The infrared spectra of the complexes, tabulated in Table III, also show that $(C_6H_6)_2Cr^+$ has been formed during the course of the reaction as well as marked changes in the position of the bands associated with the Lewis acids. In particular it should be noted that the asymmetric stretching frequency of the nitro group, which occurs at 1567 cm.$^{-1}$ in trinitrobenzene, is shifted and split to give a doublet at 1547 and 1534 cm.$^{-1}$. The splitting of the $-NO_2$ frequency suggests that the ring and the $-NO_2$ group are no longer coplanar, which could arise because of either lattice-packing effects or the dimerization of the trinitrobenzene radical ions.

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Properties of Metal-to-Oxygen Multiple Bonds, Especially Molybdenum-to-Oxygen Bonds[1]

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Principally on the basis of structural and infrared data for Mo–O bonds, derived from recent studies in this laboratory, several aspects of multiple bonds from oxygen to transition metals have been examined. It is found that for MO_n groups, where $n > 1$, a positive M–O to M–O stretching interaction constant in the range 0.2–0.7 mdyne/Å. is generally necessary to account for the observed M–O stretching frequencies, although the actinyl ions are exceptions. Assignments of M–O stretching frequencies in a number of compounds are proposed, and with these assignments force constants are computed. For Mo–O bonds it is shown that the force constants are related to the bond distances and to estimated bond orders by smooth curves which have physically reasonable shapes.

1. Introduction

Several years ago, Barraclough, Lewis, and Nyholm[2] pointed out that complexes containing metal-to-oxygen multiple bonds seemed generally to have strong infrared absorption bands in the region of 900–1100 cm.$^{-1}$ and proposed that these bands be assigned to the metal–oxygen stretching frequencies. Since then, such bands have been observed and so assigned in some other molecules, but no further attempts appear to have been made to elaborate the general analysis and understanding of the M–O stretching modes. In particular, the problems of (1) interaction between two or more such M–O oscillators, either equivalent or not, and (2) the interdependence of metal–oxygen force constants, bond lengths, and bond orders seem to merit investigation. This report will deal first with the interaction problem and stretching force constants will be calculated for some relatively simple metal–oxygen compounds. The interesting cases in which one oxygen atom is present as a bridging group in a linear M–O–M system will be briefly discussed, and the infrared spectra of some more complex compounds, which contain a variety of metal–oxygen bond types, will be interpreted. Finally, relationships between the force constants, lengths, and orders of Mo–O bonds will be presented.

2. The Normal Coordinate Analyses and Stretch–Stretch Interactions

In order to interpret the spectra of molecules having two or more M–O oscillators with a common metal atom, it is necessary to consider the manner in which the vibration in one oscillator interacts with the vibration(s) in the other(s). Metal–oxygen π bonding can presumably be attributed to the overlap of the filled $p\pi$ orbitals of oxygen with empty $d\pi$ orbitals on the metal and each of the latter will, in general, be expected to be available to two or more of the oxygen atoms. Thus as one M–O bond stretches, lessening the involvement of some of the $d\pi$ orbitals in π bonding to that oxygen atom, these same $d\pi$ orbitals will become more available for π bonding to the other oxygen atoms, and the π bonding to them will become stronger. Consequently, the stretch–stretch interaction constants should be positive.

Using available data for several isoelectronic tetrahedral MO_4^{n-} species, force constants have been computed using simplified F matrices[3,4] in which only the M–O stretching constant and the stretch–stretch inter-

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[1] Supported in part by the National Institutes of Health and the National Science Foundation.

[2] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[3] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

[4] The effect of omitting the bend and the bend–stretch interaction constants from the F_2 factored block on the stretch and stretch–stretch interaction constants was checked and found to be insignificant. Also due to the large difference in frequencies very little mixing of the stretching and bending modes occurred. This is fortunate because for most of the cases to be considered here the necessary data for including the bend–stretch interaction are not available.

Table I

Secular Equations and Related Information on Metal–Oxygen Stretching Modes in Some Selected Metal–Oxo Compounds

Species	M–O skeletal symmetry	Vibration class	Activity[a]	Secular equation[b]
(a) Substituted Tetrahedral ($n = 4$) or *cis*-Octahedral ($n = 6$) Cases				
$L_{n-1}MO$	$C_{\infty v}$	A_1	IR, R	$\lambda = (\mu_O + \mu_M)k$
$L_{n-1}MO_2$	C_{2v}	A_1	IR, R	$\lambda = [\mu_O + \mu_M(1 + \cos\phi)](k + k_i)$
(angle = ϕ)		B_2	IR, R	$\lambda = [\mu_O + \mu_M(1 - \cos\phi)](k - k_i)$
$L_{n-3}MO_3$	C_{3v}	A_1	IR, R	$\lambda = [\mu_O + \mu_M(1 + 2\cos\phi)](k + 2k_i)$
(angle = ϕ)		E	IR, R	$\lambda = [\mu_O + \mu_M(1 - \cos\phi)](k - k_i)$
(b) Tetrahedral Case				
MO_4	T_d	A_1	R	$\lambda = \mu_O(k + 3k_i)$
		F_2	IR, R	$\lambda = (\mu_O + {}^4/_3\mu_M)(k - k_i)$
(c) *trans*-Octahedral Case				
L_4MO_2	D_{4h}	A_{1g}	R	$\lambda = \mu_O(k + k_i)$
		A_{2u}	IR, R	$\lambda = (\mu_O + 2\mu_M)(k - k_i)$
(d) M–O–M Bridges				
Linear	$D_{\infty h}$	Σ_g^+	R	$\lambda = \mu_M(k + k_i)$
		Σ_u^+	IR	$\lambda = (\mu_M + 2\mu_O)(k - k_i)$
Bent	C_{2v}	A_1	IR, R	$\lambda = [\mu_M + \mu_O(1 + \cos\phi)](k + k_i)$
(angle = ϕ)		B_1	IR, R	$\lambda = [\mu_M + \mu_O(1 - \cos\phi)](k - k_i)$

