TABLE III

BOND ANGLES IN GROUP V TRIHALIDES[a]

Halide	N Angle, deg	N Method	P Angle, deg	P Method	As Angle, deg	As Method	Sb Angle, deg	Sb Method
F	102.17 ± 0.04	MW[39]	97.8 ± 0.2	ED[b]	96.1 ± 0.2	ED[40]	(88)	XD[42]
					95.8 ± 0.7	ED[41]		
Cl	...		100.27 ± 0.09	ED[43]	98.7 ± 0.3	ED[45]	99.5 ± 1.5	MW[6]
			100.1	MW[44]	98.4	MW[44]		
Br	...		(101.5)	ED[46]	$99.6_6 \pm 0.2_6$	ED[47]	(97)	ED[48,49]
I	...		(102)	ED[49]	100.2 ± 0.4	ED[50]	99.1 ± 2	ED[51]

[a] Abbreviations: ED, electron diffraction; MW, microwave spectroscopy; XD, X-ray diffraction (crystal). [b] Present study.

considerable contribution of double-bond character for the fluorides; according to his argument,[12] the above anomaly may be attributed to "the unshared pairs of fluorine having a strong tendency to delocalize into the incomplete shell of the central atom, thereby giving the bonds some double-bond character and, therefore, increasing the size of the bonding orbitals and hence the bond angle." From the present result for PF_3, along with the recent results for AsF_3 by Bartell and Clippard[40] and by Konaka and Kimura,[41] their bond angles fit in regular series, so that the rules governing the bond angles in group V trihalides can be simplified.

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The Characterization of Metal–Oxygen Bridge Systems[1]

BY R. M. WING AND K. P. CALLAHAN

The vibrational spectra of various types of metal–oxygen bridge systems are assigned by normal-coordinate analysis and discussed in terms of geometry. The results of this analysis are shown to be a powerful tool for the characterization of metal–oxygen bridged complexes. The synthesis of a new dioxo-bridged molybdenum(V) complex is described and a structure is proposed on the basis of its infrared spectrum.

Introduction

In the course of our work on molybdenum(V) chemistry we have frequently been faced with the problem of distinguishing between the several types of oxygen-bridged dimers that occur in this system.[2-4] Infrared spectral measurements were thought to be the solution to this problem.

However, the ir spectral characteristics of metal-to-oxygen multiply bonded systems have been discussed in detail only for those compounds in which the oxo ligand is in a terminal position.[5-7] An abbreviated analysis of monooxo bridged systems, both linear and bent, was discussed by Cotton and Wing,[6] and Hewkin and Griffith[8] have tabulated a considerable amount of infrared and Raman data for compounds containing a single oxo bridge.

It is the purpose of this paper to present a general analysis of the mono- and dioxobridged systems and to illustrate how infrared spectra in the bridge metal–oxygen region (ca. 850–200 cm^{-1}) can be used to predict structures. Of prime importance in a consideration of these bridge systems is the fact that the vibrational frequencies are strongly sensitive to the M–O–M bond angle. It is in fact this angular dependence which permits one to distinguish between mono- and dioxobridged systems.

Normal-Coordinate Analyses and Angular Dependence of Frequencies

The general monooxo-bridged metal dimer, treated for simplicity as a three-body system, is bent at an angle ϕ and exhibits two bridge vibrations. Such a system can be characterized by a two-constant potential field. The first constant pertains to the metal–oxygen

(1) Supported in part by the National Science Foundation under Grant GP-8055.
(2) L. Sacconi and R. Cini, *J. Am. Chem Soc.*, **76**, 4239 (1954).
(3) G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 663 (1962).
(4) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).
(5) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).
(6) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).
(7) D. Grandjean and R. Weiss, *Bull. Soc. Chim. France*, 3058 (1967).
(8) D. J. Hewkin and W. P. Griffith, *J. Chem. Soc., A*, 472 (1966).

stretch, and the second to cross oxygen (M–O–M) stretch–stretch interaction.[6]

The addition of another bridging oxygen to the monobridged system gives rise to a perturbation of the system which can be characterized by one additional force constant, namely, a cross-metal (O–M–O) stretch–stretch interaction constant. (Cross-ring interactions are assumed to be insignificant.) The perturbed system gives rise to four bridge vibrations, which are linear combinations of the symmetric and antisymmetric vibrations of two isolated monobridged species. Symmetry coordinates for these systems are given in Table I, and secular equations, in Table II.

