un ensemble de forces de van der Waals à caractère attractif. Cependant, contrairement à la structure du dérivé méthylé, on observe ici un certain nombre de contacts à caractère répulsif entre les cycles *A* et *C* de molécules non homologues: O(33)···C(62) 3,29; C(3)···C(62) 3,43; C(53)···C(12) 3,47 Å.

La projection de la structure cristalline suivant l'axe *b* est représentée sur la Fig. 3.

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Références

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Busetta, B., Comberton, G., Courseille, C. & Hospital, M. (1974). *Acta Cryst.* **B30**, 2759–2761.

Acta Cryst. (1975). **B31**, 2294

Contributions to the Chemistry of Mo and W. XIV.* The Mo-O Bond Length/Bond Order Relationship. A Systematical Treatment†

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M–O and O–M–O bond-distance values have been collated from all the relevant crystal structure determinations reported so far. The values could be separated into groups which gave characteristic distances on averaging. Based upon four fundamental coordination polyhedra all 'types' of Mo–O distances could be classified. After four points of definition were established the bond distance/bond order correlation equation $d_{\mathrm{Mo-O}} = 1{\cdot}87_4 - 0{\cdot}60_0 \log \mathrm{BO}_{\mathrm{Mo-O}}$ was obtained. For all known, totally O-coordinated polyhedra the sums of the bond orders were calculated, permitting a differentiation between the several differently distorted coordination octahedra of Mo in collective structures, as in *e.g.* Mo_4O_{11}.

Introduction

Cotton & Wing (1965*a*) have proposed a correlation diagram between the length of a Mo–O bond and the corresponding bond order. This was done on the assumption that the degenerate 4*d*-orbital levels are split in an octahedral field of ligands to leave the three t_{2g} orbitals for π bonding. This led to further assumptions. Where only one terminal O atom (O_t) is bonded to a Mo atom this bond was given a bond order of 3, corresponding to one σ bond plus two π bonds. In those compounds in which two *cis* Mo–O_t bonds occur, each bond was given a bond order of 2·5 (one σ and $\frac{3}{2}\pi$ bonds). In the compounds of the type MoO_3.dien (dien = diethylenetriamine) (Cotton & Elder, 1964) where three Mo–O_t occur, each bond was given a bond order of 2 (one σ and one π bond). The same bond order was attributed to each Mo–O bond in the MoO_4^{2-} complex ion. These arrangements are shown in Fig. 1. The Mo–O distances which were attributed to these bond orders were 1·65, 1·69 (and 1·70), 1·736 (and 1·77) Å, respectively. A bond order of 1 was attributed by these authors to a distance of 2·08 Å, which was deduced from the Mo–O distance of coordinated oxalato groups in the compounds $K_2\{[MoO_2(C_2O_4)H_2O]_2O\}$ and $Ba\{[MoO(C_2O_4)H_2O]_2O_2\}.3H_2O$.

Later (Le Carpentier, Mitschler & Weiss, 1972), it was concluded that a distance of 1·917(7) Å should correspond to 'a bond order close to one' *i.e.* a pure Mo–O (σ) single bond.

A further consideration by Perloff (1970) achieved no progress in the understanding of the Mo–O bond distance/bond order relationship. The recent general treatment by Brown & Shannon (1973), which gives an excellent review of earlier papers on this problem, does not include the case Mo–O but only the related system V–O.

We have been investigating (Schröder, 1973) the results of all crystal structure determinations of adequate accuracy of compounds containing Mo–O bonds. With few exceptions, all these compounds contain Mo in the oxidation state +6, +5 or, formally, states between the two. From these data, characteristic values of bond distances can be derived, which give the first consistent picture of the structural aspects of Mo–O bonding.

Results

(I) *Derivation of characteristic distances*

(*A*) *Terminal* Mo–O *bonds*

Cotton & Wing (1965*a*) showed from structural data that Mo–O_t bonds, having Mo in different oxidation states, can be 'scaled' upon one another. They found

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* Part XIII: *Z. Naturforsch.* (1973). **28b**, 216.

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Table 1. *d(Mo–O$_t$) in Å for structures of compounds containing only one* O$_t$ (O$_t$ = *terminal oxygen*) *per* Mo

Figures in brackets in this and all following tables are standard deviations in units of the last digit. Remarks: (*a*) This value was not used for calculating the mean of all distances (*b*) This structure determination is incomplete (*c*) This structure determination corresponds to an *R* value of 0·1–0·15; the intensities were determined by film methods (*d*) The deviation of this value could not be explained in the original paper. A = ethylenediaminetetraacetato-.

