Versatility of the Co-ordination Behaviour of 1-Methylpyrimidine-2-thione towards Metal Ions of the First Transition Series

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The preparations are reported of complexes of 1-methylpyrimidine-2-thione (L) with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. A combination of *X*-ray, electronic spectral, i.r., and e.s.r. studies has been employed to deduce the co-ordination geometries. The complexes $[ML_4][ClO_4]_2{\cdot}2Me_2CO$ (M = Mn, Co, or Zn) contain tetrahedral $[ML_4]^{2+}$ ions with L co-ordinated *via* N. Zero-field splitting parameters have been evaluated for the manganese complex. The thione ligand chelates *via* N and S in a range of complexes such as $[CoL_3][ClO_4]_2$, $[CuLX_2]$ (X = Cl or Br) and, with varying degrees of distortion, in metal halide complexes ML_2X_2 (M = Mn, Co, or Ni). Copper(II) perchlorate or tetrafluoroborate are reduced by L to give $Cu^{I}{}_2L_3X_2$ (X = ClO_4 or BF_4).

As a continuation of our studies [1,2] on the co-ordination behaviour of pyrimidinethione derivatives with heavy-metal ions we report here some complexes of 1-methylpyrimidine-2-thione (L). Since we had previously found [1] that the parent ligand pyrimidine-2-thione co-ordinated to some first-row transition-metal ions strongly by the unprotonated ring nitrogen and more weakly by the exocyclic sulphur atom, to give a four-membered chelate

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[1] J. Abbot, D. M. L. Goodgame, and I. Jeeves, *J.C.S. Dalton*, 1978, 880.

[2] D. M. L. Goodgame and G. A. Leach, *Inorg. Chim. Acta*, 1977, **25**, L127.

ring, we were interested to see what effect *N*-methylation would have on the co-ordination by sulphur with these same metal ions.

The introduction of an *N*-methyl group would produce a steric effect tending to increase the extent of metal–sulphur interaction, but, opposing this, 1-methylpyrimidine-2-thione can no longer have some thiol character and thus, compared with pyrimidine-2-thione (pymt), the tendency towards *S*-co-ordination should be diminished.

TABLE 1

Analytical and low-frequency i.r. data for the complexes of 1-methylpyrimidine-2-thione

		Analysis (%)						Infrared bands (cm^{-1})	
		Found			Calc.				
Complex	Colour	C	H	N	C	H	N	ν(M-X)	ν(M-L)
[MnL_2Cl_2]	Yellow	31.5	3.0	14.6	31.8	3.2	14.8	256s,br	*a*
[MnL_2Br_2]	Orange-yellow	26.1	2.8	12.1	25.7	2.6	12.0	213	233
[MnL_4][ClO_4]$_2$·2 Me_2CO	Yellow	36.3	4.3	13.6	35.7	4.15	12.8		218
[CoL_2Cl_2]	Dark green	32.55	3.4	15.0	31.4	3.2	14.7	288, 270	*a*
[CoL_2Br_2]	Dark green	25.75	2.4	12.0	25.5	2.6	11.9	221	*a*
[CoL_4][$CoBr_4$]	Red	26.2	2.6	11.65	25.5	2.6	11.9	225vs	*a*
$CoL_2(NO_3)_2(OH_2)_2$	Orange-brown	25.9	3.5	18.3	25.65	3.2	17.9		*b*
[$CoL_2(OH_2)_2$][ClO_4]$_2$	Orange-brown	22.3	2.9	10.35	22.4	2.8	10.4		*b*
[CoL_3][ClO_4]$_2$	Brown	28.3	3.1	13.1	28.3	2.85	13.2		
[CoL_4][ClO_4]$_2$·2 Me_2CO	Red	35.8	4.1	13.8	35.5	4.1	12.75		224
[NiL_2Cl_2]	Yellow-green	31.7	3.1	14.4	31.4	3.2	14.7	284	*a*
[NiL_2Br_2]	Yellow-brown	25.6	2.6	12.0	25.5	2.6	11.9	203	261 [c]
$NiL_3(NO_3)_2$	Green	32.4	3.5	20.4	32.1	3.2	20.0		
[$CuLCl_2$]	Light green	23.6	2.3	10.9	23.0	2.3	10.75	318, 299	*a*
[$CuLBr_2$]	Pink–brown	18.4	1.8	7.7	17.2	1.7	8.0	268, 244	*a*
$Cu_2L_3(ClO_4)_2$	Red	25.9	2.5	11.9	25.6	2.6	11.9		
$Cu_2L_3(BF_4)_2$	Red	26.35	2.8	12.15	26.5	2.7	12.4		
[ZnL_4][ClO_4]$_2$·2Me_2CO	Yellow	35.3	4.0	13.0	35.3	4.1	12.7		210