[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 a.m.u. $\lambda = (5.889 \times 10^{-7})\nu^2$, where ν^2 is the frequency in wave numbers. k then has units of mdynes/Å.

action constant were included. The secular equations for this case and several others of interest are given in Table I, and the data and results for the tetrahedral cases are given in Table II. It can be seen that all of the interaction constants are indeed positive and lie in the range 0.2–0.6 mdyne/Å. The stretching force constants themselves are all reasonable and indicate that the various M–O bonds are similar.

Table II

Frequencies and Approximate Force Constants for Some Isoelectronic MO_4 Species

		Observed frequencies, cm.$^{-1}$				Force constants, mdynes/Å.	
Species	Source	ν_1	ν_2	ν_3	ν_4	k	k_i
VO_4^{3-}	*a*	870	345	825	480	5.16	0.63
CrO_4^{2-}	*a*	847	348	884	368	5.60	0.39
MnO_4^-	*a*	840	. . .	908	500	5.89	0.29
MoO_4^{2-}	*b, d*	894	407	833	318	5.67	0.32
TcO_4^-	*b*	912	. . .	912	325	6.8	0.35
RuO_4	*a*	880	. . .	913	330	6.65	0.16
WO_4^{2-}	*a, b*	931	405	833	320	6.43	0.57
ReO_4^-	*b, c*	971	. . .	916	340	7.55	0.45
OsO_4	*a*	971	328	960	328	8.07	0.27

[a] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963. [b] R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **44,** 215 (1964). [c] H. H. Claassen and A. J. Zielen, *ibid.*, **22,** 707 (1954). [d] H. Siebert, *Z. anorg. allgem. Chem.*, **275,** 225 (1954).

Within groups of isoelectronic MO_4^{n-} species containing metal atoms from the same row of the periodic table, there is an increase in force constant with increasing atomic number of the metal atom. These variations are shown in Figure 1. The increases in force constants are approximately linear with atomic number except for that of TcO_4^-, which is either incorrect or genuinely anomalous. These linear variations in force constant will be used later.

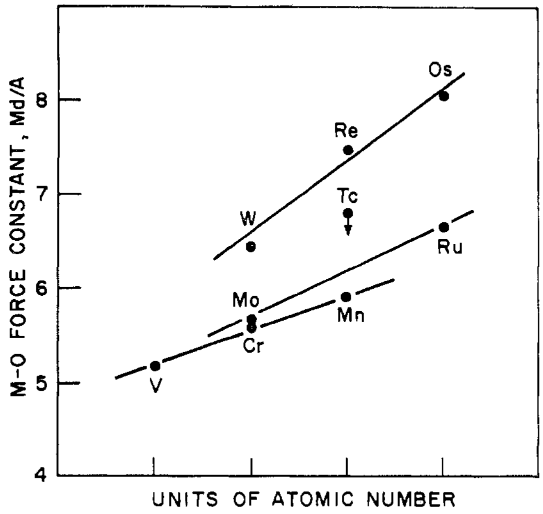

Figure 1.—The dependence of force constants on the atomic number of the metal atom in MO_4^{n-} species.

The force constants for some *trans* dioxo compounds, Table III, are not in accord with the preceding discussion, since the interaction constants are negative. For the actinide compounds the data and assignments seem unambiguous,[5,6] and for these species, the interaction constants are all negative. For the *trans*-$[OsO_2Cl_4]^{2-}$ ion the interaction constant appears to be positive, but the assignment of the symmetric stretching frequency is insecure[7] and thus this result must be considered as tentative. For the rhenium compound only the antisymmetric frequency has been reported. The reason for the qualitatively different behavior of the dioxygenyl actinide species is not known. While there can be no doubt that the metal–oxygen bonds have appreciable π character in these cases, just

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(5) L. H. Jones, *J. Chem. Phys.*, **23,** 2105 (1955).

(6) For additional references and discussion of the assignments see F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 329.

(7) W. P. Griffith, *J. Chem. Soc.*, 245 (1964).

