known to hinder the chemisorption of small molecules on metal surfaces and to dramatically decrease the rate of catalytic reactions.[27] From a number of experiments the preference for atomic adsorption at the highest coordination site on clean transition-metal surfaces has been established,[28] and specifically, chalcogen adsorption at the nickel (100) 4-fold hollow is well documented.[29] Such 4-fold bridging modes of sulfur (or selenium) are encountered in some molecular compounds, e.g. $[Ni_9S_9(PEt_3)_6]^{2+}$,[16] $[Ni_8Cl_2S_6(PPh_3)_6]$,[29] $[Ni_8S_6(PPh_3)_6]$,[30] $[Ni_8S_5(PPh_3)_7]$,[30] $[Ni_{12}Se_{11}(PPh_3)_8Cl]^{2+}$,[31] and $[Ni_{34}Se_{22}(PPh_3)_{10}]$.[32] A 4-fold coordination of a disulfide group as in $[Ni_4(S_2)(edt)_4]^{2-}$ has not been detected on metal surfaces yet. One might speculate an S_2 group to be existent in the initial reaction steps on sulfided metal surfaces.

Acknowledgment. This work has been supported by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Bundesminister für Forschung und Technologie (BMFT), under Contract No. 05339GAB/3, and the Fonds der Chemischen Industrie. W.T. thanks the European Molecular Biology Organization (EMBO) for a Postdoctoral Fellowship.

Registry No. 2, 106828-48-2.

Supplementary Material Available: Thermal parameters of the anion (Table S-I), positional and thermal parameters of the cations and solvate molecules (Table S-II), distances and angles within the cations and solvate molecules (Table S-III), and a stereoscopic view of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion with thermal ellipsoids (Figure S-1) (8 pages); observed and calculated structure factors (Table S-IV) (32 pages). Ordering information is given on any current masthead page.

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(27) For recent reviews on poisoning and promotion see: (a) Martin, G. A. In *Metal Support and Metal—Additive Effects in Catalysis*; Imelik, B., Ed.; Elsevier: Amsterdam, 1982, p 315. For the different mechanisms of poisoning see: (b) Goodman; D. W.; Kiskinowa, M. *Surf. Sci.* **1981**, *108*, 54. (c) Johnson, S.; Madix, R. J. *Surf. Sci.* **1981**, *108*, 77.

(28) For example, see: van Hove, M. A. In *The Nature of the Surface Chemical Bond*; Rhodin, T. N., Ertl, G., Eds.; North-Holland: Amsterdam, 1979; p 277.

(29) (a) Fisher, G. B. *Surf. Sci.* **1977**, *62*, 31. (b) Perdereau, M.; Oudar, J. *Surf. Sci.* **1970**, *20*, 80. (c) Demuth, J. E.; Jepsen, D. W.; Marcus, P. M. *Phys. Rev. Lett.* **1973**, *31*, 540. (d) Anderson, S. *Surf. Sci.* **1979**, *79*, 385. (e) Hagstrum, H. D.; Becker, G. E. *J. Chem. Phys.* **1971**, *54*, 1015; *Phys. Rev. Lett.* **1969**, *22*, 1054.

(30) Fenske, D.; Ohmer, J.; Hachgenei, J. *Angew. Chem.* **1985**, *97*, 684; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 706.

(31) Fenske, D.; *Nachr. Chem., Tech. Lab.* **1986**, *34*, 432.

(32) Fenske, D.; Ohmer, J.; Hachgenei, J. *Angew. Chem.* **1985**, *97*, 993; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993.

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Metal-Oxygen Multiple Bond Lengths: A Statistical Study

James M. Mayer

Received January 11, 1988

The factors that influence metal-oxygen multiple-bond distances have been explored by examining the structures of more than 600 complexes. Mean M-O distances for monooxo compounds have been determined for 11 different metals from titanium to osmium. These mean values decrease on moving from left to right across the periodic table, with the exception of unusually long bonds observed for d^4 octahedral complexes of iron and ruthenium. The bond lengths in di- and trioxo species are on average longer than those in monooxo species, with the general order monooxo < d^0 *cis*-dioxo < *fac*-trioxo < d^2 *trans*-dioxo. For a particular metal, the M-O bond lengths in monooxo compounds fall in a narrow range and describe a fairly smooth and regular distribution. The M-O distance is in general not a sensitive function of the coordination number or the oxidation state of the metal. These observations are discussed with use of simple ligand field descriptions of the metal-oxygen multiple bonds.

