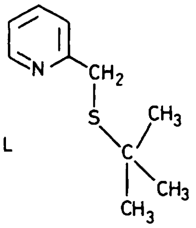
Sulphur-ligand–Metal Complexes. Part 14.[1] Bis[2-(3,3-dimethyl-2-thiabutyl)pyridine] Complexes of Copper(II) and Related Metal Ions

By **Eric W. Ainscough,* Andrew M. Brodie,*** and **Nigel G. Larsen**, Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North, New Zealand

Complexes of the type $[CuL_2X_2]$ [L = 2-(3,3-dimethyl-2-thiabutyl)pyridine; X = Cl, Br, ClO_4, or BF_4], $[CuL_2X]BF_4$(X = Cl or Br), $[ML_2X_2]$ (M = Co or Ni, X = Cl or Br), $[ML_2(H_2O)(ClO_4)]ClO_4$ (M = Co or Ni), and $[NiL_2(H_2O)_2][ClO_4]_2$ have been prepared and characterized by electronic, i.r., and e.s.r. spectroscopy. It is proposed that in the solid state all the complexes have distorted octahedral structures except $[CuL_2X]BF_4$ complexes which are five-co-ordinate. In methanol the $[CuL_2X_2]$ (X = Cl or Br) complexes ionize to give $[CuL_2X]^+$ species whereas for X = ClO_4 and BF_4 the complexes also show evidence of ligand dissociation.

COPPER complexes containing thioether ligands continue to attract interest as a result of the *X*-ray structural studies on the blue copper proteins plastocyanin [2] and azurin [3] confirming the presence of Cu–S thioether bonding. As a continuation of our interest in sulphur ligands,[1] we have examined copper complexes of the ligand 2-(3,3-dimethyl-2-thiabutyl)pyridine, L, which contains a bulky tertiary butyl substituent on the thioether sulphur. An earlier synthetic study of Livingstone and co-workers [4] reported complexes of the related methyl-substituted ligand, 2-(2-thiapropyl)pyridine. We have been able to prepare a wider variety of copper complexes than in this previous work, and moreover the greater solubility of the tertiary butyl-substituted thioether complexes allows more detailed spectroscopic studies to be carried out. Recently we published the synthesis and structural characterization of the copper(I) complexes of this ligand, *viz.* $[CuL_nBr]$ (n = 1 or 2) and $[\{Cu(HL)X_2\}_2]$ (X = Cl or Br),[5] and the mono-ligand copper(II) complexes, *viz.* $[(CuLX_2)_2]$ (X = Cl or Br).[6] We now report the isolation and characterization of a series of bis-ligand complexes with the same ligand L, *viz.* $[CuL_2X_2]$ (X = Cl, Br, ClO_4, or BF_4) and $[CuL_2X]BF_4$ (X = Cl or Br). To assist with spectral interpretations the related complexes of Co^{II} and Ni^{II} have also been included.

L



EXPERIMENTAL

Physical measurements and the synthesis of L have been described previously.[5]

Preparations.—$[ML_2X_2]$ (M = Cu, Co, *or* Ni, X = Cl *or* Br; M = Cu, X = ClO_4 *or* BF_4), $[NiL_2(H_2O)_2][ClO_4]_2$, *and* $[ML_2(H_2O)(ClO_4)]ClO_4$ (M = Co *or* Ni). These were obtained by similar methods of which the following is typical.

Copper(II) chloride dihydrate (0.340 g, 2 mmol), dissolved in the minimum volume of absolute ethanol, was added to L (0.725 g, 4 mmol) in the same solvent. Concentration of the solution, using a rotary evaporator, followed by cooling in ice, yielded $[CuL_2Cl_2]$ as a lime green precipitate which was filtered off, washed with small volumes of absolute ethanol, followed by diethyl ether, and then dried *in vacuo*. Yield 0.655 g (66%). For M = Co or Ni and X = ClO_4, the monoaqua-complexes were isolated from solutions containing triethyl orthoformate,[7] a dehydrating agent.

$[CuL_2X]BF_4$ (X = Cl *or* Br). To copper(II) tetrafluoroborate hexahydrate (0.345 g, 1 mmol), dissolved in the minimum volume of acetone containing L (0.363 g, 2 mmol), was added LiCl (0.042 g, 1 mmol), dissolved in an ethanol–acetone mixture. The lime green solution was concentrated, using a rotary evaporator, and cooled to yield the crude product. Recrystallization was achieved from absolute ethanol. The bromide was prepared in a similar manner using LiBr with triethyl orthoformate as a dehydrating agent. Yields were <20%.