[a] Not observed. [b] Band at 356 cm^{-1} assigned as ν(Co—OH_2). [c] Tentative assignment (see text).

TABLE 2

Reflectance spectral band energies (cm^{-1}) of some complexes of 1-methylpyrimidine-2-thione (L)

[CoL_4][ClO_4]$_2$·2 Me_2CO	18 350	10 420	*a*	
[CoL_4][$CoBr_4$]	18 350	14 300	10 260	5 000 [b]
[CoL_3][ClO_4]$_2$	18 690	8 475		
[$CoL_2(OH_2)_2$][ClO_4]$_2$	*ca.* 19 000(sh) [c]	*ca.* 16 800(sh)	*ca.* 10 500(sh)	7 810
$CoL_2(NO_3)_2(OH_2)_2$	*ca.* 18 600(sh) [c]	*ca.* 15 700(sh)	8 260	
[CoL_2Cl_2]	16 400 [d]	10 400	6 500	*ca.* 5 360br,(sh)
[CoL_2Br_2]	17 240	15 800	7 520	5 500
$NiL_3(NO_3)_2$	*e*	16 500	9 250	
[NiL_2Cl_2]	*ca.* 21 400(sh) [c]	13 800	8 360	
[NiL_2Br_2]	*e*	13 700	8 330	
[$CuLCl_2$]	12 900			
[$CuLBr_2$]	20 800	12 900		

[a] Possible weak electronic absorption (ν_1?) in the 5 000—6 000 cm^{-1} region, but assignment uncertain because of vibrational bands. [b] Centre of gravity of broad multicomponent peak; see for example, ref. 11. [c] On edge of strong u.v. band. [d] Centre of gravity of multicomponent peak. [e] Expected band not resolved from strong u.v. band.

RESULTS AND DISCUSSION

The complexes isolated are listed in Table 1. We shall discuss first the results for the perchlorates and nitrates.

The perchlorates of Mn^{II}, Co^{II}, and Zn^{II} each formed a complex of stoicheiometry $ML_4(ClO_4)_2$·2Me_2CO, and for cobalt 3 : 1 and hydrated 2 : 1 complexes were also obtained. Attempts to isolate a solid complex of nickel perchlorate were unsuccessful. The thione ligand reduced copper(II) perchlorate and tetrafluoroborate to give red crystals of the copper(I) complexes $Cu_2L_3X_2$ (X = ClO_4 or BF_4).

The general form of the electronic spectrum of solid $CoL_4(ClO_4)_2$·2Me_2CO (Table 2) suggested that the metal ion was tetrahedrally surrounded by nitrogen atoms with a very strong value of 10*Dq* (6 280 cm^{-1}, B' = 660 cm^{-1}; parameters calculated using equations quoted in ref. 3). Since *X*-ray powder photographs showed that the complexes $ML_4(ClO_4)_2$·2Me_2CO (M = Mn, Co, or Zn) are isomorphous, and good crystals of the zinc complex could be obtained, a single-crystal structural determination of the zinc complex has been carried out by Mr. K. A. Woode of this Department. Full crystallographic details will be published elsewhere,[4] but we note here that the *X*-ray study confirms that in these complexes only the free ring-nitrogen atoms of the thione ligands are co-ordinated to the metal, with a geometry very close to tetrahedral (Zn–N 2.06 Å; N–Zn–N 107—113°, mean 109.9°). The zinc–nitrogen bond length is slightly longer than those found[5] for other tetrahedral zinc complexes, because of steric interactions between the

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[3] F. A. Cotton and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777.