The change in vibrational frequencies of the bridge modes as a function of M–O–M angle was calculated for *illustrative purposes only* and is shown in Figure 1. For these calculations the mass of the metal was taken as that of molybdenum, the M–O stretching force constant was set at 3.8 mdyn/Å,[6] and interaction constants were assumed to be 0.2 mdyn/Å.

The energy–geometry dispersion as we discuss it here is qualitative, and the dangers of associating quantitative significance with the curves of Figure 1 cannot be overemphasized. Thus we mention briefly how the details of this correlation are influenced by two factors.

First, the angle ϕ is sensitive to the choice of force constants. The effect that an error of 0.2 mdyn/Å in either k or k_{MOM} has on the angle ϕ ranges from $\pm 20°$ at $\phi = 180°$, $\pm 10°$ at $\phi = 145°$, to only $\pm 5°$ at $\phi = 90°$.

Table I

1. Symmetry Coordinates for M_2O

$$\overset{\Delta_1}{\underset{M}{}}\!\!\!\overset{O}{\underset{\phi}{}}\!\!\!\overset{\Delta_2}{\underset{M}{}}$$
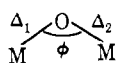
A_1: $s_1 = \dfrac{1}{\sqrt{2}}(\Delta_1 + \Delta_2)$

B_2: $s_2 = \dfrac{1}{\sqrt{2}}(\Delta_1 - \Delta_2)$

2. Symmetry Coordinates for M_2O_2

$$\begin{array}{c}\Delta_1 \;O\; \Delta_2 \\ M \qquad M \\ \Delta_3 \;O\; \Delta_4\end{array}$$
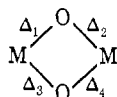
A_g: $S_1 = \dfrac{1}{2}(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)$

$\qquad = \dfrac{1}{\sqrt{2}}(s_1{}^1 + s_1{}^2)$

B_{3g}: $S_2 = \dfrac{1}{2}(\Delta_1 - \Delta_2 - \Delta_3 + \Delta_4)$

$\qquad = \dfrac{1}{\sqrt{2}}(s_2{}^1 - s_2{}^2)$

B_{1u}: $S_3 = \dfrac{1}{2}(\Delta_1 + \Delta_2 - \Delta_3 - \Delta_4)$

$\qquad = \dfrac{1}{\sqrt{2}}(s_1{}^1 - s_1{}^2)$

B_{2u}: $S_4 = \dfrac{1}{2}(\Delta_1 - \Delta_2 + \Delta_3 - \Delta_4)$
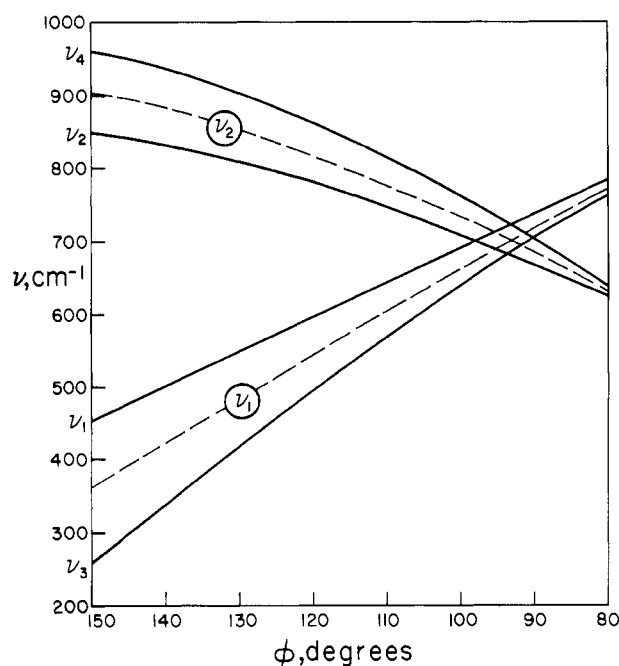
$\qquad = \dfrac{1}{\sqrt{2}}(s_2{}^1 + s_2{}^2)$

Figure 1.—Variation in metal–oxygen bridge vibrations as a function of the M–O–M angle. Calculated from equations in Table II using $M = Mo$, $k_B = 3.8$ mdyn/Å, and $k_i = 0.2$ mdyn/Å: solid line, dioxo-bridged species; dashed line, monooxo-bridged species.

