagnetic and that there is anti-ferromagnetic interaction. On this evidence structures (II) and (III) are improbable, since there would be little likelihood of anti-ferromagnetic interaction. Structure (IV) is suggested as being the most probable, as the anti-ferromagnetic behaviour would be accounted for by interaction between cobalt atoms of adjacent dimeric units. The insolubility of the complex is in accordance with this postulate.

For comparison, the magnetic susceptibility of the chloro-complex CoCl$_2$mpbt was determined over the range 83-293°K. This compound obeys the Curie-Weiss Law with a small value (−12°) for θ (Table III), indicating the absence of anti-ferromagnetic interaction.

Table III. Magnetic Data for Cobalt Complexes

Co(NCS)$_2$mpbt

T°K	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
393	6109	164.1	4.40
373	6435	155.6	4.40
343	6867	146.0	4.36
313	7392	135.3	4.32
293	7783	128.5	4.29
272	8191	122.1	4.24
243	8974	111.4	4.19
213	9908	100.9	4.13
183	11122	89.9	4.05
153	12663	79.0	3.95
123	14543	68.8	3.80
87	17543	57.0	3.51

CoCl$_2$mpbt

T°K	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
293	8854	112.9	4.57
263	9693	103.2	4.54
233	10893	91.8	4.53
203	12356	80.9	4.50
173	14356	69.6	4.48
143	17136	58.1	4.44
113	21194	47.2	4.40
83	27827	35.9	4.32

Attempts to prepare the complexes CoX$_2$mpbt (X= SeCN, OCN) were unsuccessful.

Nickel Complexes. The complexes NiX$_2$mpbt (X= Cl, Br, I) and Ni(SCN)$_2$(mpbt)$_2$ were isolated. No bis-ligand halide complexes or tris-ligand complexes, such as were obtained with the benzothiazole pbt, were isolated.

The infrared spectrum of the thiocyanato complex Ni(SCN)$_2$(mpbt)$_2$ shows one band, at 2090 cm^{-1}, in the C≡N stretching region. This frequency is characteristic of terminal *N*-bonded thiocyanate.[14] The electronic spectrum displays bands at 15880 and 9800

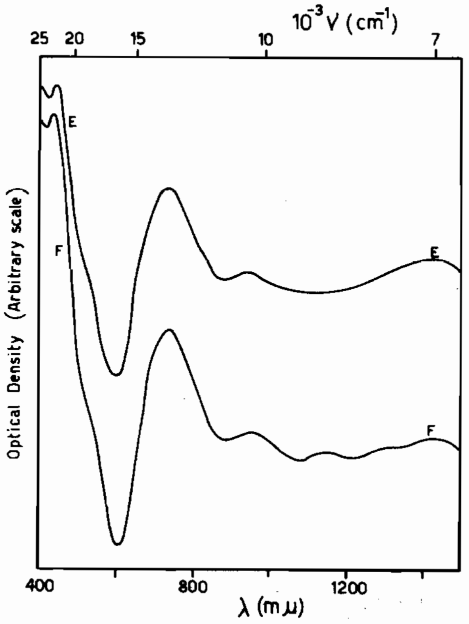

Figure 2. Electronic spectra: (E), NiCl$_2$mpbt; (F), NiBr$_2$-mpbt.

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(14) P. C. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960); M. M. Chamberlain and J. C. Bailar, *J. Amer. Chem. Soc.*, *81*, 6412 (1959); A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 959 (1965).

(15) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, *88*, 5180 (1966).

cm^{-1} and the magnetic moment is 3.19 B.M. These data are similar to those for Ni(SCN)$_2$py$_4$,[16] which has been shown to possess a *trans*-octahedral structure. However, a *cis*-octahedral structure is more probable for Ni(SCN)$_2$(mpbt)$_2$, since molecular models show that two molecules of mpbt cannot be accommodated in a square plane without considerable steric hindrance.

