Contribution from the School of Chemistry, The University of New South Wales Kensington, N.S.W., Australia

Metal Chelates of α-Diimines Containing a Benzothiazole Moiety. I. Complexes of 2-(2-Pyridyl)benzothiazole

L. F. Lindoy and S. E. Livingstone

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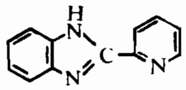
2-(2-Pyridyl)benzothiazole (pbt) acts as a bidentate ligand, coordinating through both nitrogen atoms. Cobalt(II) forms the tetrahedral complexes $CoX_2(pbt)$ ($X=Cl$, Br) and the high-spin octahedral complexes $CoX_2(pbt)_2$ ($X=Cl$, Br, I) and $[Co(pbt)(H_2O)_4]SO_4$. Nickel(II) forms mono-, bis-, and tris-ligand complexes. The tris complex $[Ni(pbt)_3](ClO_4)_2$ and the bis complexes $NiX_2(pbt)_2$ ($X=Cl$, Br, SCN, NO_3) are octahedral with moments in the range 3.1-3.3 B.M. The mono complexes $NiCl_2(pbt)$ and $Ni(CH_3CO_2)_2(pbt)(H_2O)_2$ have moments in the range 3.3-3.6 B.M.; the spectrum of $NiCl_2(pbt)$ indicates that the complex is tetragonal and polymeric with chloro bridges. The mono complex $[Ni(pbt)(H_2O)_4]SO_4$ was also isolated. With palladium(II) and platinum(II) the mono complexes $MX_2(pbt)$ ($M=Pd$, $X=Cl$, Br, SCN, NO_2; $M=Pt$, $X=Cl$, Br, SCN) and one bis complex $PtI_2(pbt)_2$ were obtained. The copper(II) complex $Cu(pbt)_2(ClO_4)_2 \cdot H_2O$ has one perchlorate group coordinated in the solid state and in nitrobenzene solution. The spectra of the mono complexes $CuX_2(pbt)$ ($X=Cl$, Br, SCN, NO_3) indicate five- or six-coordination. The thiocyanato complex contains a bridging SCN group. The insoluble copper(I) complex $CuI(pbt)$ is probably dimeric with iodo bridges. Mono complexes $MX_2(pbt)$ ($M=Zn$, $X=Br$, I; $M=Cd$, $X=Cl$, Br, I, SCN) and bis complexes $Zn(SCN)_2(pbt)_2$ and $CdI_2(pbt)_2$ were isolated. The spectra of $Zn(pbt)_2(ClO_4)_2 \cdot H_2O$ and $Cd(pbt)_2(ClO_4)_2$ indicate perchlorate coordination.

Introduction

The coordinating ability of bidentate ligands containing the α-diimine grouping $-N=\overset{|}{C}-\overset{|}{C}=N-$ has been extensively studied and the behaviour of ligands of this type with iron(II), cobalt(II), and nickel(II) has recently been reviewed.[1] It is known that heterocyclic α-diimines containing a five-membered ring have their nitrogen atoms less favourably positioned for coordination to a metal ion than are the donor nitrogens in, for example, 2,2-bipyridyl.[1]

Although metal chelates of 2-(2-pyridyl)benzimidazole (I) have been studied in considerable detail,[2-5] to our knowledge no complexes of 2-(2-pyridyl)benzothiazole (II; pbt) have been reported. Substitution of a sulphur atom for the –NH– group in the benzimidazole ring of (I) would be expected to result in electronic effects with a resultant alteration of the chelating ability of the donor nitrogen atoms.



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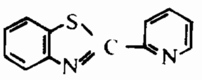

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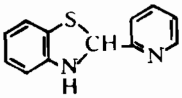

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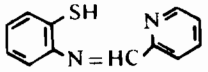

(IV)

We have recently reported reactions of 2-(2-pyridyl)benzothiazoline (III) with zinc, cadmium, mercury, and nickel.[6,7] In some cases rearrangement of the ligand occurs, to yield intensely coloured metal complexes of the tautomeric Schiff base, *N*-2-mercaptophenyl-2′-pyridylmethyleneimine (IV), which contains the α-diimine grouping. The benzothiazole (II) can be obtained by the aerial oxidation of the benzothiazoline (III) in alcohol.[6]

The compound (II) and other benzothiazoles have been investigated as fungicidal agents.[8]

Results and Discussion

A number of metal chelates of the benzothiazole (II) have been prepared in this investigation; they are listed in Table I.

Interaction with Iron(II). Reaction of an excess of (II) with a solution of ferrous perchlorate yields a

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(1) L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Revs.*, *2*, 173 (1967).
(2) J. L. Walter and H. Freiser, *Anal. Chem.*, *26*, 217 (1954).
(3) T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, *J. Amer. Chem. Soc.*, *78*, 260 (1956).
(4) T. R. Harkins and H. Freiser, *J. Amer. Chem. Soc.*, *78*, 1143 (1956).
(5) B. Chiswell, F. Lions, and B. S. Morrls, *Inorg. Chem.*, *3*, 110 (1964).
(6) L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, *1*, 365 (1967).
(7) L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.*, *7*, 1149 (1968).
(8) H. Faikachi and T. Hisano, *Yakugaku Zasshl*, *81*, 64 (1961).

Table I. Metal Complexes of 2-(2-Pyridyl)benzothiazole

Compound	Colour	Λ_{1000}[a] in $PhNO_2$ (25°)	Room Temperature Magnetic Moment	
			χ'_M[c]	μ(B.M.)
$CoCl_2(pbt)$	dark blue	i	9410	4.74
$CoBr_2(pbt)$	greenish bule	i	9440	4.76
$CoCl_2(pbt)_2$	brown	i	10800	5.10
$CoBr_2(pbt)_2$	brown	i	9730	4.83
$CoI_2(pbt)_2$	brown	17.3	9580	4.79
$Co(SCN)_2(pbt)_2$	orange brown	6.4	10620	5.03
$[Co(pbt)(H_2O)_4]SO_4$	orange	i	10310	4.95
$[Ni(pbt)_3](ClO_4)_2$	buff	52.4	4150	3.12
$NiCl_2(pbt)_2$	green	3.0	4090	3.10
$NiBr_2(pbt)_2$	green	8.0	4190	3.15
$Ni(NO_3)_2(pbt)_2$	blue green	14.3	4550	3.27
$Ni(SCN)_2(pbt)_2.{}^3/_2DMF$ [b]	green	i	4560	3.29
$Ni(SCN)_2(pbt)_2$	blue green	i	4530	3.24
$Ni(CH_3CO_2)_2(pbt)(H_2O)_2$	blue green	i	4720	3.36
$NiCl_2(pbt).½DMP$ [d]	green	i	5170	3.50
$NiCl_2(pbt)$	yellow green	i	5400	3.57
$[Ni(pbt)(H_2O)_4]SO_4.½H_2O$	blue green	i	4400	3.23
$PdCl_2(pbt)$	yellow	0.1	n	
$PdBr_2(pbt)$	yellow	0.1	n	
$Pd(SCN)_2(pbt)$	yellow	i	n	
$Pd(NO_2)_2(pbt)$	yellow	0.1	n	
$PtCl_2(pbt)$	yellow	0.1	n	
$PtBr_2(pbt)$	yellow	0.6	n	
$Pt(SCN)_2(pbt)$	orange	i	n	
$PtI_2(pbt)_2$	orange brown	0.9	n	
$Cu(pbt)_2(ClO_4)_2.H_2O$	yellow green	34.4	1730	2.01
$CuCl_2(pbt)$	green	0.5	1390	1.81
$CuBr_2(pbt)$	brown red	5.0	1430	1.85
$Cu(SCN)_2(pbt)$	brown	i	1420	1.84
$Cu(NO_3)_2(pbt).H_2O$	green	i	1530	1.90
$CuI(pbt)$	brown	i	n	
$Zn(pbt)_2(ClO_4)_2.H_2O$	pale yellow	i	n	
$ZnBr_2(pbt)$	pale yellow	2.3	n	
$ZnI_2(pbt)$	pale yellow	2.3	n	
$Zn(SCN)_2(pbt)_2$	pale yellow	9.1	n	
$Cd(pbt)_2(ClO_4)_2$	white	39.6	n	
$CdI_2(pbt)_2$	pale yellow	i	n	
$CdCl_2(pbt)$	pale yellow	i	n	
$CdBr_2(pbt)$	pale yellow	i	n	
$CdI_2(pbt)$	yellow orange	i	n	
$Cd(SCN)_2(pbt)$	pale yellow	i	n	

