The Preparations of some μ-Peroxo Binuclear Cobalt(III) Complexes of Macrocyclic Tetra-aza-ligands and Studies of the Oxygenation and Deoxygenation Reactions

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Received September 20, 1983

*The preparations of μ-peroxo complexes of the type $[(H_2O)LCoO_2CoL(H_2O)]^{4+}$ where L = C-*meso *and C-*racemic*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane, $Me_2[14]dieneN_4$ and $Me_4[14]dieneN_4$ are described. The oxygenation of the yellow low spin cobalt(II) complexes of the macrocycles is discussed. The deoxygenation of the μ-peroxo complexes in acidic solution has been studied kinetically.*

Introduction

Peroxo-bridged dicobalt(III) complexes are often regarded as models for biological oxygen carriers [1–3]. In recent years a number of peroxo-bridged dicobalt(III) complexes of macrocyclic ligands have been characterised in the solid state [4–6, 11]. Cobalt(II) complexes of 14-membered tetra-aza have been reported as low spin ($t_{2g}{}^6e_g{}^1$) $[Co(N_4)(OH_2)_2]^{2+}$ species. Thus $[Co(Me_6[14]dieneN_4)(OH_2)_2]^{2+}$ is described as a yellow low spin species prior to oxygenation [7].

The reaction of dissolved oxygen with cobalt(II) complexes of macrocycles is a rapid process (eqns. 1 and 2):

$$Co^{II}L + O_2 \overset{K_1}{\rightleftharpoons} Co^{III}LO_2^{\cdot-} \qquad (1)$$

$$Co^{III}LO_2^{\cdot-} + Co^{II}L \overset{K_2}{\rightleftharpoons} [LCo^{III}O_2{}^{2-}Co^{III}L] \qquad (2)$$

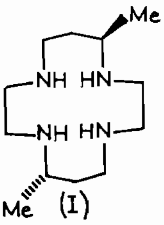
Thus Wong *et al.* [8] have shown that the reaction of $[Co(Me_2[14]dieneN_4)(OH_2)_2]^{2+}$ with O_2 leads to apparently quantitative formation of the μ-peroxo complex in less than 1 minute.

Breakdown of $[(H_2O)Co(Me_2[14]dieneN_4)]_2O_2{}^{4+}$ occurs in acidic media by a two step reaction neither step showing a dependence on $[H^+]$ over the acidity range 0.05–0.5 *M* $[H^+]$. The products are $[Co(OH_2)_6]^{2+}$ and $LH_2{}^{2+}$ [9]. These reactions appear to involve the reverse of eqns. 1 and 2 coupled with the further reaction 3:

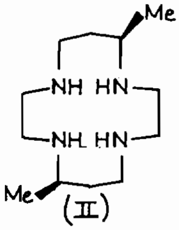
$$[CoL]^{2+} + 2H^+ \longrightarrow [Co(H_2O)_6]^2 + LH_2{}^{2+} \qquad (3)$$

Similar conclusions have been reached with the complex $[(en)_2(NH_3)Co^{III}(\mu\text{-}O_2{}^{2-})Co^{III}(NH_3)(en)_2]^{4+}$ [10]. Decomposition to Co(II) and O_2 is first order in the concentration of the complex and is independent of $[H^+]$ over the pH range 1.1–10.2 with $k = 4.9 \times 10^{-3}\ s^{-1}$ at 25 °C ($\Delta H^{\ddagger} = 132$ kJ mol^{-1} and $\Delta S^{\ddagger} = 151$ J K^{-1} mol^{-1}).

The present paper discusses the synthesis of a number of μ-peroxo complexes of the type $[(H_2O)LCoO_2CoL(H_2O)]^{4+}$ where L = C-*meso* Me_2cyclam (I), C-*racemic* Me_2cyclam(II), $Me_2[14]dieneN_4$ (III) and $Me_4[14]dieneN_4$ (IV). The decomposition of some of the μ-peroxo complexes in acidic solution has been studied kinetically and O_2 uptake by the cobalt(II) complexes investigated.



