Complexes of Pyrimidine-2-thione with some Bivalent Metal Halides of the First Transition Series

By **John Abbot, David M. L. Goodgame,*** and **Ian Jeeves,** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The preparations are reported of complexes of pyrimidine-2-thione (Hpymt) with halides of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II}. The complexes have stoicheiometry ML_2X_2. A combination of *X*-ray, electronic spectral, i.r., e.s.r., and, for iron, Mössbauer studies shows that, in most cases, the sulphur atom, as well as the non-protonated ring nitrogen atom, of the thione ligand co-ordinates to the metal to give a four-membered chelate ring. Some inner complexes $[M(pymt)_2]$ (M = Co, Ni, or Zn) are also reported.

To complement our work [1] on the co-ordination of heavy metal ions to nucleotides and related components of nucleic acids we have examined a wide range of substituted pyrimidines and purines as ligands. Those bases containing sulphur atoms form a particularly interesting group. The thio-bases 2- and 4-thiouracil (uracil = pyrimidine-2,4-diol) and 2-thiocytosine (cytosine = 4-aminopyrimidin-2-ol) are normal constituents of some t-RNA species,[2-4] but their function is not well understood. They appear to be essential components, but they can, under certain conditions, inhibit RNA synthesis, leading to anti-tumour and anti-thyroid activity.[5-7] A similar inhibitory behaviour has been found [8] for pyrimidine-2-thione (Hpymt).

Pyrimidinethiones are also of interest because of their potentially ambidentate ligand nature. 2-Thiouracil has been reported [9] to co-ordinate *via* N and S or N and O, the particular mode of co-ordination being influenced

TABLE 1

Analytical and low-frequency i.r. data for complexes of pyrimidine-2-thione

Complex	Colour	Analysis (%) [a] C	H	N	I.r. bands (cm^{-1}) ν(M–X)	ν(M–L)
$Mn(Hpymt)_2Cl_2$	Yellow	27.6 (27.4)	2.4 (2.3)	16.1 (16.0)	210br, 228br	*b*
$Mn(Hpymt)_2Br_2$	Yellow	21.9 (21.9)	2.0 (1.8)	12.9 (12.8)	166, 180(sh)	231
$Fe(Hpymt)_2Cl_2$	Dark brown	27.4 (27.35)	2.55 (2.3)	15.8 (16.0)	215, 238(sh)	250(sh)
$Fe(Hpymt)_2Br_2$	Dark brown	22.0 (21.8)	1.8 (1.8)	12.8 (12.7)	168, 177(sh)	246
$Co(Hpymt)_2Cl_2$	Dark green	27.1 (27.1)	2.3 (2.3)	15.8 (15.8)	232, 246(sh)	261
$Co(Hpymt)_2Br_2$	Dark green	22.0 (21.7)	1.7 (1.8)	12.8 (12.65)	176, 188(sh)	254
$Co(pymt)_2$	Red	34.0 (34.2)	2.3 (2.15)	19.65 (19.9)		
$Ni(Hpymt)_2Cl_2$	Yellow-green	27.5 (27.15)	2.65 (2.3)	15.75 (15.8)	204(sh), 216	265
$Ni(Hpymt)_2Br_2$	Deep yellow	22.1 (21.7)	2.2 (1.8)	12.9 (12.65)	179, 205 [c]	265
$Ni(pymt)_2$	Yellow-green	34.35 (34.2)	2.1 (2.15)	20.2 (19.9)		
$Zn(Hpymt)_2Cl_2$	Pale yellow	26.7 (26.45)	2.2 (2.2)	15.9 (15.5)	238, 252	260(sh)
$Zn(pymt)_2$	Pale yellow	33.7 (33.4)	2.0 (2.1)	19.7 (19.5)		
$Cd(Hpymt)_2Cl_2$	Pale yellow	23.7 (23.6)	2.0 (2.0)	13.8 (13.75)		
$Cd(Hpymt)_2Br_2$	Pale yellow	19.4 (19.35)	1.6 (1.6)	11.3 (11.3)		
$Cd(Hpymt)_2I_2$	Cream	16.2 (16.3)	1.4 (1.4)	9.55 (9.5)		

[a] Calculated values are given in parentheses. [b] ν(M–L) presumed hidden under strong, broad, ν(Mn–Cl) bands. [c] Tentative assignment (see text).