Compound	Ref.*	*d*(Mo–O) exp	Av. dist.	Reduced av. dist.	Remarks
		Mo VI			
$MoO_2Cl_2.H_2O$	1	1·60 (3), 1·63 (3)	1·62		
$(MoO_2Cl_2.H_2O)_3.KCl$	2	1·68 (1)	1·68		*a,b,c*
		Mo V			
$MoOCl_3$	3	1·60 (2), 1·63 (4)	1·62	1·59	Values of two independent structure determinations
$MoOBr_3$	4	1·65 (1)		1·62	
$[MoO(C_2H_5OCS_2)_2]_2O$	5	1·644 (28), 1·649 (29)	1·646	1·62	
$(MoOC_5H_5)_2S_2$	6	1·673 (8), 1·685 (8)	1·679	1·65	
$Mo_2O_4(SO_2NC_5H_{10})_2$	7	1·669 (16), 1·657 (19)	1·663	1·63	CN = 5 (trig. bipyr.)
$Mo_2O_2S_2(SO_2NC_4H_8)_2$	8	1·650 (30), 1·779 (26) *a,d*		1·62	CN = 5 (trig. bipyr.)
$Mo_2O_3[SP(OC_2H_5)_2]_4.2C_6H_4Cl_2$	9	1·647 (14)		1·62	
K_2MoOCl_5	10	1·67 (4)		1·64	
$KMoOCl_4.H_2O$	10	1·72 (5)		1·69	*a,c*, partially bridging
$(NH_4)_2MoOBr_5$	11	1·86 (3)		1·83	*a,b,c*
$[(C_6H_5)_4As][MoOBr_4(OH_2)]$	12	1·78 (7)		1·75	*a*, should be 1·62–3 Å according to IR
$Cs_2[Mo_2O_2S_2A].2H_2O$	13	1·683 (6)		1·65	See headnote for A
$Na_2[Mo_2O_2S_2(O_4C_6H_{10}N_2)].2H_2O$	14	1·550 (25), 1·690 (25)	1·62	1·59	*c,d*
$Mo_4O_6Cl_4(OC_3H_7)_6$	15	1·617 (15), 1·634 (16)	1·626	1·60	
$MoOCl_3(SPPh_3)$	90	1·647 (3)		1·62	
$MoO_2S_2(l\text{-histidine})_2 1{\cdot}5H_2O$	41	1·686 (6), 1·666 (6)	1·676	1·646	
		Mo IV			
$[MoOCl(PhP(CH_2)_2PPh_2)_2]^+$ $[ZnCl_3.Az]^-$	16	1·69		1·62	Az = $OC(CH_3)_2$
$MoOCl_2(PMe_2Ph)_3]$	17	1·676 (7)		1·61	
$[MoOCl_2(PEt_2Ph)_3]$	18	1·801 (9)		1·73	*a*, conform. isom. from Me comp.

* References in this and following tables are:

(1) Schulz & Schröder (1973). (2) Atovmyan & Krasochka (1971). (3) Drew & Tomkins (1970*a*); Ferguson, Mercer & Sharp (1969). (4) Drew & Tomkins (1970*b*). (5) Blake, Cotton & Wood (1964). (6) Stevenson & Dahl (1967). (7) Drew & Kay (1971*a*). (8) Drew & Kay (1971*b*). (9) Knox & Prout (1969*b*). (10) Gloviak (1967). (11) Atovmyan, D'yachenko, Lobkovskii (1970). (12) Scane (1967). (13) Spivack & Dori (1973). (14) Brown & Jeffreys (1973). (15) Beaver & Drew (1973). (16) Adam, Gregory, Kilbourn (1970). (17) Manojlović-Muir (1971). (18) Manojlović-Muir & Muir (1972). (19) Kihlborg (1963/4*a*). (20) Åsbrink & Brandt (1971); Krebs (1972). (21) Atovmyan & Krasochka (1972). (22) Böschen, Buss & Krebs (1974). (23) Allcock, Bissell & Shawl (1973). (24) Kihlborg (1963/4*b*). (25) Kihlborg (1963/4*c*). (26) Mumme & Watts (1970). (27) Wilhelmi (1969). (28) Pierce, McKinzie, Vlasse & Wold (1970); Pierce & Vlasse (1971). (29) Edwards & Steventon (1968). (30) Stomberg (1968). (31) Le Carpentier, Schlupp & Weiss (1972). (32) Stomberg (1970). (33) Grandjean & Weiss (1967*a*). (34) Larking & Stomberg (1970). (35) Stomberg, Trysberg & Larking (1970). (36) Grandjean & Weiss (1967*b*). (37) Kierkegaard & Longo (1970). (38) Cotton & Morehouse (1965). (39) Knox & Prout (1969*a*). (40) Delbaere & Prout (1971). (41) Spivack & Dori (1974). (42) Kopwillem & Kierkegaard (1969). (43) Fenn (1969). (44) Florian & Corey (1968). (45) Seleborg (1967). (46) Magarill & Klevtsova (1972). (47) Seleborg (1966). (48) Gatehouse & Leverett (1971). (49) Gatehouse & Leverett (1970). (50) Böschen & Krebs (1974). (51) Mattes, Müller & Becher (1972). (52) Atovmyan, Krasochka & Rahlin (1971). (53) Grandjean & Weiss (1967*c*). (54) Kierkegaard & Holmen (1964). (55) Kierkegaard (1961*a*). (56) Linnros (1970). (57) Kierkegaard (1961*b*). (58) Smith & Ibers (1965). (59) Jeitschko & Sleight (1973). (60) van der Elzen & Rieck (1973*a*). (61) Schröder, Scherle & Hazell (1975). (62) Atovmyan & Sokolova (1969). (63) Kojić-Prodić, Ružić-Toroš, Grdenić & Golič (1974). (64) Atovmyan & Krasochka (1970). (65) Cotton, Morehouse & Wood (1964). (66) Atovmyan & Bokii (1963). (67) Day & Hoard (1968). (68) Park, Glick & Hoard (1969). (69) Leciejewicz (1965). (70) Klevtsova & Klevtsov (1971). (71) Gatehouse & Leverett (1969). (72) Jeitschko (1972). (73) Abrahams & Reddy (1965). (74) Abrahams (1967). (75) Abrahams, Bernstein & Jamieson (1968). (76) Ibers & Smith (1964). (77) Eick & Kihlborg (1966). (78) Gonschorek & Hahn (1973). (79) Jeitschko (1973). (80) Kihlborg (1963/4*d*). (81) Kihlborg (1963). (82) van der Elzen & Rieck (1973*b*). (83) Le Carpentier, Mitschler & Weiss (1972). (84) Larking & Stomberg (1972). (85) Perloff (1970). (86) Hedman (1973). (87) Sjöbom & Hedman (1973). (88) Strandberg (1973). (89) Peytavin & Philippot (1973). (90) Boorman, Garner & Mabbs (1974). (91) Cotton & Elder (1964). (92) Strandberg (1974). (93) Villa, Coghi, Manfredotti & Guastini (1974). (94) Atovmyan, Tkachev & Shishova (1974). (95) Fischer, Ricard & Toledano (1974). (96) Klevtsova, Kozeeva & Klevtsov (1974). (97) Kihlborg, Norrestam & Olivecrona (1971). (98) Evans (1968).

that increasing the oxidation number by one causes a shortening of this Mo–O$_t$ distance by 0·02–0·04 Å. We subtracted 0·03 Å from these bond distances in Mo^{V} compounds and 0·07 Å in Mo^{IV} compounds to obtain reduced distances comparable with those in Mo^{VI} compounds.

(i) *Single* Mo–O$_t$ *bond per* Mo *atom*:* Tables 1 and 2 show all the bonds measured, together with the reduced distances, for structures which contain only one Mo–O$_t$ bond. The values of both tables are seen to vary over a wide range. However, if the compounds are separated into groups, with respect to the type of the remaining ligand atoms of Mo, the distances within each group fall fairly close together. Table 1 contains those compounds in which some or all the other ligands of Mo are third- or higher-row elements, *viz*. P, S, Cl or Br. In Table 2 only N, O and F occur as further ligand atoms. To summarize, the Mo–O$_t$ distances in Table 1 are shorter than those in Table 2, evidently because the other ligand atoms of the compounds of Table 2 cause a greater stress on the total (π–) electron system around the central Mo, than do those of Table 1. The mean value of the Mo–O$_t$ distances of Table 1 is 1·62 Å which is fairly well approximated by most of the individual values.

In Table 2 there is a mean value of 1·67 Å for d(Mo–O) with additional strongly bonded ligand atoms (with $d\pi$–$p\pi$ interaction) which weaken the π bonding of Mo–O$_t$. d(Mo–O) in $MoOF_4$ (*cf*. Table 2) is substantially shorter, because the F ligand atoms with their high electronegativity draw electron density from the oxygen lone-pair electrons into the Mo–O$_t$ bond which is thus strengthened. The same effect is produced by additional positive partners, as can be seen from the values for $Cs_{0.25}MoO_3$ (Mumme & Watts, 1970); this is not yet understood.

The outlined characteristics of a single Mo–O$_t$ bond are largely independent of the coordination number (CN) of Mo. As Tables 1 and 2 show, a single Mo–O$_t$ bond has been found with CN 5 (trigonal bipyramid, tetragonal pyramid), 6 (distorted hexagon) and with several peroxo-compounds in which Mo may have a CN of 7 or 5.