[a] $Ohm^{-1}\,cm^2\,mole^{-1}$; [b] DMF = dimethylformamide; [c] corrected for diamagnetism; [d] DMP = 2,2′-dimethoxypropane; [i] insoluble; [n] magnetic susceptibility was not measured.

bright red colour which is characteristic of tris(α-diimine)iron(II) complexes[1] but attempts to isolate this complex were unsuccessful.

Cobalt(II) Complexes. The cobalt-halide complexes of (II) are readily decomposed by water and their isolation is only possible under anhydrous conditions. The conductivities of the complexes $CoX_2(pbt)_2$ ($X=$ SCN, I) show that appreciable dissociation occurs in nitrobenzene. The electronic reflectance spectra of the cobalt complexes are reproduced in Figures 1 and 2.

High-spin cobalt(II) complexes commonly have either tetrahedral or octahedral stereochemistries.[9] Tetrahedral complexes are usually deep blue or green[10] and have magnetic moments in the range 4.4-4.8 B.M.[11]

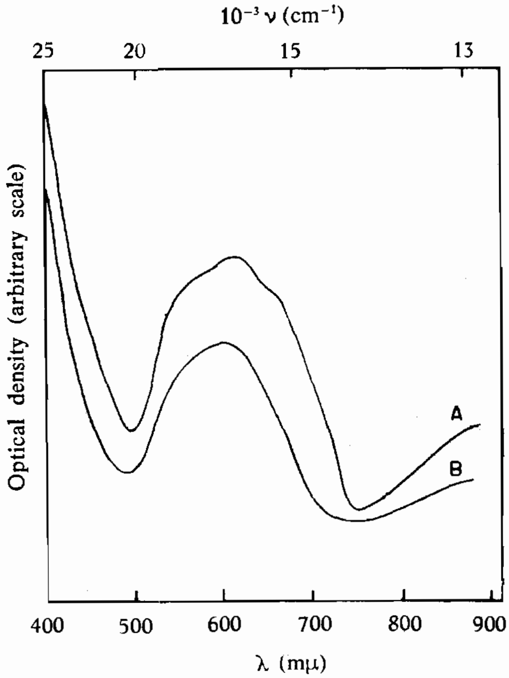

Figure 1. Solid state electronic spectra of cobalt complexes. A, $CoBr_2(pbt)$; B, $CoCl_2(pbt)$.

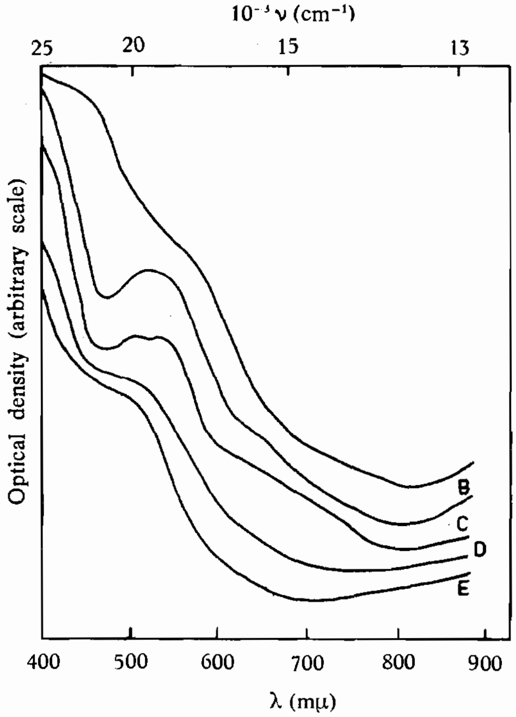

Figure 2. Solid state electronic spectra of cobalt complexes. A, $CoI_2(pbt)_2$; B, $CoBr_2(pbt)_2$; C, $CoCl_2(pbt)_2$; D, $Co(SCN)_2(pbt)_2$; E, $[Co(pbt)(H_2O)_4]SO_4$.

Their visible spectra normally display bands in the 600-700 mμ region.[9,10] Octahedral complexes are usually lilac or pink[10] and have magnetic moments in the range 4.7-5.3 B.M.[11] Their visible spectra usually display bands below *ca.* 600 mμ and thus this absorption

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(9) R. L. Carlin, *Transition Metal Chemistry, 1,* 1 (1965).

(10) D. P. Graddon and E. C. Watton, *Austral. J. Chem., 18,* 507 (1965); D. P. Graddon, K. B. Heng, and E. C. Watton, *Austral. J. Chem., 21,* 121 (1968).

(11) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem., 6,* 185 (1964).

generally occurs at lower wavelengths than in tetrahedral complexes.[9,10] The magnetic moments and the spectra indicate that the complexes $CoX_2(pbt)$ ($X = Cl$, Br) are tetrahedral, whereas the complexes $CoX_2(pbt)_2$ ($X = SCN$, Cl, Br, I) are octahedral. It is unlikely that the complexes $CoX_2(pbt)$ are salts of the type $[Co(pbt)_2][CoX_4]$, since the values of their magnetic moments would require that both cation and anion are tetrahedral. To our knowledge, no tetrahedral cationic complexes of cobalt(II) are known.