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[1] B. A. Cartwright, D. M. L. Goodgame, I. Jeeves, and A. C. Skapski, *Biochim. Biophys. Acta*, 1977, **477**, 195 and refs. therein.

[2] J. A. Carbon, L. Hung, and D. S. Jones, *Proc. Nat. Acad. Sci. U.S.A.*, 1965, **53**, 979.

[3] M. N. Lipsett, *Biochem. Biophys. Res. Comm.*, 1965, **20**, 224.

[4] J. A. Carbon, H. David, and M. H. Studier, *Science*, 1968, **161**, 1146.

[5] J. F. Holland, R. Guthrie, P. Sheeke, and H. Tieckelmann, *Cancer Res.*, 1958, **18**, 776.

[6] C. B. Lozzio, *Exp. Cell Res.*, 1971, **69**, 377; *J. Cell Physiol.*, 1971, **78**, 25.

[7] M. Y. W. Yu, J. Sedlak, and R. H. Lindsay, *Arch. Biochem. Biophys.*, 1973, **155**, 111.

[8] I. Votruba, A. Holý, and K. Jošt, *F.E.B.S. Letters*, 1972, **22**, 287; A. Holý, I. Votruba, and K. Jošt, *Coll. Czech. Chem. Comm.*, 1974, **39**, 634.

[9] I. P. Khuller and U. Agarwala, *Austral. J. Chem.*, 1974, **27**, 1877; 1975, **28**, 1529; *Indian J. Chem.*, 1974, **12**, 1096.

by the nature of the metal atom and by the extent of deprotonation of the base. Moreover, the formation of a four-membered chelate ring involving N and S as donor atoms has been demonstrated with anionic 4,6-dimethylpyrimidine-2-thione [10] as well as with deprotonated pyridine-2-thione.[11–13]

We report here the synthesis of some complexes of Hpymt with some first-row transition-metal ions, and structural and spectral studies on them to determine the extent to which the sulphur atom takes part in co-ordination.

RESULTS AND DISCUSSION

The solid complexes we have isolated are listed in Table 1. Attempts were made to prepare complexes with relatively non-co-ordinating anions, such as perchlorate, but the analytical results on the products were poor and irreproducible. Inner complexes of formula [M(pymt)$_2$] could, however, be readily isolated using the corresponding metal acetate as starting material. Copper(II) complexes could not be prepared because of the reducing power of the thione ligand.

Room-temperature magnetic moments and reflectance spectral band energies of the iron, cobalt, and nickel complexes are given in Table 2. The results for the cobalt halide complexes Co(Hpymt)$_2$X$_2$ (X = Cl or Br) are, at first sight, similar to those of well established distorted tetrahedral complexes such as [Co(quinoline)$_2$X$_2$]. The magnetic moments are in the range usually observed for such a geometry, although toward the higher end of that range, and the electronic spectra (Figure 1) have an intense multicomponent band at 15 000—17 000 cm^{-1} and bands of medium intensity in the near-i.r. region. However, the splitting of the band components below 12 000 cm^{-1} is much greater than expected [14] for a tetrahedral CoN$_2$X$_2$ chromophore. Indeed, as may be seen from Figure 1, the spectrum of Co(Hpymt)$_2$Cl$_2$ is quite similar to that [15] of the distorted six-co-ordinate [16] complex [Co(PPh$_3$O)$_2$(NO$_3$)$_2$], although for the latter all the bands are at somewhat higher energy.

TABLE 2

Magnetic moments and reflectance spectral band energies of some complexes of pyrimidine-2-thione

Complex	$\mu_{eff.}$ [a]/B.M.	Reflectance spectra (cm^{-1})
Fe(Hpymt)$_2$Cl$_2$	5.25	5 480, 8 200
Fe(Hpymt)$_2$Br$_2$	5.42	5 120, 8 770
Co(Hpymt)$_2$Cl$_2$	4.62	5 530, 6 640, 10 530, 15 630, 17 240
Co(Hpymt)$_2$Br$_2$	4.75	5 240, 6 150, 11 490, 14 810, 17 180
Ni(Hpymt)$_2$Cl$_2$	3.21	8 260, 13 610 [b]
Ni(Hpymt)$_2$Br$_2$	3.20	8 260, 13 510 [b]
Co(pymt)$_2$		5 200br,w, 10 100br, 18 350
Ni(pymt)$_2$		8 970, 15 270(sh) [b]

[a] At room temperature. 1 B.M. ≈ 9.27 × 10^{-24} A m^2. [b] Higher-energy region obscured by intense electron-transfer transition.