(I)



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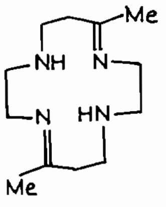

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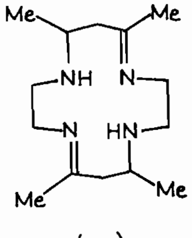

(IV)

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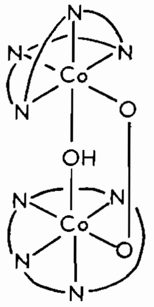
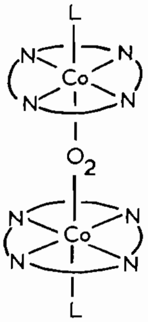
With macrocyclic ligands it has been possible to identify a variety of structures for the O_2 adducts. The μ-peroxo-μ-hydroxo structure (V) occurs with [12]aneN_4 and [13]aneN_4, as ligand folding to give a *cis*-complex is required [18]. The μ-peroxo structure (VI) is well established with [14]aneN_4 where a planar ligand stereochemistry is favoured [11]. The superoxo-adduct (VII) has been noted with Me_6[14]dieneN_4 [7] and dioxocyclam [19] in the presence of bases such as pyridine and imidazole which act as the axial ligand.



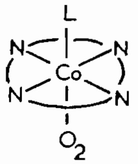
μ-PEROXO-μ-HYDROXO

(V)



μ-PEROXO

(VI)



SUPEROXO ADDUCT

(VII)

Experimental

The ligand salts Me_2[14]diene$N_4 \cdot 2HClO_4$ [15], Me_4[14]diene$N_4 \cdot 2HClO_4$ [17] and Me_6[14]diene-$N_4 \cdot 2HBr \cdot 2H_2O$ [16] were prepared as previously described. C-*meso* and C-*racemic*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane were prepared essentially as described by Kolinski and Korybut-Daskiewicz [15].

Trans-*[(H_2O)LCoO_2CoL(H_2O)](ClO_4)$_4 \cdot H_2O$ (L = C-*meso *or* C-rac *Me_2cyclam)*

The C-*meso* or C-*racemic*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane (0.23 g) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.37 g) were individually dissolved in the minimum volume of water. The two solutions were then mixed, when the solution immediately became brown. Sodium perchlorate (1 g) was added and the solution cooled in ice. On standing in ice for *ca.* 0.5 hr, a brown precipitate formed which was filtered off, washed with ethanol, then diethyl ether and dried *in vacuo. Anal.* Calcd. for $C_{24}H_{62}N_8O_{21}Cl_4Co$: C, 27.23; H, 5.90; N, 10.58. Found: C, 27.29; H, 5.81; N, 10.20 (C-*meso* ligand) and C, 27.24; H, 5.77; N, 10.24% (C-*racemic* ligand).

The μ-peroxo complexes with Me_2[14]dieneN_4 and Me_4[14]dieneN_4 were prepared by a similar method. *Anal.* Calcd. for $C_{28}H_{60}N_8Cl_4O_{20}Co_2$: C, 30.90; H, 5.56; N, 10.29. Found: C, 30.78; H, 5.45; N, 10.06 (Me_4[14]dieneN_4 ligand). Calcd. for $C_{24}H_{52}N_8Cl_4O_{20}Co_2$: C, 27.92; H, 5.08; N, 10.85. Found: C, 27.31; H, 4.90; N, 10.55% (Me_2[14]-dieneN_4 ligand).