Table II

Secular Equations for Oxo-Bridged Metal Systems

Species	M–O skeletal symmetry	Vibration class	Activity[a]	Secular eq[b]
		A_1	R, ir	$\lambda = [\mu_M + \mu_O(1 + \cos\phi)](k + k_{\text{MOM}})$
M_2O	C_{2v}	B_2	R, ir	$\lambda = [\mu_M + \mu_O(1 - \cos\phi)](k - k_{\text{MOM}})$
		A_g	R	$\lambda = \{\mu_M[1 + \cos(180 - \phi)] + \mu_O(1 + \cos\phi)\}(k + k_{\text{MOM}} + k_{\text{OMO}})$
M_2O_2	D_{2h}	B_{3g}	R	$\lambda = \{\mu_M[1 - \cos(180 - \phi)] + \mu_O(1 - \cos\phi)\}(k - k_{\text{MOM}} - k_{\text{OMO}})$
		B_{1u}	Ir	$\lambda = \{\mu_M[1 - \cos(180 - \phi)] + \mu_O(1 + \cos\phi)\}(k + k_{\text{MOM}} - k_{\text{OMO}})$
		B_{2u}	Ir	$\lambda = \{\mu_M[1 + \cos(180 - \phi)] + \mu_O(1 - \cos\phi)\}(k - k_{\text{MOM}} + k_{\text{OMO}})$

[a] R, Raman active; ir, infrared active. [b] μ_M and μ_O are reciprocals of the masses of the metal atom and the oxygen atom, respectively, in amu. $\lambda = (5.889 \times 10^{-7})\nu^2$, where ν is the frequency in cm^{-1}. k is the bridge M–O force constant; k_{MOM} is the M–O–M bridge interaction constant; k_{OMO} is the O–M–O bridge interaction constant.

TABLE III

BRIDGE VIBRATIONAL MODES OF LINEAR AND
BENT MONOOXO-BRIDGED SPECIES[a]

Linear

Species	ν_{anti}, cm^{-1}	ν_{sym}, cm^{-1}
$Ru_2OCl_{10}{}^{4-}$	886	226
$Ru_2OBr_{10}{}^{4-}$	860	222
$Re_2OCl_{10}{}^{4-}$	855	230
$Cr_2O(NH_3)_{10}{}^{4+}$	873	215
$Mo_2O_3(C_2O_4)_2(H_2O)_2{}^{2-}$ [b]	860	—
$Mo_2O_3(C_2H_5OCS_2)_2{}^c$	946	—
$C_{74}H_{42}Mn_2N_{18}O \cdot 2C_5H_5N^{d,e}$	820	—

Bent

Species	ν_{anti}, cm^{-1}	ν_{sym}, cm^{-1}	M–O–M angle, deg.
$V_2O_7{}^{4-}$ ^{f}	810	503	—
$Cr_2O_7{}^{2-}$	770	560	115^g
$W_2O_{11}(H_2O)_2{}^{2-}$	790^h	556	139^i
$Sn_2OF_{10}{}^{4-}$ ^{i}	833	452	—

[a] Data from ref 8 unless otherwise noted. [b] Reference 6. [c] We prefer this assignment instead of Selbin's suggestion (J. Selbin, *Angew. Chem. Intern. Ed. Engl.*, **5**, 717 (1966)) that this vibration is due to terminal oxygens and that ν_{anti} appears at 765 cm^{-1}. Our preference is based on the more reasonable force constant calculated for the 946-cm^{-1} band (4.09 mdyn/Å *vs.* 2.75 mdyn/Å for the 765-cm^{-1} vibration) and the fact that the Mo–O$_t$ bonds are unusually short which is in agreement with the higher frequency assigned to their vibration (1046 cm^{-1}). [d] μ-oxo-bis(phthalocyanatopyridinemanganese(III)) dipyridinate: J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959). [e] Mn–O–Mn angle is 178°: L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966). [f] Presumed to be bent on the basis of this evidence: W. P. Griffith and T. D. Wickins, *J. Chem. Soc., A*, 1087 (1966). [g] A. Bystrom and K.-A. Wilhelmi *Acta Chem. Scand.*, **5**, 1003 (1951). [h] Listed as 750 cm^{-1} by W. P. Griffith, *J. Chem. Soc.*, 5345 (1963). [i] F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, **17**, 1127 (1964). [j] Presumed[8] to be bent on the basis of this evidence.