Since the spectral evidence indicated a distortion from tetrahedral toward octahedral co-ordination, and therefore some degree of Co–S bonding, a crystal-structure determination was carried out [17] on Co(Hpymt)$_2$Cl$_2$.

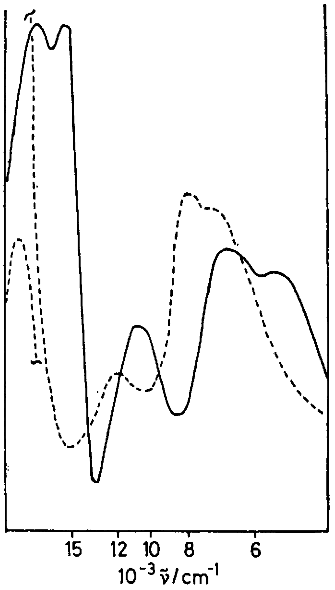

FIGURE 1 Reflectance spectra of Co(Hpymt)$_2$Cl$_2$ (——) and [Co(PPh$_3$O)$_2$(NO$_3$)$_2$] (– – –)

TABLE 3

Selected bond angles and bond lengths of the Co(Hpymt)$_2$Cl$_2$ molecule with estimated standard deviations in parentheses

Angles (°)	
Cl–Co–Cl′	98.58(7)
Cl–Co–S	89.36(5)
Cl–Co–N(1)	105.26(14)
Cl–Co–N(1′)	99.10(13)
Cl–Co–S′	158.18(3)
S–Co–S′	90.65(6)
S–Co–N(1′)	93.39(14)
S–Co–N(1)	59.12(13)
N(1)–Co–N(1′)	142.32(17)
S–C(2)–N(1)	116.2(3)
Co–N(1)–C(2)	111.8(3)
C(2)–S–Co	71.9(2)
Lengths (nm)	
Co–Cl	0.2369(2)
Co–S	0.2960(2)
Co–N(1)	0.2098(4)
N(1)–C(2)	0.1388(8)

Full crystallographic details will be published elsewhere [18] but the main features of the molecular geometry

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[10] B. A. Cartwright, D. M. L. Goodgame, I. Jeeves, P. D. Langguth, jun., and A. C. Skapski, *Inorg. Chim. Acta*, 1977, **24**, L45.

[11] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.

[12] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3224.

[13] C. K. Brown, D. Georgiou, and G. Wilkinson, *J.C.S. Dalton*, 1973, 929.

[14] See, for example, D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4**, 139.

[15] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.

[16] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

[17] J. C. McConway, Ph.D. Thesis, University of London, 1975.

[18] J. C. McConway and D. Rogers, unpublished work.

relevant to the present discussion are shown in Figure 2 and listed in Table 3.

The co-ordination about the cobalt atom is best described as very distorted octahedral. It is far from tetrahedral, as shown by the large N(1)–Co–N(1′) angle of *ca.* 142°. The Co–Cl and Co–N bond lengths are, moreover, appreciably greater than those found[19] for essentially tetrahedral [CoL_2Cl_2] molecules involving nitrogen-donor ligands L {*e.g.* for [$Co(imidazole)_2Cl_2$]: Co–Cl 2.24 and 2.26 Å, Co–N 2.00 and 1.99 Å (ref. 19*a*)}. However, the Co–S distance is too long for it to be regarded as a strong bond, and Co–Cl is shorter than might be expected for a truly six-co-ordinate cobalt(II) complex {*cf.* Co–S 2.50 and 2.53, Co–Cl 2.47 Å for [$Co(thiourea)_4Cl_2$] [20]}. Further geometrical evidence for a definite, although weak, Co–S bonding interaction is provided by the S–C(2)–N(1) angle of 116.2° and the Co–N(1)–C(2) angle of 111.8°.