TABLE III

FREQUENCIES AND APPROXIMATE FORCE CONSTANTS OF SOME *trans*-MO_2L_4 SPECIES

Species	Source	Frequencies, cm.$^{-1}$ Sym. str.	Asym. str.	Force constants, mdynes/Å. k	k_i
$[UO_2(CH_3CO_2)_3]^-$	*a*	856	931	7.06	−0.15
$[NpO_2(CH_3CO_2)_3]^-$	*a*	844	934	7.00	−0.29
$[PuO_2(CH_3CO_2)_3]^-$	*a*	818	930	6.75	−0.43
$[AmO_2(CH_3CO_2)_3]^-$	*a*	749	914	6.14	−0.85
$[ReO_2py_4]Br \cdot 2H_2O$	*b*	. . .	819	5.67[e]	0.25
$K_2[OsO_2Cl_4]$	*c*	808[d]	837	5.89	0.25

[a] References 5 and 6. [b] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964). [c] Reference 7. [d] Deduced from the observed value of the antisymmetric mode and a band at 1645 cm.$^{-1}$ which was assigned as a summation of the symmetric and antisymmetric modes. [e] k_i given an arbitrary value of 0.25.

as they do in oxygenyl compounds of the d-block elements, the nature of the π bonding, particularly in regard to the nature of the metal orbitals used, may well be qualitatively different. It may be relevant that the U–O stretching frequencies in the uranyl ion are very sensitive to the nature of the other ligands.[8] This is an indication that the uranium-to-oxygen bonding cannot be treated independently of the bonding of uranium to the other ligands present. The rather simple argument leading to the expectation of a positive interaction constant, which treats the M–O bonds without reference to the other metal–ligand bonds, could thus be quite unreliable for these actinide species.

In Tables IV, V, and VI are listed force constants for other oxygenyl species. In all cases where an interaction constant, k_i, could be calculated it turned out to be positive.

TABLE IV

FREQUENCIES AND APPROXIMATE FORCE CONSTANTS OF SOME M–O SPECIES

Species	Source	ν_{A_1}, cm.$^{-1}$	k, mdynes/Å.
$VO(acac)_2$	*a*	995	7.10
$OVBr_3$	*b*	1025	7.64
$OVCl_3$	*c*	1035	7.70
K_2CrOCl_5	*d*	952	6.54
$(NH_4)_2MoOCl_5$	*e*	975	7.68
$CpMoOCl_2$	*f*	949	7.26
$K_2NbF_5O \cdot H_2O$	*g*	935	7.00

[a] K. Nakamoto, *et al.*, *J. Am. Chem. Soc.*, **83**, 4533 (1961). [b] F. A. Miller and L. R. Cousine, *J. Chem. Phys.*, **26**, 329 (1957). [c] F. A. Miller and W. K. Baer, *Spectrochim. Acta*, **17**, 115 (1961). [d] Reference 2. [e] This study. [f] M. Cousins and M. H. L. Green, *J. Chem. Soc.*, 1567 (1964). [g] O. L. Keller, *Inorg. Chem.*, **2**, 783 (1963).

TABLE V

FREQUENCIES AND APPROXIMATE FORCE CONSTANTS FOR SOME *cis*-MO_2 SPECIES

Species	Source	Obsd. frequencies, cm.$^{-1}$ ν_{A_1}	ν_{B_2}	Force constants, mdynes/Å. k	k_i
O_2CrF_2	*a*	1016	1006	7.43	0.65
O_2CrCl_2	*b*	984	994	7.10	0.48
O_2CrClF	*c*	1000	990	7.18	0.62
$O_2Mo(S_2CN(CH_3)_2)_2$	*d*	908	873	6.71	0.77
$O_2ClMo(\pi\text{-}C_5H_5)$	*e*	920	887	6.61	0.49
O_2ReBr_2	*f*	938	875	7.16	0.68

[a] W. E. Hobbs, *J. Chem. Phys.*, **28**, 1220 (1958). [b] H. Stammreich, K. Kawai, and Y. Tavares, *Spectrochim. Acta*, **15**, 438 (1959). [c] G. D. Flesch and H. J. Svec, *J. Am. Chem. Soc.*, **80**, 3189 (1958). [d] F. A. Cotton and J. A. McCleverty, to be published. [e] Table IV, footnote *f*. [f] F. A. Cotton, *et al.*, *Science*, **145**, 1305 (1964).

TABLE VI

FREQUENCIES AND APPROXIMATE FORCE CONSTANTS FOR SOME *cis*-MO_3 SPECIES

Species	Source	Obsd. frequencies, cm.$^{-1}$ A_1	E	Force constants, mdynes/Å k	k_i
$KCrO_3F$	*a*	910	946	6.37	0.37
$KCrO_3Cl$	*a*	910	946	6.37	0.37
	b	907	954	6.43	0.31
Cr_2O_7	*c*	904	946	6.33	0.33
MoO_3dien	*d*	839	839	5.7	0.23
$ClReO_3$	*e*	1001	960	8.26	0.45
$BrReO_3$	*e*	997	963	8.27	0.42

[a] T. Dupuis, *Compt. rend.*, **246**, 3332 (1958). [b] H. Stammreich, O. Sala, and K. Kawai, *Spectrochim. Acta*, **17**, 226 (1961). [c] H. Stammreich, D. Bassi, O. Sala, and H. Siebert, *ibid.*, **13**, 192 (1958). [d] This work. [e] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **16**, 1148 (1960).