Table II. Selected Infrared Assignments for Complexes of 2-(2-Pyridyl)benzothiazole

Compound	Band (cm^{-1})	Assignment
$Co(SCN)_2(pbt)_2$	2070 s	ν(C—N)
$[Co(pbt)(H_2O)_4]SO_4$	3200 br	ν(O--H)
	1070 br	ν(S—O)
$[Ni(pbt)_3](ClO_4)_2$	1080 br	ν(Cl—O)
$Ni(NO_3)_2(pbt)_2$	815	δ(NO_3)
$Ni(SCN)_2(pbt)_2 . {}^3/_2DMF$	2080 s	ν(C—N)
	1670 s	ν(C—O)
$Ni(SCN)_2(pbt)_2$	2078 s	ν(C—N)
$Ni(CH_3CO_2)_2(pbt)(H_2O)_2$	3250 br	ν(O—H)
	1550, 1340	ν(C—O)
$[Ni(pbt)(H_2O)_4]SO_4 . ½H_2O$	3200 br	ν(O—H)
	1070 br	ν(S—O)
$Pd(SCN)_2(pbt)$	2115 s	ν(C—N)
$Pd(NO_2)_2(pbt)$	824 s, 815 s	δ(NO_2)
$Pt(SCN)_2(pbt)$	2115 s	ν(C—N)
$Cu(pbt)_2(ClO_4)_2 . H_2O$	3320 br	ν(O—H)
	1095 s, 1060 sh	ν(Cl—O)
$Cu(SCN)_2(pbt)$	2115, 2075	ν(C—N)
$Cu(NO_3)_2(pbt) . H_2O$	3200 br	ν(O—H)
	818 m, 812 sh	δ(NO_3)
$Zn(pbt)_2(ClO_4)_2 . H_2O$	3300 br	ν(O—H)
	1110 br, 1048 br	ν(Cl—O)
$Zn(SCN)_2(pbt)_2$	2100	ν(C—N)
$Cd(pbt)_2(ClO_4)_2$	1125 br, 1030 br	ν(Cl—O)
$Cd(SCN)_2(pbt)$	2100	ν(C—N)

The C—N stretching mode of $Co(SCN)_2(pbt)_2$ (Table II) indicates *N*-bonded thiocyanate.[12,13] The C—S stretching frequency, which normally occurs in the region 690-780 cm^{-1} for *N*-bonded complexes, was not observed owing to strong ligand absorptions which obscure this region. The infrared spectrum of (II) is quite complex and has many strong bands in the region 1600 cm^{-1} to 400 cm^{-1}. For many of the complexes prepared in this study, the assignment of specific bands in this region has often been difficult or even impossible owing to interference from the strong ligand bands.

By using the centre (λ_c) of the envelope of bands at *ca.* 600 mμ in the spectra of cobalt(II) halide complexes of pyridine and its substituted derivatives as a guide to the relative ligand-field strengths of the halides in these complexes, Graddon *et al.*[10] obtained the order $I^- < Br^- < Cl^- < SCN^-$. The spectra of the cobalt complexes of (II) (Figures 1 and 2) also suggest a similar order of ligand-field strengths.

Reaction of a solution of (II) in alcohol with cobalt sulphate in water yields the orange complex $Co(pbt)SO_4 . 4H_2O$. The water molecules are not removed over phosphorus pentoxide *in vacuo* and are only lost when the complex is heated to 200°. The visible spectrum (Figure 2) and magnetic moment (Table I) indicate an octahedral stereochemistry. The single broad absorption at 1070 cm^{-1} in the infrared spectrum shows that the sulphate is ionic.[14] Accordingly this compound is formulated as $[Co(pbt)(H_2O)_4]SO_4$.

The benzimidazole (I) forms bis- and tris-ligand octahedral cobalt(II) complexes[3,5] but no mono-ligand, tetrahedral complexes have been reported.

Nickel(II) Complexes. Whereas only tris- and bis-ligand nickel complexes of (I) have been reported,[3,5] tris-, bis-, and mono-complexes of (II) were obtained. The tris-ligand complex is a bi-univalent electrolyte in nitrobenzene (Table I) and the infrared spectrum (Table II) shows an intense absorption at 1080 cm^{-1} (broad), indicating ionic perchlorate groups.[15] The magnetic moment (Table I) and visible reflectance spectrum of this compound (Figure 3) are typical of high-spin, octahedrally coordinated nickel. This compound is analogous to the tris-ligand compounds formed by many other α-diimines with nickel perchlorate.[1] Its isolation confirms that the benzene ring of the benzothiazole moiety does not cause significant inter-ligand steric interference such as occurs with 2-(2-pyridyl)-quinoline.[16]

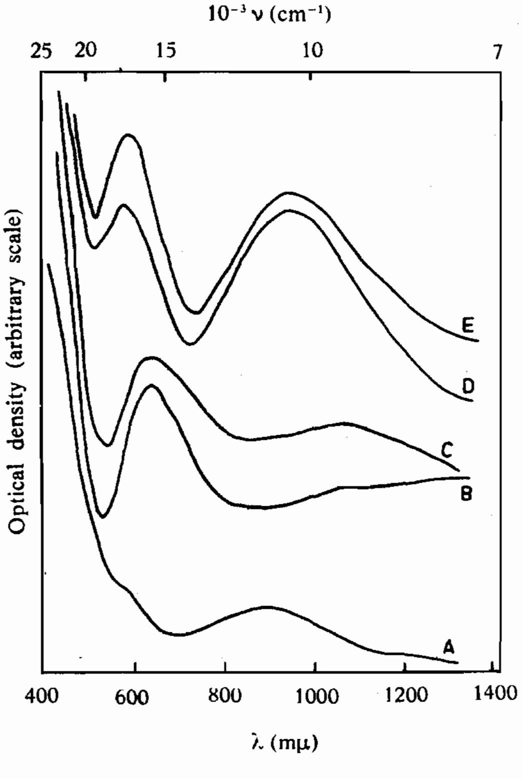

Figure 3. Solid state electronic spectra of nickel complexes. A, $[Ni(pbt)_3](ClO_4)_2$; B, $NiCl_2(pbt)_2$; C, $NiBr_2(pbt)_2$; D, $Ni(SCN)_2(pbt)_2$; E, $Ni(NO_3)_2(pbt)_2$.

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[12] S. E. Livingstone, *Quart. Revs.*, *19*, 386 (1965).

[13] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

[14] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, Section II-8 (1963).

[15] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[16] R. J. Charlton, C. M. Harris, H. Patil, and N. C. Stephenson, *Inorg. Nucl. Chem. Letters*, *2*, 409 (1966).