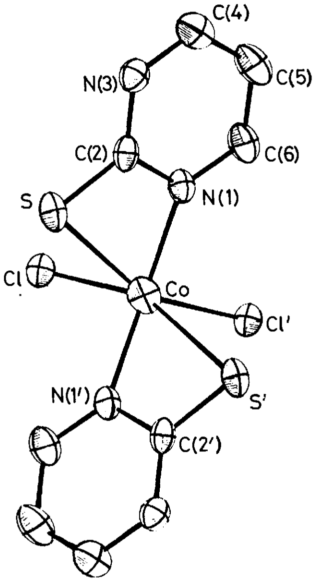

FIGURE 2 Molecular structure of $Co(Hpymt)_2Cl_2$

The electronic spectrum of the cobalt bromide complex is similar to that of the chloride but with somewhat greater band splittings, so it presumably has the same type of structure.

X-Ray powder photographs of the halide complexes of manganese, iron, and nickel were alike; the patterns of the cobalt complexes were similar to those of the other three metals, but were not close enough to establish isomorphism.

The electronic spectra of the iron(II) complexes show two intense bands in the near-i.r. region (Table 2, Figure 3). The spectra are unlike those of pseudo-tetrahedral iron(II) complexes such as $Fe(quinoline)_2Cl_2$ [21] in that one band is at relatively high energy (8 000—9 000 cm^{-1}) for such a geometry. The band energies resemble more closely those of six-co-ordinate complexes involving two stronger and four weaker donors as in polymeric halide-bridged complexes such as [{$Fe(4CN\text{-}py)_2Cl_2$}$_n$] (py = pyridine) which has bands[22] at 9 850 and 6 250 cm^{-1}. However, the bands of $Fe(Hpymt)_2X_2$ are much stronger than those of the polymeric species (Figure 3), pointing to a non-centrosymmetric co-ordination geometry. These observations are consistent with a molecular structure generally similar to that observed for $Co(Hpymt)_2Cl_2$, with weak Fe–S interaction producing a relatively weak ligand field intermediate between distorted octahedral and tetrahedral.

Further support for this is provided by the Mössbauer spectrum of $Fe(Hpymt)_2Cl_2$, which, at room temperature, consists of a quadrupole-split doublet (Δ 3.05 mm s^{-1}) with an isomer shift, δ, of 0.99 mm s^{-1} relative to iron metal. This isomer-shift value lies between the range found (1.10—1.22 mm s^{-1}) for six-co-ordinate high-spin iron(II) [FeL_2X_2] complexes containing halide bridges[23] and those for tetrahedral [FeL_2]X_2 compounds involving *N*-donor (0.78—0.87 mm s^{-1})[24] or *S*-donor (0.71—0.81 mm s^{-1})[25] ligands.

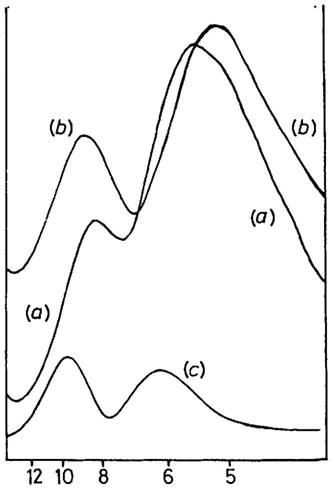

FIGURE 3 Reflectance spectra of (*a*) $Fe(Hpymt)_2Cl_2$, (*b*) $Fe(Hpymt)_2Br_2$, and (*c*) $Fe(4CN\text{-}py)_2Cl_2$

A polymeric structure involving halide bridges can also be ruled out for the $Mn(Hpymt)_2X_2$ (X = Cl or Br) complexes, since their *X*-band e.s.r. spectra (Figure 4) do not show the simple $g_{eff.} = 2$ type of spectrum observed[26] for such polymers (because of the consequent

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[19] (*a*) C. J. Antti and B. K. S. Lundberg, *Acta Chem. Scand.*, 1972, **26**, 3995; (*b*) M. Laing and G. Carr, *Acta Cryst.*, 1975, **B31**, 2683.

[20] J. E. O'Connor and E. L. Amma, *Inorg. Chem.*, 1969, **8**, 2367.

[21] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 454.

[22] D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, 1966, **5**, 635.

[23] T. Birchall and M. F. Morris, *Canad. J. Chem.*, 1972, **50**, 201.