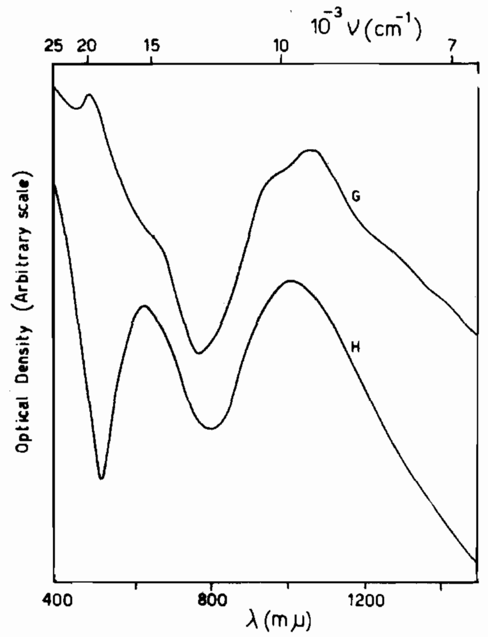

Figure 3. Electronic spectra: (G), NiI$_2$mpbt; (H), Ni(SCN)$_2$(mpbt)$_2$.

The diffuse reflectance spectra of the halide complexes are shown in Figures 2 and 3 and the maxima are listed in Table II. The spectra of the chloro and bromo complexes do not display unambiguously the features expected for a tetrahedral stereochemistry.[17-20] However, the spectra resemble those of some polymeric halide-bridged nickel complexes.[19,21] On the basis of their stoichiometry, low solubility, spectra, and magnetic moments, a six-coordinate tetragonal configuration, involving halide bridges, is assigned to these complexes.

The iodo-complex NiI$_2$mpbt is only slightly dissociated in nitrobenzene (Table I). Its spectrum is different from those of the chloro and bromo-complexes but is essentially similar to those of NiX$_2$L$_2$ (X=Cl, Br; L=amine), which have been shown to possess a tetragonal configuration.[22] The magnetic moment is not unusually high for a tetragonal complex and therefore this complex is considered to be tetragonal also.

Copper Complexes. The magnetic moments of the copper complexes lie within the range 1.86-1.96 B.M. Their diffuse reflectance spectra, which are shown in Figures 4 and 5, are similar to the spectra of complexes which contain either five- or six-coordinate copper,[23,24] in that they display a band at *ca.* 11500 cm.$^{-1}$ On the other hand, the spectra of the square-planar complexes Cu(Me$_4$en)X$_2$ and Cu(Me$_4$pn)X$_2$ (Me$_4$en = N,N,N',N'-tetraethylmethylenediamine; Me$_4$pn = N,N,N',N'-tetramethyl-1,2-propylenediamine; X = Cl, Br) display maxima at 14400 to 15000 cm^{-1}.[25]

The infrared spectrum of the thiocyanato complex shows strong bands at 2095 and 2145 cm^{-1}, indicating that both terminal and bridging thiocyanato groups are present.[14,26] The magnetic susceptibility of this compound was measured over the range 80-290°K (Table IV). The compound obeys the Curie-Weiss Law but the numerical value of θ is large (−73°) and thus the compound is anti-ferromagnetic. Its structure is probably the same as that of the cobalt complex Co(SCN)$_2$mpbt.

Table IV. Magnetic Data for Cu(SCN)$_2$mpbt

T°K	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
293	1540	649.4	1.91
263	1691	591.3	1.89
233	1869	535.0	1.87
203	2083	480.1	1.85
173	2306	433.7	1.79
143	2618	382.0	1.74
113	2992	334.2	1.65
79	3581	279.3	1.51

