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The Coordination Chemistry of Molybdenum and Tungsten. Part V.[1,2] Open-Chain Tetrathioether Complexes of Molybdenum(IV) and (V) and Tungsten(IV) and (V)

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The tetrathioethers α,ω-bis(methylthioalkylthio)-alkanes, $CH_3S(CH_2)_nS(CH_2)_mS(CH_2)_nSCH_2$ (n = m = 2; n = 2, m = 3; n = 3, m = 2, n = m = 3, ligand), yield seven-co-ordinate [MCl_4(ligand)] (M = Mo, W), seven-coordinate [$WoCl_3$(ligand)] in which the thioethers act as tridentate ligands, and six-co-ordinate [$(MoOCl_3)_2$(ligand)] in which the ligand acts in a tetraligate bimetallic manner. 2-5-Dithiahexane (dth) similarly yielded [MCl_4(dth)(RCN)] and [$MoOCl_3$(dth)]. The electronic, infared and electron paramagnetic resonance spectral properties of these complexes are reported and discussed.

Introduction

A number of reactions of mono- and bi-dentate thioether ligands with various halides and oxide halides of molybdenum and tungsten have been reported in recent years [3, 4] and complexes of stoichiometries $MoOCl_3(R_2S)$ [5], $WCl_6(Me_2S)_2$ [6], $WCl_4(Et_2S)$ [7], $Mo_6Cl_{12}(dth)_2$ [8], $WCl_6(dth)$ [6] and $WBr_5(dth)$ [6] (dth = 2,5-dithiahexane) have been characterized. Under certain conditions tungsten halides promote dealkylation of the thioethers, and $[R_3S]_2[WCl_6]$ complexes have been obtained [9]. As part of a continuing study of the coordination chemistry of bi-and multidentate ligands with early transition metals we report here the reactions of four openchain tetrathioethers, $CH_3S(CH_2)_nS(CH_2)_m$-$S(CH_2)_nSCH_3$ {n = m = 2 (2,2,2); n = 2, m = 3 (2,3, 2); n = 3, m = 2 (3,2,3); n = m = 3 (3,3,3)} and of 2,5-dithiathexane with $MoCl_4(PrCN)_2$, WCl_4-$(MeCN)_2$, $MoOCl_3(THF)_2$ and $WOCl_3(THF)_2$.

Experimental

Physical measurements were made as described previously [1, 10]. The tetrathioethers were prepared as reported [11] and dth was obtained by a similar method from 1,2-ethanedithiol, sodium methoxide and iodomethane. All reactions were conducted under a dry dinitrogen atmosphere using standard dry-box and Schlenk tube techniques, in predried solvents. Initially, considerable difficulty was encountered in obtaining reproducible carbon analyses by normal combustion techniques; commonly, duplicate determinations differed by ±2% and were usually 5–10% low on the calculated value. Use of a flux greatly improved accuracy and reproducibility of the determinations. Other analytical data were obtained without difficulty. All the complexes decompose in moist air and the molybdenum(IV) and tungsten(IV) complexes also react rapidly with dioxygen. The complexes were made by the same general methods, one example of each being given below.

Hexachlorodioxo {1,2-bis(2-methylthioethylthio)ethane}dimolybdenum(V), [$(MoOCl_3)_2$(2,2,2)]

Oxotrichlorobis(tetrahydrofuran)molybdenum(V) [5] (2.3 g, 6.2 mmol) was suspended in toluene (20 cm^3) and 2,2,2 (1.5 g, 6.2 mmol) in 1:1 toluene: dichloromethane (20 cm^3) was slowly added with vigorous stirring. A brown solid separated immediately, and after stirring for 3 h this was filtered off, rinsed with toluene/dichloromethane (10 cm^3, 1:1) and pentane (10 cm^3) and dried *in vacuo*. Yield ~50%, based on $MoOCl_3(THF)_2$. Reversal of the order of addition did not change the nature of the product.

Tetrachloro {1,2-bis(2-methylthioethylthio)ethane}-molybdenum(IV), $MoCl_4$(2,2,2)

Tetrachlorobis(butyronitrile)molybdenum(IV) [12] (0.43 g, 1.3 mmol) was suspended in toluene (20 cm^3) and 2,2,2 (0.31 g, 1.3 mmol) in 1:1 toluene:dichloromethane (20 cm^3) was added dropwise with stirring. After stirring for a further 3 h the precipitate was filtered off, washed with toluene/-dichloromethane (10 cm^3, 1:1) and pentane (10 cm^3) and dried *in vacuo*. Yield ~80%.

