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Oxy-complexes and their Vibrational Spectra

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The vibrational spectra of a number of monomeric oxy-complexes of the form $(MO_nX_{6-n})^{x-1}$ (n = 2, 3, 4, and 6) have been measured, and also the spectra of dinuclear species involving one or two bridging oxygen atoms. The factors influencing the structures of such complexes are discussed.

BOTH the stretching and deformation vibrations of metal-oxygen bonds give strong and characteristic bands in the i.r. and Raman spectra of oxy-complexes, and thus vibrational spectroscopy is a valuable method for the determination of the structures of such species; since terminal metal-oxygen bonds are multiple their vibrational frequencies should be sensitive to changes in the degree of metal-oxygen π -bonding. Thus M=O stretches are found near 950 cm.⁻¹ for mono-oxy-species,¹ near 820 cm.-1 for trans-dioxo-,2,3 and near 930 and 890 cm.⁻¹ for *cis*-dioxo-species.⁴ Raman spectra are also valuable for studying the structures of oxy-complexes in aqueous solution where crystal-splitting effects are avoided. We now extend studies on this topic to a variety of mono- and di-nuclear oxy-complexes and attempt to account for their observed structures.

The three types of complexes studied are (I), (II), and

¹ D. Brown, J. Chem. Soc., 1964, 4944; J. Selbin, L. H. Holmes, and S. P. McGlynn, J. Inorg. Nuclear Chem., 1963, **25**, 1359.

² W. P. Griffith, J. Chem. Soc., 1964, 245.
 ³ N. P. Johnson, C. J. Lock, and G. Wilkinson, J. Chem. Soc.

1964, 1054.

⁴ W. P. Griffith and T. D. Wickins, J. Chem. Soc. (A), 1968, 400.

(III); the numbering systems for the ligands are also defined in the diagrams.

Mononuclear Complexes (I).—Dioxo-complexes

 $(MO_2X_4)^{x-}$. For these we expect two metal-oxygen stretching modes, one symmetric [v^s(MO₂)] and one asymmetric $[v^{as}(MO_2)]$, and a deformation $[\delta(MO_2)]$. For *cis*-dioxo-species (symmetry C_{2n}) $\nu^{s}(MO_{2})$ and $\delta(MO_2)$ are A_1 modes, polarised in the Raman, and $v^{as}(MO_2)$ is B_1 , depolarised in the Raman; all three are active in the Raman and i.r. For trans-dioxo-species, which are centrosymmetric and have D_{4h} symmetry, $v^{s}(MO_{2})$ is an A_{1g} mode, polarised in the Raman but inactive in the i.r., while $v^{as}(MO_2)$ (A_{2u}) and $\delta(MO_2)(E_u)$ are i.r.-active only. Table 1 shows the three modes for a number of trans-dioxo-complexes; a number of the complexes listed therein are known to have this structure from X-ray studies $\{viz., K_2[OsO_2(OH)_4], 5\}$ $K_2[OsO_2Cl_4]$, $K_3[ReO_2(CN)_4]$, and $K_4[MoO_2(CN)_4]$ and

- ⁶ F. H. Kruse, Acta Cryst., 1961, **14**, 1035. ⁷ K. Lukaszewicz and T. Glowniak, Bull. Acad. polon. Sci., 1961, 9, 613.
 - ⁸ S. J. Lippard and B. J. Russ, Inorg. Chem., 1967, 6, 1943.

⁵ N. A. Porai-Koshits, L. A. Atovyman, and V. G. Adrianov, J. Struct. Chem. U.S.S.R., 1960, 2, 686.

J. Chem. Soc. (A), 1969



these show, as expected, one Raman and two i.r. (MO_2) vibrations. The intensity of the Raman bands near 880 cm.⁻¹ and the fact that they vary little in frequency whatever the nature of other ligands present suggests that this is indeed the polarised A_{1g} mode; the two i.r.

bands have previously been assigned for most of these complexes. The other complexes in Table 1 show bands in similar positions with similar activities and may be assumed to have the trans-dioxo-structure as well.