RESULTS AND DISCUSSION

Copper(II) *Halide and Related Complexes.*—The halide complexes, $[ML_2X_2]$ (M = Cu, Co, or Ni; X = Cl or Br), were prepared by the reaction of L with the appropriate metal salt in ethanol, whereas the $[CuL_2X]BF_4$ (X = Cl or Br) complexes were prepared by the addition of LiX to $[CuL_2(BF_4)_2]$ prepared *in situ*. Analytical data, colours, melting points, and conductivity data are given in Table 1.

Overall, the evidence presented below suggests that the $[CuL_2X_2]$ (X = Cl or Br) complexes may have a distorted *cis*-octahedral arrangement of the halide donors about copper(II). Conductivity studies in nitromethane and nitrobenzene (Table 1) give Λ values considerably lower than expected [8] for 1 : 1 electrolytes, indicating that only partial ionization occurs in these solvents and the copper is six-co-ordinate in the solid state. The powder e.s.r. spectrum of $[CuL_2Cl_2]$ shown in the Figure is rhombic in character, exhibiting three peaks corresponding to powder g values for g_x, g_y, and g_z, clearly resolved (Table 3). The linewidths are surprisingly small for powder spectra, but such linewidth narrowing appears to be characteristic of copper complexes containing thioether ligands, since it has been noted previously for $[Cu(CH_3SCH_2CH_2SCH_3)_2(BF_4)_2]$ [9] and the related perchlorate,[10] where it was explained in terms of an electron-exchange process in the crystal. The

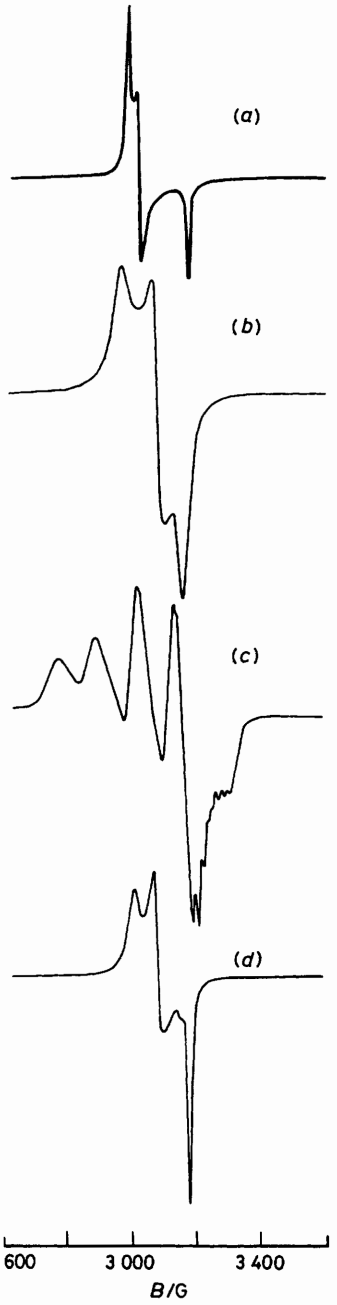


FIGURE E.s.r. spectra (77 K) for: (*a*) [CuL_2Cl_2] powder, (*b*) [CuL_2Cl]BF_4 powder, (*c*) [CuL_2Cl_2] in 20% glycerol–MeOH, and (*d*) [$CuL_2(BF_4)_2$] powder