(ii) *Two cis* Mo–O$_t$ *bonds per* Mo *atom*: Table 3 shows the values of all known examples of two *cis* Mo–O$_t$. They exclusively comprise Mo^{VI} compounds. The first three compounds have no additional π-interacting (or barely $d\pi$–$d\pi$ interacting) ligands. This leads again to shorter Mo–O$_t$ distances. The average value of the five distances for these first three compounds is 1·68$_3$ Å. The average value for the other Mo–O$_t$ of Table 3 is 1·70$_5$ Å. The Mo–O$_t$ in two of the three fluorine-containing compounds seem to be also shortened somewhat for the reasons discussed in (i).

(iii) *Three* Mo–O$_t$ (1,2,3) *and four* Mo–O$_t$ (*tetrahedron*) *per* Mo *atom*: Table 4 shows the values of the corresponding bonds. The resulting characteristic distance of three Mo–O$_t$ is 1·738(7) Å which is about 0·03 Å shorter than the characteristic average distance of 1·77 Å in isolated MoO_4^{2-} ions. Of these, the most reliable value is considered to be that of $PbMoO_4$ (Leciejewicz, 1965). Its value, together with those from the other molybdates is also given in Table 4.

In $Na_2Mo_2O_7$ the average over two Mo–O$_t$ (2 × 1·684 Å) from the octahedron and two Mo–O$_t$ (1·708, 1·752 Å) from the linked tetrahedron is 1·707 Å, precisely the mean of Table 3, while the four distances at the tetrahedron give an average of 1·757 Å, not far from that obtained in Table 4. In α-$ZnMoO_4$ (Abrahams, 1967) one Mo–O tetrahedron, through the influence of the Zn cations, is so distorted that two distances [1·707(9), 1·716(10) av. 1·711 Å] average close to the 1·70$_5$ Å for the two *cis* Mo–O$_t$, while the mean of all the distances is 1·76$_1$ Å, close to the average value of Table 4.

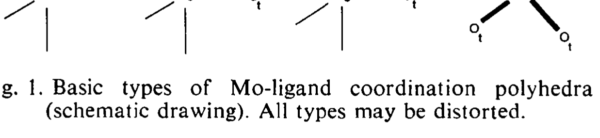

Fig. 1. Basic types of Mo-ligand coordination polyhedra (schematic drawing). All types may be distorted.

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* The tables in this paper do not include any of the Mo–O distances obtained for the following structures: $K_{0.26}MoO_3$ (Stephenson & Wadsley, 1965); $K_{0.28}MoO_3$ (Graham & Wadsley, 1966); $(NH_4)_6Mo_7O_{24}.4H_2O$ (Shimao, 1967; Evans, 1968); $(NH_4)_2H_6(CeMo_{12}O_{42}).12H_2O$ (Dexter & Silverton, 1968); $LiCd[MoO_4]OH$ (Kobtsev, Kharitonov, Pobedimskaya & Belov, 1968); $Na_{0.9}Mo_6O_{17}$ (Stephenson, 1966); $(NH_4)_4Mo_4O_{11}(C_4H_3O_5)_2.6H_2O$ (Porai-Koshits, Aslanov, Ivanova & Polynova, 1968); $(NH_4)_2MoO_3F_2$ (Mattes & Müller, 1973) $KR(MoO_4)_2(R^{3+}=Al, Sc, Fe)$ (Klevtsova & Klevtsov, 1971); U_2MoO_8 (Serezhkin, Kovba & Trunov, 1973*a*); γ-$U_3Mo_{20}O_{64}$ (Serezhkin, Kovba & Trunov, 1973*b*); γ-$U_3Mo_{20}O_{64}$ (Serezhkin, Kovba & Trunov, 1973*c*); $UO_3.2MoO_3.3H_2O$ (Serezhkin, Chuvaev, Kovba & Trunov, 1973); $[(CO_3)Mo(CO)(PMe_2Ph)_3]_2$ (Chatt, Kubota, Leigh, March, Mason & Yarrow, 1974); $K_6Mo_7O_{24}.4H_2O$ (Gatehouse & Leverett, 1968); $K_xV_xMo_{1-x}O_3$ (Darriet & Galy, 1973). $(NH_4)_2Mo_2O_7$ (Knöpnadel, Hartl, Hunnius & Fuchs, 1974); $MoO_2(O_2C_5H_7)_2$ (Kamenar, Penavić & Prout, 1973); $K_5La(MoO_4)_2$ (Efremov & Trunov, 1975); $[MoO_2Cl.2DMF]O_2$ and $K_2[MoO_2(C_6H_4O_2)_2].2H_2O$ (Atovmyan, Sokolova & Tkachev, 1970); $Li_8Mo_{10-x}O_{34-3x}$ (Magarill, Klevtsova & Bakakin, 1975); $H_2Mo_2O_5C_6H_{10}O_6.3H_2O$ (Hedman, 1974); $UMo_{10}O_{32}$ (Serezhkin, Kovba & Trunov, 1974). These structures can be shown to be in error and/or of poor accuracy.