The study of compounds with metal-ligand multiple bonds—metal-oxo, -sulfido, -nitrido, -imido, -alkylidyne, -alkylidene, and related complexes—has become one of the fastest growing areas of inorganic chemistry.[1] There is increasing interest in these compounds as reagents or catalysts for organic reactions and as models for the active sites in heterogeneous processes. Oxo, imido, sulfido, and related ligands also appear to be involved in the catalytic cycles of a variety of metalloenzymes, for instance those of cytochrome P-450,[2] nitrogenase,[3] and xanthine oxidase.[4]

Structural studies, in particular single-crystal X-ray diffraction, have played a major role in the development of this area. In most cases a structural study is the primary evidence for a metal-ligand multiple bond, and the bond length is the starting point for a discussion of the nature of the multiple bond. In the course of preparation of a monograph on this topic,[1] a large table has been compiled listing structural data for complexes with metal-oxygen, metal-nitrogen, and metal-carbon multiple bonds; the metal-oxo portion alone contains over 600 structures. The metal-oxo table and accompanying references are available as supplementary material, and the whole table appears in the monograph.

In this report, the wealth of data in the table is used to explore some of the factors that influence metal-oxygen multiple-bond distances. The importance of the nature of the metal, its oxidation state and coordination number, and the formal M-O bond order have been examined. Because of the large number of structures (290 for molybdenum alone!), the data have been analyzed with use of simple statistical procedures.

Results and Discussion

Methodology. The structural data used in this study derive primarily from X-ray crystallography, with a few structures determined by electron diffraction or microwave spectroscopy. Only terminal oxo complexes are considered; bridged species, heteropolyanions, and nonmolecular structures (e.g. MoO_3) have in general not been included. For each complex the data tabulated include the metal-oxygen multiple-bond length and its estimated standard deviation (σ)[5] and the coordination number[6] and oxidation state of the metal center.[7]

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(1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.

(3) *New Trends in the Chemistry of Nitrogen Fixation*; Chatt, J., da Camara Pina, L. M., Richards, R. L., Eds.; Academic: London, 1980. Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703.

(4) *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1985.

(5) A number of workers (see: Taylor, R.; Conrad, O. *Acta Crystallogr., Sect. B: Struct. Sci.* **1986**, *B42*, 112) have noted that reported estimated standard deviations are often not an excellent measure of true errors. Inaccurate values would not, however, bias the conclusions in the present analysis because average bond distances (Table I) are essentially the same whether they are weighted by the estimated errors[10] or not. (See also ref 8.)

(6) The coordination number is defined in the usual fashion, with the following special cases: cyclopentadienyl groups are counted as tridentate ligands, peroxide (O_2^{2-}) and related species as bidentate ligands, and olefin and acetylene as monodentate ligands.

(7) The table also includes information about the angle(s) cis to the multiply bonded ligand and references.

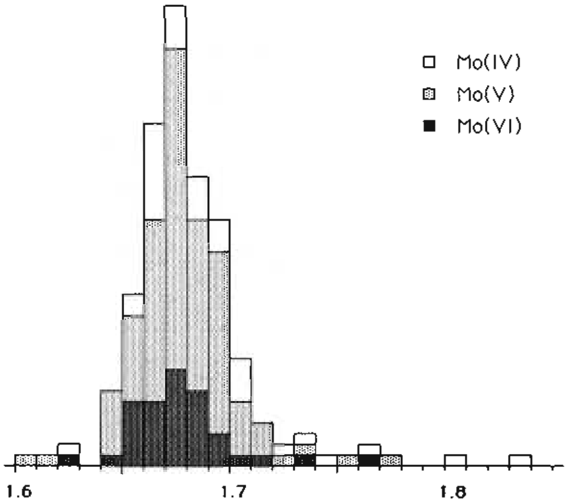

Figure 1. Distribution of molybdenum–oxygen distances (Å) for monooxo complexes in the oxidation states +4, +5, +6 (reproduced from ref 1). Only bond lengths with standard deviations less than 0.015 Å are included.