spectral profile is consistent with a distorted *cis*-octahedral structure, although the lowest *g* value is not less than 2.03 as often found for copper(II) nitrogen–oxygen donor ligand systems with a d_{z^2} ground state.[11,12] For [CuL_2Cl_2] the *R* value [= $(g_2 - g_1)/(g_3 - g_2)$ where $g_3 > g_2 > g_1$] of 4.0 is as expected for an approximately d_{z^2} ground state [13] and is identical to the value calculated from powder e.s.r. data for [$Cu(bipy)_2(ONO)$]NO_3, which has a *cis*-octahedral stereochemistry.[11] However, in some cases it has been pointed out that such evidence should be treated with caution.[14] In the far-i.r. spectrum (Table 2), bands are assignable essentially to Cu–X stretching frequencies for equatorial Cu–X bonds.[15,16] While two bands are expected for a *cis*-$CuCl_2$ unit,[17] only one distinct absorption is observed in each case, in contrast to the two well resolved bands seen for the related [ML_2X_2] (M = Co or Ni) complexes. The reflectance spectra (Table 2) of the copper complexes show *d–d* band maxima in the 700—800 nm region, with shoulders at lower energies, and the spectra of the cobalt and nickel analogues are typical of distorted octahedral geometries for these metal ions.[18-21] Space-filling molecular models suggest that the binding of the halide ions will be less sterically hindered if the 2-(3,3-dimethyl-2-thiabutyl)pyridine ligands are in a *cis* arrangement around the metal ion. However, the exact arrangement of the L donor atoms relative to the *cis*-halide ions is not known, but the rhombic structure is favoured.

The [CuL_2X]BF_4 (X = Cl or Br) complexes appear to have distorted square-pyramidal structures. In the i.r., the observation of the $\nu_3(BF_4^-)$ as a single unbroadened band (Table 2) is good evidence for its ionic nature [22] and this is supported by molar conductivity values (Table 1) which are characteristic of 1 : 1 electrolytes. The reflectance spectra show *d–d* bands near 800 nm with shoulders discernable at *ca.* 950 nm (Table 2). The fact that the lower energy transition is less intense than the main band is in line with an approximate square-pyramidal rather than a trigonal-bipyramidal environment.[23,24] The three-line powder e.s.r. spectrum for [CuL_2Cl]BF_4 (see Figure) is different from that observed for [CuL_2Cl_2], and not inconsistent with that expected for a distorted square-based pyramidal stereochemistry with a $d_{x^2-y^2}$ ground state predominating.[12]

In methanol solution the spectroscopic properties of [CuL_2X_2] and [CuL_2X]BF_4 (X = Cl or Br) are remarkably similar, suggesting a [CuL_2X]$^+$ chromophore predominating in all cases. Molar conductivity measurements in methanol would give credence to this idea, with the [CuL_2X_2] complexes approaching 1 : 1 electrolyte values (Table 1). The e.s.r. spectra (Table 3) recorded as frozen solutions, in methanol and 20% glycerol–methanol, yield similar parameters, but the latter solvent system gave improved resolution. Spectral parameters are unchanged on the addition of excess of L, thus ruling out ligand dissociation. For the chloro-complexes, [CuL_2Cl_2] (see Figure) and [CuL_2Cl]BF_4, the $g_{\parallel}$ ($\approx$ 2.185) and $A_{\parallel}$ ($\approx 125 \times 10^{-4}$ cm^{-1}) values are characteristic of complexes having distorted square-pyramidal geometries, where $A_{\parallel}$ has been lowered from typical tetragonal values (150×10^{-4}—200×10^{-4} cm^{-1}) by increased axial interactions.[25-27] In addition, the two clearly resolved *d–d* bands which are observed at 90 K in the same solvent system (Table 2) can be associated with an intermediate geometry.[28,29] For the bromo-complexes [CuL_2Br_2] and [CuL_2Br]BF_4 an additional species is observed in the e.s.r. spectrum with $g_{\parallel} \approx 2.23$ and $A_{\parallel} \approx 105 \times 10^{-4}$ cm^{-1}. The low $A_{\parallel}$ value could point to a tetrahedral geometry about copper(II) [9] but it cannot be the Br^- ion that is ionized as molar conductivities for the related