[4] A. C. Skapski and K. A. Woode, unpublished work.

[5] C. A. Bear, K. A. Duggan, and H. C. Freeman, *Acta Cryst.*, 1975, **B31**, 2713.

thione ligands. The zinc–sulphur distances (3.20 and 3.25 Å) are much longer than Co–S (2.96 Å) in Co(pymt)$_2$Cl$_2$.[6] The acetone molecules are not co-ordinated, an observation in agreement with the fact that the crystals tend to crumble to a powder, with acetone loss, on exposure to the air for *ca.* 1 d.

As far as we are aware, [MnL$_4$][ClO$_4$]$_2$·2Me$_2$CO is the first example of a manganese(II) complex for which there is *X*-ray evidence for an N$_4$ donor set approaching quite closely a tetrahedral geometry. We were, therefore, interested to compare its e.s.r. spectrum and zero-field splitting parameters, *D* and λ (= *E*/*D*), with those of more distorted tetrahedral manganese(II) complexes previously reported from these laboratories.[7,8]

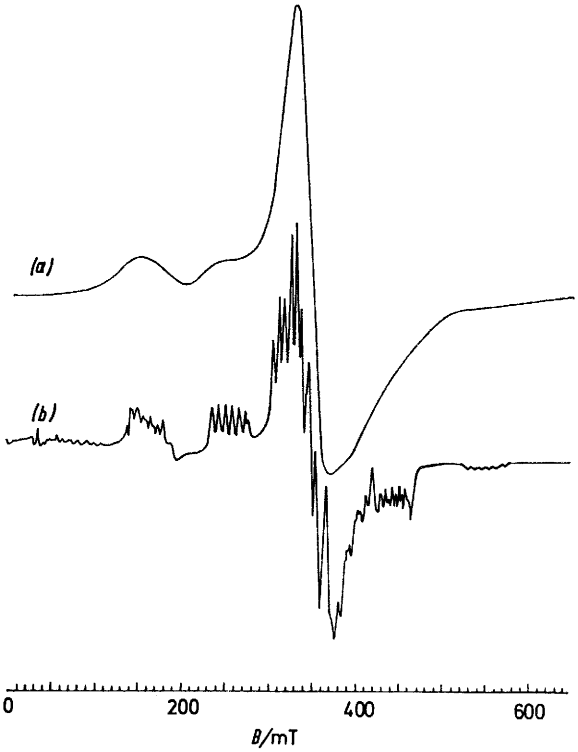

FIGURE Room-temperature *X*-band e.s.r. spectra of (*a*) [MnL$_4$][ClO$_4$]$_2$·2Me$_2$CO, and (*b*) [Zn(Mn)L$_4$][ClO$_4$]$_2$·2Me$_2$CO (L = 1-methylpyrimidine-2-thione)

A manganese(II) ion in a rigorously tetrahedral ligand field would show one band (excluding nuclear-hyperfine components) at $g_{\text{eff.}} = 2$. The *X*-band e.s.r. spectrum of polycrystalline [MnL$_4$][ClO$_4$]$_2$·2Me$_2$CO has a strong band in the $g_{\text{eff.}} = 2$ region [Figure (*a*)] but there are weaker bands at lower field and a pronounced shoulder at higher field. The zero-field splitting is more clearly seen in the spectrum of manganese(II) doped (nominal 2%) into the isomorphous zinc analogue [Figure (*b*)]. Analysis of this latter spectrum using the program ESRS[8] yields values $D = 0.047$ cm^{-1} and $\lambda = 0.30$ (Table 3). Because of the relatively low *D* value the transitions expected in the 300—360 mT region overlap appreciably and it was not possible accurately to resolve them all. The dominant ones in the experimental spectrum are listed in Table 3. However, the evaluation of *D* and λ depends more critically on the bands at higher and lower fields and these are well resolved.