Oxotrichloro {1,2-bis(2-methylthioethylthio)ethane}-tungsten(V), $WOCl_3$(2,2,2)

Oxotrichlorobis(tetrahydrofuran)tungsten(V) [13] (1.3 g, 2.9 mmol) was suspended in toluene (40

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TABLE I. Analytical Data, Physical and Spectroscopic Properties of the Complexes.

Compound	Colour	C%[a]	H%[a]	Cl%[a]	X%[a]	ν(M=O), cm^{-1}	ν(M–Cl), cm^{-1}	$E_{max} \times 10^3$, cm^{-1} [b]	μ_{eff}, B.M.
$[MoCl_4(dth)C_3H_7CN]$[c]	Yellow–Green	21.5(22.5)	3.8(3.9)	32.7(33.1)			345, 330sh, 310sh	20.2sh, 23.8, 25.6sh	2.70
$[MoCl_4(2,2,2)]$	Yellow–Green	19.6(20.0)	3.7(3.8)	29.5(29.5)	26.7(26.7)[d]		340, 325, 300	21.0sh, 24.1, 26.3	2.62
$[MoCl_4(2,3,2)]\,1/4CH_2Cl_2$	Yellow–Green	21.4(21.3)	3.2(3.9)	34.8(33.1)			345, 330sh, 310sh	20.0sh, 23.0, 24.0sh	2.84
$[MoCl_4(3,2,3)]\,1/2CH_2Cl_2$	Yellow–Green	21.1(20.8)	3.7(4.2)	30.9(32.2)			345, 330sh, 305sh	21.8sh, 25.0	2.74
$[MoCl_4(3,3,3)]$	Yellow–Green	24.7(25.3)	3.8(4.6)	27.5(27.2)			340, 320sh, 300	21.2sh, 23.0sh, 24.8	2.80
$[MoOCl_3(dth)]\,1/4THF$	Brown	15.3(16.7)	3.0(3.3)	29.1(29.6)		960	355sh, 345, 315sh	13.4, 22.7, 25.6sh	1.62
$[(MoOCl_3)_2(2,2,2)]\,1/4THF$	Brown	15.4(15.5)	2.9(2.9)	29.6(30.5)	27.2(27.3)[e]	975	350, 325	13.6, 20.8, 27.0sh	1.40
$[(MoOCl_3)_2(2,3,2)]\,1/4THF$	Brown	16.6(16.8)	3.2(3.1)	29.8(29.9)	27.5(27.0)[e]	980	355, 330	13.5, 20.8, 25.8sh	1.30
$[(MoOCl_3)_2(3,2,3)]\,THF$	Brown	20.9(21.6)	3.9(3.9)	26.7(27.3)		970	330, 320sh, 305sh	13.2, 21.0, 25.0sh	1.35
$[(MoOCl_3)_2(3,3,3)]\,THF$	Brown	22.2(22.2)	4.1(4.0)	26.6(26.8)		980	335, 310sh, 300sh	12.7, 16.3sh, 21.0, 26.7 sh	1.31
$[WCl_4(dth)\cdot MeCN]$[f]	Brown	14.9(14.7)	2.6(2.7)	30.4(29.0)			335sh, 318, 306sh	19.8sh, 22.0	1.67
$[WCl_4(2,2,2)]\,1/2CH_2Cl_2$	Brown	15.8(16.6)	3.1(3.1)	29.0(29.0)			330sh, 315, 307sh	22.6	1.98
$[WCl_4(2,3,2)]\,1/2CH_2Cl_2$	Brown	17.0(18.2)	3.1(3.2)	27.7(28.2)			340sh, 320, 310sh	22.0	1.85
$[WCl_4(3,2,3)]\,1/2CH_2Cl_2$	Brown	18.4(19.6)	4.1(3.7)	28.4(27.6)			330sh, 320, 310sh	19.0sh, 21.9	1.89
$[WCl_4(3,3,3)]\,CH_2Cl_2$	Brown	19.8(20.6)	4.1(3.7)	29.9(30.6)			333sh, 310, 295sh	22.0	1.90
$[WOCl_3(dth)\cdot THF]$[g]	Blue	19.5(19.2)	3.0(3.6)	21.0(21.1)		980	330sh, 310, 295sh	~13.5, 21.8, 25.3sh	1.20
$[WOCl_3(2,2,2)]\,1/4CH_2Cl_2$	Blue	16.9(17.4)	3.1(3.2)	22.3(21.8)	22.3(22.5)[d]	982	350sh, 325, 315sh	~14.8, 17.8sh, 20.8, 24.5	1.32
$[WOCl_3(2,3,2)]\,1/4CH_2Cl_2$	Blue	17.9(18.9)	3.1(3.4)	21.3(21.2)		987	350sh, 315, 305sh	~13.0sh, 21.8, 26.7	1.28
$[WOCl_3(3,2,3)]$	Blue	19.9(20.8)	3.7(3.8)	18.4(18.4)		980	330sh, 315, 305sh	~13.0sh, 21.8, 26.7	1.21
$[WOCl_3(3,3,3)]\,1/4CH_2Cl_2$	Blue	21.4(22.4)	4.1(4.5)	19.6(20.0)		975	340sh, 320, 295sh	~13.0sh, 22.6, 26.2	1.19