TABLE 1

Colours, analytical, m.p., and conductivity data for the complexes

Complex	Colour	Analysis [a]/%			M.p./°C	Λ [b]/S cm² mol⁻¹	
		C	H	N		$MeNO_2$	MeOH
$[CuL_2Cl_2]$	Lime green	48.2 (48.2)	6.2 (6.1)	5.55 (5.6)	89—90	22	65 (4 [c])
$[CuL_2Br_2]$	Green	41.1 (41.0)	5.3 (5.2)	4.9 (4.8)	91—93	36	73
$[CuL_2(ClO_4)_2]$	Dark green	38.95 (38.4)	5.0 (4.8)	4.6 (4.5)	*d*	165	28 [c]
$[CuL_2(BF_4)_2]$	Dark green	40.05 (40.05)	5.2 (5.0)	4.7 (4.7)	149—150	170	30 [c]
$[CuL_2Cl]BF_4$	Green	43.3 (43.8)	5.6 (5.5)	4.85 (5.1)	112—113	86	101
$[CuL_2Br]BF_4$	Lime green	40.6 (40.5)	5.2 (5.1)	4.65 (4.7) [e]	123—124	92	100
$[CoL_2Cl_2]$	Mauve	48.8 (48.8)	6.2 (6.1)	5.7 (5.7)	152—155	22	126 (2 [c])
$[CoL_2Br_2]$	Mauve	41.2 (41.3)	5.2 (5.2)	4.7 (4.8)	148—150	26	138
$[CoL_2(H_2O)(ClO_4)]ClO_4$	Mauve	37.6 (37.6)	5.0 (5.05)	4.4 (4.4)	*d*	168	*d*
$[NiL_2Cl_2]$	Blue-green	48.7 (48.8)	6.2 (6.1)	5.5 (5.7)	212—213	7	138
$[NiL_2Br_2]$	Pale green	41.4 (41.3)	5.3 (5.2)	4.8 (4.8)	191—193	20	145
$[NiL_2(H_2O)(ClO_4)]ClO_4$	Pale green	37.6 (37.6)	5.2 (5.05)	4.15 (4.4)	*d*	169	*d*
$[NiL_2(H_2O)_2][ClO_4]_2$	Pale blue	36.7 (36.6)	5.5 (5.2)	4.0 (4.3)	*d*	168	*d*

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm⁻³ solutions. Values expected [8] for 1 : 1 electrolytes are 75—95 ($MeNO_2$), 80—115 (MeOH), and 20—30 S cm² mol⁻¹ ($PhNO_2$). [c] In $PhNO_2$. [d] Not recorded. [e] Br 14.0 (13.5)%.

TABLE 2

Electronic and infrared spectral data for the complexes

Complex	U.v.–visible absorptions [a] (nm)			Infrared absorptions [b] (cm⁻¹)	
	Charge transfer	*d–d*	State	Metal–halogen	BF_4^-/ ClO_4^- anion
$[CuL_2Cl_2]$	410 (sh)	730, 970 (sh)	Solid	277 (sh), 270	
	361 (1 480)	810 (209), 965 (sh) (200)	MeOH		
	372	750, 1 010	20% Glycerol–MeOH [c]		
$[CuL_2Br_2]$	450 (sh)	840, 1 000 (sh)	Solid	184	
	310 (1 890), 342 (sh)	800 (350), 940 (sh) (310)	MeOH		
	366 (2 610), 395 (sh) (1 800)	780 (915), 1 020 (860)	20% Glycerol–MeOH [c]		
$[CuL_2Cl]BF_4$	375	810, 960 (sh)	Solid	292	1 054 (ν_3)
	363 (1 470)	800 (212), 950 (194)	MeOH		
	376 (2 450)	762 (455), 1 025 (630)	20% Glycerol–MeOH [c]		
$[CuL_2Br]BF_4$	419	840, 975 (sh)	Solid	183	1 055 (ν_3)
	355 (1 610)	805 (300), 950 (sh) (255)	MeOH		
	365, 396 (sh)	780 (710), 1 020 (670)	20% Glycerol–MeOH [c]		
$[CuL_2(ClO_4)_2]$	435	600	Solid		1 090, 1 050 (ν_3), 933 (ν_1)
	390	600 [d]	CH_2Cl_2		
	346 (1 020)	750 (60), 900 (sh) (40)	MeOH		
$[CuL_2(BF_4)_2]$	430	595	Solid		1 098, 1 061, 991 (ν_3)
	370 (sh), 387	595 [d]	CH_2Cl_2		
	344 (1 090)	745 (75), 900 (sh) (55)	MeOH		
$[CoL_2Cl_2]$		470 (sh), 542 (sh), 590, 675 (sh), 970, 1 330	Solid	249, 222	
$[CoL_2Br_2]$		510 (sh), 542 (sh), 680	Solid	228, 192	
$[CoL_2(H_2O)(ClO_4)]ClO_4$		490 (sh), 507, 628 (sh), 875	Solid		1 123, 1 016 (ν_3), 921 (ν_1)
$[NiL_2Cl_2]$		405, 645, 1 080, 1 300 (sh)	Solid	253, 230	
$[NiL_2Br_2]$		410 (sh), 690, 1 100	Solid	210, 194	
$[NiL_2(H_2O)(ClO_4)]ClO_4$		390 (sh), 645, 900	Solid		1 126, 1 022 (ν_3), 929 (ν_1)
$[NiL_2(H_2O)_2][ClO_4]_2$		390 (sh), 630, 900	Solid		1 090 (ν_3)

[a] Absorption coefficients (ϵ/dm³ mol⁻¹ cm⁻¹) are given in parentheses; sh = shoulder. [b] As Nujol mulls. [c] At 90 K. [d] Insufficiently soluble to record ϵ.