TABLE 3

X-Band e.s.r. spectrum (mT) of [Zn(Mn)L$_4$][ClO$_4$]$_2$·2Me$_2$CO

	Calc. for $D = 0.047$ cm^{-1}, $\lambda = 0.30$		
Obs.	Field	Transition *	
141.5	145.6	$\frac{3}{2} \rightarrow \frac{5}{2}$	*z*
152.0	157.4	$-\frac{5}{2} \rightarrow -\frac{3}{2}$	*y*
241.5	240.4	$\frac{1}{2} \rightarrow \frac{3}{2}$	*z*
244.0	245.1	$-\frac{3}{2} \rightarrow -\frac{1}{2}$	*y*
	315.2	$-\frac{1}{2} \rightarrow \frac{1}{2}$	*x*
309.0	319.5	$-\frac{3}{2} \rightarrow -\frac{1}{2}$	*x*
	328.4	$\frac{1}{2} \rightarrow \frac{3}{2}$	*x*
326.0	334.9	$-\frac{1}{2} \rightarrow \frac{1}{2}$	*y*
	336.5	$-\frac{1}{2} \rightarrow \frac{1}{2}$	*z*
358.0	342.3	$-\frac{5}{2} \rightarrow -\frac{3}{2}$	*x*
	361.6	$\frac{3}{2} \rightarrow \frac{5}{2}$	*x*
431.5	429.2	$\frac{1}{2} \rightarrow \frac{3}{2}$	*y*
445.5	436.0	$-\frac{3}{2} \rightarrow -\frac{1}{2}$	*z*
	533.5	$\frac{3}{2} \rightarrow \frac{5}{2}$	*y*
543.0	543.0	$-\frac{5}{2} \rightarrow -\frac{3}{2}$	*z*

* Small admixtures of other levels to wavefunctions not included, for simplicity of presentation.

The *D* value observed here is much smaller than those found[7,8] for most other tetrahedral manganese(II) complexes which, although of essentially tetrahedral geometry, have usually contained chemically inequivalent donor atoms. A very similar *D* value (0.045 cm^{-1}) was however found[7] for the complex Mn(AsPh$_3$O)$_2$(NCS)$_2$. More recently, Matsuda and Murakami[9] have analysed the *K*-band spectrum of bis[bis(3,5-dimethylpyrrol-2-yl)methanato-*NN'*]manganese(II) and find $D = 0.12$ cm^{-1} and $\lambda = 0.27$. In that complex the presence of chelate rings would be expected to cause a deviation from strict T_d symmetry about Mn^{II} in addition to any distortion towards a plane from the bonding requirements in dipyrromethene complexes of this general type. It would be useful to have an *X*-ray structural study of the pyrrolyl complex for comparison with [MnL$_4$][ClO$_4$]$_2$·2Me$_2$CO.

It is interesting that the λ value we observe (0.30) for the [MnL$_4$]$^{2+}$ ion is close to the maximum value of $\frac{1}{3}$. High λ values seem to be a consistent feature of the distorted tetrahedral manganese(II) complexes studied to date.

The low-frequency i.r. spectra of the complexes [ML$_4$][ClO$_4$]$_2$·2Me$_2$CO (Table 1) each show one band in the 210—224 cm^{-1} region assignable as ν(M–N) (ν_3 F$_2$ in T_d) although it will not, of course, have pure M–N stretching character.

Cobalt perchlorate also forms complexes of stoicheiometry CoL$_3$(ClO$_4$)$_2$ and CoL$_2$(OH$_2$)$_2$(ClO$_4$)$_2$, which, from their electronic spectra, are six-co-ordinate. In neither case is there any significant splitting of the perchlorate ν_3 and ν_4 i.r. bands, but the low-frequency spectrum of the hydrate, and also that of CoL$_2$(NO$_3$)$_2$(OH$_2$)$_2$, has a

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

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

[8] D. Vivien and J. F. Gibson, *J.C.S. Faraday II*, 1975, 1640.