The complex perchlorate was obtained as a yellowish-green dihydrate and in a brown anhydrous form which is explosive when struck or heated. The infrared spectrum of the brown form displays no band in the region 3000-3500 cm^{-1}, while the spectrum of the yellowish-green form displays ν(OH) at 3350 cm^{-1}. The molar conductivities of both forms in nitrobenzene have values (Table I) which are only slightly greater than those found for uni-univalent electrolytes in this solvent. This indicates that the complexes exist in nitrobenzene solution as [Cu(mpbt)$_2$ClO$_4$]ClO$_4$. Further evidence to support this postulate of a fire-coordinate complex was obtained by the isolation of the complex [Cu(mpbt)$_2$Cl]ClO$_4$, which is a uni-univalent electrolyte in nitrobenzene. The infrared spectrum of [Cu(mpbt)$_2$Cl]ClO$_4$ shows a strong broad band at 1095 cm^{-1}, indicative of ionic perchlorate (T$_d$ symmetry).[27] The infrared spectra of [Cu(mpbt)$_2$ClO$_4$]ClO$_4$. nH$_2$O (n=0,2) show two maxima in this region. The spectrum of the anhydrous complex displays maxima at 1095 cm^{-1} (s) and 1133 cm^{-1} (m), while that of the dihydrate has maxima at 1090 cm^{-1} (s)

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(18) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.* (*A*), 1676 (1967).
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(20) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 6, 262 (1967).
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(24) L. Sacconi and I. Bertini, *Inorg. Chem.*, 5, 1520 (1966).
(25) I. Bertini and F. Mani, *Inorg. Chem.*, *2*, 2032 (1967).
(26) R. H. Toeniskoetter and S. Solomon, *Inorg. Chem.*, 7, 617 (1968).
(27) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

and 1134 cm^{-1} (m). This splitting of the ν(Cl—O) band into two components is consistent with the C_{3v} symmetry of a unidentate coordinated perchlorato group.[27,28] The greater intensity of the band at *ca.* 1095 cm^{-1} is attributed to the presence of an ionic perchlorate in both these compounds.

The perchlorato complexes display similar electronic spectra which exhibit a very broad band at a lower frequency (9900 cm^{-1}) than the halide complexes CuX_2mpbt (X=Cl, Br) and $[Cu(mpbt)_2Cl]ClO_4$ (*ca.* 10500 cm^{-1}). This can be attributed to perchlorate coordination—*i.e.* the substitution of the perchlorato group for the chloro group in $[Cu(mpbt)_2Cl]^+$ shifts the absorption band to a lower frequency (see Table II and Figures 4 and 5).

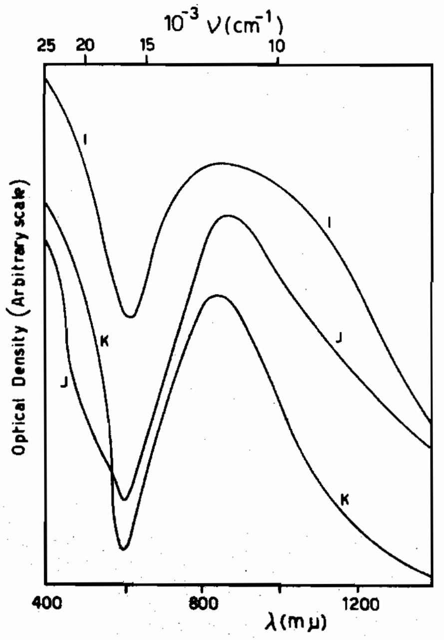

Figure 4. Electronic spectra: (I), $Cu(SCN)_2$mpbt; (J), $CuCl_2$-mpbt; (K), $CuBr_2$mpbt.