[a] Found (calculated). [b] Diffuse reflectance spectra. [c] ν(CN) 2280 cm^{-1}. [d] S%. [e] Mo%. [f] ν(CN) 2275 cm^{-1}. [g] ν(COC) 1030, 855 cm^{-1}.

The following dth absorptions are present in:

$MoOCl_3(dth)\cdot 1/4THF$	1420(s), 1415sh, 1323(s), 1255(m), 1030(vs), 971(s), 890(w), 840(m), 725(s)
$WCl_4(dth)\cdot MeCN$	1415sh, 1320(m), 1260(m), 1025(s), 980(s), 895(vw), 840(w), 728(s)
$WOCL_3(dth)\cdot THF$	1418(s), 1405sh, 1315(m), 1250(w), 1030(s), 890(w), 840(s), 730(s)
$[MoCl_4(dth)\cdot C_3H_7CN$	1420(s), 1415sh, 1318(m), 1260(m), 1032(s), 980(s), 895(w), 842(m), 730(s).

TABLE II. Electron Paramagnetic Resonance Results.

	g_{iso}	$A_{iso} \times 10^4$ cm^{-1}	$g_{\parallel}$	$g_{\perp}$
$MoOCl_3(dth)\cdot 1/4THF$	1.948	48	1.948	1.948
$(MoOCl_3)_2(2,2,2)\cdot 1/4THF$	1.949	48	1.980	1.949
$(MoOCl_3)_2(2,3,2)\cdot 1/4THF$	1.949	48	1.980	1.947
$(MoOCl_3)_2(3,2,3)\cdot THF$	1.951	48	1.978	1.945
$(MoOCl_3)_2(3,3,3)$	1.942	48	1.948	1.945
$MoOCl_3(THF)_2$	1.940[a]	b	1.940	1.940
$WOCl_3(dth)(THF)$	1.778		1.835	1.763
$WOCl_3(2,2,2)\cdot 1/4CH_2Cl_2$	1.766		1.824	1.746
$WOCl_3(2,3,2)\cdot 1/4CH_2Cl_2$	1.761		1.820	1.738
$WOCl_3(3,2,3)$	1.744		1.795	1.730
$WOCl_3(3,3,3)\cdot 1/4CH_2Cl_2$	1.744		1.835	1.732
$WOCl_3(THF)_2$	1.73[a]		1.73[a]	1.73[a]

[a] Broad. [b] Not observed.

cm^3) and 2,2,2 (0.7 g, 2.9 mmol) in dichloromethane (20 cm^3) was added with vigorous stirring. After continuing to stir for 3 h pentane (20 cm^3) was added and the mixture stirred for a further 8 h. The blue solid formed was filtered off, rinsed with dichloromethane (10 cm^3) and pentane (10 cm^3) and dried *in vacuo*. Yield ~50%.

Tetrachloro {1,2-bis(2-methylthioethylthio)ethane} tungsten(IV), $WCl_4(2,2,2)$

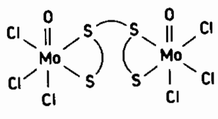
Tetrachlorobis(acetonitrile)tungsten(IV) [12] (0.41 g, 1 mmol) was suspended in toluene (20 cm^3) and 2,2,2 (2.4 g, 1 mmol) in dichloromethane (20 cm^3) was added with vigorous stirring. After 8 h pentane/20 cm^3 was added and the brown solid which was deposited was filtered off, rinsed with dichloromethane (10 cm^3) and pentane (10 cm^3) and dried *in vacuo*. Yield 63%.