Table 1 also shows metal-oxygen stretching force

TABLE 1 Vibrational spectra of dioxo- and trioxo-complexes

		vibration	ai specifa (or uloxo-	and thoso-complexes		
trans-Dioxo		$\nu^{\rm g}({ m MO}_2)$	$\nu^{as}(MO_2)$	$\delta(MO_2)$	Other strong bands	k	k_{i}
Cs ₂ [OsO ₂ (OH) ₄]	R	852(10)		,	$372(4)(\nu_{O_{8}-O}), 245(3)(\delta_{O_{8}-O})$	6.03	0.79
	I.r.	004/0	806vs	299s	$1052m(\delta_{OB-OH}), 440vs(\nu_{OB-O})$	a a=	
$K_2[OsO_2OI_4]$	К* Т-	904(6)p	82710	208110	$313(10,p)(\nu_{Os-Cl}), 300(4)dp(\nu_{Os-Cl}), 200(1)(\delta_{Os-Cl})$	6.67	1.03
(pvH) [OsO (OH) Cl.]	R	900(10)	00103	00003			
$K_2[OsO_2Br_4]$	R	899(5)			$193(10)(\nu_{\text{Os-Br}}), \ 182(4)(\nu_{\text{Os-Br}})$	6.68	0.96
	R *	900(10)	0.40	205	192(10)p		1 1
$\operatorname{Us}_{2}[(\operatorname{Us}_{2}\operatorname{Br}_{4}] \dots \dots$	I.r. R		842vs	290s	$220 \mathrm{W}(\nu_{\mathrm{Os-Br}})$	6.62	1.01
112[0302(01()4]	R*	886(10)p			$430(3)(\nu_{O8-C})$	6·47	0.92
	I.r.		830vs	280s	$437(\nu_{OB-O}), 455(\nu_{OB-C}), 353$ vs		
$[OsO_2(NH_3)_4]Cl_2$	R	865(10)	07	9701		6.55	0.49
K [OsO ov.]	I.r. R	910(10) 8	07VS	2700	$482 m(\nu_{OS-N}), 200 VS, D$ $440(3)(\nu_{OS-N})$	6.62	1.11
	I.r.	510(10)	824vs		±±0(0)(P08-0)	0.02	
$K_2[OsO_2(OH)_2 \text{ ox}]$	\mathbf{R}	881(10)			$400(2)(\nu_{O8-O})$	6.21	1.10
[D-0]C]	I.r.	200/10)	796vs	316s	$407 m(\nu_{0s-0})$	0 00	1 01
$[\text{ReO}_2 \text{ en}_4] \text{O}_2 \dots \dots \dots$	к Тт	* 890(10)	790ws	3215		0·20	1.21
$K_3[ReO_2(CN)_A]$	R	871(10)	10013		2141(10), 2130(4)($\nu_{C=N}$), 420(1)(ν_{Be-C})	6.02	1.28
	R *	. 881(10)p	-		2141(8)p, 2130(2)($\nu_{C=N}$), 431(1)(ν_{Re-C}), 230(1)(δ_{Re-C}))	
K (Ba O (CN) 1 4H O	L.r.	1 069(10)	768vs	258m	019(4)() 490b()		
$M_6[M_2O_3(ON)_8], 411_3O$	Lr.	808(10)	781s. 746s	249	$2123s, 2080s, b, 909s(v_{Re=0}), 476, 467(v_{Re=0}) 335s$		
K ₄ [MoO ₂ (CN) ₄]	R	779(10)	,		$602(\frac{1}{2}), 394(1)(\nu_{Mo-C})$	5.27	0.50
	I.r.		826s	317s	2083s, 2072s($\nu_{C\equiv N}$), 912m, 513w(ν_{Mo-C}), 238s		
cis-Dioxo *		$\nu^{\rm s}({\rm MO}_{\rm s})$	$v^{as}(MO_{a})$	δ(MO ₂)			
		$(A_1)^{2/2}$	(B_2)	$(A_1)^{(A_1)}$			
Na ₂ [WO ₂ F ₄]	R *	958(10)p	904(7)dp	378(1)		7.53	0.41
$Cs_2[WO_2Cl_4]$	R	935(10)	886(7)	370(2)		7.46	0.67
$Na_2[MoO_2F_4]$	К *	951(10)p	920(7)dp	385(1)		7.05	0.23
$\operatorname{Na}_{2}[\operatorname{MOO}_{2}\operatorname{Cl}_{4}]$	л т р	904(10)p	920(0)up	392(1)		5.0	0.30
$\mathbf{R}_{3}[\mathbf{VO}_{2}\mathbf{F}_{4}]$	К	928(10)	890(3)	301(2)		9.9	0.24
(1,2,3)-Trioxo		v ^s (MO ₃) v ^{ss})M(O_3) $\delta^{s}(MO_3)$	$ u^{\rm as}({ m MO}_3)$	Other strong bands	k	ki
	_	$(A_1) \qquad (E)$	(A_1)	(E)			
$K[OsO_3F_3]$	R	935(10) $918(0)$	6) 345(5)	329(3)	$594(1)(\nu_{0s-F}), 387(6)(\delta_{0s-F})$	7.35	0.81
K.[WO.F.]	R I.r.	931(10) 828($\frac{5}{3}$ 328(10)	328(10)	$575S(\nu_{OB-F}), 465S(\nu_{OB-F})$	6.39	0.54
	I.r.	926w 833v	s 322s	322s			
$(NH_4)_3[MoO_3F_3]$ †	R	900(10) 824(8	B) 365(2)	365(2)	$652(1)(\nu_{Mo-F})$	5.81	0.35
$MoO_3(dien)$ †	<u>R</u> *	892(10)p 839(3)dp $317(7)$	317(7)		6.71	0.83
$Na_2[MO_2O_6(EDTA)]$	K D*	892(10) 815(8	340(10)	374(3)		0.04	0.18
	к* Т-	802m 840-	#)ap 330(10)				
	1.1.	0000111 04011	1 0443				

* Aqueous solution; all other spectra on solid samples. Bands due to ammonia, oxalate, pyridine, EDTA, and dien not listed; p = polarised; dp = depolaried. \dagger Ref. 4. \ddagger Ref. 3.

constants (k) and stretch-stretch interaction force constants (k_i) for these trans-species and also for some cis-complexes; the secular equations of Cotton and Wing ⁹ were used for these calculations. It is apparent from the values and also from the $v^{s}(MO_{2})$ frequencies that the *cis*-species have higher k values than the *trans*consistent with the fact that three metal t_{2g} orbitals are available to the oxygen $2p_{\pi}$ orbitals in the *cis*-structure and only two for the trans.⁴ The k values, among trans-species, decrease in the sequence osmium(vi) >rhenium(v) > molybdenum(iv) as would be expected since the electron-attracting power of the metal for oxygen $2p_{\pi}$ electrons decreases in this sequence; a similar effect was observed with cis-dioxo-complexes of sexi- and quinque-valent species.⁴ All the interaction constants k_i for these and other complexes studied here are positive, as expected for transition-metal complexes.⁹

Most of the transition-metal dioxo-complexes reported in the literature have d^0 or d^2 electron configurations for the transition-metal atoms and all the d^0 complexes we have studied have the cis-structure and d^2 the trans. There are however old reports of a few d^1 dioxo-species such as $(pyH)[MoO_2Cl_2(H_2O)_2]$,¹⁰ $Li[MoO_2Br_2(H_2O)]$, aq,¹¹ (pyH)₂[WO₂(NCS)₃],¹² and (pyH)₂[MoO₂(NCS)₃].¹³ On the basis of former arguments⁴ we might expect such complexes to take the trans-structure with the single d electron entering a ' non-bonding ' d_{xy} orbital, but we find that their Raman and i.r. spectra show only one band in the metal-oxygen stretching region rather than the two expected for either a cis- or a trans-dioxo-system. This, together with the presence of bands near 500 cm.⁻¹, which may be associated with bridging oxygen systems (see below), suggests that the compounds may well be dimers of the form $(M_2O_4X_6)^{x-}$ involving two bridging oxy-ligands and one terminal oxy-ligand per metal (III); to minimise competition for metal t_{2q} orbitals these terminal ligands are probably in positions 1 [M(1)] and 10 [M(2)]. The spectra of Na₂[Mo₂O₄(EDTA)] are consistent with a similar structure for this compound (a similar conclusion has been reached from ¹H n.m.r. and preliminary X-ray data 14,15).