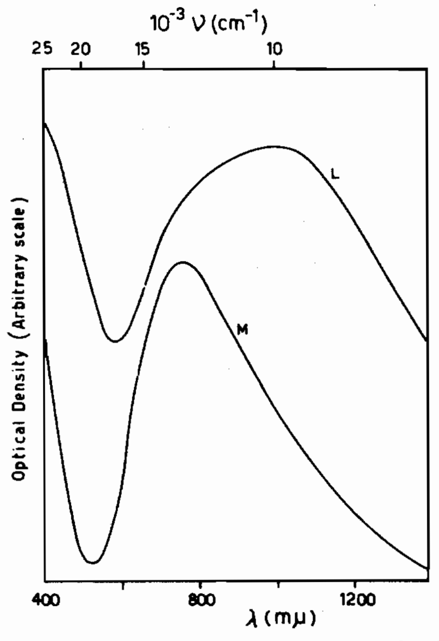

Figure 5. Electronic spectra: (L), $[Cu(mpbt)_2ClO_4]ClO_4$; (M), $[Cu(mpbt)_2Cl]ClO_4$.

Steric Effect of the Methyl Group. A comparison of the results obtained with the two benzothiazoles pbt and mpbt shows differences which can be attributed to the steric effect of the methyl group of mpbt.

Ferrous ion gives the intense red colouration, characteristic of tris(α-diimine)iron(II) complexes,[1] with pbt[2] but not with mpbt. 2-9-Dimethyl-1,10-phenanthroline and 6,6′-dimethyl-2,2′-bipyridyl also fail to produce an intense red colour with ferrous ion and these results have been explained on the basis of the methyl groups causing steric hindrance which inhibits the formation of tris-chelated complexes.[1]

The high energy component of ν_2 in the spectra of tetrahedral cobalt(II) has been shown to be sensitive to steric hindrance and moves to lower energy.[6] This effect has been observed for the cobalt complexes of mpbt and pbt. This band occurs at 11180 cm^{-1} for $CoCl_2$pbt but at 9800 cm^{-1} for $CoCl_2$-mpbt and at 10820 cm^{-1} for $CoBr_2$pbt but at 9430 cm^{-1} for $CoBr_2$mpbt. There is a shift to lower energy of *ca.* 1385 cm^{-1} for both of the mpbt complexes.

It has been found for a series of *N*-methyl-substituted ethylenediamine complexes of copper(II) that the position of maximum absorption is shifted progressively to lower frequency as the number of methyl groups on the ligand increases.[23] This phenomenon has been attributed to the increased steric requirements of the *N*-substituted ligands.[23] A similar situation occurs with the ligands pbt and mpbt: the maxima in the spectra of the copper complexes of mpbt occur at lower frequencies than those of the copper complexes of pbt.[2] This effect is due to the steric influence of the methyl group of mpbt.

Experimental Section

Analyses. Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales.

Physical Measurements. The infrared spectra were obtained from Nujol or halocarbon mulls on a Perkin-Elmer 337 spectrophotometer. The diffuse reflectance spectra were measured on a Zeiss PMQ II spectrophotometer with magnesium oxide as the reference. The magnetic susceptibilities were determined on a Newport Variable-temperature Gouy Balance. The X-ray diffraction patterns were obtained on a Philips 100 X-ray diffractometer from a layer of powdered specimen; CuK_α radiation ($\lambda = 1.5418$Å) was used.

2-(6-methyl-2-pyridyl)benzothiazole. A solution of *o*-aminobenzenethiol (11.5g) in alcohol (15 ml) was added to 6-methylpyridine-2-aldehyde (10g) in alcohol (15 ml). After 2 min crystals commenced to form. The product was filtered off, washed with a little alcohol, and recrystallized from alcohol to yield pale cream crystals of *2-(methyl-2-pyridyl)benzothiazo-*

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(28) D. H. Brown, R. H. Nuttall, J. McAvoy, and D. W. A. Sharp, *J. Chem. Soc., A,* 892 (1966); W. A. McWhinnie, *J. Inorg. Nucl. Chem.*, 26, 21 (1964); S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4, 1091 (1965); S. Buffagui, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, 3, 671 (1964); L. M. Vallarino, W. E. Hill, and J. V. Quagliano, *Inorg. Chem.*, 4, 1588 (1965).

line; yield 20.0g; m.p. 87°. *Anal.* Calcd. for $C_{13}H_{12}N_2S$: C,68.4; H,5.3; N,12.3%. Found: C,68.1; H,5.2; N,12.1.