* There is one further noticeable result: in only three of the compounds listed in Tables 1, 2 and 3 do the O$_t$ show electron-donating properties in so far as they are involved in hydrogen bonding. These are $MoO_3.2H_2O$ (Åsbrink & Brandt, 1971), α-$MoO_3.H_2O$ (Böschen & Krebs, 1974), and $(NH_4)_6Mo_8O_{27}.4H_2O$ (Böschen, Buss & Krebs, 1974) where comparatively long Mo–O$_t$ distances have been found. These O$_t$ are involved in complicated hydrogen-bonding systems.

(*B*) *Bridging* Mo–O *bonds*

(i) *Derivation from one* $Mo–O_t$ *and two cis* $Mo–O_t$: In the previous section, the O_t were included in the scheme already used by Cotton & Wing (1965*a*) and which is presented in Fig. 1. In this section it will be shown that the same scheme can be used for describing $Mo–O_{br}$ bonds. This can be done by looking at the $Mo–O_t$ of the coordination polyhedra of Fig. 1 as if they become subsequently $Mo–O_{br}$. The definitions are: O atoms with neighbouring Mo atoms closer than about 2·4 Å (an upper limiting value, given by the experimental results) are called O_{br}, while O atoms bonded to only one central atom (although they may still act as accepting atoms in hydrogen bridges) are called O_t.

In these derivations we expect the following possibilities:

(*a*) a single $Mo–O_{br}$
(*b*) two $Mo–O_{br}$
(*c*) one $Mo–O_t$ plus one $Mo–O_{br}$.

The possibilities (*a*) and (*b*) have never been found, *e.g.* a dimeric arrangement of the type $X_5Mo–O–MoX_5$ does not occur. Only arrangement (*c*), formally derived from two *cis* $Mo–O_t$, is known.

The sum of the average values for two *cis* $Mo–O_t$ bonds is $2\times1{\cdot}68_3=3{\cdot}36_6$ Å or $2\times1{\cdot}70_5=3{\cdot}41$ Å. Are there examples for which this last value is also realized by the sum of one $Mo–O_t$ plus one $Mo–O_{br}$ bond length? The results given (in Table 6) show that this can be so.

The compounds with the shortest $Mo–O_{br}$ together with one $Mo–O_t$, are given in Table 5. They again contain ligands such as S, Cl, *etc.* The shortest $Mo–O_{br}$ distance has an average value of 1·83 Å. It is found in symmetrical, quasi-symmetrical (both distances equal within σ) bridges, as well as in chains with slightly alternating distances. The distance *trans* at the O atom to the $Mo–O_{br}$ in such chains is no longer than about 2·10 Å.

Terminal O atoms with a small electron-donating character are found in three coordination polyhedra of Mo_8O_{23} (Table 6). Their distances to a second Mo atom are about 2·36 Å. Such O_t atoms are named quasi-O_t or qO_t. The average of the sum of $Mo–qO_t+Mo–O_{br}$ is consequently slightly higher (mean $3{\cdot}51_1$ Å).

Table 2. *d*($Mo–O_t$) *in* Å *for structures of compounds containing only one* O_t *per one* Mo

(*a*)–(*d*) as in Table 1; (*e*) Peroxo compound.