The preparation[9] and structure[10] of $MoO_3 \cdot$dien have recently been reported. Only one band which could be reasonably assigned as an M–O stretch was found in the infrared spectrum.[9] The spectrum has been carefully reinvestigated using $Mo(CO)_3 \cdot$dien and $[Ni(dien)_2]Cl_2$ for comparison, and we agree with Marzluff that no second M–O stretching band can be identified. Since an MoO_3 group with C_{3v} symmetry should have two infrared-active M–O stretching modes and there appears to be no *a priori* reason for either to be weakly absorbing, this result was at first puzzling. It has been satisfactorily explained, however, by assuming that the A_1 and E Mo–O stretching modes are accidentally degenerate. (See Table VI for observed frequency and force constants.) The calculated force constants are comparable with those for the MoO_4^{2-} ion and thus indicate that this explanation is reasonable.

3. Metal–Oxygen–Metal Bridge Systems

Discussion of this topic will be limited to singly-bridged systems. As seen in Table I, the antisymmetric M–O–M stretching vibration must have a higher frequency than the symmetric one in both the linear and bent systems for any reasonable values of k and k_i.

Even if k and k_i are the same in a bent system as in a linear one, the antisymmetric mode would have a lower frequency, by a factor of approximately $[(1 - \cos \phi)/2]^{1/2}$, in the bent system. Moreover, the extensive metal-to-oxygen π bonding which is possible in a linear system[11] must be less extensive in the bent system. This is an additional reason to expect that the antisymmetric mode of a linear system must occur at a higher

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(8) S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961).

(9) W. F. Marzluff, *Inorg. Chem.*, **3**, 395 (1964).

(10) F. A. Cotton and R. C. Elder, *ibid.*, **3**, 397 (1964).

(11) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

frequency than any other type of M–O stretching mode in either type of M–O–M group.

The most attractive compounds for study of M–O–M bridge systems are those in which the stretching frequencies for the bonds *to* other ligands and *within* other ligands are not in the same range as M–O–M stretching vibrations. Such compounds are those containing the $[Cl_5RuORuCl_5]^{4-}$, $[Cl_5ReOReCl_5]^{2-}$, and $[Br_5RuORuBr_5]^{4-}$ ions, the first two of which have been shown by X-ray studies[12,13] to contain linear M–O–M groups. Unfortunately, data are still limited. Table VII, based on studies by Griffith[14] and Woodhead and Fletcher,[15] summarizes some data and force constants derived therefrom. These data and results provide tentative ranges in which antisymmetric M–O–M stretches and M–O force constants for such linear systems may be expected to lie. For bent systems, firm data are still scarcer at present. For the dichromate ion[16] the antisymmetric frequency appears to be 772 cm.$^{-1}$, *i.e.*, lower than the frequencies for linear systems given in Table VII, in agreement with preceding considerations.

TABLE VII

FREQUENCIES AND APPROXIMATE FORCE CONSTANTS FOR SOME LINEAR M–O–M BRIDGE SYSTEMS

Species	Ref.	Obsd. frequencies, cm.$^{-1}$		Force constants, mdynes/Å.		
		$\nu\Sigma_g^+$	$\nu\Sigma_u^+$	$k - k_i$	k	k^a
$[Cl_5RuORuCl_5]^{4-}$	14, 15	240?	888	3.43	3.43	3.73
$[Cl_5ReOReCl_5]^{4-}$	14	...	855	3.30	...	3.60
$[Br_5RuORuBr_5]^{4-}$	14	...	860	3.24	...	3.54
$[Cl_5OsOOsCl_5]^{4-}$	14	...	840	3.18	...	3.48

[a] Assuming the symmetric stretch in the first case is at 260 cm.$^{-1}$ giving $k_i = 0.3$ mdyne/Å., and assuming $k_i = 0.3$ mdyne/Å. for the other cases.

The above brief discussion will be adequate for our purposes later in this paper. The work of Griffith[14] should lead to more extensive correlations.

4. Assignment of Mo–O Stretching Frequencies in Some More Complex Molecules

The structure of $K_2\{[MoO_2(C_2O_4)H_2O]_2O\}$ has recently been reported.[17] Each Mo atom is octahedrally surrounded by two terminal oxygen atoms, O_t, the bridging oxygen atom, O_b, the oxygen atom of a water molecule, and two oxalate oxygen atoms. The infrared spectrum, recorded using a hydrocarbon oil mull by Mrs. S. M. Morehouse, has, in addition to oxalate bands,[18] strong absorption bands at 960, 920, and 860 cm.$^{-1}$, which may be assigned as Mo–O_t and Mo–O_b stretching bands. From the X-ray work,[17] the analysis of Mo–O vibrations may be conducted by treating the molecule as an $O_2Mo–O–MoO_2$ system with C_{2v} symmetry, a linear Mo–O_b–Mo bridge system, and taking all other O–Mo–O angles as 105°. Three force constants, k_t for Mo–O_t bonds, k_b for Mo–O_b bonds, and k_i for all three types of Mo–O to Mo–O interactions, were used. The bands at 960 and 920 cm.$^{-1}$ were assigned to symmetric and antisymmetric modes within MoO_2 groups (coupling between these being neglected in the simplified force field used), and the band at 860 cm.$^{-1}$ was assigned to the antisymmetric Mo–O–Mo stretching mode. The following force constants (mdynes/Å.) were then calculated: $k_t = 7.01$, $k_b = 3.84$, and $k_i = 0.44$. These seem reasonable in the light of the preceding discussions (sections 2 and 3).