The only reported dioxo-complex with more than two bonding d electrons is $K_4[ReO_2(CN)_4]$, formed by the action of potassium cyanide on K2(ReCl6); the formula was given on the basis of carbon and nitrogen analyses only, and no magnetic or spectroscopic information was reported.¹⁶ The only other established Group VIIa cyano-complex of the (+iv) state is $K_{4}[Tc(OH)_{3}(CN)_{4}]$.¹⁷ We find that the correct formula for the rhenium compound appears to be closer to K₆[Re₂(CN)₈O₃],4H₂O; the magnetic moment is very low ($\chi_g=4{\cdot}81~\times~10^{-7}$

- ⁹ F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, 4, 867.
 ¹⁰ R. G. James and W. Wardlaw, *J. Chem. Soc.*, 1927, 2153.
 ¹¹ F. G. Angell, R. G. Jones, and W. Wardlaw, *J. Chem. Soc.*, 1929, 2153.

- ¹² A. Rosenheim and E. Dehn, Ber., 1915, **48**, 1168.
 ¹³ R. G. Jones and W. Wardlaw, J. Chem. Soc., 1928, 2726.
 ¹⁴ P. C. H. Mitchell, Quart. Rev., 1966, **20**, 103; D. T. Sawyer
 ¹⁵ J. W. Wardlaw, J. Chem. 1966, **20**, 103; D. T. Sawyer
- and J. M. McKennie, *J. Amer. Chem. Soc.*, 1960, **82**, 4191. ¹⁵ L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, 1967, **6**, 2146.

c.g.s.u.); from the above molecular formula the magnetic moment per rhenium atom is 1.25 B.M. The Raman and i.r. spectra (Table 1) show bands which may be assigned to v^s and v^{as}(MO₂) at 868 cm.⁻¹ and 760 cm.⁻¹ of a trans-ReO₂ group, as in K₃[ReO₂(CN)₄]; there is also a band, apparent in both the Raman and i.r. at 909 cm.⁻¹ which we assign to a terminal Re=O stretch. A structure consistent with the spectra and magnetic properties of the complex is (IV). It may therefore be a

$$\begin{bmatrix} O & O \\ \parallel & \parallel \\ (CN)_{3}Re-C\equiv N-Re(CN)_{4} \end{bmatrix}^{6-}$$
(IV)

mixed valence state complex of rhenium(v) and rhenium(III); hence the dark colour, often associated with mixed oxidation states, and the low moment, since the rhenium(v) dioxo part will be diamagnetic. The i.r. band at 2123 cm.⁻¹ presumably arises from the linear cyanide bridge. Thus the dioxo part of the molecule has a d^2 configuration and the necessity to promote electrons to an antibonding orbital is avoided.

Trioxo-complexes, $(MO_3X_3)^{x-}$. We have suggested that d^0 trioxo-complexes will take up the (1,2,3) C_{3v} cis rather than the (1,2,6) C_{2v} structure; ⁴ this is known to be so for MoO_3 (dien) from X-ray studies,¹⁸ and for the potassium and ammonium salts of $(MoO_3F_3)^{-4}$ Table 2 shows the spectra of $K(OsO_3F_3)$, $K_3(WO_3F_3)$, and $Na_4[Mo_2O_6(EDTA)]$. For the (1,2,3) C_{3v} structure we expect two Raman-polarised A_1 modes, v^{s} and $\delta^{s}(MO_3)$, and two E modes, v^{as} and $\delta^{as}(MO_3)$, all active in the Raman and i.r. [the $(1,2,6)C_{2v}$ form would require 6 bands, 3 polarised in the Raman]. The spectra support the C_{3v} rather than the C_{2v} configuration in each case, as expected. For Na₄[Mo₂O₆(EDTA)], for which the (1,2,3) configuration for the oxygen atom has been suggested,¹⁴ we assume C_{3v} local symmetry.

Again we list k and k_1 values calculated from Cotton and Wing's equations.⁹ As expected the k values are somewhat lower for these cis-trioxo-species than for the cis-dioxo-complexes, since in the former case 3 oxyligands compete for the metal t_{2g} orbitals rather than 2. The higher k value for $K(OsO_3F_3)$ than for $K_3(WO_3F_3)$ is consistent with the higher oxidation state of osmium in the complex.

No mononuclear trioxo-species with one or more delectrons has been reported.

Tetraoxy-complexes, $(MO_2X_4)^{x-}$. Three unstable species of this type have been reported: $[OsO_4(OH)_2]^{2-19}$ (potassium, caesium, and barium salts), $Cs_2(OsO_4F_2)$,¹⁹ and $Ba[ReO_4(OH)_2]$; ²⁰ the last two complexes could be examined only by Raman spectroscopy since they are

¹⁶ P. H. L. Walter, J. Kleinberg, and E. Griswold, *Inorg. Chem.*, 1962, **1**, 10.