Compound	Ref.	*d*(Mo–O) exp.	Av. dist.	Red. av.dist.	Remarks
Mo VI					
MoO_3	19	1·671 (8)			
$MoO_3.2H_2O$	20	1·693 (2), 2 × 1·695 (2) 1·698 (2)	1·694		
$(NH_4)_4Mo_8O_{26}.4H_2O$	21	1·60 (4), 1·64 (4), 1·67 (4), 2 × 1·71 (4), 1·73 (4)	1·68		
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	1·697 (7)	1·697		
$[HN_3P_3(NMe_2)_6^+]_2\,[Mo_6O_{19}^{2-}]$	23	6 × 1·676 (5)–1·679 (5)	1·678		
Mo_8O_{23}	24	1·683 (6), 2 × 1·695 (6), 1·700 (6)	1·693		
$Mo_{18}O_{52}$	25	1·700 (25), 2 × 1·690 (30), 2 × 1·630 (30), 1·650 (35), 1·710 (35), 2 × 1·680 (30), 1·670 (25), 3 × 1·660 (25), 1·640 (35), 1·540 (35), 2 × 1·720 (25)	1·666		
$Cs_{0.25}MoO_3$	26	1·59 (4), 1·64 (4)	1·61		*a*,*c*
$Mo_4O_{10}(OH)_2=H_2Mo_4O_{12}$	27	1·687 (30)			
$Mo_4O_{11.2}F_{0.8}$	28	1·650 (11)			
$MoOF_4$	29	1·65 (1), 1·62 (1)	1·64		*a*
$K_2[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	30	1·664 (12), 1·662 (10)	1·663		*e*, CN = 7
$MoO(O_2)_2OP[N(CH_3)_2]_3.H_2O$	31	1·662 (5)			*e*, CN = 7
$MoO(O_2)_2OP[N(CH_3)_2]_3.C_5H_5N$	31	1·658 (12)			*e*, CN = 7
$(pyH^+)_2([MoO(O_2)_2H_2O]_2O)$	83	1·674 (7)			*e*, CN = 7
$(pyH^+)_2[MoO(O_2)_2OOH]_2$	83	1·669 (6)			*e*, CN = 7
$K_2[MoO(O_2)_2(C_2O_4)]$	32	1·678 (14)			*e*, CN = 7
$K_2[MoO(O_2)F_4].H_2O$	33	1·64 (3)			*e*, CN = 7
$(NH_4)_3F[MoO(O_2)F_4]$	34	1·67 (2)			*e*, CN = 7
$K_6[Mo_7O_{22}(O_2)_2].8H_2O$	84	1·64			*c*,*e*
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	4·713			
Mo V					
$K_2MoOF_5.H_2O$	36	1·666 (26)		1·64	
$MoOPO_4$	37	1·652 (5)		1·62	*a*, tetrag. pyr.
$Ba([MoO(C_2O_4)H_2O]_2O_2).3H_2O$	38	1·70 (1)		1·67	
$Na_2\{Mo_2O_4[SCH_2CH(NH_2)CO_2]\}.$ $5H_2O$	39	1·706 (18) 1·712 (16)	1·709	1·68	
Mo_2O_4(*l*-histidine)$_2.3H_2O$	40	1·71		1·68	
$Mo_2O_2S_2$(histidine)$_2.H_2O$	41	1·70 (2), 1·72 (2)	1·71	1·68	

The almost constant sums of the bond distances in Table 6 must be interpreted in such a way that the bonding relations of these Mo–O_{br} plus Mo–O_t (or qMo–O_t) are practically the same as for two *cis* Mo–O_t.

(ii) *Derivation from three* Mo–O_t: The sum of the bond lengths of three Mo–O_t (1,2,3) bonds as given in Table 4 is $3\times1{\cdot}738(7)=5{\cdot}21_4$ Å. From this arrangement, the following derivative structural situations which might be possible, are considered:

(*a*) two O_t plus one O_{br}

(*b*) one O_t plus two O_{br}

(*c*) three qO_t (quasi O_t, each with a distance of about 2·36 Å to a second Mo atom; *cf.* definition of qO_t above)

(*d*) three O_{br} (each with a more or less equal distance to a second Mo atom).

Table 3. *d*(Mo–O_t) *in* Å *for structures of compounds containing two cis* O_t *per one* Mo

(*a*)–(*e*) as in the previous tables.