For μ-oxo-bis(dioxo)cyclopentadienylmolybdenum(VI), molybdenum–oxygen stretching bands have been reported[19] to occur at 930, 898, and 850 cm.$^{-1}$. With assignments, assumptions as to bond angles, and choice of force field analogous to those described above for the oxalato complex the following force constants (mdynes/Å.) are obtained: $k_t = 6.63$, $k_b = 3.68$, and $k_i = 0.37$.

The structure of the oxomolybdenum(V) ethyl xanthate compound, $[(C_2H_5OCS_2)_2MoO]_2O$, has recently been reported.[11] It contains a linear Mo–O–Mo bridge group and the O_t–Mo–O_b–Mo–O_t group has very nearly C_{2v} symmetry, with O_b–Mo–O_t angles of 104°. The infrared spectrum, together with that of $Ni(S_2COC_2H_5)_2$ for comparison, is shown in Figure 2. These spectra were kindly supplied by Dr. A. B. Blake. It is evident that there are only two strong bands in the region 800–1100 cm.$^{-1}$ which can be assigned to Mo–O stretching modes, *viz.*, those at 1046 and 946 cm.$^{-1}$, both marked with small arrows in the figure. The coupling between the two Mo–O_t oscillators, to give symmetric and antisymmetric modes, should be very

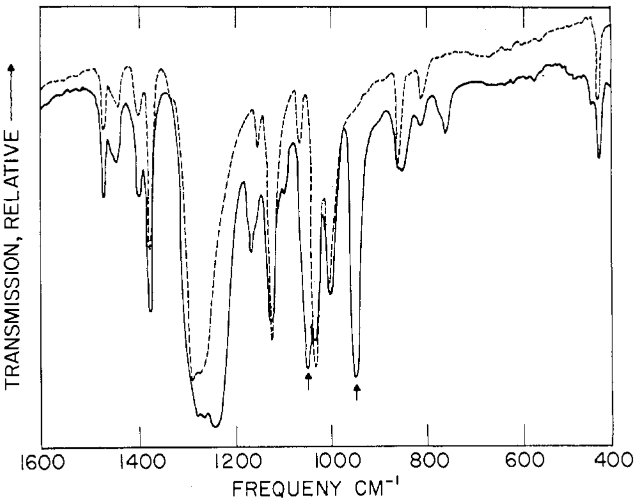

Figure 2.—Infrared absorption spectra of $Mo_2O_3(S_2COC_2H_5)_4$, solid curve, and $Ni(S_2COC_2H_5)_2$, broken curve. Both spectra were recorded using mineral oil mulls. The small arrows indicate the bands at 946 and 1046 cm.$^{-1}$ which are assigned to Mo–O stretching modes.

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[12] A. M. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

[13] J. C. Morrow, *ibid.*, **15**, 851 (1962).

[14] W. P. Griffith, private communications. Dr. Griffith is carrying out a more general study of oxygen-bridged systems.

[15] J. L. Woodhead and J. M. Fletcher, United Kingdom Atomic Energy Authority Research Group Report, AERE-R4123. A copy of this report was kindly supplied by Dr. Fletcher.

[16] H. Stammreich, D. Bassi, O. Sala, and H. Siebert, *Spectrochim. Acta*, **13**, 192 (1958).

[17] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

[18] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963.

[19] M. Cousins and M. H. L. Green, *J. Chem. Soc.*, 1567 (1964).

slight, although coupling of the terminal modes with the corresponding modes of the bridge system need not be small. However, since there are only two bands, one of which must be the antisymmetric bridge mode, we assume that there is no resolved separation of the Mo–O_t modes. Therefore, the 1046 cm.$^{-1}$ band is assigned to both the Mo–O_t stretching modes and the 946 cm.$^{-1}$ band to antisymmetric Mo–O_b–Mo stretching. With the structural arrangement described above and using a value of 0.2 mdyne/Å. for the Mo–O_b to Mo–O_b interaction constant, the values of k_t = 9.0 mdynes/Å. and k_b = 4.1 mdynes/Å. have been calculated.

Finally, the structure of the doubly-bridged anion, $\{[MoO(C_2O_4)(H_2O)]O_2\}^{2-}$, as it occurs in the barium salt, has recently been determined[20] and the infrared spectrum recorded. A strong band which can be assigned to Mo–O_t stretching occurs at 975 cm.$^{-1}$; by treating the Mo–O_t groups as isolated harmonic oscillators, this frequency leads to k_t = 7.7 mdynes/Å. The lengths of the crystallographically independent Mo–O_t bonds are both 1.70 Å., each with a standard deviation of 0.04 Å.