Results and Discussion

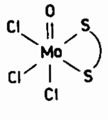
All of the complexes isolated decompose rapidly in moist air and thus had to be manipulated under a dry dinitrogen atmosphere and stored in sealed ampoules. Many of the complexes were obtained as solvates from which the solvate molecules were not removable by prolonged pumping at ambient temperatures. On quite gentle heating the complexes changed colours and sometimes partially liquified, probably due to S-dealkylation, and hence could not be desolvated in the usual manner.

Oxotrichloromolybdenum(V) Complexes

The reaction of $MoOCl_3(THF)_2$ with the tetrathioethers in toluene/dichloromethane in a 1:1 Mo:-ligand molar ratio yields $(MoOCl_3)_2$(ligand)·nTHF (L = 2,2,2, 2,3,2, 3,2,3, 3,3,3), whilst 2,5-dithiahexane forms $MoOCl_3(dth)\cdot 1/4THF$. The infrared spectra of the complexes exhibit strong ν(Mo=O) at 960–980 cm^{-1} (Table I) consistent with terminal Mo=O bonds [5] and strong partially resolved ν(Mo–Cl) vibrations at 350–300 cm^{-1} The $\nu(COC)_{asym}$ and $\nu(COC)_{sym}$ of the THF are only very slightly shifted from the values for free THF (1078 and 909 cm^{-1}), indicating that the THF is only present in the lattice since coordination shifts these frequencies to lower energy by ≤60 cm^{-1} [14]. The complexes are only very slightly soluble in halocarbon solvents and decompose in polar solvents such as N,N-dimethylformamide and alcohols. This lack of solubility precluded attempts to measure molecular weights, conductivities and n.m.r. spectra. The mass spectrum of $(MoOCl_3)_2$ (2,2,2) shows only monometallic ions, the ion of highest m/e corresponding to $MoOCl_3(MeSCH_2CH_2SCH_2)^+$, the product of β-fission of the ligand backbone [15]. The diffuse reflectance spectra of all five complexes are very similar consisting of a weak band at ~13500 cm^{-1} and a strong absorption at 20–22000 cm^{-1}, assigned as $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$, respectively, in O_h symmetry [16]. Consistent with the proposed six-co-ordinate structures, the infrared spectrum of $MoOCl_3(dth)$ shows the



(i)



(ii)

presence of the *gauche* conformer of the ligand and hence dth is chelating [8, 17, 18]. The magnetic moment of $MoOCl_3(dth)$ is 1.62 B.M. consistent with the other values reported for d^1 oxomolybdenum(V) complexes [3]; the tetrathioether complexes have slightly lower moments, 1.3–1.4 B.M., although the reason is not clear.

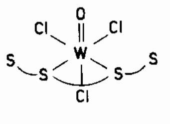
We thus assign these complexes hexaco-ordinate structures, probably of the type shown, (i) and (ii);

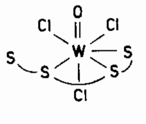
less symmetric isomers or a [cation] [anion] formulation being ruled out by the e.p.r. spectra (Table II) (*q.v.*) which show that only one molybdenum(V) environment is present.

Oxotrichlorotungsten(V) Complexes

The reaction of dth with [$WOCl_3(THF)_2$] forms [$WOCl_3$(dth)(THF)], whilst the tetrathioethers (1:1 W:ligand ratio) afford $WOCl_3$(ligand) (ligand = 2,2,2, 2,3,2, 3,2,3, 3,3,3). The products are blue microcrystalline solids which exhibit ν(W=O) at ~980 cm^{-1} and ν(W–Cl) at 350–300 cm^{-1} consistent with terminal W=O and W–Cl bonds. Once again the complexes are insufficiently soluble for either molecular weight or n.m.r. measurements to be obtained, all but for [$WoCl_3$(dth)(THF)] which is soluble enough (~10^{-4} *M*) in nitromethane and in which it is a nonelectrolyte (Λ_M = 10 ohm^{-1} cm^2 M^{-1}) [19]. The infrared spectrum of [$WOCl_3$(dth)(THF)] confirms that the dth ligand is present in the gauche conformation [8, 17, 18] (Table I) and also, unlike the case of the Mo(V) analogue, the ν(COC) vibrations of the THF are absent in the ~1070 and ~909 cm^{-1} regions, but a new set of bands appear at 1030 and 855 cm^{-1}, the shift in frequency being consistent with O-co-ordinated THF (*cf.* in $WOCl_3(THF)_2$ where ν(COC) occurs at 1049 and 856 cm^{-1}). Thus, the [$WOCl_3$(dth)(THF)] is clearly seven-co-ordinate.