The benzothiazoline was further characterized by the isolation of the complexes formed by zinc and cadmium acetates. *Anal.* Calcd for $ZnC_{13}H_{11}N_2S \cdot CH_3CO_2 \cdot 1/2H_2O$: C,50.0; H,4.2; N,7.8%. Found: C,50.0; H,4.8; N,7.7. Calcd. for $CdC_{13}H_{11}N_2S \cdot CH_3CO_2 \cdot H_2O$: C,43.2; H,3.9; N,6.7%. Found: C,43.2; H,4.1; N,6.6.

Air was passed through a warm solution of 6-methyl-2-(2-pyrydyl)benzothiazoline (10g) in alcohol (200 ml) for 10 hr. After concentration of the solution, *2-(6-methyl-2-pyridyl)benzothiazole* formed as cream crystals; yield 8.lg; m.p. 146°. *Anal.* Calcd. for $C_{13}H_{10}N_2S$: C,69.0; H,4.5; N,12.4%. Found: C,69.2; H,4.5; N,12.0.

Preparation of the Metal Complexes. Unless otherwise stated, the complexes were prepared by the same general method. A solution of 2-(6-methyl-2-pyridyl)-benzothiazole (2 mmoles) in alcohol (20 ml) was added slowly to a hot solution of the metal halide (2 mmoles) in alcohol (20 ml). The mixture was then heated, whereupon the complex was filtered off, washed with ethanol, and dried *in vacuo* over phosphoric oxide.

Dichloro-2-(6-methyl-2-pyridyl)benzothiazolecobalt-(II). *Anal.* Calcd. for $C_{13}H_{10}CoCl_2N_2S$: C, 43.8; H, 2.8; N, 7.9%. Found: C, 44.0; H, 3.1; N, 7.8.

Dibromo-2-(6-methyl-2-pyridyl)benzothiazolecobalt-(II). *Anal.* Calcd. for $C_{13}H_{10}CoBr_2N_2S$: C, 35.1; H, 2.2; N, 6.3%. Found: C, 35.2; H, 2.2; N, 6.2.

Diiodo-2-(6-methyl-2-pyridyl)benzothiazolecobalt(II). *Anal.* Calcd. for $C_{13}H_{10}CoI_2N_2S$: C, 29.0; H, 1.9; N, 5.2%. Found: C, 28.7; H, 2.0; N, 5.3.

Dithiocyanato-2-(6-methyl-2-pyridyl)benzothiazole-cobalt(II). *Anal.* Calcd. for $C_{15}H_{10}CoN_4S_3$: C, 44.9; H, 2.5; N, 14.0%. Found: C, 45.1; H, 2.9; N, 13.9.

Dichloro-2-(6-methyl-2-pyridyl)benzothiazolenickel-(II). *Anal.* Calcd. for $C_{13}H_{10}Cl_2N_2NiS$: C, 43.9; H, 2.8; N, 7.9; Ni, 16.5%. Found: C, 44.3; H, 3.1; N, 8.0; Ni, 16.4.

Dibromo-2-(6-methyl-2-pyridyl)benzothiazolenickel-(II). *Anal.* Calcd. for $C_{13}H_{10}Br_2N_2NiS$: C, 35.1; H, 2.3; N, 6.3; Ni, 13.2%. Found: C, 35.3; H, 2.5; N, 6.5; Ni, 13.1.

Diiodo-2-(6-methyl-2-pyridyl)benzothiazolenickel(II). *Anal.* Calcd. for $C_{13}H_{10}I_2N_2NiS$: C, 29.0; H, 1.9; N, 5.2; Ni, 10.9%. Found: C, 28.6; H, 1.9; N, 5.2; Ni, 10.9.