*[(OH)LCoO_2L(OH)](ClO_4)$_2$ (L = C-*meso*-Me_2cyclam)*

C-*meso*-5,12-dimethyl-1-4,8,11-tetra-azacyclotetradecane (0.25 g) was dissolved in the minimum volume of water (*ca.* 2 cm^3) and treated with a few drops of diethylamine. Cobalt(II) nitrate hexahydrate (0.25 g) was added with stirring. Air was bubbled through the solution for *ca.* 1 hr and the deep brown solution so obtained filtered. Addition of excess $NaClO_4$ (*ca.* 1 g) to the filtrate and standing for *ca.* 1 hr gave the crystalline complex which was filtered off, washed with isopropanol, then ether and dried *in vacuo. Anal.* Calcd. for $C_{24}H_{58}N_8Cl_2O_{12}Co_2$: C, 34.34; H, 6.96; N, 13.35. Found: C, 34.58; H, 6.56; N, 13.31%.

The decomposition of $[(H_2O)L_MCoO_2CoL_M(H_2O)]^{4+}$ (L_M = C-*meso*-Me_2cyclam) was monitored spectrophotometrically using the absorbance decrease at 340 nm. The initial fast reaction was followed by stopped flow techniques using a Durrum Gibson instrument interfaced with a transient recorder and desk top computer. The slower second step was monitored using a Gilford 2400S spectrophotometer. Decomposition of $[(H_2O)L_RCoO_2L_R(H_2O)]^{4+}$ (L_R = C-*racemic*-Me_2cyclam) was monitored at 315 nm using a Gilford instrument. Stopped flow measurements in this case did not reveal an initial rapid reaction. Oxygen evolution was studied using an oxygen electrode. Oxygen evolution was quite slow and it was difficult to obtain quantitative estimations due to leakage of O_2 over extended periods. Decomposition of the μ-peroxo complexes was studied in both HCl and $HClO_4$ solutions ($[H^+]$ = 0.01 *M* to 0.5 *M* with I = 0.1 *M* to 0.5 *M* adjusted with NaCl and $NaClO_4$ respectively). Measurements of oxygen uptake were determined using an oxygen electrode. The zero point was calibrated with 5% $NaHSO_3$ aqueous solution and the 100% point with air saturated water. Air saturated water is 0.222, 0.258 and 0.397 m*M* at 35, 25 and 5 °C respectively [26]. Oxygen uptake was studied at pH 8.2 with a lutidine–HCl buffer. The cobalt(II) complex (10^{-6} mol) in 0.1 cm^3 of buffer (prepared under argon) was injected using a microsyringe into the vessel which contained 10 cm^3 of buffer. The solution was

TABLE I. Charge Transfer Absorption Spectra of Binuclear μ-Peroxo Complexes $[L_5CoO_2CoL_5]^{4+}$.

L_5[a]	λ_{max} (nm)	log ϵ (M^{-1} cm^{-1})	Ref.
$(Me_2[14]dieneN_4)(OH_2)$	320	3.59	6
$(Me_2[14]dieneN_4)(SCN^-)$	295	3.60	6
$(NH_3)_2(dien)$	295	3.60	6
$(NH_3)_2(pn)_2$	298	3.8	6
$(NH_3)_2(tn)_2$	298	3.8	6
$(NH_3)_2(bn)_2$	300	–	6
(pn)(dien)	301	4.0	12
(tn)(dien)	299	4.0	6
$(dien)_2$	301	3.51	6
(NH_3)trien	300	–	12
$(NH_3)(en)_2$	300	–	
tetren	311	4.10	12
(en)(dien)	300	3.98	12
(NH_3)(tren)	303	3.96	13
$(dpK{\cdot}H_2O)_2(py)$	305	4.0	14
(pydien)	319	3.78	14
(pydpt)	319	3.78	14

[a] pydien = 1,9-bis(2-pyridyl)-2,5,8-triazanonane; pydpt = 1,11-bis(2-pyridyl)-2,6,10-triazaundecane; $dpK{\cdot}H_2O$ = hydrate of di-2-pyridyl ketone, $(C_5H_5N)_2C(OH)_2$.

stirred and the decrease in the O_2 concentration monitored at 25 °C. Thus for the $Me_2[14]dieneN_4$ complex 19% of the oxygen was rapidly absorbed (minutes). The quantity of O_2 bound to the complex is $10.0 \times 0.258 \times 0.195 \times 10^{-6}$ mol = 0.49×10^{-6} mol, confirming the 2:1 CoL:O_2 stoichiometry. Similar stoichiometries were obtained with Me_4-$[14]dieneN_4$, *C-meso* and *C-racemic* Me_2cyclam.