These data are not from a random sampling of structures—they are from an essentially complete compilation.[8] It is interesting to note that the reported structures reflect both the interests of workers in this area and the ease of preparation of oxo complexes. For instance, the large number of molybdenum–oxo structures are the result of the stability of these compounds and their use as enzyme models. The use of a large number and a wide variety of structurally characterized complexes, as for molybdenum, lends credence to the statistical approach and supports the generality of the conclusions. In a few areas, however, the statistics must be considered tentative because only a few oxo complexes of a particular type have been structurally characterized. For instance, there are only three accurate structures of titanium–oxo complexes, all with porphyrin or phthalocyanine ligands.

The structures have been divided into categories, by metal and by the number of oxo groups, separating into monooxo, d^0 dioxo, d^2 dioxo, and trioxo compounds. The categories with a large number of structures, such as molybdenum monooxo structures (122), have been further subdivided and analyzed by coordination number and/or d electron count.

For each category there is a distribution of metal–ligand bond distances (see Figure 1). The distributions are characterized by an average bond length (the mean), a width (defined[9] as twice the standard deviation from the mean), and the median (the middle value). These values are given in Table I. Also included is a crude estimate of the average error in the individual bond lengths, the average of the individual σ values.[5] The weighted mean of the distribution is also calculated, with each bond length weighted by $1/\sigma^2$, so that the more accurately determined bond distances are weighted more heavily.[10] In all cases the weighted mean is quite close to the mean, the difference being less than one-fourth of the width of the distribution.

Distributions of Metal–Oxo Bond Lengths. In most of the categories, the distribution of M–O distances is quite regular in shape, almost Gaussian. This is illustrated in Figure 1 for monooxo molybdenum compounds. The regularity is indicated by the fact that the median of the distributions is always very close to the mean, the difference being less than 0.01 Å in almost every case. In other words, the distributions do not "tail" to longer or shorter bond lengths. It is because of this regularity that the simple statistical treatment of the data is useful.

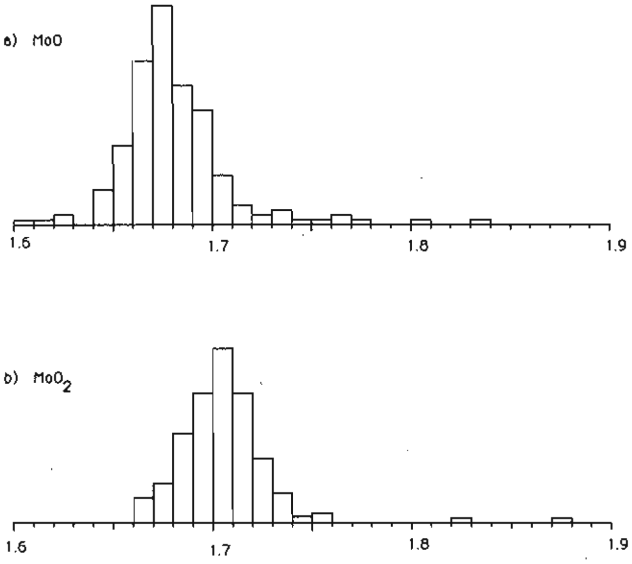

Figure 2. Distribution of molybdenum–oxygen distances (Å) in (a) monooxo and (b) *cis*-dioxo (d^0) complexes (reproduced from ref 1). Only bond lengths with standard deviations less than 0.015 Å are included.

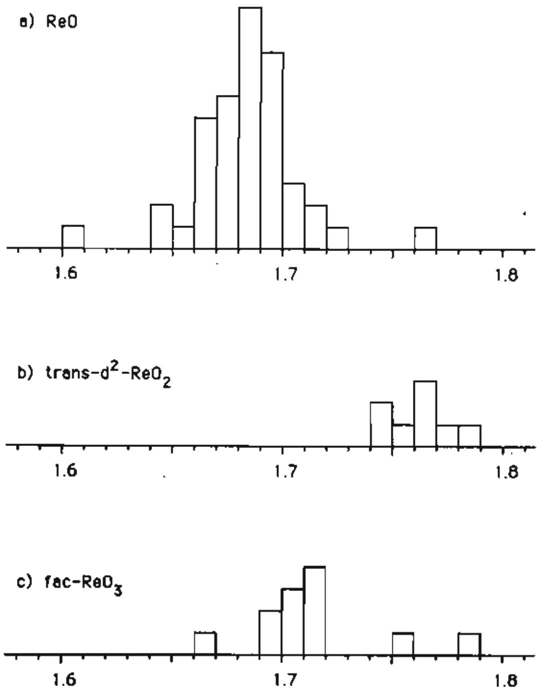

Figure 3. Distribution of rhenium–oxygen distances (Å) in (a) monooxo, (b) *trans*-dioxo (d^2), and (c) *fac*-trioxo (d^0) complexes. Only bond lengths with reported standard deviations less than or equal to 0.02 Å have been included.