Dithiocyanato-bis[2-(6-methyl-2-pyridyl)benzothiazole]nickel(II). *Anal.* Calcd. for $C_{28}H_{20}N_6NiS_4$: C, 53.6; H, 3.2; N, 13.4; Ni, 9.4%. Found: C, 53.8; H, 3.4; N, 13.4; Ni, 9.5.

Dichloro-2-(6-methyl-2-pyridyl)benzothiazolecopper-(II). *Anal.* Calcd. for $C_{13}H_{10}Cl_2CuN_2S$: C, 43.3; H, 2.8; Cu, 17.6; N, 7.8%. Found: C, 43.3; H, 3.2; Cu, 17.8; N, 8.1.

Dibromo-2-(6-methyl-2-pyridyl)benzothiazolecopper-(II). *Anal.* Calcd. for $C_{13}H_{10}Br_2CuN_2S$: C, 34.7; H, 2.2; N, 6.2%. Found: C, 35.1; H, 2.2; N, 6.0.

Dithiocyanato-2-(6-methyl-2-methyl)benzothiazole-copper(II). 2-(6-Methyl-2-pyridyl)benzothiazole (0.45 g) in alcohol (20 ml) was added to a hot solution of copper nitrate 3-hydrate (0.48 g) in alcohol (20 ml). To the resultant solution was added lithium thiocyanate (1 g) in alcohol (5 ml). After the mixture was heated, brown crystals of the *complex* deposited. These were collected and washed with alcohol (*Anal.* Calcd. for $C_{15}H_{10}CuN_4S$: C, 44.4; H, 2.5; Cu, 15.6; N, 13.8%. Found: C, 44.2; H, 2.3; Cu, 15.7; N, 13.5).

Perchloratobis-[2-(6-methyl-2-pyridyl)benzothiazole]-copper(II) Perchlorate Dihydrate. 2-(6-Methyl-2-pyridyl)benzothiazole (0.45 g) in alcohol (20 ml) was added to copper(II) perchlorate 6-hydrate (0.74 g) in alcohol (15 ml) at room temperature. The solution, on standing for 2 days, deposited yellowish green crystals of the *complex*. These were collected, washed with alcohol, and dried over calcium chloride (*Anal.* Calcd. for $C_{26}H_{24}Cl_2CuN_4O_{10}S_2$: C, 41.6; H, 3.2; Cu, 8.4%. Found: C, 42.0; H, 3.7; Cu, 8.4).

Perchloratobis-[2-(6-methyl-2-pyridyl)benzothiazole]-copper(II) Perchlorate. 2-(6-Methyl-2-pyridyl)benzothiazole (0.45 g) in alcohol (20 ml) was added to a boiling solution of copper(II) perchlorate 6-hydrate (0.74 g) in alcohol (20 ml). Brown crystals of the *anhydrous complex* deposited during the next few minutes. The crystals were collected, washed with alcohol and dried over phosphoric oxide (Calcd. for $C_{26}H_{20}Cl_2CuN_4O_8S_2$: Cu, 8.9%. Found:* Cu, 8.4).

Chlorobis-[2-(6-methyl-2-pyridyl)benzothiazole]-copper(II) Perchlorate. Perchloratobis-[2-(6-methyl-2-pyridyl)benzothiazole]copper(II) perchlorate (0.23 g) was suspended in boiling acetone (20 ml) and water was added dropwise until solution was complete. The hot solution was filtered and lithium chloride (0.02 g) in acetone (5 ml) was added. The solution was allowed to cool and after 2 days the green *complex* was filtered off and washed with alcohol (Calcd. for $C_{26}H_{20}Cl_2CuN_4O_4S_2$: C, 48.0; H, 3.1%. Found: C, 47.5; H, 3.7).

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(*) Microanalyses for carbon and hydrogen were unsuccessful due to the exlposive nature of the compound.