TABLE 3

E.s.r. data for the copper(II) complexes

Complex	State [a]	$g_{\parallel}$	$10^4 A_{\parallel}/\text{cm}^{-1}$	$g_{\perp}$
$[CuL_2Cl_2]$	Powder	2.174 (g_3)		2.149 (g_2), 2.044 (g_1)
	20% glycerol–MeOH	2.179	124	2.051
$[CuL_2Br_2]$	20% Glycerol–MeOH	2.175 [b]	144	
		2.227 [c]	109	
$[CuL_2Cl]BF_4$	Powder	2.182 (g_3)		2.103 (g_2), 2.049 (g_1)
	20% Glycerol–MeOH	2.191	126	2.056
$[CuL_2Br]BF_4$	20% Glycerol–MeOH	2.180 [b]	142	
		2.225 [c]	104	
$[CuL_2(ClO_4)_2]$	Powder	2.133 (g_3)		2.088 (g_2), 2.036 (g_1)
$[CuL_2(BF_4)_2]$	Powder	2.149 (g_3)		2.099 (g_2), 2.033 (g_1)
	MeOH	2.296 [b]	150	
		2.363 [c]	151	
	MeOH + excess of L	2.252 [b]	173	
		2.194 [c]	164	

[a] At 77 K. [b] Major species. [c] Minor species.

chloro- and bromo-complexes are the same (Table 1). Moreover, complete L dissociation is precluded since the addition of excess of L does not alter the spectrum. It is possible that a thioether sulphur is removed from the co-ordination sphere.

$[CuL_2X_2]$ ($X = ClO_4$ *or* BF_4) *and Related Complexes.*—The complexes $[CuL_2X_2]$ ($X = ClO_4$ or BF_4) and $[NiL_2(H_2O)_2][ClO_4]_2$ were prepared from the interaction of the ligands with the appropriate metal salt in ethanol. The addition of the dehydrating agent triethyl orthoformate allowed the isolation of the monoaquo-complexes $[ML_2(H_2O)(ClO_4)]ClO_4$ (M = Co or Ni). For the copper complexes, spectral evidence points to a tetragonal co-ordination about the metal. Conductivity data in nitrobenzene indicate co-ordination of the anion, since the molar conductivity values ($\Lambda \approx 30$ S cm^2 mol^{-1}) (Table 1) fall well below the range expected [8] for 2 : 1 electrolytes (Λ 50—60 S cm^2 mol^{-1}). This is confirmed by i.r. measurements of the anion absorptions (Table 2) as the splitting of the ν_3 band is about that expected for weak co-ordination of the anion to copper(II).[22,30,31] The nickel diaquo-complex is formulated as $[NiL_2(H_2O)_2][ClO_4]_2$, on the basis of the ionic nature of the $\nu_3(ClO_4^-)$ band, whereas the monoaqua-complexes clearly show features expected for co-ordinated ClO_4^-,[22,32] and are therefore formulated as $[ML_2(H_2O)(ClO_4)]ClO_4$ (M = Co or Ni).

Electronic reflectance spectra of the $[CuL_2X_2]$ ($X = ClO_4$ or BF_4) complexes (Table 2) show a broad band near 600 nm which is assignable as a *d–d* absorption envelope and is typical of tetragonal copper(II) [33] [although the band may also include a $\pi(S) \longrightarrow Cu$ charge-transfer transition].[34] Additional strong absorptions at *ca.* 430 nm can be assigned to $\sigma(S) \longrightarrow Cu$ charge-transfer bands, by analogy with other copper thioether complexes.[6,10,34,35] The profiles of the e.s.r. spectra of the powdered complexes (see Figure) are similar, including the narrow linewidths, to those reported for the tetragonal complexes $[Cu(CH_3SCH_2CH_2SCH_3)_2X_2]$ ($X = ClO_4$ or BF_4).[9,10]