- 17 K. Schowchau and W. Herr, Z. anorg. Chem., 1962, 318, 198.
- F. A. Cotton and R. C. Elder, Inorg. Chem., 1964, 3, 397.
 E. Fritzmann and L. Tchugaev, Z. anorg. Chem., 1938, 172, 213; F. Krauss and D. Wilken, *ibid.*, 1925, 145, 151.
- ²⁰ B. Scharnor, Z. anorg. Chem., 1933, 145, 151.

stable only in the presence of aqueous solutions containing fluoride and hydroxide ions respectively.

For cis-complexes of this type (C_{2v}) we expect 4 M=O stretches $(2A_1 + B_1 + B_2)$, all active in the Raman and i.r. with the A_1 modes Raman-polarised, and 6 deformations $(2A_1 + 2B_1 + 2B_2)$, while for the centrosymmetric trans (D_{4h}) form we expect 3 stretches (A_{1g}) , polarised and active in the Raman only; B_{1g} , depolarised and Raman-active; B_{1u} , i.r.-active), and 4 deformations $(A_{2u} + E_u, \text{ i.r., and } B_{2g} + E_g, \text{ Raman})$. claimed there is no evidence for their being pentacoordinate. The spectra of $K_3(\text{ReO}_5)$, $K_3(\text{OsO}_5)$, and $K_3(\text{IO}_5)$ (the three are isomorphous ²¹) together with those of Na₃(ReO₅) are listed in Table 4. The lack of coincidences of Raman and i.r. bands of the rhenium and iodine complexes (the osmium salt is too dark to record the Raman spectrum) suggests a centrosymmetric structure. This, the fact that the number of M=O stretching bands is too large for either a square based pyramidal or a trigonal bipyramidal structure (both

	Vi	brationa	l spectra	of tetra	- and h	nexa-oxy-	comple	xes					
cis -Tetraoxy $\nu^{s}(MO_{a})$		$\nu^{s}(MO_{A})$	$\nu^{\rm as}({ m MO}$	D_{4}) $\nu^{as}(MO_{4})$		δ(MO ₄)				Other strong bands			
$Ba[OsO_4(OH)_2] \dots R 878(10) \\ I.r. 885m \\ 875n$		864(4) 865m	860(] 858m	\tilde{b} 820($\frac{1}{2}$) 825s		306w, 279w 348m, 325vs, 318s				m(v _{0s-0})	, 240w,t	ο(δ _{Os-O})	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	875(10)p 945(10) 903(10)	929(3) 882(4)	921(2) $860(\frac{1}{2})$	820)) 82:	0(1) 2(3) :	380(7) 399(2) 373	$\begin{array}{cc} 325(2) \\ 5(3) & 34 \end{array}$	310(1) 5(1) 299	(2) 450	(2) (v _{Re-0}	5)		
Hexa-oxy				$\nu(MO_{e})$						δ(N	IO.)		
Na ₅ [ReO ₆] R I.r. 90	872(4) 3s	815(4)	759(10)	645vs		563(2)	519(1)		$378(\frac{1}{2})$ 363s	310m	07		
$Ba_{5}[OsO_{6}]_{2}$ I.r. 89 $K_{5}[IO_{6}]$ R	3m 855m 782(1)	819w	729(10)	645m 686(1)	662(6)	555vs 580w	483w $451(\frac{1}{2})$	465s 431(1)		390m	350s 319vw	33 5s	
$Ba_3[OsO_6]$ I.r. 87 Ba_[WO] Ba_1 [WO] Ba_1 [WO] Ba_2 [WO]	7m 3m 862m	752vs 828w 810(7)	708(0)	685s 694w 765(10)		602vs 588vs	440s 508w	490 w	420s 469w	400/0	320s	261 s	
$Ba_{3}[WO_{6}]$ R Ba_[MoO_{6}] R	7s 904vs	812(3)	797(2)	705(10)	588vs 727(10	558vs	521vs	478w	421(0)	$341(\frac{1}{2})$	335s 334(1)	275s	
I.r. 909 Hg ₃ [TeO ₆] R	9w 855m	806vs	(-)	683(5)	625(1)	690m	606m	507m 511(1)	424(10)	225m	$\begin{bmatrix} 318(\frac{1}{2}) \\ 319s \\ 262(7) \\ 271m \end{bmatrix}$	285 s	

TABLE 2

* Aqueous solution spectra; all other spectra in solid samples.

TABLE 3

Linear complexes		$\nu^{as}(M_2O)$	$\nu^{s}(M_{2}O)$	$\delta(M_2O)$	Other strong bands	k	ki
K ₄ [Ru ₂ OCl ₁₀]	R		254(7)	138w?	$357(5), 289(10)(\nu_{Ru-Cl}), 194(1), 180(3)(\delta_{Ru-Cl})$	3.74	0.25
	I.r.	886s			461m, $323vs(\nu_{Ru-Cl})$, $233w,b$		
K ₄ [Ru ₂ OBr ₁₀]	I.r.	860s					
$K_4[Re_2OCl_{10}]$	R	055-	200(1)		$356(8), 296(1)(\nu_{\text{Re-Cl}}), 176(10)(\delta_{\text{Re-Cl}})$	3.39	1.00
$K_{2}[Mo_{2}O_{5} ox_{2}(H_{2}O)_{2}]$	R R	0005	235(4)		$958(6), 919(10)(\nu_{M_0O_0}), 385(4)(\delta_{M_0O_0})$	3.12	0.01
	I.r.	851s	()		962vs, 917vs($\nu_{M0=0}$)		
$(NH_4)_4[Os_2OCl_{10}]$	\mathbf{R}		224(7)		$340(1), 330(\frac{1}{2}), 290(3)(\nu_{Os-Cl})$	4.42	1.16
	I.r.	848m			317vs, $306vs(\nu_{Os-Cl})$		
$(\mathrm{NMe}_4)_4[\mathrm{Os}_2\mathrm{OCl}_6\mathrm{Br}_4]$	R		223(2)		$339(10)(\nu_{Os-Cl}), 191(7)(\delta_{Os-Cl}), 183(3), 165(10), 157(3)(\nu_{Os-B})$	4.41	1.17
	I.r.	846w			310s, 290s(ν_{Os-Cl})		
NEt ₄) ₄ [Os ₂ OBr ₁₀]	\mathbf{R}		237(4)	136(1)?	$185(10)(\nu_{Os-Br})$	4.70	1.50
	I.r.	846w					