The benzothiazole (II) yields the bis-complexes $NiX_2(pbt)_2$ (X=Cl, Br, SCN, NO_3). The electronic reflectance spectra of these compounds (Figure 3) each display the two absorptions—at *ca.* 600 mμ and *ca.* 1000 mμ—which are characteristic of six-coordinated nickel(II). The magnetic moments fall between 3.1 B.M. and 3.3 B.M. and are within the range expected for high-spin octahedral nickel(II). The conductivities of the compounds in nitrobenzene indicate a tendency to ionise which increases in the order $Cl < Br < I \simeq NO_3$. The infrared spectrum of the thiocyanate complex has ν(C–N) at 2080 cm^{-1}; this frequency is within the range normally found for terminal *N*-bonded thiocyanate groups.[12,13]

The mono-complex $NiCl_2(pbt)$. ½DMP was also prepared. The DMP can be removed on the thermogravimetric balance to yield the unsolvated complex. The moments of both the solvated and unsolvated products are above the range (3.0-3.3 B.M.) generally found for octahedral complexes. On the basis of their high moments these compounds could be assigned pseudotetrahedral structures. Although the overall pattern of the spectra of these two compounds is similar, the positions of the band maxima are different (Figure 4 and Table III) and thus the possibility that the dimethoxypropane is bonded in the solvated complex cannot be discounted. Neither spectrum shows unambiguously the features expected for a tetrahedral stereochemistry.[17,18] Moreover both spectra resemble the spectra of some tetragonal halogen-bridged complexes; for example, the tetragonal compounds $NiCl_2$(ligand) (where ligand = *N,N,N′,N′*-tetramethylethylenediamine or propylenediamine) have solid state spectra which show absorption peaks at *ca.* 400, 690, 1100 and 1350 mμ.[18] Both these complexes have moments of 3.45 B.M. A large number of complexes of the type $NiCl_2(amine)_2$ also have moments in the range 3.3-3.5 B.M.[19] and their visible spectra are similar to the above complexes. These latter complexes have also been assigned polymeric tetragonal structures.[20] Consequently the complex $NiCl_2(pbt)$ is considered to be tetragonal.

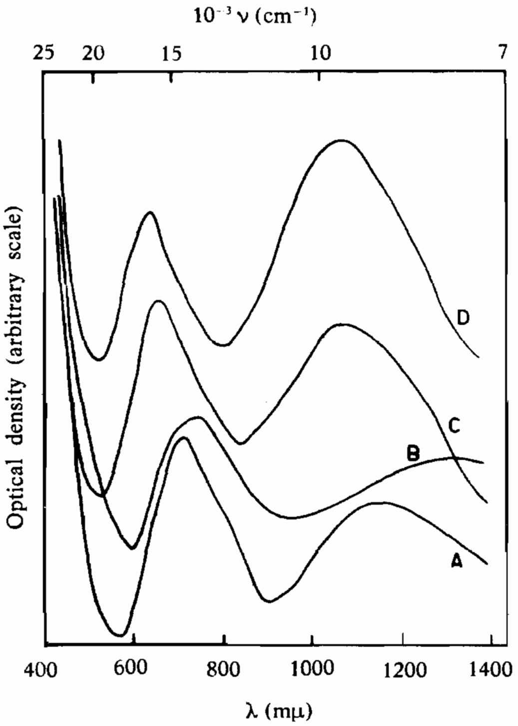

Figure 4. Solid state electronic spectra of nickel complexes. A, $NiCl_2(pbt)$. ½DMP; B, $NiCl_2(pbt)$; C, $Ni(CH_3CO_2)_2(pbt)(H_2O)_2$; D, $[Ni(pbt)(H_2O)_4]SO_4$. ½H_2O.

Table III. Electronic Absorption Bands of Nickel(II) Complexes

	Bands			
Compound	λ_{max} (mμ)		ν_{max} (cm^{-1})	
$[Ni(pbt)_3](ClO_4)_2$	590sh	~ 990 br	17000	10100
$NiCl_2(pbt)_2$	630	~1050 br	15900	9500
$NiBr_2(pbt)_2$	640	~1050 br	15600	9500
$Ni(SCN)_2(pbt)_2$	580	~ 950 br	17300	10500
$Ni(NO_3)_2(pbt)_2$	585	~ 950 br	17100	10500
$NiCl_2(pbt)$. ½DMP	690	~1150 br	14500	8700
$NiCl_2(pbt)$	740	~1300 br	13500	7700
$Ni(CH_3CO_2)(pbt)(H_2O)_2$	640	~1060 br	15600	9400
$[Ni(pbt)(H_2O)_4]SO_4$. ½H_2O	630	~1050 br	15900	9500

The mono-ligand complex $Ni(CH_3CO_2)_2(pbt)(H_2O)_2$ has been prepared. Its infrared spectrum displays bands at 1550 cm^{-1} and 1340 cm^{-1} which are assigned to ν_{asym} and ν_{sym} of the acetate group. The difference of 210 cm^{-1} between the positions of these two bands is consistent with monodentate acetate groups.[21] The broad band at *ca.* 3200 cm^{-1} is due to ν(O–H) of the water molecules. The electronic spectrum of this compound (Figure 4) indicates that it is six-coordinate; however, its magnetic moment (3.36 B.M.) is slightly above the normal range of octahedral complexes.

The green octahedral complex $[Ni(pbt)(H_2O)_4]SO_4$. ½H_2O is analogous to the cobalt(II) complex $[Co(pbt)(H_2O)_4]SO_4$. The magnetic moment and solid state spectrum indicate that the complex is octahedral. The sulphate band (ν_3) in the infrared spectrum is not split, indicating and ionic sulphate group.[14] The water is quantitatively lost on heating the complex to 210°.

Palladium(II) and Platinum(II) Complexes. The yellow complexes $MX_2(pbt)$ (M=Pd, X=Cl, Br, SCN, NO_2]; M=Pt, X=Cl, Br, SCN) have been prepared. The soluble complexes are non-electrolytes in nitrobenzene. The infrared spectra of both thiocyanate complexes have ν(C–N) at frequencies which indicate *S*-bonded thiocyanate.[12,13] The bis-complex $PtI_2(pbt)_2$ is a non-electrolyte in nitrobenzene and its dark colour confirms that the iodide ions are coordinated.

Copper Complexes. The copper(II) complexes have magnetic moments in the range 1.8-2.0 B.M. Reaction of (II) with copper perchlorate hexahydrate in alcohol

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(17) J. Ferguson and B. O. West, *J. Chem. Soc.*, (A), 1565, 1569 (1966).

(18) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, *6*, 263 (1966) and references therein.

(19) A. B. P. Lever, *Inorg. Chem.*, *4*, 763 (1965).

(20) A. B. P. Lever, S. M. Nelson, and T. M. Shephard, *Inorg. Chem.*, *4*, 810 (1965).

(21) M. J. O'Connor and B. O. West, *Austral. J. Chem.*, *20*, 2077 (1967).

yields the yellowish-green crystalline complex $Cu(pbt)_2(ClO_4)_2 \cdot H_2O$. Its infrared spectrum shows ν(O–H) of the water molecule at 3320 cm^{-1}. The conductivity in nitrobenzene is only slightly higher than that expected for a uni-univalent electrolyte. In addition the perchlorate band at *ca.* 1100 cm^{-1} is not symmetrical and shows a very pronounced shoulder at 1060 cm^{-1}. Perchlorate coordination is known to result in a splitting of this band[15] and thus both these observations suggest that the complex should be formulated as $[Cu(pbt)_2(ClO_4)]ClO_4 \cdot H_2O$. However, the water molecule, which was not removed over phosphorus pentoxide *in vacuo,* may also occupy a coordination site.