[24] C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (*A*), 1968, 1074.

[25] T. Birchall and M. F. Morris, *Canad. J. Chem.*, 1972, **50**, 211; F. Petillon, J. E. Guerchais, and D. M. L. Goodgame, *J.C.S. Dalton*, 1973, 1209.

[26] R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame, and P. J. Hayward, *Nature*, 1968, **219**, 1037.

magnetic concentration). Instead, they show fine structure due to zero-field splitting, with bands well away from the $g = 2$ region. The breadth of the bands precludes accurate determination of the zero-field splitting parameters, D and E, but, for the bromide, numerical analysis followed by computer simulation * of the spectrum (Figure 4) suggests $D \sim 0.2$ cm^{-1} and λ ($= E/D$) ~ 0.25. The shift of the main band to higher field in the spectrum of the chloride indicates that this complex has a lower D value (*ca.* 0.09—0.1 cm^{-1}). A similar lowering of D on changing from bromide to chloride in related complexes has been observed previously for both distorted octahedral [27] and tetrahedral [28] geometries.

The electronic spectra of the solid complexes Ni(Hpymt)$_2$X$_2$ (X = Cl or Br) are virtually identical and are somewhat unusual. As may be seen from Figure 5 they are unlike those of tetrahedral complexes such as [Ni(quinoline)$_2$Cl$_2$] or of six-co-ordinate [NiL$_2$X$_2$] complexes containing halide bridges such as [Ni(pyridine)$_2$Cl$_2$]. The bands are relatively intense, again suggesting a non-centrosymmetric ligand environment about the metal ion, and the greater intensity of the band at 8 260 cm^{-1} compared with the band in the visible region is unusual. If, here too, the geometry involves distorted octahedral co-ordination of a N$_2$S$_2$Cl$_2$ donor set, then the band intensities and energies are understandable.

The electronic spectrum of the inner complex [Co(pymt)$_2$] suggests that the metal atom is tetrahedrally surrounded by nitrogen atoms as in bis(benzimidazolato)cobalt(II).[29] However, the spectrum of [Ni(pymt)$_2$] indicates octahedral co-ordination, so in this case the sulphur atoms are also bonded to the metal.

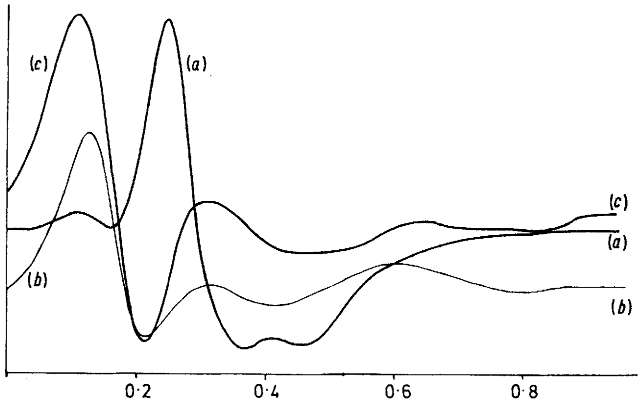

FIGURE 4 X-Band e.s.r. spectra of (*a*) Mn(Hpymt)$_2$Cl$_2$, (*b*) Mn(Hpymt)$_2$Br$_2$, and (*c*) computed simulation of (*b*) with D = 0.2 cm^{-1} and λ = 0.25

Further information in support of postulated distorted six-co-ordinate structures for the manganese, iron, and nickel halide complexes is provided by their metal–halogen stretching frequencies (Table 1). From its structure, two ν(Co–Cl) bands would be expected for the complex Co(Hpymt)$_2$Cl$_2$. By comparison with the spectra of the free ligand and the bromide analogue, the ν(Co–Cl) bands may be clearly assigned at 232 and 246 cm^{-1}, with the ν(Co–Br) bands at 176 and 188 cm^{-1}. In each case these wavenumbers are well below those reported [30] for tetrahedral [CoL$_2$X$_2$] complexes, although above those found for polymeric [{CoL$_2$X$_2$}$_n$] with halide bridges.[31] This range of wavenumbers for ν(Co–Cl) is in accord with the observed bond lengths. The low-frequency i.r. spectra of the manganese, iron, and nickel halide complexes are completely analogous to those of the cobalt complexes, except for the nickel bromide complex for which the band at 205 cm^{-1} assigned as ν(Ni–Br) in Table 1 seems rather high compared with the other ν(M–Br) bands. These i.r. results support the conclusions from other physical measurements that the halide complexes contain a distorted octahedral N$_2$S$_2$X$_2$ donor set.