Thus the distinction between the two possible structures is not as clear as for dioxo- and trioxo-species; and this, with the difficulty of obtaining spectra of these salts, prevents an unequivocal assignment of bands. Nevertheless the coincidence of a number of Raman and i.r. lines for Ba $[OsO_4(OH)_2]$ suggests that this does not have a centre of symmetry, and the presence of two strong Raman bands in the M=O stretching region also supports a C_{2v} symmetry for these complexes rather than D_{4h} (Table 2).

Penta- and hexa-oxy complexes, $(MO_5)^{z-}$ and $(MO_6)^{z-}$. Although a number of pentaoxy-species have been would require four M=O stretches), and the presence of bands near 500 cm.⁻¹ which may arise from bridging dioxo-modes, suggests that these have dimeric structures of the type (III).

The complexity of the spectra of the hexaoxy-complexes listed in Table 3 clearly indicates the presence of a low site symmetry and no attempt at assignment of modes beyond the splitting of stretches and deformations has been attempted; the lack of coincidences of Raman

²¹ R. Scholder and K. L. Huppert, Z. anorg. Chem., 1964, 334, 209; R. Scholder, Angew. Chem., 1958, 70, 583; R. Scholder and G. Schatz, Angew. Chem., 1963, 2, 264.

and i.r. frequencies does however suggest the retention of a centre of symmetry, so perhaps C_i (for which 6 A_g Raman modes, and 9 A_u i.r. modes would be expected) represents the symmetry of most of them. The only simple spectrum is that of $Hg_3(TeO_6)$ which is known from X-ray studies to have D_3 symmetry and a Te-O bond length of 1.98 Å; ²² Na₅(IO₆), Na₅(ReO₆), and Na₅(OsO₆) are isomorphous.²¹ A number of the bands since 6 oxy-ligands compete for 3 t_{2q} orbitals in the octahedral complexes while in tetrahedral species π -bonding is possible from the 4 oxy-ligands to all five *d* orbitals, giving a higher metal-oxygen bond order.

Dinuclear complexes (II and III).-With one oxygen bridge (II). If we regard complexes of the type $(X_5M-O-MX_5)^{x-}$ as 'three-body' systems the three vibrations which mainly involve the M-O-M linkage are,

							-							
	۲	Vibrationa	l spect	tra of d	inucle	ar com	plexes	with	two o:	xygen	bridges	5		
D_{2h} Symmetry		$\nu^{\rm s}({\rm M_2O_2}) \nu^{\rm a}$	(M_2O_2)	(A)		<i>v</i> <u>M</u> =0				δ <u>m</u> =	₌ο, δ(M₂	2O2)		Other strong
$K_4[As_2O_2F_8]$	R	548(2)	(D _{2u})	(21 19)							290(3)			$\begin{array}{c} 697(10), \\ 601(1)(\nu_{As-F}) \\ 404(3) \end{array}$
	I.r.		492s 495vs								309s			689s, 637vs, 595m, 381s
$Ba_2[Mo_2O_4 ox_2(H_2O)_2] \dots$	R Ir	499(3)	578w	971(10) 975ys							305(2)	224(2)		
$K_4[Os_2O_6(NO_4)_4]$	R I.r.	540(2)	887m 841s	884(10)							245m,	Ъ		557m, 505m(ν_{Os-N}), 245
K ₄ [Te ₂ O ₈ (OH) ₂]	R	655(2)		682(10)					403(4)	384(3)	$341(\frac{1}{2})$			$552(2)(\nu_{\rm Te-O})$
K ₆ [Re ₂ O ₁₀]	1.r. R I	661(10)	581vs	867(10)	725s 942(2)	897(3)	077-	814w	465(2)	452(3)	3555 351(3)	240w 337(4)	204-	
Na ₆ [Re ₂ O ₁₀]	R I.r.	627(3) 625s	588vb	815(10) 926s 909ys	891(6)	901VS 873(6)	742(2)	676(2) 662m	420w 425w	374(4)	335(2)	299w	2945	
K ₆ [I ₂ O ₁₀]	R I.r.	663(4)	541m 562vs	733(10)	909s	795(2) 784w	719vs		452(1) 446w	433(3) 431w	401w 399vs	388(1)	336(2)	
K ₆ [Os ₂ O ₁₀]	I.r.	617w	518w	884m	769vs	741vs					333w	321m 307w	270w	
C_{2k} Symmetry $K_4[I_2O_8(OH)_2]$ $Na_2[Mo_2O_4(EDTA)]$ $(pyH)_4[W_2O_4(NCS)_6]$	R I.1 R R I.1	$ \nu^{s}(\mathbf{M}_{2}O_{2}) (A_{g}) 654(8) (A_{2}) (A_{2})$	$ $	O ₂) (A ₂ 730(953(963(963(952) 952(952)) 10) 781 757 10) 10) 10) 10) 75	ν <u>m</u> = 749; w	=0 (1) 703((2) 433 410 400	δ _{M=} 390 s 378 (1) 390 b 365	$\begin{array}{c} \text{co, } \delta(M_2) \\ (4) & 332 \\ \text{s} & 352 \\ (1) & 314 \\ & 312 \\ (4) \\ & 335 \\ & 335 \end{array}$	O ₂) (2) 280 m 285 320 (7) (7) s	(2) 518 m m	Other s (7)(v _{I-0})	trong bands 1, 432(v _{I-0})
$(pyH)_{2}[Mo_{2}O_{4}(RCS)_{6}]$ $(pyH)_{2}[Mo_{2}O_{4}Cl_{4}(H_{2}O)_{2}]$ $Li_{2}[Mo_{2}O_{4}Br_{4}(H_{2}O)_{2}]$	R	r. r.	490s 485s 602s	932(943) 978) 978(75 75 2)					285 295 295 295	m m m	210	(10) (vmo 78(1)	о-вг), 194(1),
	I. 1	r.		9695	'S							230	b(имо-в	.)