Results and Discussion

Aerial oxidation at room temperature of solutions containing simple cobalt(II) salts and amine ligands commonly give characteristically brown binuclear cobalt(III) complexes with a bridging peroxo group of the general formula $[L_5CoO_2$-$CoL_5]^{n+}$ (n = 4 for neutral ligands L, or dibridged species of the general type $[L_4Co(O_2, X)CoL_4]^{m+}$ (m = 3 for neutral ligands L) containing a μ-hydroxo or μ-amido bridge in addition to the μ-peroxo bridge. One electron oxidation of the μ-peroxo complexes gives an analogous range of normally less stable, dark green μ-superoxo complexes. Reaction of mixtures of cobalt(II) salts and amine ligands at low temperatures in non-aqueous solvents can give unstable mononuclear superoxo complexes in which the dioxygen is coordinated as a σ-bonded 'bent' unidentate ligand [1].

Previous work [6, 11] has shown that 14-membered macrocyclic tetraaza ligands form relatively stable μ-peroxo complexes which are readily isolated in the solid state. The complexes are brown in colour due to an intense charge transfer absorption assigned as $\pi^*O_2^{2-} \rightarrow d_{z^2}Co(III)$ transition in the u.v. 'tailing' into the visible region. The charge transfer maximum for the monobridged complexes occurs in the region 295–311 nm with an ϵ of 4000 to 10000 M^{-1} cm^{-1}, Table I. The $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ band occurs as a shoulder in the visible, near 500 nm, or is hidden by the tail of the strong charge transfer band.

The present complexes show the expected charge transfer band near 300 nm, Table II, confirming the μ-peroxo formulation (the $[L_4Co(O_2,OH)CoL_4]^{3+}$ complexes have the charge transfer band in the 350–360 nm region [6]), Table III. In the infra-red, the complexes have bands at *ca.* 3420 cm^{-1} due to coordinated water and perchlorate bands at 623 and 1100(br) cm^{-1}. The μ-peroxo derivative of Me_2-$[14]dieneN_4$ has a sharp band due to $\nu C{=}N$ at 1650 cm^{-1} absent in the complexes of the Me_2cyclams. The μ-peroxo derivative of $Me_4[14]dieneN_4$ has $\nu C{=}N$ at 1655 cm^{-1}.

Oxygenation

Mixing deaerated aqueous solutions of $Me_2[14]$ diene$\cdot 2HClO_4$ and $Co(ClO_4)_2{\cdot}6H_2O$ gives a yellow solution which turns brown on aeration. A constant absorption is reached after *ca.* 15 min aeration at room temperature. The product spectrum displays a shoulder at *ca.* 455 nm on the charge transfer band at 320 nm. The spectral parameters are in good agreement with those for $[(H_2O(Me_2[14]dieneN_4)Co]_2O_2^{4+}$ where λ_{max} = 320 nm (log ϵ = 3.59) with a shoulder at 460 nm (log ϵ = 2.52) assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition [6]. Quantitative O_2 consumption measurements using an O_2 electrode (see Experimental) confirm the 2:1 CoL:O_2 stoichiometry, and similar results were obtained with $Me_4[14]dieneN_4$ and *C-racemic* and *C-meso* Me_2-cyclam.

Cobalt(II) complexes of 14-membered tetrazamacrocycles have been reported as low spin $[CoN_4$-$(OH_2)_2]^{2+}$ species. Thus $[Co(Me_6[14]dieneN_4)$-$(OH_2)_2]^{2+}$ is described as a yellow low spin species before oxygenation [7]. Mixing deaerated aqueous solutions of $Me_6[14]$diene$\cdot$2HBr and $Co(ClO_4)_2{\cdot}$ $6H_2O$ gives a yellow solution which on aeration changes very slowly to brown with the formation of a shoulder at *ca.* 500 nm on the charge transfer band, presumably the $^1A_{1g} \rightarrow {}^1T_{1g}$ of cobalt(III). Some two hours are required for a constant absorbance to be reached.