The visible spectra of this and the other copper(II) complexes are reproduced in Figure 5. All are similar to the spectra of complexes in which the copper ion is either five- or six-coordinate.[22,23]

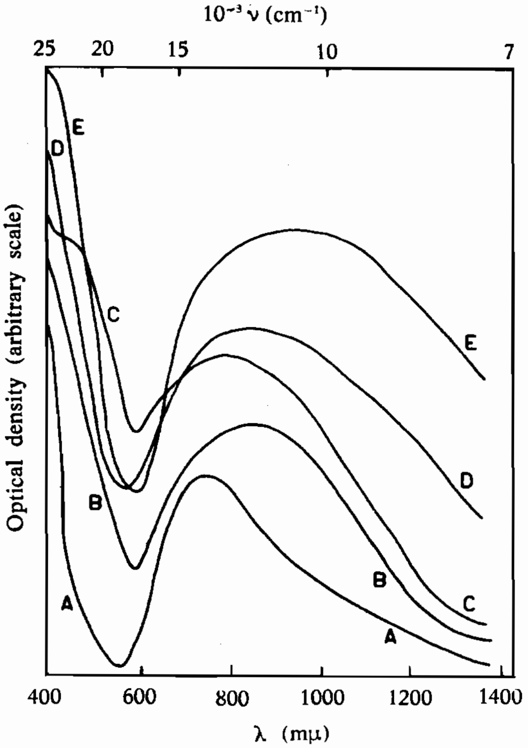

Figure 5. Solid state electronic spectra of copper complexes. A, $CuCl_2(pbt)$; B, $CuBr_2(pbt)$; C, $Cu(NO_3)_2(pbt)$; D, $Cu(SCN)_2(pbt)$; E, $Cu(pbt)_2(ClO_4)_2 \cdot H_2O$.

The C–N stretching mode of the thiocyanate complex is split into two bands at 2115 cm^{-1} and 2075 cm^{-1}. The copper atom in this compound may achieve a coordination number greater than four by bridge formation which involves only one of the thiocyanate groups. Similar halogeno-bridged dimeric or polymeric structures are possible for the compounds $CuX_2(pbt)$ (X=Cl, Br). Attempts to form pyridine adducts of several of these complexes were unsuccessful. The compounds were recrystallized from acetone which contained a small excess of pyridine and in all cases ligand exchange occurred, yielding the corresponding pyridine complexes.

Reaction of cuprous iodide with (II) in methanol yields CuI(pbt) which has only a slight conductivity in nitrobenzene. This compound may well be dimeric with iodo-bridges between the adjacent copper atoms.

Zinc and Cadmium Complexes. Mono-ligand complexes of the type $MX_2(pbt)$ (M=Zn; X=Br, I, and M=Cd; X=Cl, Br, I, SCN) have been prepared. The soluble compounds have only small conductances in nitrobenzene. The infrared spectrum of the complex $Cd(SCN)_2(pbt)$ exhibits a single band at 2100 cm^{-1}, indicating that the thiocyanato groups are terminal.[12,13] The bis complexes $Zn(pbt)_2X_2$ (X=SCN, ClO_4) and $Cd(pbt)_2X_2$ (X=I, ClO_4) were isolated. The low conductivity of $Zn(SCN)_2(pbt)_2$ shows that the thiocyanato groups are not ionic and the infrared spectrum shows a single C–N stretch at 2100 cm^{-1}. If the benzothiazole is behaving as a bidentate ligand, then the metal atom is six-coordinate in this complex. The cadmium complex $CdI_2(pbt)_2$ is insoluble.

The infrared spectra of the zinc and cadmium perchlorate complexes both show ν(Cl–O) bands which are split (Table II). The zinc complex is insoluble in nitrobenzene; however, the value of the conductivity of the cadmium complex in this solvent is between that expected for a uni-univalent and a bi-univalent electrolyte. It seems that at least one of the perchlorate groups is coordinated in each of the solid complexes.

Experimental Section

Unless otherwise stated, all compounds were washed with absolute alcohol and dried *in vacuo* over phosphorus pentoxide.

2-(2-Pyridyl)benzothiazole. This compound was prepared as previously reported;[6] m.p. 133.5° (Found: C, 67.9; H, 3.8; N, 12.9. Calcd. for $C_{12}H_8N_2S$: C, 67.9; H, 3.8; N, 13.2%).

Dichloro-2-(2-pyridyl)benzothiazolecobalt(II). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot alcohol (30 ml) was added to a solution of cobalt chloride hexahydrate (0.6 g) in a 1:1 alcohol/2,2′-dimethoxypropane mixture (20 ml). The *compound* deposited as deep blue crystals; yield, 0.6 g (Found: C, 42.2; H, 2.6; Co, 16.9; N, 8.2. $C_{12}H_8Cl_2CoN_2S$ requires C, 42.1; H, 2.4; Co, 17.2; N, 8.2%).

Dibromo-2-(2-pyridyl)benzothiazolecobalt(II). By a similar procedure cobalt bromide hexahydrate (1.1 g) yielded the *bromo-complex* as dark green-blue crystals; yield, 0.8 g (Found: C, 33.0; H, 2.3; N, 6.5. $C_{12}H_8Br_2CoN_2S$ requires C, 33.4; H, 1.9; N, 6.5%).

Dichlorobis[2-(2-pyridyl)benzothiazole]cobalt(II). 2-(2-Pyridyl)benzothiazole (0.9 g) in hot alcohol (60 ml) was added to a solution of cobalt chloride hexahydrate (0.2 g) in a hot 1:1 alcohol/2,2′-dimethoxypropane mixture (10 ml). The *complex* deposited as brown crystals; yield, 0.4 g (Found: C, 51.9; H, 3.2; N, 9.9. $C_{24}H_{16}Cl_2CoN_4S_2$ requires C, 52.0; H, 2.9; N, 10.1%).

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(22) D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*, *4*, 584 (1965).
(23) L. Sacconi and I. Bertini, *Inorg. Chem.*, *5*, 1520 (1966).

Dibromobis[*2-(2-pyridyl)benzothiazole*]*cobalt*(*II*). By a similar procedure cobalt bromide hexahydrate (0.6 g) yielded the *complex* as brown crystals; yield, 1.0 g (Found: C, 45.3; H, 2.6; Co, 9.1; N, 8.4. $C_{24}H_{16}Br_2CoN_4S_2$ requires C, 44.8; H, 2.5; Co, 9.2; N, 8.7%).

Diidobis[*2-(2-pyridyl)benzothiazole*]*cobalt*(*II*). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot alcohol (90 ml) was added to a solution of cobalt nitrate hexahydrate (0.6 g) in a mixture of alcohol (15 ml) and 2,2′-dimethoxypropane (5 ml). Lithium iodide (1 g) was added to the solution, which was then concentrated to 10 ml, whereupon the *complex* deposited as brown crystals; yield, 0.4 g (Found: C, 38.8; H, 2.2; Co, 7.7; N, 7.8. $C_{24}H_{16}CoI_2N_4S_2$ requires C, 39.1; H, 2.2; Co, 8.0; N, 7.6%).