[9] Y. Matsuda and Y. Murakami, *Bull. Chem. Soc. Japan*, 1977, **50**, 2321.

band at 356 cm^{-1} assignable as ν(Co–OH$_2$). It appears that the 3 : 1 complex contains the tris(chelate) cation [CoL$_3$]$^{2+}$ analogous to that formed by 1,4,6-trimethylpyrimidine-2-thione.[2] There is no detectable splitting of the ν$_1$ band in the electronic spectrum of [CoL$_3$][ClO$_4$]$_2$ which may well indicate a *fac*-ligand arrangement in the cation [as found [10] in the cobalt(III) inner complex of the related ligand 4,6-dimethylpyrimidine-2-thione]. Nickel nitrate also forms a 3 : 1 complex, NiL$_3$(NO$_3$)$_2$, but, since the principal nitrate i.r. bands were hidden by the organic ligand bands, the probable presence of the corresponding [NiL$_3$]$^{2+}$ cation could not be confirmed. However, it may be noted that the electronic spectrum shows very little splitting of the ν$_1$ band.

There are five possible geometric isomers for the cation in [CoL$_2$(OH$_2$)$_2$][ClO$_4$]$_2$, but the evidence available does not allow a reliable assignment of the geometry.

Halide Complexes.—The chlorides and bromides of Mn, Co, and Ni each form complexes of stoicheiometry ML$_2$X$_2$. Two different complexes of composition CoL$_2$Br$_2$ could be isolated. A dark green form separated from cold ethanolic solutions of the stoicheiometric amounts of hydrated cobalt bromide and L, but a red isomer precipitated when such solutions were heated. (The red form could also be obtained by strongly grinding the dark green form.) The electronic spectrum of the red isomer (Table 2) showed that its correct formulation is [CoL$_4$][CoBr$_4$], since the spectrum was a composite of those observed for [CoL$_4$][ClO$_4$]$_2$·2Me$_2$CO and the [CoBr$_4$]$^{2-}$ ion.[11] There was also a very strong band at 225 cm^{-1} in the i.r. spectrum, assignable as the ν$_3$(Co–Br) stretch of the anion.[12]

The electronic spectrum of CoL$_2$Cl$_2$ is very similar to that of Co(pymt)$_2$Cl$_2$ in which there is a weak Co–S interaction leading to a very distorted six-co-ordinate geometry about the cobalt atom.[1] The frequencies of the ν(Co–Cl) bands at 270 and 288 cm^{-1} are also in accord with this type of structure as they are in between the ranges found [13] for ν(Co–Cl) for tetrahedral and octahedral complexes respectively.

Interpretation of the spectral results for the green form of CoL$_2$Br$_2$ is less clear-cut. The far-i.r. spectrum (Table 1) indicates the presence of terminal rather than bridging bromides,[13] but the bands in the near-i.r. region of the electronic spectrum are much less intense than is usually the case for pseudo-tetrahedral cobalt complexes. Although these observations would seem to indicate a monomeric, distorted, octahedral structure, as in the chloride, the electronic spectrum has no component in the 10 000—12 000 cm^{-1} region, in contrast to the chloride and to the complexes Co(pymt)$_2$X$_2$ (X = Cl or Br).[1]

The *X*-band e.s.r. spectra of the complexes MnL$_2$X$_2$ (X = Cl or Br) each show the effects of zero-field splitting and this suggests that halide bridges are absent [further indicated by the ν(M–X) bands in their i.r. spectra (Table 1)]. The e.s.r. spectrum of the chloride consists of a main band in the $g_{\text{eff.}} = 2$ region but with pronounced shoulders at *ca.* 130 and *ca.* 500 mT. The bromide has a strong band in the $g_{\text{eff.}} = 4$ region and there are very weak bands at higher fields. The general form of each of these spectra is similar to that previously found [1] for the analogous complex with pymt, and we conclude that the 1-methylpyrimidine-2-thione complexes also have distorted octahedral geometry. However, the fine structure for the MnL$_2$X$_2$ complexes is insufficient for reliable evaluation of the zero-field splitting parameters and no suitable, isomorphous, host lattice could be found for studies on manganese-doped samples.

The nickel halide complexes are hygroscopic and several hydrates can be isolated; only the anhydrous complexes NiL$_2$X$_2$ (X = Cl or Br) will be discussed here. Their electronic spectra are typical of octahedral systems. The highest-energy spin-allowed band is partly hidden by an intense parity-allowed band in the near u.v. but the other two bands show no sign of the splitting found for halide-bridged polymers such as Ni(py)$_2$Cl$_2$ (py = pyridine),[14] nor do they have the unusually high intensity found [1] for the analogous complexes with pymt.