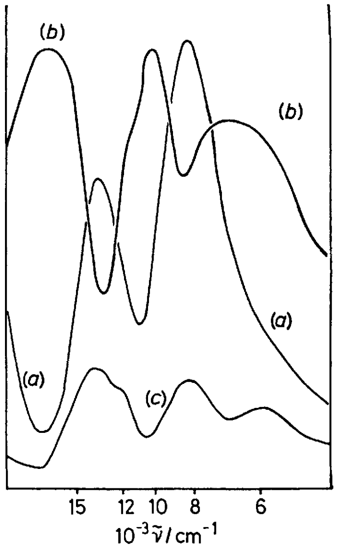

FIGURE 5 Reflectance spectra of (*a*) Ni(Hpymt)$_2$Cl$_2$, (*b*) Ni(quinoline)$_2$Cl$_2$, and (*c*) Ni(py)$_2$Cl$_2$

The ν(Zn–Cl) bands are at higher energies than ν(M–Cl) for any of the other complexes. Although the values (238 and 252 cm^{-1}) are still below those normally associated [30,32] with tetrahedral [ZnL$_2$Cl$_2$] complexes, this higher frequency may well indicate that the sulphur atoms are interacting less strongly with zinc than with the other metal ions, permitting a closer approach to distorted tetrahedral geometry.

The bands assigned as ν(M–L) in Table 1 probably have

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* Using the program SHAPE 9.

[27] R. D. Dowsing, J. F. Gibson, M. Goodgame, and P. J. Hayward, *J. Chem. Soc.* (*A*), 1969, 187.

[28] R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame, and P. J. Hayward, *J. Chem. Soc.* (*A*), 1969, 1242.

[29] M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, 1962, **84**, 1543.

[30] J. R. Ferraro, ' Low Frequency Vibrations of Inorganic and Coordination Compounds,' Plenum, New York, 1971.

[31] C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatako, and K. Nakamoto, *Inorg. Chem.*, 1969, **8**, 1851.

[32] D. M. L. Goodgame, M. Goodgame, and G. W. Rayner Canham, *Inorg. Chim. Acta*, 1969, **3**, 406.

an appreciable contribution of ν(M–N) character, since the Co–S distance found for the cobalt chloride complex suggests that ν(Co–S) would occur at very low frequencies. However, the ν(M–L) bands cannot, of course, be assigned as pure M–N stretching frequencies.

EXPERIMENTAL

Preparations.—Dried and deoxygenated solvents were used throughout. The general method of preparation was to treat the appropriate metal halide (2 mmol) with a deficit (3.2—3.5 mmol) of pyrimidine-2-thione in hot stirred ethanol. Because of the poor solubility of the thione, it was generally necessary to avoid a large solvent volume by using a solution or suspension of the thione and heating and stirring until reaction was complete. The products were filtered off under nitrogen, washed with ethanol and diethyl ether, and dried *in vacuo* over P_4O_{10}. The iron(II) complexes were prepared under nitrogen throughout. The inner complexes [M(pymt)$_2$] (M = Co or Ni) were prepared as for the halides but using the corresponding metal acetate. Analyses were by the Microanalytical Laboratory, Imperial College.

Physical Measurements.—Diffuse-reflectance spectra were recorded on Beckman DK2 and Cary 14 spectrometers, i.r. spectra on Perkin-Elmer 325 (200—4 000 cm^{-1}) and Beckman FS 720 (40—400 cm^{-1}) spectrometers. Magnetic susceptibilities were determined using the Evans modification [33] of the Gouy–Rankine balance. *X*-Band e.s.r. spectra were obtained as described previously.[28] *X*-Ray powder photographs were taken by Dr. R. S. Osborn of the University of London Intercollegiate *X*-ray service. The Mössbauer spectrum of Fe(Hpymt)$_2$Cl$_2$ was recorded by Mr. E. Niven.

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[33] D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 1670; *J. Phys.* (*E*), 1974, **7**, 247.