The distributions are remarkably narrow, with widths on the order of 0.06 Å. In many cases the standard deviation of the distribution (half the width) is only 4 or 5 times larger than the average of the σ's of the individual values. The narrow distributions are noteworthy because of the wide variety of compounds that are included. For the molybdenum monooxo complexes shown in Figure 1, the coordination numbers vary from 4 to 7 and the oxidation states from +6 to +4. The ancillary ligands range from fluoride to cyanide to thiolate, from water to phosphines to acetylenes, from Schiff bases to dithiocarbamates to cyclopentadienyl. That all of these complexes have bond lengths in the same narrow range indicates that the nature of the ancillary ligands does not have a pronounced effect on the metal–oxygen multiple bond length. This insensitivity to the other ligands is probably a result

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(8) Seriously disordered structures and structures with quite high R values have been excluded.

(9) The width is taken as 1 standard deviation on both sides of the mean, i.e. twice the standard deviation of the distribution. Roughly 70% of the values lie within this range.

(10) The weighted mean is defined as $[\sum(\text{bond length})/\sigma^2]/\sum(1/\sigma^2)$. Weighting by $1/\sigma$ gives values for the weighted mean that are very similar to those obtained by weighting with $1/\sigma^2$. The latter is the statistically most valid procedure: Parratt, L. G. *Probability and Experimental Errors in Science*; Wiley: New York, 1961; p 118.

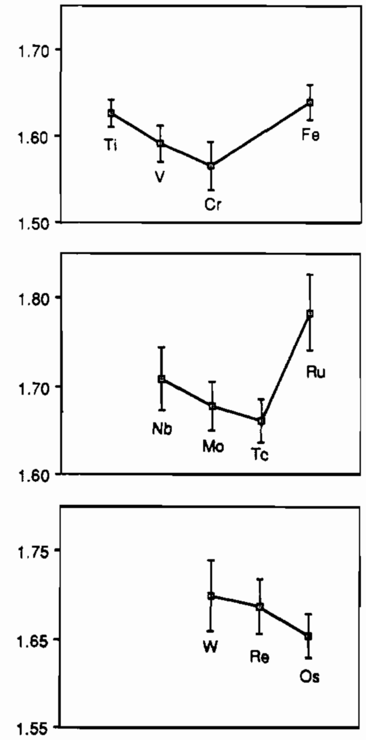


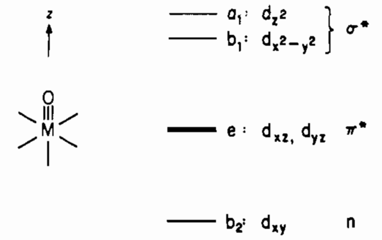
Figure 4. Graphs showing the average M–O distance for monooxo complexes of transition metals in the fourth, fifth, and sixth periods. Bond lengths are in angstroms; the error bars indicate the widths of the distributions.

of the high M–O bond strength.[11] The narrow distributions of metal–oxo bond distances contrast with those for most metal–ligand distances, which range over a few *tenths* of angstroms.[12] For instance, metal–chloride bond lengths can vary, even within a single molecule, by more than 0.2 Å.[13]

The sharpness and regularity of the distributions indicate that the categories have been chosen correctly. If, for example, molybdenum monooxo and d^0 dioxo compounds were combined, the distribution would be much broader and would almost have two resolved peaks (Figure 2). Similarly, Re–O distances in monooxo and d^2 dioxo compounds (Figure 3) fall in different ranges. Thus, the metal–oxygen bond distance, while not strongly influenced by most ancillary ligands, is affected by the presence of a second oxo group.[14]

There are, however, a few exceptionally long metal–oxygen bonds, well outside the normal range. Surprisingly, these bonds are not found in complexes with unusual electronic configurations or coordination geometries. Very long bonds have instead been observed in complexes that are very similar to species with normal M–O bond lengths.[15] In a few cases long bonds have been found in *isomers* of "normal" complexes; Chatt has coined the term "distortional isomers" for these remarkable compounds.[15a] Although there are only a few of these compounds, the long bonds skew the distribution of bond lengths, so for some distributions Table I gives two sets of statistics, the second without the long bond distances.