Dithiocyanatobis[*2-(2-pyridyl)benzothiazole*]*cobalt*(*II*). This *compound* was prepared as above except that lithium thiocyanate was substituted for lithium iodide; yield, 0.3 g (Found: C, 51.8; H, 2.8; N, 13.8. $C_{26}H_{16}CoN_6S_4$ requires C, 52.1; H, 2.7; N, 14.1%).

Tetraaqua-2-(2-pyridyl)benzothiazolecobalt(*II*) *Sulphate*. 2-(2-Pyridyl)benzothiazole (0.6 g) in alcohol (30 ml) was added to a solution of cobalt sulphate heptahydrate (0.6 g) in water (20 ml) to give an orange precipitate of the *complex;* yield, 0.6 g (Found: C, 32.6; H, 3.7; N, 6.5; S, 14.5; H_2O, 16.3. $C_{12}H_{26}CoN_2O_8S_2$ requires C, 32.8; H, 3.7; N, 6.4; S, 14.6; H_2O, 16.4%).

Tris[*2-(2-pyridyl)benzothiazole*]*nickel*(*II*) *Perchlorate*. 2-(2-Pyridyl)benzothiazole (0.8 g) in hot acetone (60 ml) was added to a solution of nickel perchlorate hexahydrate (0.4 g) in hot acetone (15 ml). The resulting solution was evaporated to 15 ml and treated with excess 2,2′-dimethoxypropane. The brown oil which separated was isolated and triturated with ether to yield the *complex* as a buff powder; yield, 0.7 g (Found: C, 48.1; H, 3.3; N, 9.2; Ni, 6.5. $C_{36}H_{24}Cl_2N_6NiO_8S_3$ requires C, 48.3; H, 2.7; N, 9.4; Ni, 6.6%).

Dichlorobis[*2-(2-pyridyl)benzothiazole*]*nickel*(*II*). 2-(2-Pyridyl)benzothiazole (0.5 g) in hot alcohol (8 ml) was added to a hot solution of nickel chloride hexahydrate (0.3 g) in a 2:1 2,2′-dimethoxypropane/alcohol mixture (15 ml). To this hot solution was added 2,2′-dimethoxypropane until the solution became turbid. Green crystals formed as the solution cooled. On drying over phosphorus pentoxide, the crystals crumbled to give the *complex* as a hygroscopic green powder; yield, 0.6 g (Found: C, 51.5; H, 3.3; Ni, 10.5; N, 9.9. $C_{24}H_{16}Cl_2N_4NiS_2$ requires C, 52.0; H, 2.9; Ni, 10.6; N, 10.1%).

Dibromobis[*2-(2-pyridyl)benzothiazole*]*nickel*(*II*). 2(-2-Pyridyl)benzothiazole (0.8 g) in hot acetone (50 ml) was added to a solution of nickel bromide trihydrate (0.5 g) in hot 95% acetone (50 ml). A green crystalline product formed which, after drying at 160°, yielded the anhydrous green *complex*; yield, 1.1 g (Found: C, 44.6; H, 2.8; N, 8.8. $C_{24}H_{16}Br_2N_4NiS_2$ requires C, 44.8; H, 2.5; N, 8.7%).

Dithiocyanatobis[*2-(2-pyridyl)benzothiazole*]*nickel*(*II*). 2-(2-Pyridyl)benzothiazole (0.6 g) in hot alcohol (10 ml) was added to a hot solution of nickel nitrate hexahydrate (0.9 g) in alcohol (40 ml). The addition of lithium thiocyanate (1 g) in alcohol (10 ml) produced a green precipitate which was recrystallized from dimethylformamide to yield the complex which contained one and a half molecules of dimethylformamide; yield, 0.5 g (Found: C, 51.7; H, 4.0; N, 14.6. $C_{30.5}H_{26.5}N_{7.5}NiO_{1.5}S_4$ requires C, 51.7; H, 3.7; N, 14.8%). The unsolvated *complex* was obtained by heating the solvated compound to 160° on the thermogravimetric balance. (Loss on heating: 15.0. Calcd. for 1.5 DMF, 15.5%) (Found for unsolvated complex: C, 52.2; H, 2.9; N, 14.0; Ni, 9.6. $C_{26}H_{16}N_6NiS_4$ requires C, 52.1; H, 2.7; N, 14.0: Ni, 9.8%).

Dinitratobis[*2-(2-pyridyl)benzothiazole*]*nickel*(*II*). 2-(2-Pyridyl)benzothiazole (0.5 g) in hot alcohol (8 ml) was added to a hot solution of nickel nitrate hexahydrate (0.15 g) in a 2:1 2,2′-dimethoxypropane/alcohol mixture (15 ml) to give a green precipitate of the *complex;* yield, 0.3 g (Found: C, 47.1; H, 2.7; N, 14.0; Ni, 9.4. $C_{24}H_{16}N_6NiO_6S_2$ requires C, 47.5; H, 2.7; N, 13.8; Ni, 9.7%).

Diacetatodiaqua-2-(2-pyridyl)benzothiazolenickel(*II*). Nickel acetate dihydrate (0.5 g) in hot methanol (100 ml) was added to a solution of 2-(2-pyridyl)benzothiazole (0.4 g) in methanol (20 ml). The solution was concentrated to 5 ml whereupon the green *complex* separated out; yield, 0.15 g (Found: C, 45.0; H, 4.2; N, 6.7; Ni, 14.0. $C_{16}H_{18}N_2NiO_6S$ requires C, 45.2; H, 4.3; N, 6.6; Ni, 13.8%).

Dicholoro-2-(2-pyridyl)benzothiazolenickel(*II*). 2-(2-Pyridyl)benzothiazole (0.5 g) in hot 3:1 alcohol/2,2′-dimethoxypropane mixture (20 ml) was added to a solution of nickel chloride hexahydrate (0.5 g) in the same solvent (10 ml). The solution was concentrated to 25 ml whereupon green crystals deposited; yield, 0.6 g. After drying over phosphorus pentoxide *in vacuo*, this product contained half a molecule of 2,2′-dimethoxypropane (Found: C, 43.8; H, 3.9; N, 7.1. $C_{14.5}H_{14}Cl_2N_2NiOS$ requires C, 44.2; H, 3.6; N, 7.1%). The unsolvated *complex* was obtained by heating the solvated product to 200° on the thermogravimetric balance. (Loss on heating: 12.8; Calcd. for 0.5 DMP, 13.2%) (Found for unsolvated product: C, 41.8; H, 2.6; N, 8.2. $C_{12}H_8Cl_2N_2NiS$ requires C, 42.2; H, 2.4; N, 8.2%).