5. Correlations of Stretching Force Constants, Bond Lengths, and Bond Orders for Molybdenum-to-Oxygen Bonds

For bonds between pairs of light atoms, *e.g.*, C and C, C and O, C and N, N and N, etc., there exist relationships, in the form of smooth, monotonic curves, between the bond orders, the stretching force constants, and the bond lengths. It seems reasonable to assume that it is a necessary though not sufficient criterion for the correctness of any two sets of these parameters that they be so related. For bonds between transition metal atoms and lighter atoms, only one such study has been made, namely, that of Mo–C bonds,[21] where it was found that the expected relationships were well obeyed.

There are now accurate bond lengths known[10,11,17,20] for several compounds containing MoO, MoO_2, MoO_3, and MoOMo groups as well as for MoO_4^{2-} in lead molybdate,[22] and for all of these same compounds Mo–O stretching force constants have been estimated in earlier sections of this paper. The compounds are listed in Table VIII, together with the bond lengths and stretching force constants.

We turn first to the relationship between the more or less experimental quantities, bond lengths and force constants. Figure 3 shows a plot of these, with a smooth curve which transects the elipses of uncertainty for all the points. The two elipses at the largest bond length values (those without points in them) require special explanation.

The elipse near the bond length 2.1 Å. pertains to the bonds from molybdenum to the oxygen atoms of oxalate groups in compounds 2 and 5 of Table VIII. There are six crystallographically independent bonds of this type altogether, those in compound 2 being 2.08 and 2.18 Å. in length, those in compound 5 all being 2.11 ± 0.03 Å. A mean value of 2.08 Å. was used, equal to the mean of 2.11 Å. less 0.03 Å. to correct for the change from sp^2 hybridization of oxygen in the oxalate oxygen atoms to sp hybridization, which is presumably that used by oxygen atoms in the other compounds for σ bonding. There is, however, no direct measure of the bond force constants in these particular compounds. In order to obtain a plausible range, adequate for this correlation, the results of Fujita, Martell, and Nakamoto[23] for other oxalato complexes were used. In these studies, the metal–oxygen stretching force constants ranged from 1.9 to 2.7 mdynes/Å. for $[Pt(C_2O_4)_2]^{2-}$ to $[Cr(C_2O_4)_3]^{3-}$, respectively.

TABLE VIII

MO–O DISTANCES AND FORCE CONSTANTS

	Compound	Bond[a]	Ref.	Bond length, Å.[b]	Force constants, mdynes/Å.
1a.	$[MoO(S_2COC_2H_5)_2]_2O$	Mo–O_t	11	1.65 ± 0.02	9.0
1b.		Mo–O_b	11	1.86 ± 0.03	4.1
2a.	$K_2\{[MoO_2(C_2O_4)H_2O]_2O\}$	Mo–O_t	17	1.69 ± 0.02	7.0
2b.		Mo–O_b	17	1.876 ± 0.002	3.8
3.	dienMoO_3[c]	Mo–O_t	10	1.737 ± 0.005	5.7
4.	$PbMoO_4$	Mo–O_t	22	1.77 (± 0.01)[d]	5.7
5.	$Ba\{[MoO(C_2O_4)H_2O]O_2\}$	Mo–O_t	20	1.70 ± 0.03	7.7

[a] O_t represents a terminal oxygen atom, while O_b represents a bridging oxygen atom. [b] Intervals are standard deviations. [c] dien represents diethylenetriamine. [d] No s.d. given, but it is presumably ≤0.02.

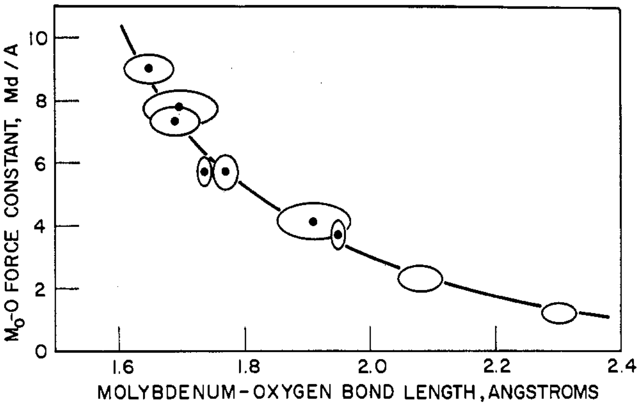

Figure 3.—Mo–O bond lengths plotted against Mo–O force constants. Data are from Table VIII. Uncertainty intervals are taken to be twice the listed standard deviations in bond lengths and ±0.5 mdyne/Å. in the force constants.

In two of the compounds listed in Table VIII there are Mo–OH_2 bonds, whose lengths are thus known, but the corresponding Mo–OH_2 stretching frequencies have not been assigned. However, from the general study of M–OH_2 stretching modes by Nakagawa and Shimanouchi,[24] it seems likely that this frequency lies in the range 400 ± 50 cm.$^{-1}$. Using the simple harmonic oscillator model for an isolated Mo–O bond, this leads to 1.3 ± 0.35 mdynes/Å. for the force constant of the

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Mo–OH_2 bond; the bond lengths in each case are 2.30 ± 0.02 Å.