Chart I. Schematic Molecular Orbital Level Diagram for an Octahedral Monooxo Complex



Monooxo Complexes. The average metal–oxygen bond distances in general follow a simple periodic trend, as illustrated in Figure 4. They decrease on traversing a row of the transition elements from left to right, for instance from niobium to technetium. The bond lengths increase on descending a triad, with first-row transition metal ≪ second row ≤ third row. These trends are consistent with the well-known changes in metal radius.[16]

There are two obvious and important exceptions to the trends (Figure 4): iron and ruthenium monooxo compounds have average M–O distances roughly 0.1 Å longer than would be expected. This is due to the unusual electronic configuration of all eight of the reported iron and ruthenium monooxo structures: all are d^4 octahedral complexes. In fact, these are the only d^4 octahedral complexes among the 606 structures that are considered in this study; all of the other structurally characterized oxo compounds have d^0, d^1, or d^2 electronic configurations, except for four tetrahedral d^4 ruthenium–oxo–acetylene complexes.

The importance of the electronic configuration is revealed on examination of the d orbital splitting pattern for octahedral monooxo complexes (Chart I), which is well established from spectroscopic and theoretical studies.[17] In d^0, d^1, and d^2 complexes, the metal–oxygen interaction is best described as a triple bond, with one σ and two π bonds, the latter arising from overlap of the two oxygen p_π orbitals with the metal d_{xz} and d_{yz} orbitals.[18,19] Up to two d electrons can be accommodated in the nonbonding d_{xy} orbital. In d^4 complexes, however, two electrons occupy metal–oxygen π-antibonding orbitals, reducing the M–O bond order from 3 to 2. This results in substantially longer M–O bonds (and reduced M–O stretching frequencies[20]).

It should be noted that the long iron– and ruthenium–oxo bond lengths are not simply due to the high d electron count: tetrahedral d^4 rhenium compounds have bond lengths identical with those of d^2 rhenium–oxo species because in the tetrahedral structure the four d electrons do not occupy π^* orbitals.[17a] Similarly, the long bond lengths cannot be some sort of peculiarity of the iron triad, since osmium monooxo (and ruthenium and osmium dioxo) bond lengths fall right on the periodic trend.

Thus, octahedral d^4 monooxo complexes have much longer metal–oxygen bonds than d^0, d^1, and d^2 species that do not have

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(11) Sanderson, R. T. *Inorg. Chem.* **1986**, *25*, 3518.

(12) Most metal–ligand distances are strongly affected by the nature of the trans ligand (the trans effect); see: Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Yu. A. *Coord. Chem. Rev.* **1975**, *17*, 1 and references therein.

(13) See, for example: Bright, D.; Ibers, J. *Inorg. Chem.* **1969**, *8*, 709.

(14) (a) The M–O distance appears to be affected not only by another oxo group but also by a nitrido or imido ligand, in other words, by the presence of a second metal–ligand multiple bond. (b) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459. (c) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413.

(15) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 655. (b) Wieghardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777. Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594. Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848 and references therein.

(16) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; pp 71 ff, 256 ff. Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(17) (a) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454 and references therein. (b) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436. (c) See also ref 14b, 18, and 23.

(18) Bond orders in metal–oxo complexes have been described by a number of workers, including: Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203. Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656. Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29. See also ref 14b, 23a, and references therein.

(19) It should be noted that the metal–oxygen bond order used in this paper is quite different from the bond valence or Pauling bond strength used in the discussion of solid-state structures. The bond order used here refers to orbital occupancy in a molecular orbital sense and is derived from a ligand field description.[18] The Pauling bond strength is an apportionment of bond valences among the bonds to a central atom and is empirically determined from the observed bond distances; see: Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1957. Bart, J. C. J.; Ragani, V. *Inorg. Chim. Acta* **1979**, *36*, 261.

(20) Reference 1, p 117.