Second, the factoring of the metal–oxygen bridge vibrations from the other vibrations of a molecule could be dangerous in some cases. We have checked this approximation out for the specific cases discussed in this paper, and find the errors introduced to be much less than those arising from an error in the primary force constants, *vide supra*.

The M–O–M angle for monobridged systems has never been found to be less than 115°. Thus, from Figure 1 it may be inferred that ν_{anti} will appear at a frequency at least 215 cm^{-1} higher than ν_{sym}. Conversley, dioxo-bridged systems show M–O–M angles less than 90° but are not expected to decrease much below 80°. For these systems Figure 1 predicts that the bridge metal–oxygen vibrations would occur at lower frequencies and would be distributed over a narrower range than for the monobridged species. Tables III and IV show frequencies observed for several examples of these systems.

Vibrations for doubly bridged systems are highly symmetry sensitive; a centrosymmetrical structure makes ν_1 infrared inactive. Thus for the EDTA[9] and oxalate[10] complexes containing the Mo_2O_4 unit and

(9) R. M. Wing and K. P. Callahan, unpublished results.
(10) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).

TABLE IV

BRIDGE VIBRATIONAL MODES
DIOXO-BRIDGED COMPOUNDS[a]

Compd	ν_1	ν_3	ν_4	M–O–M angle, deg
	cm^{-1}			
$Ba[(MoO_2(C_2O_4)(H_2O))_2O_2]$	745	722	612	83^b
$Na_2Mo_2O_4(EDTA)$	759	736	635	83^c
$[(CH_3)_4N]_2Mo_2O_4Cl_4(OH_2)_2$	729	705	675	...
$Mo_2O_4Cl_2(bipy)_2$	742	721	e	...
$[(\pi\text{-}C_5H_5)MoO_2]_2{}^f$	e	710	600	...

[a] All data from this work unless noted. [b] Reference 10. [c] Reference 9. [d] Reference 14. [e] See text. [f] Reference 12.

exhibiting C_{2v} symmetry, three bands attributable to bridge modes are found in the infrared spectra: ν_1 and ν_3 at *ca.* 750–700 cm^{-1} and ν_4 at *ca.* 600 cm^{-1}, or about 100 cm^{-1} lower in frequency. The probably centrosymmetrical[11] compound $Mo_2O_4(\pi\text{-}C_5H_5)_2$ shows only two bands assignable to bridge vibrations,[12] which we must assign as ν_3 and ν_4 since the splitting observed for these bands is only about 100 cm^{-1} as compared to the 300 cm^{-1} or more splitting observed in the mono-bridged systems (*vide supra*).

Application to Compounds of Unknown Structure

Colton and Rose[13] have recently reported the synthesis of the compound $R_2Mo_2O_3Cl_8$ (R = $(C_2H_5)_4N^+$, Cs$^+$), which shows infrared absorptions at 983, 958, 735, and 516 cm^{-1}. The first two can be assigned to symmetrical and antisymmetrical stretching of the terminal oxygens. The latter two absorptions are assigned to bridge vibrations, and their frequencies and splittings would indicate a bent monobridge system with a Mo–O–Mo angle of about 130°.

The probability that the compound $Mo_2O_4Cl_2(bipy)_2$[14] has a dioxo bridge is emphasized by the correspondence between its infrared spectrum and those of known dibridged compounds. No spectrum extending lower than 700 cm^{-1} has been reported for this compound, thereby precluding comparison between ν_4's.

We have succeeded in synthesizing a simpler version of the former compound. $((CH_3)_4N)_2Mo_2O_4Cl_4(OH_2)_2$ is assigned a dioxo-bridged structure primarily on the basis of infrared evidence.