In CH_2Cl_2 solution the *d–d* bands for the $[CuL_2X_2]$ ($X = ClO_4$ or BF_4) complexes are unchanged from the wavelengths observed in the solid state, however, more polar solvents (*e.g.* methanol) cause shifts to lower energy (Table 2). E.s.r. spectra in frozen methanol confirm that the complexes have broken down, at least two species being observed and on addition of excess of ligand, changes occur (Table 3). Presumably solvated ions such as $[CuL_2(MeOH)_x]^{2+}$ and $[CuL(MeOH)_x]^{2+}$ are formed, but the absence of a species with $g_{\parallel} = 2.430$ and $A_{\parallel} = 126 \times 10^{-4}$ cm^{-1} rules out complete solvation to $[Cu(MeOH)_6]^{2+}$ as was observed for the mono-ligand complexes $[(CuLX_2)_2]$ (X = Cl or Br) in methanol.[6]

We thank the New Zealand University Grants Committee for support, Dr. G. A. Bowmaker (University of Auckland) for assistance in recording far-infrared spectra, and Dr. E. N. Baker for useful discussions.

[1/1462 *Received, 18th September,* 1981]

REFERENCES

[1] Part 13, E. W. Ainscough, A. M. Brodie, N. G. Larsen, A. Gin, and M. A. Weiner, *Inorg. Chim. Acta*, 1981, **53**, L271.

[2] P. M. Colman, G. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature*, 1978, **272**, 319.

[3] E. T. Adman, R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, 1978, **123**, 35.

[4] P. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, 1967, **20**, 239.

[5] E. W. Ainscough, E. N. Baker, A. M. Brodie, N. G. Larsen, and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1981, 1746.

[6] E. W. Ainscough, E. N. Baker, A. M. Brodie, and N. G. Larsen, *J. Chem. Soc., Dalton Trans.*, 1981, 2054.

[7] P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 145.

[8] W. J. Geary, *Coord. Chem. Rev.*, 1971—1972, **7**, 81.

[9] U. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 1979, 600.

[10] M. M. Olmstead, W. K. Musker, and R. M. Kessler, *Inorg. Chem.*, 1981, **20**, 151.

[11] B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 1969, 2219.

[12] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

[13] W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.

[14] W. E. Estes, D. P. Gavel, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1978, **17**, 1415.

[15] A. B. P. Lever and B. S. Ramaswamy, *Can. J. Chem.*, 1973, **51**, 1582.

[16] A. B. P. Lever and E. Mantovani, *Inorg. Chem.*, 1971, **10**, 817.

[17] K. Nakamoto, ' Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley, New York, 1978, p. 321.

[18] J. Abbot, D. M. L. Goodgame, and I. Jeeves, *J. Chem. Soc., Dalton Trans.*, 1978, 880.

[19] S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, 1970, **23**, 1553.

[20] W. Levason, C. A. McAuliffe, F. P. McCullough, and A. M. Werfalli, *Inorg. Chim. Acta*, 1977, **25**, 247.

[21] J. H. Worrell, J. J. Genova, and T. D. Dubois, *J. Inorg. Nucl. Chem.*, 1978, **40**, 441.

[22] I. M. Proctor, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1968, 1678.

[23] M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint, and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1981, 1342.

[24] N. Ray, L. Hulett, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1463.

[25] A. Bencini, I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, 1978, **17**, 3194.

[26] R. Barbucci, A. Mastroianni, and M. J. M. Campbell, *Inorg. Chim. Acta*, 1978, **27**, 109.

[27] R. Barbucci and M. J. M. Campbell, *Inorg. Chim. Acta*, 1976, **16**, 1667.

[28] B. J. Hathaway, N. Ray, D. Kennedy, N. O'Brien, and B. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 1371.

[29] W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1556.

[30] A. M. Brodie and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, 1979, 199.

[31] A. P. Gaughan, Z. Dori, and J. A. Ibers, *Inorg. Chem.*, 1974, **13**, 1665.

[32] K. Nakamoto, ' Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley, New York, 1978, p. 242.

[33] B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 1196.

[34] V. M. Miskowski, J. A. Thich, R. Solomon, and H. J. Shugar, *J. Am. Chem. Soc.*, 1976, **98**, 8344.

[35] A. R. Amundsen, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, 1977, **99**, 6730.