TABLE 4

* Aqueous solution spectra; all other spectra on solid samples. Bands due to oxalate, nitro, thiocyanate, pyridinium, or EDTA modes not listed.

near 400 cm.⁻¹ probably arise from cation-oxygen stretches.

If we assume that the strongest Raman bands in the M=O stretching region correspond to the totally symmetric MO_6 stretch it is found that these values are significantly lower than for the corresponding v_1 values for MO_4^{x-} complexes; thus, v_1 for $(IO_6)^{5-}$ is at 729 cm.⁻¹ and at 791 cm.⁻¹ for $(IO_4)^-$; 759 for $(ReO_6)^{5-}$ and 966 for $(\text{ReO}_4)^-$; 765 for $(\text{WO}_6)^{6-}$ and 931 for $(\text{WO}_4)^{2-}$; 727 for $(MoO_6)^{6-}$ and 897 for $(MoO_4)^{2-}$. This is to be expected

 ²² M. T. Falqui, *Ricerca sci.*, 1963, A, 3, 627.
 ²³ D. J. Hewkin and W. P. Griffith, J. Chem. Soc. (A), 1966, 472.

for linear and bent systems, as shown in Figure 1 and 2.

We showed 23 that i.r. spectra of linear systems gave v^{as}(M₂O) frequencies near 860 cm.⁻¹ if M is a transition metal; v^s is active in the Raman only and was not observed. In the case of bent complexes all three modes are Raman- and i.r.-active, and vs, vas, and $\delta(M_{2}O)$ modes were found near 550, 750, and 220 cm.⁻¹ for $Cr_2O_7^{2-24}$ and $(V_2O_7)^{4-25}$.

²⁴ H. Stammreich, D. Bassi, O. Sala, and H. Siebert, Spectrochim. Acta, 1958, 13, 192.
 ²⁵ W. P. Griffith and T. D. Wickins, J. Chem. Soc. (A), 1966, 2007

1087.

Table 3 gives the spectra of a number of linear complexes of this type. For these $v^{as}(M_2O)$ is, as expected, found in the i.r. only and $v^{s}(M_{2}O)$ in the Raman; the deformation $\delta(M_2O)$ was not observed since our i.r. measurements do not extend below 200 cm.⁻¹, but the weak Raman modes near 130 cm.⁻¹ may perhaps be due to this mode, activated in the Raman by crystal effects. The k and k_1 values for these species (Table 3) show that the stretching force constant is about half that expected for terminal M=O stretches, which is to be expected since the $2p_{\pi}$ electron density of the oxy-bridge is distributed between two, rather than one, metal atoms. Of the complexes in Table 3 $K_4(Ru_2OCl_{10})$,²⁶ $K_4(Re_2OCl_{10})$,²⁷ and $K_2[Mo_2O_5 \text{ ox}_2 (H_2O)_2]$ ²⁸ are known from X-ray

such bridges {viz., X-ray studies to have $K_4(AsO_2F_8),^{33}$ $K_4[Os_2O_6(NO_2)_4]$,³⁴ $K_{4}[I_{2}O_{8}(OH)_{2}]^{35}$ $K_4[Te_2O_6(OH)_4]$,³⁶ and $Ba(Mo_2O_4 ox_2(H_2O)_2)^{37}$. These all have centrosymmetric D_{2h} structures for the anions with the exception of $K_4[I_2O_8(OH)_2]$, which has the centrosymmetric C_{2h} structure.

For all these complexes we would expect two stretching modes associated with the M2O2 bridge (Figure 3), one active in the i.r. and the other in the Raman, v^{ns} and $v^{as}(M_2O_2)$. We find bands in the 500-600 cm.⁻¹ region in these complexes which we assign to such modes; we have shown earlier that $v^{as}(CoO_{2}M)$ modes (M = Cr, Mo, S, P) occur near 500 cm.^{-1.38} Bands in this region are also found for the 'pentaoxy'-species $(MO_5)^{x-1}$



results to contain linear M-O-M bridges, and the similarity of their spectra with those of the other complexes in Table 3 suggest that these compounds also have this type of structure. Although

 $K_2[Mo_2O_5 \text{ ox}_2 (H_2O_2)]$ has a $4d^0$ configuration for the molybdenum atoms while the other complexes have two or more d electrons the v^{s} and $v^{as}(M_{2}O)$ frequencies and k-values are not markedly different; this may be attributed to the greater electronegativity of the sexivalent molybdenum than the other metals. Thus, in (NMe₄)₂(Zr₂OCl₁₀),²⁹ (Cp₂TiCl)₂O,³⁰ and (Cp₂ZrCl)₂O³¹ the $v^{as}(M_2O)$ values are near 750 cm.⁻¹; these contain metals in the d^0 , quadrivalent state. In $K_4(Ru_2OCl_{10})$ v^{as}(M₂O) shifts from 888 to 843 cm.⁻¹ on ¹⁸O substitution,³² which establishes this band as $v^{as}(M_2O)$.

With two oxygen bridges (III). There are very few data on the vibrational spectra of such species. Table 4 lists the spectra of complexes which are known from

²⁶ A. M. Mathieson, D. P. Mellor, and N. C. Stephenson, Acta Cryst., 1952, 5, 185. ²⁷ J. C. Morrow, Acta Cryst., 1962, 15, 851. ²⁸ F. A. Cotton, S. M. Morehouse, and J. S. Wood, Inorg.