TABLE II. Electronic Spectra of the μ-Peroxo Complexes in Water.

Complex	λ_{max} (nm)	(ϵ) (M^{-1} cm^{-1})
$[(H_2O)L_MCoO_2CoL_M(OH_2)](ClO_4)_4$	530sh	(151)
(L_M = C-*meso* Me_2cyclam)	430sh	(316)
	305sh	(3200)
	220	(14,100)
$[(H_2O)L_RCoO_2CoL_R(OH_2)](ClO_4)_4$	525sh	(165)
(L_R = C-*racemic* Me_2cyclam)	440sh	(336)
	300sh	(2600)
	222	(34,300)
$[(HO)L_MCoO_2CoL_M(OH)](ClO_4)_2$	520sh	(73)
	310sh	(2400)
	220	(13,300)
$[(H_2O)LCoO_2CoL(OH_2)](ClO_4)_4$	534	(166)
L = Me_4[14]dieneN_4	418sh	(182)
	358sh	(279)
	220	(37,700)
$[(H_2O)LCoO_2CoL(OH_2)](ClO_4)_4$	455sh	(457)
L = Me_2[14]dieneN_4	318	(6200)
	218	(27,000)

The spectral parameters must be regarded as somewhat approximate as the complexes slowly decompose in aqueous solution.

TABLE III. Charge Transfer Absorption Spectra of Binuclear $[L_4Co(O_2,OH)CoL_4]^{3+}$ Complexes.[a]

L_4	λ_{max} (nm)	log ϵ (M^{-1} cm^{-1})
$(pn)_2$	352	3.68
$(tn)_2$	353	3.70
$(en)_2$	357	3.69
tren	350	3.86

[a] Data taken from Ref. 6.

Although stirring aqueous solutions of a cobalt(II) salt with the macrocyclic ligands cyclam [11] Me_2[14]dieneN_4 and Me_4[14]dieneN_4 leads to rapid formation of the μ-peroxo complexes at room temperature, Lawrance and Lay have reported [6] that attempts to prepare the analogous complexes of Me_6[14]dieneN_4 were unsuccessful presumably as a result of steric effects due to methyl substitution. Steric inhibition of μ-peroxo complex formation has been reported for certain non-cyclic Schiff base ligands [20–22]. Formation of brown *cis*-$[(NH_3)(Me_6[14]dieneN_4)Co]_2O_2\cdot(ClO_4)_4$ in strongly ammoniacal solutions occurs [6] presumably as a result of epimerisation of the two chiral nitrogen centres to give the N-*racemic* configuration required for *cis*-complexes. Formation of the *cis*-complex significantly reduces steric interactions in Me_6[14]dieneN_4 complexes [23]. *Cis*-$[CoL(O_2,OH)CoL]^{3+}$ complexes (L = cyclen and [13]aneN_4) occur on oxygenation of the cobalt(II) complexes of these ligands [18]. The second (μ-hydroxo) bridge is spontaneously formed in aqueous solution whenever a site *cis* to the peroxo bridge is available. Me_6[14]dieneN_4 appears to act like a 'picket fence' porphyrin for a planar ligand stereochemistry. Thus equilibrium studies have indicated that reaction of O_2 with cobalt(II) complexes of cyclam and Me_6[14]dieneN_4 in the presence of various trans axial donors (py, imidazole, NH_3, CN^- and H_2O) has a 2:1 stoichiometry with cyclam, (*i.e.* μ-peroxo complex) with a strong correlation between axial ligand basicity and O_2 affinity; but a 1:1 stoichiometry occurs with Me_6[14]diene [7]. Thus complexes (VII) and (V) can be formed with Me_6[14]dieneN_4 in planar and folded ligand stereochemistries respectively.