Cotton[15] has proposed that the compound $Re_2O_3(py)_4Cl_4$ has a linear *trans*-dioxo-μ-oxo structure because of the low frequency at which the Re–O–Re bridge vibration is observed (710–675 cm^{-1}). The electron-withdrawing power of oxo groups *trans* to the bridging oxygen was said to cause the frequency decrease. Unfortunately the published spectrum did not extend below 600 cm^{-1} and thus a decision between a linear (ν_1 absent) or bent ($\nu_1 \sim 500$ cm^{-1}) structure

(11) Presumably isostructural with the sulfur-bridged analog; see D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3721 (1967).
(12) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1567 (1964).
(13) R. Colton and G. G. Rose, *Australian J. Chem.*, **21**, 883 (1968).
(14) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1963).
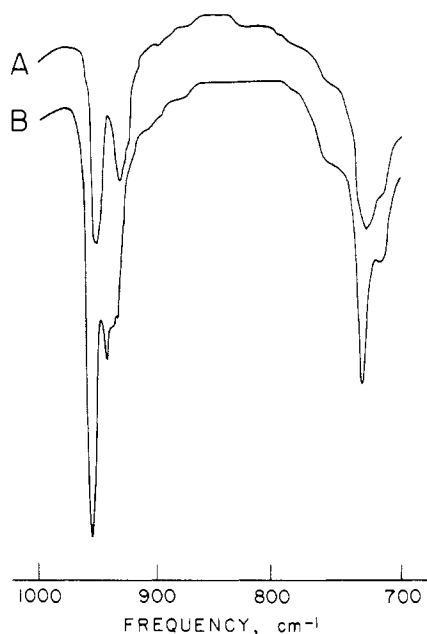(15) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

Figure 2.—Infrared spectra of (a) $Cs_2Mo_2O_4Cl_4(OH_2)_2$ and (b) $[(CH_3)_4N]_2Mo_2O_4Cl_4(OH_2)_2$ in the Mo–O stretch region.

cannot be made. A similar problem is faced with the $Re_2O_3Cl_8{}^{2-}$ ion, which shows[16] a bridge metal–oxygen vibration at 740 cm^{-1} [$(C_2H_5)_4N^+$ salt]. On the basis of the very low frequency of the observed band, we would predict qualitatively that both of these systems

are bent. We have checked to what extent the presence of *trans* oxo groups would depress ν_2 and found that no reasonably sized stretch–stretch interaction constant could explain its low frequency.

Experimental Section

Preparation of $[(CH_3)_4N]_2Mo_2O_4Cl_4(OH_2)_2$.—A standard solution of Mo(V) was prepared by the reduction of an acidic solution ($\sim$4 M HCl) of sodium molybdate with mercury.[17] To 69 ml of a 0.5 F Mo(V) solution was added 4.6 g of tetramethylammonium chloride dissolved in the minimum quantity of water. The solution was stirred a short while and then 20 ml of ether was added, forming an immiscible layer. A large volume of acetone was poured into the reaction mixture and a red-brown oil separated out. The supernatant liquid was removed by decantation and the oil was solidified by the addition of more acetone and scratching. The solid was repeatedly recrystallized from methanol but the dark red-brown rhombs did not give a completely satisfactory analysis. The compound slowly decomposes in air and more rapidly in aqueous solution. *Anal.* Calcd for $[(CH_3)_4N]_2Mo_2O_4Cl_4(OH_2)_2$: C, 16.50; H, 4.81; Cl, 24.38. Found: C, 17.68; H, 3.29; Cl, 24.61.

Molecular Weight Determination.—A single crystal was mounted in a borosilicate capillary and unit cell dimensions were determined from oscillation, precession, and Weissenberg films. The crystal was monoclinic with $a_0 = 19.69$, $b_0 = 15.88$, $c_0 = 13.38$ Å, $\beta = 96°$, and ρ_{obsd} (flotation) $= 1.86$ g/cm^3. Assuming $Z = 8$, the molecular weight is 582 (calcd for $[(CH_3)_4N]_2Mo_2O_4Cl_4(OH_2)_2$, 582). The space group is B_{2_1}/n, a nonstandard setting which can be reduced to P_{2_1}/c.

Infrared Spectra.—All new data reported in this paper were obtained on a Perkin-Elmer 621 grating infrared spectrophotometer. Samples were run as Nujol mulls or KBr pellets. (See Figure 2.)

(16) B. J. Brisdon and D. A. Edwards, *Inorg. Chem.*, **7**, 1898 (1968).

(17) D. E. Carritt, Ph.D. Thesis, Harvard University, 1947.