Compound	Ref.	*d*(Mo–O) exp.	Av. dist.	Remarks
		Mo VI		
$MoO_2[(C_5H_5)_2NCS_2]_2$	42	2 × 1·634 (25)	1·634	
$MoO_2Br_2C_{10}N_2H_8$	43	1·643 (17), 1·826 (18)	1·73	*d*
$MoO_2Cl_2(OCHN(CH_3)_2)_2$	44	2 × 1·68 (1)	1·68	
$Na_2Mo_2O_7$	45	2 × 1·684 (19)	1·684	
$K_2Mo_2O_7$	46	1·75, 1·76, 1·75, 1·77	1·76	*a,c*
$K_2Mo_3O_{10}$	47	2 × 1·71 (3), 1·64 (3), 1·70 (3)	1·69	
$K_2Mo_4O_{13}$	48	2 × 1·67 (3), 1·68 (3), 1·71 (3), 1·72 (3), 2 × 1·74 (3), 1·75 (3)	1·71	
$Ag_6Mo_{10}O_{33}$	49	2 × 1·69 (3), 1·71 (3), 2 × 1·72 (3), 2 × 1·73 (3), 1·74 (3), 1·75 (3), 1·76 (3)	1·72	
α-$MoO_3.H_2O$	50	1·688 (7), 1·687 (7)	1·688	
$(NH_4)_4Mo_8O_{26}.4H_2O$	21	1·60 (4), 1·64 (4), 1·67 (4), 2 × 1·71 (4), 1·73 (4)	1·68	
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	1·697 (7), 1·707 (7), 1·714 (7), 1·716 (7), 1·725 (7), 1·732 (7)	1·715	
$Na_3(CrMo_6O_{24}H_6).8H_2O$	85	1·703 (4), 1·708 (4), 1·699 (4), 1·716 (3), 1·695 (3), 1·720 (4)	1·707	
$K_4[Mo_4O_{12}(O_2)_2]$	35	1·69, 1·70, 4 × 1·71	1·70	
$K_6[Mo_7O_{22}(O_2)_2].8H_2O$	84	1·66 (3), 1·68 (3), 1·73 (3), 1·75 (3)	$1{\cdot}70_5$	*e*
$Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$	86	1·697 (8), 2 × 1·701 (8), 2 × 1·702 (8), 1·703 (8), 1·709 (10), 1·713 (9), 1·715 (9), 1·735 (8)	$1{\cdot}70_8$	
$Na_6Mo_7O_{24}(H_2O)_{14}$	87	1·67 (2), 1·69 (2), 2 × 1·70 (2), 2 × 1·71 (2), 2 × 1·72 (2), 1·74 (2), 2 × 1·75 (2)	1·71	
$Na_6Mo_5P_2O_{23}(H_2O)_{13}$	88	4 × 1·72 (1), 2 × 1·73 (1)	1·72	
$CsMoO_2F_3$	51	2 × 1·68 (6)	1·68	
$NH_4MoO_2F_3$	52	1·65 (4), 2 × 1·66 (4), 3 × 1·68 (4), 2 × 1·69 (4), 1·70 (4), 1·71 (4)	1·68	
$K_2MoO_2F_4.H_2O$	53	1·688 (24), 1·733 (14)	1·71	
$AgMoO_2PO_4$	54	1·73 (11), 1·76 (11), 1·79 (12), 1·80 (6)	1·77	*a,c*
$NaMoO_2PO_4$	55	$2\times1{\cdot}7_8$, $1{\cdot}8_7$, $1{\cdot}9_7$	$1{\cdot}8_5$	*a,c*
$LiMoO_2AsO_4$	56	1·683 (10), 1·707 (12)	1·695	
$MoO_2(PO_3)_2$	57	$2\times1{\cdot}7_7$	$1{\cdot}7_7$	*a,c*
$CoMoO_4$	58	2 × 1·726 (8), 2 × 1·719 (8)	1·722	
$HgMoO_4$	59	2 × 1·722 (4)	1·722	
$Bi_2(MoO_4)_3$	60	1·68 (1), 1·69 (1), 2 × 1·72 (1), 1·73 (1), 1·78 (1)	1·72	CN = 5 (trig. bipyr.)
$MoO_2(OC_2H_4OH)_2$	61	1·722 (11), 1·723 (10), 1·704 (11), 1·740 (11)	1·722	
$MoO_2(C_9H_6NO)_2$	62	2 × 1·71	1·71	
$MoO_2(O_2C_{15}H_{11})_2$	63	1·695 (8), 1·697 (8)	1·696	
$H[MoO_2(OCH_2CH_2)_3N]$	64	1·75 (4), 1·77 (4), 1·80 (4), 1·83 (4)	1·79	*a,c*
$K_2[(MoO_2(C_2O_4)H_2O)_2O]$	65	1·700 (20), 1·680 (19)	1·69	
$NaNH_4[MoO_3(C_2O_4)].2H_2O$	66	1·815 (4), 1·850 (4)	1·832	*a*
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	1·697 (9), 1·70 (1), 1·709 (9)	1·70	
$MoO_2(O_2N_2C_{17}H_{16})$	93	1·701 (4), 1·714 (4)	1·708	
$(NH_4)_2[Mo_2O_5(O_2C_6H_4)_2]$	94	2 × 1·68, 1·71, 1·73	1·70	
$[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)].3H_2O$	95	1·690 (4), 1·700 (4), 1·703 (4), 2 × 1·709 (4), 2 × 1·712 (4), 2 × 1·714 (4), 1·717 (4)	1·708	
$(NH_4)_6[TeMo_6O_{24}].Te(OH)_6.7H_2O$	98	12 × 1·714 (29)	1·71	
		Mo IV		
$NaK_3[MoO_2(CN)_4].6H_2O$	67	2 × 1·83	1·83 (Red. av. 1·76)	*a*, two *trans* O_t