The shape of the curve in Figure 3 is physically correct, especially in showing the proper limiting behavior. Thus, it asymptotically approaches the value $k = 0$ as the bond length approaches infinity, and it rises steeply as bond lengths decrease. The existence of a single such well-behaved curve which fits all of the data is good evidence for the correctness of the force constants and hence for the assignments of the spectra upon which they are based.

It is well known that when bond orders are plotted against bond lengths, a curve of the type shown in Figure 4 is to be expected. Conversely, the fact that a set of points lies consistently on such a curve can be taken as indicating that reasonable bond orders have been assigned. The rationale of assigning a bond order of 3 for point 1a, bond orders of 2.5 for points 2a and 5, and bond orders of 1.5 for points 1b and 2b has been given in detail elsewhere (see the references cited in Table VIII). The bond order 1.0 for Mo to oxalate bonds seems a reasonable assumption. The assignment of bond orders of 2.0 to points 3 and 4 is based on the following line of argument. In dienMoO_3, there are three dπ orbitals of Mo which are suitably oriented to give an average of one dπ–pπ overlap per Mo–O bond. These dπ orbitals are initially empty and the corresponding pπ orbitals initially filled. Hence each of the Mo–O σ bonds can be supplemented by one π bond. Moreover, the existence of Mo to O double bonds is in accord with the formal valences (+6 and −2) for Mo and O in this compound, so that no abnormal separation of charge is to be expected. For MoO_4^{2-}, the formation of double bonds is also in accord with the valences. In a tetrahedral species, the central atom has three dπ orbitals which overlap strongly with pπ orbitals of the ligands and two more which overlap only a little less well ($\sqrt{3}/2$ times as well). It seems plausible that the average order of the dπ–pπ bonds here may be about 1.0 or very nearly so, thus making the over-all bond orders equal, or nearly equal, to 2.0.

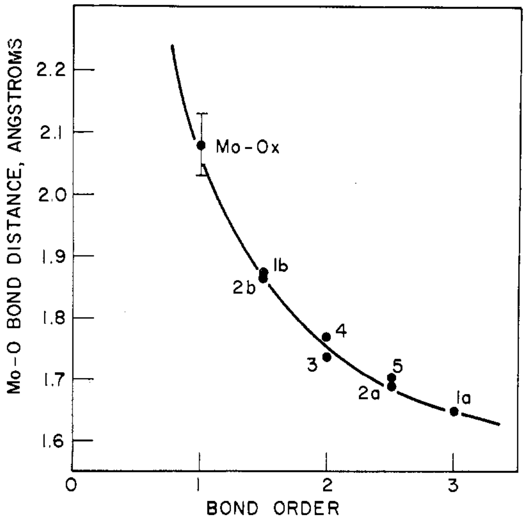

Figure 4.—The relation between Mo–O bond lengths and bond orders. Bond lengths are taken from Table VIII for numbered points.

Since the bond length–bond order and bond length–force constant relations are satisfactory, it would be expected that the third correlation, namely, that between bond orders and force constants, would be observed in a satisfactory fashion. As Figure 5 shows, this is so. In this case, allowance has been made for the fact that in compounds 1 and 5 we are dealing with molybdenum(V) whereas in all others molybdenum(VI) is concerned. As shown in Figure 1, the change from an MO_4^{n-} species to an isoelectronic one with a metal of next highest atomic number causes an increase, averaged over the three sets of points, of about 0.6 mdyne/Å. Assuming that a change from Mo(V) to Mo(VI) has about the same effect on the effective nuclear charge as a change of one unit in atomic number, the force constants for the points pertaining to Mo(V) have been increased by 0.6 mdyne/Å. and these corrected points also placed on the graph. The curve was drawn to give the best fit to the corrected Mo(V) points as well as the Mo(VI) points. This is a relatively minor matter and the method of making the correction is crude, but the points so corrected seem, nevertheless, to be more appropriate for the purpose than those without any allowance at all for the differences in oxidation state.[25]

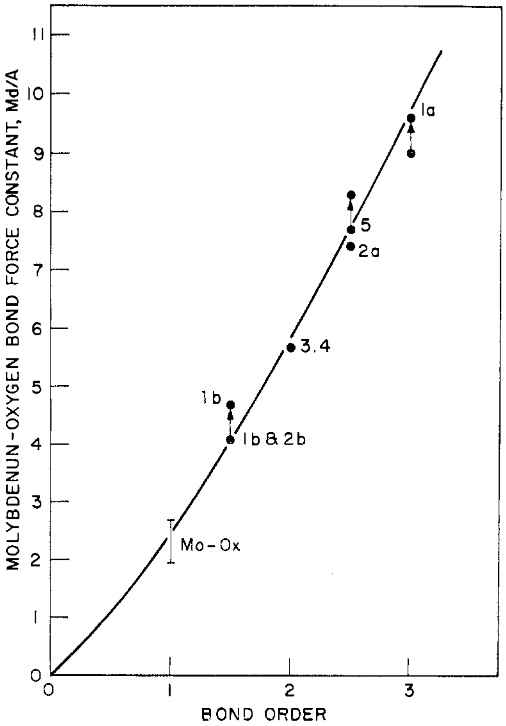

Figure 5.—The relationship between Mo–O stretching force constants and bond orders. Bond force constants are taken from Table VIII for the numbered points. See text for further explanation.