Table I. Statistical Parameters for the Distributions of Metal–Oxygen Multiple-Bond Lengths[a]

category	no. of values[b]	mean	width[c]	weighted mean	median	av σ[d]
Ti monooxo[e]	4	1.627	0.032	1.629	1.623	0.005
V monooxo	58	1.592	0.042	1.592	1.591	0.007[f]
d^0	22	1.582	0.048	1.581	1.581	0.007
d^1	36	1.598	0.032	1.599	1.599	0.007[f]
5-coord	26	1.593	0.042	1.582	1.592	0.008
6-coord	23	1.594	0.034	1.598	1.591	0.005[f]
7-coord	8	1.589	0.058	1.583	1.585	0.007
V dioxo						
d^0	46	1.629	0.050	1.634	1.628	0.005
4-coord	5	1.621	0.082	1.636	1.631	0.007
5-coord	24	1.625	0.052	1.618	1.616	0.006
6-coord	17	1.637	0.030	1.641	1.636	0.003
Nb monooxo[g]	17	1.724	0.142	1.719	1.710	0.014
bonds <1.9 Å[h]	16	1.709	0.072	1.708	1.707	0.015
Cr monooxo	10	1.566	0.056	1.560	1.565	0.011
Cr dioxo						
d^0	4	1.555	0.056	1.560	1.569	0.011
Mo monooxo	122	1.678	0.056	1.682	1.675	0.007
d^0	25	1.674	0.066	1.680	1.670	0.006
d^1	73	1.677	0.048	1.678	1.675	0.007
d^2[g]	19	1.684	0.068	1.684	1.676	0.005
d^2, bonds < 1.8 Å[h]	18	1.678	0.040	1.683	1.675	0.005
5-coord	36	1.669	0.046	1.668	1.668	0.008
6-coord	65	1.681	0.056	1.687	1.678	0.007
7-coord	19	1.677	0.052	1.689	1.677	0.005
Mo dioxo						
d^0	162	1.704	0.056	1.704	1.704	0.008[f]
5-coord	12	1.695	0.046	1.696	1.698	0.009
6-coord	146	1.704	0.054	1.705	1.705	0.007[f]
Mo trioxo	8	1.726	0.038	1.720	1.723	0.005
W monooxo[g]	34	1.711	0.122	1.699	1.700	0.013[f]
bonds <1.8 Å[h]	32	1.699	0.082	1.698	1.698	0.011[f]
d^0, bonds <1.8 Å[h]	14	1.700	0.102	1.687	1.698	0.012[f]
d^1, bonds <1.8 Å[h]	8	1.699	0.058	1.686	1.695	0.013
d^2	8	1.694	0.082	1.710	1.690	0.010
W dioxo						
d^0	11	1.709	0.038	1.714	1.712	0.008
Tc monooxo	20	1.661	0.050	1.655	1.660	0.009
Tc dioxo						
d^2	7	1.742	0.030	1.747	1.748	0.006
Re monooxo	56	1.686	0.062	1.685	1.685	0.011
d^1	9	1.671	0.082	1.666	1.671	0.011
d^2	41	1.691	0.050	1.685	1.685	0.011
d^4[i]	4	1.694	0.004	1.694	1.693	0.005
Re dioxo						
d^2	11	1.734	0.112	1.760	1.750	0.015
d^2, 6-coord	8	1.761	0.030	1.766	1.764	0.012
Re tri- and tetraoxo						
d^0	22	1.708	0.090	1.698	1.710	0.018
Iron monooxo						
d^4[j,k]	3	~1.64	~0.04			
Ru monooxo						
d^4[j]	5	1.784	0.086	1.775	1.765	0.006
Ru dioxo						
d^2	3	1.716	0.022	1.725	1.718	0.004
Os monooxo	6	1.654	0.050	1.665	1.667	0.012[f]
Os dioxo						
d^2	22	1.742	0.082	1.730	1.732	0.014[f]

[a] All distances given in angstroms. [b] Multiple values from a single-crystal structure have been included in the statistics when there is more than one independent M–O distance per molecule. [c] The width is taken as twice the standard deviation of the distribution. [d] Average of the estimated standard deviations (σ's) for the individual values. [e] One exceptionally long Ti–O bond distance is not included in the statistics because no σ was reported for this value. [f] One or more bond lengths were reported without a σ value; the value given is the average of the reported σ's. [g] Averages include one or two exceptionally long M–O bonds (see text). [h] Averages do not include one or two exceptionally long bonds. [i] Complexes are pseudotetrahedral without electrons in M–O antibonding orbitals.[17a] [j] Complexes are octahedral with two electrons formally in M–O antibonding orbitals. [k] Two structures determined by EXAFS; instead of σ's, ranges of 0.02 and 0.04 Å were reported.