Kodama and Kimura [18] have studied the oxygenation of $[CoL]^{2+}$ complexes where L represents saturated 12-, 13- and 14-membered tetraazamacrocycles. Rates for the reaction of Co(II), L and O_2 in acetate buffers are first order in Co(II) and [L] but are independent of $[O_2]$ indicating that formation of $[CoL]^{2+}$ is the slowest step in oxygen uptake. The separate reaction of $[CoL]^{2+}$ with O_2 is first order in $[CoL^{2+}]$ and $[O_2]$ with the second order rate constants being *ca.* 10^4 times faster than those for the formation of $[CoL]^{2+}$ under comparable conditions. The rate of oxygen uptake by macrocyclic cobalt(II) complexes is slower (by a factor of 10^2) compared with linear tetramines.

The yellow colour of some macrocyclic cobalt(II) complexes is indicative of low spin ($t_{2g}{}^6e_g{}^1$) ($S = ½$) cobalt(II) and such complexes are subject to Jahn–Teller distortion. Very few six-coordinate low spin cobalt(II) complexes have been reported and none appear to have been structurally characterised [24]. High spin ($t_{2g}{}^5e_g{}^2$) ($S = 3/2$) octahedral complexes are typically pale red or purple. Rates of O_2 uptake by low spin cobalt(II) complexes of macrocycles would be expected to be slower than for high spin complexes obtained from linear polyamines. The axial (low spin) cobalt(II)–ligand bond lengths will tend to be much longer than the axial cobalt(II)–ligand bond lengths resulting in a significant reorganisational barrier on reaction with O_2. The cobalt(II) complexes of [15]aneN_4 and [16]-aneN_4 are high spin [25], so that marked differences in the rates of O_2 uptake as a function of ring size are expected.

Deoxygenation Reactions

Both the *C-meso* and *C-racemic* μ-peroxo complexes decompose in acidic solutions (0.01 *M*–0.5 *M* $HClO_4$). The absorbance decreases throughout the electronic spectrum, Fig. 1. Detailed kinetic studies of the decomposition of the μ-peroxo complex derived from the *C-meso* ligand indicate a two step reaction when monitored at 340 nm. For the first step $k = 5.5 \times 10^{-2}$ s^{-1} at 25 °C and for the second step $k = 9.5 \times 10^{-4}$ s^{-1}. Both reactions are independent of the hydrogen ion concentration and occur at similar rates in HCl and $HClO_4$ solutions over the ionic strength range 0.1 *M* to 0.5 *M* adjusted with NaCl and $NaClO_4$ respectively. An analogous two step reaction has been observed for the decomposition of $[(H_2O)(Me_2[14]diene\text{-}N_4)Co]_2O_2{}^{4+}$ in acidic solution with $k_1 = 1.15 \times 10^{-1}$ s^{-1} and $k_2 = 7.3 \times 10^{-4}$ s^{-1} giving the final products $Co(H_2O)_6{}^{2+}$, O_2 and $LH_2{}^{2+}$ [9].

Studies of the decomposition of the μ-peroxo complex derived from the *C-racemic* ligand monitored at 315 nm indicated a single step with $k = 3.41 \times 10^{-3}$ s^{-1}. A fast initial step could not be detected by stopped flow measurements (mixing time *ca.* 2 ms). The single decomposition step is independent of the $[H^+]$ and $[Cl^-]$ concentration. Similar kinetic behaviour is observed with $[(H_2O)(cyclam)Co]_2O_2{}^{4+}$ in $HClO_4$ solutions with $k = 3 \times 10^{-4}$ s^{-1}. In this case the final products were different at 25 and 55 °C. At the higher temperature the final spectrum corresponded to that of $[Co(cyclam)(OH_2)_2]^{3+}$ while at lower temperatures the 'product' spectrum had relatively strong ultraviolet absorption presumably due to $O_2 \rightarrow$ Co(III) charge transfer.