- Chem., 1964, 3, 1603. 29 A. Feltz, Z. anorg. Chem., 1968, 358, 21.
- ³⁰ S. A. Giddings, *Inorg. Chem.*, 1966, 30, 684.
 ³¹ A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Mailes, *Austral. J. Chem.*, 1965, 18, 173.
 ³² J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (A), 1067, 1067, 1067
- 1967, 1043.
- ³³ M. Dunken and W. Haase, Z. Chem., 1963, 3, 433.

which, for reasons already mentioned, we regard as dimers containing M₂O₂ bridges. Terminal M=O stretching modes are not individually assigned in Table 4 apart from the very strong Raman modes which presumably arise from the totally symmetric stretches. In accordance with the centrosymmetric structures of these complexes, few coincidences of Raman and i.r. modes are observed. Table 4 also lists the spectra of the four complexes mentioned above of the type $(M_2O_4X_6)^{x-}$; these too have bands in the 500-600 cm.⁻¹ region.

Structure and Bonding in Oxy-complexes.---Mono*nuclear species.* In a previous paper we used the model of (terminal) oxygen-metal bonding of Ballhausen and Gray ³⁹ to rationalise the observed structures of dioxoand trioxo-complexes, using the principle that the oxyligands will tend to arrange themselves in such a way that competition of donor oxygen $2p_{\pi}$ orbitals for metal t_{2g} electrons is at a minimum, and any metal d electrons

- ³⁷ F. A. Cotton and S. M. Morehouse, Inorg. Chem., 1965, 4 1377.
- ³⁸ R. Coomber and W. P. Griffith, J. Chem. Soc. (A), 1968, 1128.
- 39 C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1962, 1, 111.

³⁴ L. O. Atovyman and O. A. L'yachenko, J. Struct. Chem.

U.S.S.R., 1967, 8, 143. ³⁵ A. Ferrari, A. Braibanti, and A. Tiripicchio, Acta Cryst., 1965, **19**, 629.

³⁶ O. Lindqvist and G. Lundgren, Acta Chem. Scand., 1966, 20, 2138.

will tend to avoid t_{2g} orbitals involved in π -bonding from oxygen orbitals. On this basis dioxo-complexes having no d electron will be expected to take up the $cis(C_{2v})$ positions and d^0 trioxo-species the $cis-C_{3v}$ configuration,⁴ while d^2 dioxo-complexes will be *trans*, with the two d electrons in a 'non-bonding' orbital in the plane perpendicular to the O=M=O axis.4,40 This we find to be the case in practice; we have found no case of d^1 or d^3 dioxo-species. The following discussion is concerned exclusively with metal-oxygen π interactions; for these complexes it is the π rather than the σ -bonding which will determine their stereochemistries.

For d^0 tetraoxy-species our spectra indicate a C_{2v} rather than D_{4h} structure. If we assume that the oxyligands are in positions 1,2,3 and 4 (I; the C_{2v} isomer) then the distribution of oxygen $2p_{\pi}$ electron pairs is more equal (three interact with d_{xz} and d_{xy} , two with d_{yz}) than in the D_{4h} (2,3,4,5) isomer, which requires interaction of 4 $2p_{\pi}$ electron pairs with d_{xy} and $\bar{2}$ each with d_{xz} and d_{yz} .

For hexaoxy-complexes competition for t_{2g} orbitals is at a maximum and we would expect to find such complexes existing only where the metal atom has a very high oxidation state (e.g., Os^{VII}, Os^{VI}, Re^{VII}, I^{VII}, W^{VI}, and Mo^{VI}). Few if any of these complexes retain a hexaoxy-structure in solution, so that their stability in the solid state must be ascribed to high lattice energies.

Dinuclear species. For d^0 linear complexes with one oxy-bridge (II), if the M-O-M line is taken as x-axis, the d_{xz} and d_{xy} orbitals of both M(1) and M(2) receive one electron each from the oxygen $2p_z$ and $2p_y$ orbitals respectively, and two degenerate $d_{xz}^0 - 2p_z^2 - d_{xz}^0$ and $d^{0}_{xy} - 2p^{2}_{y} - d^{0}_{xy}$ three-centre two-electron orbitals are formed. Terminal oxy-ligands will tend to avoid the use of these d orbitals as much as possible so that in K₂[Mo₂O₅ ox₂(H₂O)₂]²⁸ the two terminal ligands are cis to the Mo-O-Mo axis and take up the (3,6) and (7,8) positions.

In d^1 systems such as $[Mo_2O_3(S_2COC_2H_5)_2]^{41}$ the terminal oxy-ligands are again *cis* to Mo-O-Mo at (6, 8). If we assume the one d electron of each molybdenum(v) atom to be in d_{xy} orbitals we have a three-centre, fourelectron $d^{1}_{xy}-2p^{2}_{y}-d^{1}_{xy}$ orbital in which the two molybdenum electrons pair up; the (6,8) oxy-ligands then use d_{xz} and d_{yz} orbitals. In $(M_2OX_{10})^{x-}$ systems containing no terminal oxy-ligand the M-O-M bonding may again be explained in terms of three-centre orbitals (*e.g.*, for $(Ru_2OCl_{10})^{4-}$, $(Re_2OCl_{10})^{4-}$, and $[Cr_2O(NH_3)_{10}]^{4+,32,42}$

For $d^0 \mu \mu'$ -dioxo-systems, the M_2O_2 plane being taken as containing the x and y axes (III), only one oxygen p_{π} orbital $(2p_z$ for both bridge atoms) has the correct symmetry for π -overlap with the metal atoms; the metal

orbitals with which these will interact will be the d_{xz} and d_{yz} , and two bent three-centre two-electron orbitals will be formed. In $K_4[Te_2O_6(OH)_2]^{36}$ the 4 terminal oxy-ligands are at (4,5) and (8,9) in the M_2O_2 plane; by lying in this plane their use of the d_{xz} and d_{yz} metal orbitals is less than that of the d_{xy} , the latter orbital not being involved in bridge bonding. In K₄[I₂O₈(OH)₂] ³⁵ the 6 terminal oxy-ligands are at (1, 4, 5) and at (8, 8, 10), and the two 'extra' terminal ligands at 1 and 10 use the d_{xz} and d_{yz} orbitals already in use for the bridge electrons; it might be expected that this type of structure would be found in high oxidation state complexes only [and so also for $(M_2O_{10})^{x-}$ species]. The σ -bonds from O₂ and O₃ to M(1) and M(2) will utilise the $d_{x^2-y^2}$ orbitals of the latter.