Tetraaqua-2-(2-pyridyl)benzothiazolenickel(*II*) *Sulphate Hemihydrate*. 2-(2-Pyridyl)benzothiazole (1 g) in hot alcohol (50 ml) was added to a hot solution of nickel sulphate hexahydrate (1.3 g) in water (20 ml) to give a green precipitate of the complex; yield, 1.9 g (Found: C, 32.1; H, 3.8; N, 6.0; Ni, 13.3; S, 14.3; H_2O, 18.3. $C_{12}H_{17}N_2NiS_2O_{8.5}$ requires C, 32.2; H, 3.8; N, 6.25; Ni, 13.1; S, 14.3; H_2O, 18.1%).

Dichloro-2-(2-pyridyl)benzothiazolepalladium(*II*). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot methanol (20 ml) was added to a hot solution of potassium tetrachloropalladate(II) (0.6 g) in water (15 ml), whereupon a yellow hygroscopic product deposited; yield, 0.6 g.

This product was dried at 110° for two hours to give the pure *complex*. (Found: C, 36.7; H, 2.3; N, 7.1; Pd, 26.8. $C_{12}H_8Cl_2N_2PdS$ requires C, 37.0; H, 2.1; N, 7.2; Pd, 27.3%).

Dibromo-2-(2-pyridyl)benzothiazolepalladium(II). 2-(2-Pyridyl)benzothiazole (0.2 g) in hot methanol (10 ml) was added to potassium tetrabromopalladate(II) (0.5 g) in hot water (25 ml). A yellow precipitate of the *bromo-complex* deposited; yield, 0.4 g (Found: C, 30.1; H, 1.9; N, 5.3; Pd, 22.1. $C_{12}H_8Br_2N_2PdS$ requires C, 30.1; H, 1.7; N, 5.85; Pd, 22.2%).

Dithiocyanato-2-(2-pyridyl)benzothiazolepalladium-(II). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot alcohol (50 ml) was added to a hot solution of potassium tetrachloropalladate(II) (0.6 g) and potassium thiocyanate (1 g) in water (40 ml) to give a yellow precipitate of the *complex*; yield, 0.8 g (Found: C, 39.0; H, 1.8; N, 12.7; Pd, 24.0. $C_{14}H_8N_4PdS_3$ requires C, 38.7; H, 1.85; N, 12.9; Pd, 24.5%).

Dinitro-2-(2-pyridyl)benzothiazolepalladium(II). 2-(2Pyridyl)benzothiazole (0.5 g) in hot acetone (50 ml) was added to potassium tetranitropalladate(II) (1 g) in hot water (50 ml) to give a yellow precipitate of the complex; yield, 0.9 g (Found: C, 34.9; H, 2.2; N, 14.0; Pd, 25.9. $C_{12}H_8N_4O_4PdS$ requires C, 35.1; H, 2.0; N, 13.6; Pd, 25.9%).

Dichloro-2-(2-pyridyl)benzothiazoleplatinum(II). 2-(2-Pyridyl)benzothiazole (0.2 g) in hot methanol (10 ml) was added to a hot solution of potassium tetrachloroplatinate(II) (0.5 g) in hot water (20 ml) to yield the *complex* as a yellow precipitate which was recrystallized from acetone; yield, 0.1 g (Found: C, 30.5; H, 2.0; N, 5.7. $C_{12}H_8Cl_2N_2PtS$ requires C, 30.1; H, 1.7; N, 5.9%).

Dibromo-2-(2-pyridyl)benzothiazoleplatinum(II). By a similar procedure potassium tetrabromoplatinate(II) (0.5 g) yielded the yellow *bromo-complex;* yield, 0.4 (Found: C, 25.5; H, 1.6; N, 5.1; Pt, 34.7. $C_{12}H_8Br_2N_2PtS$ requires C, 25.4; H, 1.4; N, 4.9; Pt, 34.4%).

Dithiocyanato-2-(2-pyridyl)benzothiazoleplatinum-(II). By a similar procedure to that used for the preparation of the analogous palladium complex, potassium tetrachloroplatinate(II) (0.8 g) gave a yellow precipitate of the *complex* which was recrystallised from dimethylformamide; yield, 0.2 g (Found: C, 32.3; H, 1.6; N, 10.2. $C_{14}H_8N_4PtS_3$ requires C, 32.1; H, 1.5; N, 10.7%).

Diiodobis[2-(2-pyridyl)benzothiazole]platinum(II). To a filtered solution of potassium tetrachloroplatinate-(II) (0.4 g) and potassium iodide (1 g) in hot water (40 ml) was added 2-(2-pyridyl)benzothiazole (0.4 g) in alcohol (20 ml). The orange *complex* deposited; it was isolated and dried at 100° (Found: C, 33.2; H, 1.8; N, 6.1; Pt, 22.7. $C_{24}H_{16}I_2N_4PtS_2$ requires C, 33.0; H, 1.85; N, 6.4; Pt, 22.3%).

Bis[2-(2-pyridyl)benzothiazole]copper(II) Perchlorate Monohydrate. 2-(2-Pyridyl)benzothiazole (0.6 g) and copper perchlorate hexahydrate (0.7 g) were dissolved in hot alcohol (50 ml). The solution was concentrated to 15 ml, whereupon the *complex* deposited; yield, 0.8 g (Found: C, 40.8; H, 2.7; N, 7.6. $C_{24}H_{18}Cl_2CuN_4S_2O_9$ requires C, 40.9; H, 2.6; N, 7.95%).

Dichloro-2-(2-pyridyl)benzothiazolecopper(II). 2-(2-Pyridyl)benzothiazole (0.7 g) in hot alcohol (50 ml) was added to a hot solution of copper chloride dihydrate (0.7 g) in alcohol (40 ml) Green crystals of the *complex* deposited; yield, 1.5 g (Found: C, 41.4; H, 2.5; N, 7.7. $C_{12}H_8Cl_2CuN_2S$ requires C, 41.6; H, 2.3; N, 8.1%).

Dibromo-2-(2-pyridyl)benzothiazolecopper(II). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot acetone (15 ml) was added to a hot solution of copper bromide (0.5 g) in methanol (50 ml). The *complex* formed as brownish-red crystals; yield, 0.7 g (Found: C, 33.5; H, 2.2; Cu, 14.5; N, 6.3; S, 7.3. $C_{12}H_8Br_2CuN_2S$ requires C, 33.1; H, 1.85; Cu, 14.6; N, 6.4; S, 7.4%).

Dinitrato-2-(2-pyridyl)benzothiazolecopper(II) Monohydrate. Copper nitrate trihydrate (1.1 g) in hot alcohol (50 ml) was added to a hot solution of 2-(2-pyridyl)benzothiazole (0.9 g) in alcohol (60 ml). This solution was concentrated to 20 ml, whereupon the *complex* formed as green crystals; yield, 1 g (Found: C, 34.8; H, 2.6; N, 13.2; H_2O, 4.1. $C_{12}H_{10}CuN_4O_7S$ requires C, 34.6; H, 2.4; N, 13.4; H_2O, 4.3%).