electrons in M–O antibonding orbitals. Between d^0, d^1, and d^2 complexes, however, there is very little difference in metal–oxygen bond distance; in other words, in these electron counts the metal–oxo distance is not a strong function of oxidation state. If there is a trend, the M–O distance may be slightly longer on average in lower oxidation states. Molybdenum compounds provide the best illustration because there are a significant number of structures in three different oxidation states. The mean bond lengths for Mo(VI), Mo(V), and Mo(IV) monooxo complexes (d^0, d^1, and d^2, respectively) are 1.674, 1.677, and 1.684 Å (Table I).

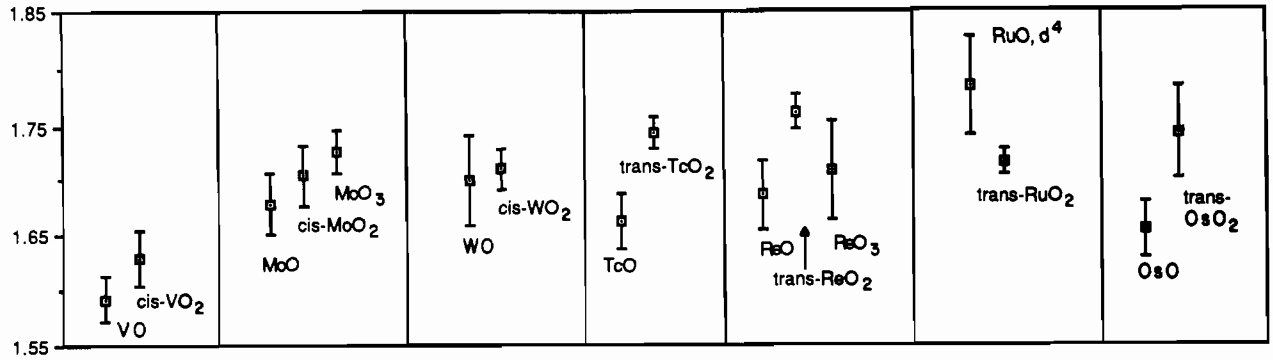

Figure 5. Graph showing, for various elements, the difference in average Mo–O bond lengths between monooxo, *cis*- or *trans*-dioxo, and trioxo complexes. Bond lengths are in angstroms; the error bars indicate the widths of the distributions. The *cis*-dioxo complexes are all d^0 and the trans species d^2; the ruthenium monooxo complexes are all d^4 octahedral compounds (see text).

The mean bond length for Mo(IV) includes two distortional isomers with Mo–O distances ≥1.8 Å; without these compounds the Mo(IV) mean is 1.678 Å. The differences among the mean Mo–O bond lengths for these oxidation states (≤0.01 Å) are much less than the variation within one oxidation state, as shown graphically in Figure 1.

Tungsten-oxo bond lengths do not show a significant oxidation-state dependence: for W(VI) and W(V) complexes the average values are 1.700 and 1.699 Å. V–O and Re–O distances are slightly longer in lower metal oxidation states, with a difference in average bond length between V(V) and V(IV) of 0.016 Å and between Re(VI) and Re(V) of 0.020 Å. These differences are less than the variation within any one category (less than or equal to half of the calculated width). The lack of a large dependence of the M–O distance on the oxidation state (for d^0–d^2 species) is completely consistent with the ligand field picture, because up to two electrons can be accommodated in a nonbonding orbital (d_{xy}, Chart I). The data are not consistent with an ionic model of metal–oxygen bonding, since the metal ionic radii are a strong function of oxidation state.[16]

Metal–oxygen bond lengths exhibit only a slight dependence on coordination number, at least in the four cases where a sufficient number of structures are available to make the statistics meaningful. For vanadium and molybdenum mono- and dioxo compounds, the mean M–O bond distance in six-coordinate complexes is 0.001–0.012 Å longer than that in five-coordinate species (Table I). Again, these differences are much less than the width of the individual distributions. M–O bonds in formally[6] seven-coordinate complexes appear to be slightly shorter than bonds in six-coordinate species, but this is based primarily on d^0 seven-coordinate complexes with peroxo (O_2^{2-}) and related ligands, a very limited sample.