For the $WOCl_3$(ligand) tetrathioether complexes there are essentially


(iii)

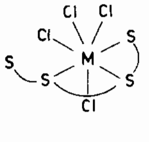

(iv)

two basic structures which are likely, a six-co-ordinate (iii) in which the ligands [3] behave as bidentates, and a seven-co-ordinate (iv) which contains a tridentate ligand. Eight co-ordination is ruled out since there are insufficient orbitals available. In the absence of n.m.r. spectra distinguishing between these two possibilities is not easy. However, the reflectance spectra of [$WOCl_3$(dth)(THF)] and [$WOCl_3$(ligand)] are very similar (Table I) and, in view of the tendency of the dth complex to become seven-co-ordinate by incorporation of a THF molecule, it is most probable that in the complexes of the tetrathioethers three of the thioether donors coordinate to achieve a similar structure. The magnetic moments of [$WOCl_3$(dth)(THF)] and [$WOCl_3$(ligand)] are ~1.2–1.3 B.M., lower than their Mo(V) analogues, but consistent with the presence of one unpaired electron. Similar moments have been observed for other tungsten(V) complexes [20].

The fact that the oxotungsten(V) complexes appear to be seven-co-ordinate, whilst the oxomolybdenum(V) species are six-co-ordinate seems to indicate that the former are more electronically disposed to achieve a higher co-ordination number. Steric effects are unlikely to account for the difference since the covalent radii of Mo(V) and W(V) are expected to be very similar due to the lanthanide contraction effect. The possibility that the difference is merely the result of solubility differences, *i.e.* that the least soluble complexes are precipitated, is unlikely since (a) the $WOCl_3$(ligand) and the (unknown) $MoOCl_3$(ligand) would not be expected to differ much in solubility and (b) the $MoOCl_3$(dth) is also six-co-ordinate, whereas if seven-co-ordination was electronically favoured it could easily have retained one THF and formed [$MoOCl_3$(dth)(THF)].

Molybdenum(IV) and Tungsten(IV) Complexes

2,5-Dithiahexane reacts with [$MoCl_4(PrCN)_2$] and [$WCl_4(MeCN)_2$] to produce [MCl_4(dth)(RCN)] (M = Mo, R = Pr; M = W, R = Me) as moisture- and air-sensitive brown powders. The complexes have only slight solubility in organic solvents, but [$MoCl_4$(dth)(PrCN)] is sufficiently soluble in dry nitromethane (~10^{-4} *M*) to obtain a conductance value (Λ_M = 18 ohm^{-1} cm^2 M^{-1}) which shows it to be a non-electrolyte [19]. The dth ligand is once again present in the gauche conformation and is thus chelating, and the nitrile ligands are coordinated since they exhibit ν(CN) vibrations (Table I) shifted to higher frequency by >40 cm^{-1}, consistent with coordination [12]. This evidence, taken together with evidence for only terminal M–Cl bonds, clearly indicates that the complexes are seven-co-ordinate, although speculation about which possible heptacoordinate structure is present is unwise in view of the likely distortions. The tetrathioethers yield [$MoCl_4$(ligand)] and [WCl_4(ligand)] which exhibit essentially similar diffuse reflectance and infrared spectra to the dth complexes, and are thus probably seven-coordinate also, (V). Once again, problems of insolubility


(v)

precluded n.m.r. measurements, and the complexities of the ligand absorptions in the infrared spectrum made attempts to distinguish co-ordinated and unco-ordinated–SMe groups unsuccessful.* The magnetic moments of the molybdenum(IV) complexes are

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*Eight-co-ordination is ruled out for high-spin molybdenum(IV) and W(IV) by lack of available metal orbitals.