Their far-i.r. spectra have strong ν(Ni–X) bands consistent with terminal halide co-ordination [ν(Ni–Cl) at 284 cm^{-1}, ν(Ni–Br) at 206 cm^{-1}]. The observation of only one ν(Ni–X) in each case, in conjunction with the low intensity of the electronic bands, indicates a *trans*-ligand arrangement leading to a centrosymmetric (or nearly so) co-ordination geometry. The i.r. spectrum of NiL$_2$Br$_2$ has a medium-intensity band at 261 cm^{-1} which is either absent in the chloride or is shifted slightly and obscured by the much stronger ν(Ni–Cl) band. This band is tentatively assigned as ν(M–L) but, since L is functioning as a chelate, not as a simple ν(M–N) mode.

In contrast to its behaviour with copper(II) perchlorate and tetrafluoroborate, 1-methylpyrimidine-2-thione did not reduce copper(II) chloride or bromide and complexes of stoicheiometry CuLX$_2$ were readily obtained. The electronic spectrum of the chloride had a strong band at 12 900 cm^{-1}. The bromide also had a band at this energy but it was significantly less intense and there was a strong band at 20 800 cm^{-1}. This spectral behaviour is very similar to that observed by Livingstone and his co-workers [15] for the complexes Cu(mtpy)X$_2$ (X = Cl or Br) formed by the chelating ligand 2-(2-methylthioethyl)pyridine (mtpy). We conclude that the thione ligand L chelates in the complexes CuLX$_2$ to give a *cis*-planar arrangement although there may also be weak Cu–X intermolecular interactions as are frequently observed in essentially planar copper halide complexes.

In conclusion it appears that 1-methylpyrimidine-

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

[11] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

[12] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1963, 1198.

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

[14] D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *J. Chem. Soc. (A)*, 1966, 1769.

[15] P. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1966, **19**, 1835.

2-thione is a fairly versatile ligand being able to co-ordinate solely through nitrogen in some cases, yielding the relatively uncommon MN_4 tetrahedral geometry, to function as a chelate in other cases, and, possibly in the case of the copper(I) complexes, to co-ordinate only by the sulphur atom.

EXPERIMENTAL

Preparations.—The ligand 1-methylpyrimidine-2-thione was prepared by the method of Fox and Van Praag.[16] Except where otherwise stated, the complexes were prepared from stoicheiometric amounts of the appropriate hydrated metal salt and the thione ligand in acetone or ethanol. The solids which formed either immediately or on cooling in a refrigerator for several days were filtered off, washed with acetone and then diethyl ether, and dried *in vacuo* (except for the perchlorates which were dried in air). Analyses (Table 1) were by the Microanalytical Laboratory, Imperial College.

Tetrakis(1-*methylpyrimidine*-2-*thione*)*cobalt*(II) *tetrabromocobaltate*(II). This red complex was precipitated on heating the green solution obtained on mixing hydrated cobalt(II) bromide and the thione ligand in 1 : 2 mol ratio. After collection the solid was dried at 80 °C for 1 h.

Tetrakis(1-*methylpyrimidine*-2-*thione*)*cobalt*(II) *perchlorate–acetone* (1/2). On mixing solutions of hydrated cobalt(II) perchlorate and the thione ligand in 1 : 4 mol ratio brown crystals of $[CoL_3][ClO_4]_2$ were first formed. These were filtered off and the red filtrate stored in a refrigerator for several hours when red needles of the *complex* were formed.

The complexes $NiL_3(NO_3)_2$ *and* $[NiL_2X_2]$ (X = Cl *or* Br). The general preparative method was followed but a small amount of 2,2-dimethoxypropane was added to remove water. The *complexes* were dried *in vacuo* at 100 °C for 2 h.

Physical measurements were made as described previously.[1,2]

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[8/175 *Received*, 2*nd February*, 1978]

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[16] J. J. Fox and D. Van Praag, *J. Amer. Chem. Soc.*, 1960, **82**, 486.