Di- and Trioxo Compounds. The mean metal–oxygen bond lengths in di- and trioxo compounds are longer than those in monooxo complexes (with the exception of the long d^4 Ru–O bonds), although the differences are on the order of the widths of the distributions (Figures 2, 3, and 5). The longer bonds in di- and trioxo (and tetraoxo) compounds are due to lower M–O bond orders, which result from the empty metal d_π orbitals having to be shared among the oxo ligands.[18]

In an octahedral complex there are three metal d orbitals of π symmetry: d_{xy}, d_{xz}, and d_{yz}. In a d^0 *fac*-trioxo complex,[21] these three orbitals interact with three oxo groups and the average metal–oxygen bond is formally a double bond (one σ plus one π). When the three d_π orbitals are shared among two oxo groups, as in a d^0 *cis*-dioxo complex,[22] the net bond order is 2.5. In d^2 dioxo compounds, however, one of the d_π orbitals is occupied with the two d electrons; a trans geometry is almost invariably adopted,[22] with formal metal–oxygen double bonds.

This simple bonding description[18] explains most of the observed trends in bond lengths (Figure 5). For instance, for molybdenum compounds, monooxo (1.678 Å) < d^0 *cis*-dioxo (1.704 Å) < facial trioxo (1.726 Å). This rough correlation of bond length with bond order has been previously noted for molybdenum–oxo compounds by a number of workers.[23] It is interesting that d^2 *trans*-dioxo compounds do not appear to simply fit this pattern: the observed bond lengths in these compounds are often much longer than those in d^0 *fac*-trioxo complexes which formally have the same bondorder. The average Re–O distance in d^2 *trans*-dioxorhenium complexes in 0.05 Å longer than in d^0 trioxo species (1.761 vs 1.708 Å, see Figure 3). While only one structure of a d^2 *trans*-dioxomolybdenum compound has been determined ($MoO_2(CN)_4^{4-}$), it has a very long bond of 1.834 (9) Å.[24] Many of these comparisons are unfortunately based on only a few structures; more data are needed to determine whether the trans-d^2 configuration displays longer bonds than would be expected on the basis of bond order, perhaps due to the large trans influence of the oxo group.[12]

Conclusions

For a particular metal, the observed metal–oxygen bond lengths in monooxo complexes fall in a narrow range, indicating that the Mo–O distance is not strongly affected by the nature of the other ligands on the metal. The only ligand that strongly influences the M–O distance is a second oxo group, with average bond lengths varying roughly with the metal–oxygen bond order: monooxo < d^0 *cis*-dioxo < d^0 *fac*-trioxo < d^2 *trans*-dioxo. Average M–O bond lengths in monooxo complexes decrease gradually on moving from left to right across the periodic table. Iron and ruthenium d^4 oxo compounds exhibit exceptionally long bonds because metal–oxygen π^* orbitals are occupied. Bond lengths in monooxo compounds are not very sensitive to the coordination number or the oxidation state of the metal, as long as metal–oxygen antibonding orbitals are not occupied. In sum, metal–oxygen bond lengths depend primarily on the formal M–O bond order, as determined by using a simple ligand field description.

Acknowledgment. W. A. Nugent is gratefully acknowledged for his encouragement and his assistance in literature searching. Support was provided by the National Science Foundation and the Chevron Research Corp. J. Wiley and Sons, Publishers, are acknowledged for permission to reproduce Figures 1 and 2 and the supplementary material.

Supplementary Material Available: A table of pertinent structural data for compounds with metal–oxygen multiple bonds and the accompanying references (39 pages). Ordering information is given on any current masthead page.

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(21) All structurally characterized octahedral trioxo compounds are d^0 and facial (see ref 14b).

(22) Transition-metal dioxo complexes with a d^0 configuration are cis; octahedral d^2 dioxo species are trans with only three well-characterized exceptions osmium (two examples): Behling, T.; Capparelli, M. V.; Skapski, A. C.; Wilkinson, G. *Polyhedron* **1982**, *1*, 840. Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357. For ruthenium (one example): Che, C.-M.; Leung, W.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 1376.

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