slightly high, μ_{eff} = 2.6–2.8 B.M., for d^2 Mo(IV), indicative of distortion and some orbital contribution, but clearly indicative of the presence of two unpaired electrons, whilst, as expected [12, 19], the tungsten(IV) analogues have lower moments, ~1.8–1.9 B.M.. If care is taken in protecting these samples from air reproducible diffuse reflectance spectra are obtainable; the [$MoCl_4$(ligand)] complexes exhibiting a band or a shoulder at ~20 000 cm^{-1} and a broad band of ~23 000 cm^{-1} with a shoulder at ~25 000 cm^{-1}; the tungsten(IV) complexes exhibit only a broad absorption at ~22 000 cm^{-1}, although in two cases a weak shoulder on the low energy side is evident. In view of the likelihood of considerable distortions from idealised geometries no particular heptacoordinate geometric assignment can be made. In the presence of air both groups of compounds oxidise rapidly, the infrared spectra subsequently showing bands assignable to ν(M=O) and the reflectance spectra also showing evidence for M(V) products.

Electron Paramagnetic Resonance Spectra

E.p.r. spectra are listed in Table II, which also includes the values we obtained for the starting materials $MOCl_3(THF)_2$ (M = Mo, W). The g values for $(MoOCL_3)_2$(ligand) and $MoOCl_3$(dth) are very similar and show the presence of only one environment for the molybdenum atom in each case. The g_{iso} values for these thioether complexes are ~1.95 which is rather lower than the values found for a series of oxotrichloromolybdenum(V) complexes of phosphorus and arsenic ligands [1] ($g_{iso} \cong$ 1.96–1.97) and higher than g_{iso} for nitrogen donor Schiff base ligands [21]. In solution all the thioether complexes exhibit the normal molybdenum hyperfine splitting of six lines (^{95}Mo, ^{97}Mo, I = 5/2), but for $MoOCl_3(THF)_2$ only one broad signal and no hyperfine splitting was observed.

The oxotrichlorotungsten(V) complexes exhibit lower g_{iso} values, as expected, ranging from 1.74–1.78 and, once again, show evidence for one type of environment for the tungsten atom. As in the case of the molybdenum analogue, $WOCl_3(THF)_2$ exhibits only one broad signal.

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References

1 Part II. W. Levason, C. A. McAuliffe and B. J. Sayle, *J. Chem. Soc. Dalton*, in press.
2 Part III. C. A. McAuliffe and B. J. Sayle, *Inorg. Chim. Acta, 14,* L43 (1975). Part IV. W. Levason, C. A. McAuliffe and F. P. McCullough, *Inorg. Nucl. Chem. Letts.*
3 D. L. Kepert, "The Early Transition Metals", Academic Press, London (1972).
4 R. A. Walton, *Prog. Inorg. Chem., 16,* 1 (1972).
5 K. Feenan and G. W. A. Fowles, *Inorg. Chem., 4,* 310 (1965).
6 P. M. Boorman, M. Islip, M. M. Reimer and K. J. Reimer, *J. Chem. Soc. Dalton,* 890 (1972).
7 M. Saheffer-King and R. E. McCarley, *Inorg. Chem., 12,* 1972 (1973).
8 R. A. Walton and D. A. Edwards, *Spectrochim. Acta, 24A,* 833 (1968).
9 P. M. Boorman, T. Chivers and K. N. Mahader, *Can. J. Chem., 53* 383 (1975).
10 L. Baracco and C. A. McAuliffe, *J. Chem. Soc. Dalton,* 948 (1972).
11 W. Levason, C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta, 17,* 247 (1976).
12 E. A. Allen, B. J. Brisdon and G. W. A. Fowles, *J. Chem. Soc. A,* 4531 (1964).
13 G. W. A. Fowles and J. L. Frost, *J. Chem. Soc. A,* 671 (1967).
14 G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Inorg. Nucl. Chem., 31,* 3119 (1969).
15 C. A. McAuliffe, S. G. Murray and R. D. Sedgwick, *Inorg. Chim. Acta,* 14, 49 (1975).
16 A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1968).
17 R. A. Walton, *J. Chem. Soc. A,* 1852 (1967).
18 R. J. H. Clark and W. Errington, *Inorg. Chem., 5,* 650 (1966).
19 W. J. Geary, *Coord. Chem. Revs., 7,* 81 (1971).
20 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem., 6,* 37 (1964).
21 W. Levason, C. A. McAuliffe, F. P. McCullough and A. C. Rice, to be published.