Dithiocyanato-2-(2-pyridyl)benzothiazolecopper(II). This compound was prepared as above except that lithium thiocyanate (2 g) was added before the solution was concentrated. The brown *complex* deposited; yield, 1.7 g (Found: C, 43.0; H, 2.3; Cu, 16.1; N, 14.0. $C_{14}H_8CuN_4S_3$ requires C, 42.9; H, 2.1; Cu, 16.5; N, 14.3%).

Iodo-2-(2-pyridyl)benzothiazolecopper(I). 2-(2-Pyridyl)benzothiazole (0.9 g) in hot methanol (50 ml) was added to a solution of cuprous iodide (0.9 g) in hot methanol (60 ml) which contained excess lithium iodide. The *complex* formed as brown crystals; yield, 1.2 g (Found: C, 35.9; H, 2.2; Cu, 16.0; N, 6.9. $C_{12}H_8CuIN_2S$ requires C, 35.8; H, 2.0; Cu, 15.8; N, 7.0%).

Bis[2-(2-pyridyl)benzothiazole]zinc(II) Perchlorate Monohydrate. 2-(2-Pyridyl)benzothiazole (0.6 g) in hot alcohol (25 ml) was added to a solution of zinc perchlorate hexahydrate (0.5 g) in hot alcohol (10 ml). The *complex* formed as pale yellow crystals; yield, 0.8g (Found: C, 41.2; H, 2.9; N, 7.4; S, 8.7. $C_{24}H_{18}Cl_2N_4O_9S_2Zn$ requires C, 40.8; H, 2.6; N, 7.9; S, 9.1%).

Dibromo-2-(2-pyridyl)benzothiazolezinc(II). 2-(2-Pyridyl)benzothiazole (0.3 g) in hot alcohol (65 ml) was added to a hot solution of zinc nitrate hexahydrate (0.5 g) in water (10 ml). To this solution was added lithium bromide (1 g) in alcohol (10 ml), whereupon the *complex* formed as a pale yellow precipitate; yield, 0.6 g (Found: C, 32.8; H, 2.1; N, 6.4; S, 6.8. $C_{12}H_8Br_2N_2SZn$ requires C, 32.95; H, 1.8; N, 6.4; S, 7.3%).

Diiodo-2-(2-pyridyl)benzothiazolezinc(II). By a similar method lithium iodide in the place of lithium bromide gave the pale yellow *iodo-complex*; yield, 0.9 g (Found: C, 27.5; H, 1.8; N, 5.0; Zn, 11.8. $C_{12}H_8I_2N_2SZn$ requires C, 27.1; H, 1.5; N, 5.3; Zn, 12.3%).

Dithiocyanatobis[2-(2-pyridyl)benzothiazole]zinc(II). 2-(2-Pyridyl)benzothiazole (0.3 g) in hot alcohol (65 ml) was added to a solution of zinc nitrate hexahydrate (0.5 g) in hot water (10 ml). To this solution was added lithium thiocyanate (1 g) in alcohol (10 ml), and the volume was then reduced to 10 ml, whereupon the *complex* deposited; yield, 0.3 g (Found: C, 51.5; H, 2.8; N, 14.2; S, 21.0. $C_{26}H_{16}N_6S_4Zn$ requires C, 51.5; H, 2.7; N, 13.9; S, 21.2%).

Bis[2-(2-pyridyl)benzothiazole]cadmium(II) Perchlorate. By a similar method to that used to prepare the zinc perchlorate complex, 2-(2-pyridyl)benzothiazole (0.5 g) and cadmium perchlorate hexahydrate (0.5 g) yielded the crystalline *complex*; yield, 0.6 g (Found: C, 38.9; H, 2.4; N, 7.7. $C_{24}H_{16}CdCl_2N_4O_8S_2$ requires C, 39.2; H, 2.2; N, 7.6%).

Diiodobis[2-(2-pyridyl)benzothiazole]cadmium(II). 2-(2-Pyridyl)benzothiazole (1 g) in hot alcohol (65 ml) was added to a solution of cadmium nitrate tetrahydrate (1.3 g) in hot water (10 ml). To this solution was added lithium iodide (2 g) in alcohol (5 ml) and the volume was then reduced to 20 ml. The *complex* formed as pale yellow flakes; yield, 0.3 g (Found: C, 35.9; H, 1.9; N, 6.9; S, 7.6. $C_{24}H_{16}CdI_2N_4S_2$ requires C, 36.45; H, 2.0; N, 7.1; S, 8.1%).

Dichloro-2-(2-pyridyl)benzothiazolecadmium(II). 2-(2-Pyridyl)benzothiazole (0.4 g) in hot methanol (25 ml) was added to a solution of cadmium chloride two and a half hydrate (0.22 g) in hot methanol (40 ml). The *complex* formed as a pale yellow precipitate; yield, 0.6 g (Found: C, 36.5; H, 2.3; Cd, 27.9; N, 7.4. $C_{12}H_8Cl_2CdN_2S$ requires C, 36.4; H, 2.0; Cd, 28.4; N, 7.1%).

Dibromo-2-(2-pyridyl)benzothiazolecadmium(II). 2-(2-Pyridyl)benzothiazole (1 g) in hot alcohol (65 ml) was added to a solution of cadmium nitrate tetrahydrate (1.3 g) in hot water (10 ml). To this solution was added lithium bromide (2 g) in alcohol (5 ml). The *complex* formed as pale yellow flakes; yield, 1.5 g (Found: C, 29.7; H, 1.9; Cd, 23.1; N, 5.8. $C_{12}H_8Br_2CdN_2S$ requires C, 29.75; H, 1.7; Cd, 23.2; N, 5.8%).

Diiodo-2-(2-pyridyl)benzothiazolecadmium(II). Cadmium nitrate tetrahydrate (1.5 g) in hot water (5 ml) was treated with 2-(2-pyridyl)benzothiazole (0.5 g) in hot alcohol (35 ml). The solution was filtered and excess lithium iodide was added to the filtrate to yield the *complex* as orange-yellow crystals; yield, 1.2 g (Found: C, 25.3; H, 1.5; Cd, 19.3; N, 5.3. $C_{12}H_8CdI_2N_2S$ requires C, 24.9; H, 1.4; Cd, 19.4; N, 4.8%).

Dithiocyanato-2-(2-pyridyl)benzothiazolecadmium(II). The *thiocyanato complex* was prepared by a similar method to the bromo complex except that lithium thiocyanate was substituted for lithium bromide; yield, 0.6 g (Found: C, 38.3; H, 2.0; N, 12.5; S, 21.6. $C_{14}H_8CdN_4S_3$ requires C, 38.1; H, 1.8; N, 12.7; S, 21.8%).

Analyses. Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne.

Spectra. The visible-ultraviolet spectra were measured on a Zeiss PMQII spectrophotometr. The infrared spectra were obtained from nujol or halocarbon mulls on a Perkin-Elmer 337 spectrophotometer.

Thermogravimetric Measurements. The measurements were made on a Stanton thermobalance model TR-01.