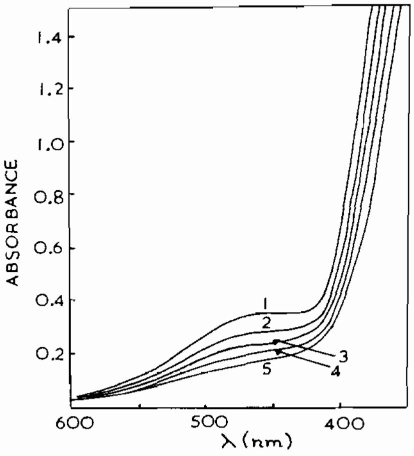


Fig. 1. Decomposition of $((H_2O)Co(Me_2[14]dieneN_4)_2\text{-}O_2{}^{4+}$ in 0.1 *M* $HClO_4$ at 25 °C; (1) = zero time, (2) = 5 min, (3) = 10 min, (4) = 15 min, (5) = 22 min.

Acknowledgement

Financial support by SERC is gratefully acknowledged.

References

1 G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976).
2 A. B. P. Lever and H. B. Gray, *Acc. Chem. Res., 11,* 348 (1978).
3 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev., 39,* 295 (1981).
4 C. G. Barraclough and G. A. Lawrance, *Inorg. Nucl. Chem. Lett., 12,* 133 (1976).
5 R. W. Hay and B. Jeragh, *J. Chem. Soc. Dalton,* 1261 (1977).
6 G. A. Lawrance and P. A. Lay, *J. Inorg. Nucl. Chem., 41,* 301 (1979).
7 G. McLendon and M. Mason, *Inorg. Chem., 17,* 362 (1978).
8 C. L. Wong, J. H. Switzer, K. P. Balakrishnan and J. F. Endicott, *J. Am. Chem. Soc., 102,* 5511 (1980).
9 C. L. Wong and J. F. Endicott, *Inorg. Chem., 20,* 2233 (1981).
10 Y. Sasaki, K. Z. Suzuki, A. Matsumoto and K. Sarto, *Inorg. Chem., 21,* 1825 (1982).
11 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem., 5,* 1514 (1966).
12 Y. Sasaki, J. Fujita and K. Sarto, *Bull. Chem. Soc. Japan, 44,* 3373 (1971).
13 C.-H. Yang and M. W. Grieb, *Inorg. Chem., 12,* 663 (1973).

14 J. D. Ortego and M. Seymour, *Polyhedron, 1,* 21 (1982).

15 R. A. Kolinski and B. Korybut-Daskiewicz, *Bull. Acad. Pol. Sci., 17,* 13 (1969).

16 R. W. Hay, G. A. Lawrance and N. F. Curtis, *J. Chem. Soc. Perkin Trans., I,* 591 (1975).

17 R. W. Hay and B. Jeragh, *J. Chem. Soc. Dalton Trans.,* 1261 (1977).

18 M. Kodama and E. Kimura, *J. Chem. Soc. Dalton Trans.,* 327 (1980).

19 K. Ishizu, J. Hirai, M. Kodama and E. Kimura, *Chem. Lett.,* 1045 (1979).

20 E. Cesarotti, M. Gullotti, A. Pasini and R. Ugo, *J. Chem. Soc. Dalton Trans.,* 757 (1977).

21 R. S. Gallard and W. P. Schaefer, *Inorg. Chem., 15,* 2759 (1976).

22 C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo and V. Valenti, *J. Chem. Soc. Dalton Trans.,* 754 (1973).

23 N. Sadasivan, J. A. Kernohan and J. F. Endicott, *Inorg. Chem., 4,* 770 (1967).

24 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd ed., Wiley, New York, N.Y. 1972.

25 See ref. 18 or ref. 8.

26 B. B. Benson, D. Krause, Jr. and M. A. Petersen, *J. Solution Chem., 8,* 655 (1979);
S. Minakami, *Igaku no Ayumi, 54,* 551 (1965).