In d^1 complexes of this type the metal d electrons may pair up to form a metal-metal bond, which is thought to occur in Ba[Mo₂O₄ ox₂(H₂O)₂] where the Mo-Mo distance is only 2.543 Å.37 In this complex the terminal oxyligands are at (1,10); these will then use the metal d_{xz} and d_{yz} orbitals, but not the d_{xy} which accommodates the metal-metal bond (the single d electron for each molybdenum atom occupies the d_{xy} orbital). We may suppose that the other d^1 complexes studies of the type $(M_2O_4X_6)^{x-}$ have this stereochemistry.

The only d^2 complex reported to be of this type is K₄[Os₂O₆(NO₂)₄]³⁴, and in this the 4 terminal oxyligands are in the plane perpendicular to M_2O_2 , at (1, 6) and 7, 10). The metal-metal distance is 3.05 Å 34 which is probably too long for a metal-metal bond; we assume that the two d electrons of Os(1) and of Os(2)pair up in the d_{xy} orbitals as in other d^2 trans-dioxocomplexes of osmium; the terminal oxy-ligands will then use d_{xz} and d_{yz} orbitals and the two bridging oxy-ligands will use their $2p_z$ orbitals to interact with d_{xz} and d_{yz} . The double occupancy of the d_{xy} orbital of each osmium atom prevents the formation of a direct metal-metal bond; hence the long Os-Os distance as compared with the Mo-Mo distance in $Ba[Mo_2O_4 ox_2(H_2O)_2]$.

EXPERIMENTAL

Osmium(VI) dioxo-complexes,² cis-dioxo-complexes of tungsten(VI), molybdenum(VI), and vanadium(V),4

 $(NH_4)_3(MoO_3F_3)$, and $MoO_3(dien)^4$ were made as described previously, and the following species were prepared by the literature methods cited: $K_2(OsO_2Br_4)$ and

 $K_4[Os_2O_6(NO_2)_4]; 4^3 (pyH)_2[OsO_2(OH)_2Cl_2] 4^4$ {this complex was formulated 44 as (pyH)₂[OsO₃Cl₂(H₂O)] but the dioxo-formulation seems more likely}; K₄[MoO₂(CN)₄]; ⁸ $K_3(WO_3F_3)$; ⁴⁵ $Na_2[Mo_2O_4(EDTA)]$ and

 $Na_4[Mo_2O_6(EDTA)]; {}^{14}K(OsO_3F_3); {}^{46}Ba[OsO_4(OH)_2],$

 $K_2[OsO_4(OH)_2]$ and $Cs_2(OsO_4F_2)$; ¹⁹ $Ba_3[ReO_4(OH)_2]_2$; ²⁰

 $Ba_3(MoO_6)$, a hitherto unreported compound, was made in 44 G. Scagliarini and A. Masetti-Zannini, Gazzetta, 1923, 53,

⁴⁰ K. A. K. Lott and M. C. R. Symons, J. Chem. Soc., 1960,

^{973.} ⁴¹ A. B. Blake, F. A. Cotton, and J. S. Wood, J. Amer. Chem. Soc., 1964, 86, 3024.
 ⁴² J. Dunitz and L. E. Orgel, J. Chem. Soc., 1953, 2594.
 ⁴³ L. Wintrebert, Ann. Chim. Phys., 1903, 28, 15.

⁴⁵ O. Schmitz-Dumont and P. Opgenhoff, Z. anorg. Chem., 1954, 275, 21.

⁴⁶ M. A. Hepworth and P. L. Robinson, J. Inorg. Nuclear Chem., 1957, 4, 24.

⁴⁷ H. P. Rooksby and E. G. Steward, Nature, 1946, 157, 548.

the same way as the tungsten analogue; $Hg_3(TeO_6)$; ²² $K_4(Ru_2OBr_{10})$, $(NH_4)(Os_2OCl_{10})$; $(NMe_4)_4(Os_2OCl_6Br_4)$, $(NEt_4)_4(Os_2OBr_{10})$; ²³ $K_2(Mo_2O_5 ox_2(H_2O)_2)$; ²⁸ $Ba_2[Mo_2O_4 ox_2(H_2O)_2]$; ³⁷ $K_4[Te_2O_8(OH)_2]$; ³⁷ and $K_4[I_2O_8(OH)_2]$. ³⁵ The complex $K_6(Re_2O_3(CN)_8)$, $4H_2O$ was made as described by Walter *et al.*¹⁶ (Found: K, 27·1, C, $10\cdot2$, N, $11\cdot6$, O, $12\cdot9\%$. Calc. for $K_6Re_2H_8C_8N_8O_7$: K, $26\cdot2$; C, $10\cdot7$; N, $12\cdot5$; O, $12\cdot5\%$).

Raman spectra were measured from 100—1200 cm.⁻¹ on a Cary Model 81 helium-neon laser spectrophotometer (6328 Å excitation) on microcrystalline samples or on saturated aqueous solutions, and i.r. spectra as Nujol mulls on Grubb-Parsons Spectromaster and DM-4 instruments. Magnetic measurements were made at room temperatures by the Gouy method.

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