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[25] No adjustment of this kind is necessary in Figure 3, since both quantities should be affected proportionately by the change in oxidation state. No correction was made in Figure 4, since (1) the magnitude of the correction is difficult to estimate even crudely, though by use of Figures 3 and 5 and the magnitude (0.6 mdyne/Å.) of the correction in force constant it might be estimated as 0.4–0.8 Å., and (2) the correction made in force constants is an upper limit which is probably about twice too big, meaning that the probable correction to bond lengths (then 0.02–0.04 Å.) is scarcely beyond the standard deviations in most of the bond lengths.

In summary, Figure 3 provides good evidence that the infrared assignments and hence the Mo–O force constants are probably correct, none being subject to any large random error. Figures 4 and 5 then show that the various estimates of bond orders are plausible and consistent over the series of compounds. Naturally, each bond order might be incorrect by several tenths of a unit, but it seems unlikely that errors, either random or systematic, could be much greater than that. Thus, Mo–O bonds appear to exhibit the same qualitative relationships between bond orders and the two observable properties, bond lengths and bond force constants, as do bonds between pairs of light atoms and the Mo–C bonds in molybdenum carbonyl and its derivatives. Similar correlations may then reasonably be expected for other series of bonds from transition metals to light atoms, and their existence should prove useful in establishing and correlating the electronic structures of compounds containing such bonds.

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A Light-Scattering Investigation of the Hydrolytic Behavior of Thorium in Aqueous Perchlorate Media

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The hydrolytic polymerization of thorium in solutions corresponding to 0.0, 1.0, 1.6, 2.0, and 3.0 bound hydroxide ions per thorium atom ($\bar{n}$ = 0.0, 1.0, etc.) has been investigated by the light-scattering technique at 25°. For each hydroxyl number, Th concentrations were varied between approximately 0.01 and 0.10 M in supporting electrolyte of 1.00 M $\mathrm{NaClO_4}$. The degree of hydrolysis of the thorium ion is found to affect markedly the magnitude and the manner in which the turbidity, refractive index increment, and density vary with thorium concentration. Changes in pH and ultraviolet absorption spectra with degree of hydrolysis are less pronounced. An unhydrolyzed and uncomplexed Th^{4+} ion is confirmed at $\bar{n} = 0.0$, while the species $[\mathrm{Th(OH)(ClO_4)_2}]^+$ is found at $\bar{n} = 1.0$. At hydroxyl numbers 1.6 and 2.0, average polymerization numbers of *ca.* 2.3 and 2.9 are found. Extremely large thorium aggregates containing 140–150 thorium atoms per particle are indicated in clear solutions at $\bar{n} = 3.0$. The measurements on all series appear to be equilibrium values at 25°, although slow kinetics cannot be ruled out for the later stages of hydrolysis.

Introduction

Prior to 1947, studies of the aqueous solution chemistry of thorium had led to uncertain or no conclusions as to the nature of the hydrolyzed thorium species present in solution. The first isopolycation of thorium, $[\mathrm{Th_4O_4}]^{8+}$, was suggested from the results of e.m.f.[2] and freezing-point depression[3] measurements on hydrolyzed thorium solutions. Alternatively, e.m.f. titration of the aqueous nitrate with NaOH led Kasper[4] to propose only the mononuclear species, $[\mathrm{Th(OH)}]^{3+}$.

Rather complete pH titration studies[5,6] have been interpreted by the "core-plus-links" hypothesis[7] in terms of chain-like thorium aggregates of general formula $[\mathrm{Th}\{(\mathrm{HO})_3\mathrm{Th}\}_n]^{(n+4)+}$. All values of n from 1 to considerably greater than 6 were found, with no upper limit to n being reached.[8] Later, $[\mathrm{Th_2(OH)_2}]^{6+}$ and $[\mathrm{Th_2(OH)}]^{7+}$ were reported[9] for the earlier stages of hydrolysis.

The hydrolysis of thorium in perchlorate and in chloride solutions was studied potentiometrically[10] as a function of acidity and thorium concentration (2.5×10^{-4} to 1.5×10^{-3} M) by Kraus and Holmberg. Their data were in agreement with those of Hietanen,[5] but their conclusions differed. A longer range of hydrolysis, with hydrolyses reversible up to $n = 2$, was concluded. The existence of unhydrolyzed Th(IV) was confirmed and stability constants for $[\mathrm{Th(OH)_2}]^{2+}$ and $[\mathrm{Th_2(OH)_2}]^{6+}$ were reported. The hydrolysis constant for the first mononuclear step was calculated as 5×10^{-5}. Ultracentrifuge experiments[11] carried out on perchlorate solutions have indicated polymeric thorium species to be the principal hydrolysis products except in early stages, where mononuclear species are probably more important. Only monomeric products have been reported elsewhere,[12,13] while the higher polymers $[\mathrm{Th_5(OH)_{12}}]^{8+}$ and $[\mathrm{Th_7(OH)_{18-21}}]^{n+}$ have been suggested as superimposing upon monomeric and dimeric species to yield an average polymerization number of four.[14] Dimeric and trimeric "core-plus-

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