Case (*d*) is not known*. Case (*c*) is found (see Table 8) if all six ligands are oxygen atoms. As regards their long bonds to Mo, these three O_{br} are similar to the three N atoms in MoO_3.dien. By using the distance of 1·83 Å for Mo–O_{br} and the characteristic distances for Mo–O_t derived before, sums of distances can be calculated. Thus we obtain for case (*a*) $2 \times 1·68_3 + 1·83 = 5·196$ Å or $2 \times 1·70_5 + 1·83 = 5·34$ Å and for (*b*) $1·62 + 2 \times 1·83 = 5·28$ Å or $1·67 + 2 \times 1·83 = 5·33$ Å. It can be seen that the sums 5·20 and 5·28 Å are fairly close to the value of the sum of three Mo–O_t. Table 8 compares the values found experimentally for the three cases. We conclude that in these cases the bonding relations between Mo and the three specified O atoms as a whole are fairly similar. Thus, the d(Mo–O_{br}) = 1·83 Å appears to be a characteristic value of Mo–O single-bridge (and chain) distances. Of course, if the distance of the Mo–O_t is altered (longer than the characteristic value) then the Mo–O_{br} can also be lowered, *e.g.* to about 1·75–1·76 Å, as the example of $MoO_3.2H_2O$ shows. Table 9 lists the values which were found for medium Mo–O_{br} distances which are longer than 1·83 Å. The largest value is 1·96 Å, practically equal to the sum of the ionic radii (0·60 Å + 1·35 Å = 1·95 Å; Shannon & Prewitt, 1969). Up to this distance symmetrical or quasi-symmetrical Mo–O_{br} bridges (or chains) in compounds with other ligand atoms, O, N *etc.*, are found.

Table 4. *d*(Mo–O_t) *in* Å *for structures of compounds containing three* O_t (1,2,3) *or four* O_t (*tetrahedral*) *per one* Mo

(*a*)–(*e*) as in the preceding tables. dien = diethylenetriamine, A = ethylenediaminetetraacetato-.

Compound	Ref.	*d*(Mo–O) exp.	Average distance
Three O_t (1,2,3)			
MoO_3.dien	91	1·739 (8), 2 × 1·735 (8)	1·736
$Na_4(O_3MoAMoO_3).8H_2O$	68	1·731 (6), 1·739 (6), 1·749 (6)	1·740
Four O_t (tetrahedral)			
$PbMoO_4$	69	4 values	1·77
$KIn(MoO_4)_2$	70	8	1·76
K_2MoO_4	71	4	1·76
$Gd_2(MoO_4)_3$	72	20	1·75
α-$MnMoO_4$	73	8	1·76
α-$ZnMoO_4$	74	12	1·76
$CuMoO_4$	75	12	1·77
$NaCo_{2.31}(MoO_4)_3$	76	9	1·77
$VOMoO_4$	77	4	1·76
Cs_2MoO_4	78	4	1·77
$La_2(MoO_4)_3$	79	18	1·77
$Na_2Mo_2O_7$	45	4	1·76
$Cs_2Mg(MoO_4)_2$	89	4	1·75
$KEu(MoO_4)_2$	96	8	1·78
$Cu_3Mo_2O_9$	97	8	1·76

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* This holds in the same way for a single O_{br} as for two O_{br}. Thus the known compounds with Mo–O double bridges (*cf.* Table 7) always carry one additional O_t per Mo atom and belong to the group of one O_t plus two O_{br}.

Table 5. *d*(Mo–O_{br}) *in* Å *for the shortest* Mo–O–Mo *bridges*

Compound	Ref.	*d*(Mo–O_{br}) exp.	Av. dist.	Red. av. dist.	Remarks
		Mo VI			
$MoO_2Cl_2.H_2O$	1	1·81 (5), 1·82 (6)	1·82		Mo–O–Mo: 171·6 (8)°, 178·3 (9)°
$(MoO_2Cl_2OH_2)_3.KCl$	2	1·83 (1)			Mo–O–Mo: 157·5° (Six-membered ring)
		Mo V			
$[MoO(C_2H_5OCS_2)_2]_2O$	5	1·851 (34), 1·872 (34)	1·861	1·83	Mo–O–Mo: 178 (4)°
$Mo_2O_3[SP(OC_2H_5)_2]_4.2C_6H_4Cl_2$	9	2 × 1·863 (12)		1·83	Mo–O–Mo: 180°

Table 6. *Sums of experimental cis d*(Mo–O) *in* Å

The distances Mo–O_t and Mo–O_{br} are 'reduced'.

Compound	Ref.	*d*(Mo–O_t) *d*(Mo–O_{br})	Sum	Av. sum
$(NH_4)_4Mo_8O_{26}.4H_2O$	21	1·61 (4) + 1·80 (3)	3·41	
$MoO_2Cl_2.H_2O$	1	1·60 (3) + 1·81 (5)	3·41	
		1·63 (3) + 1·82 (6)	3·45	3·42
$[MoO(C_2H_5OCS_2)_2]_2O$	5	1·614 (29) + 1·821 (34)	3·44	
		1·619 (28) + 1·842 (34)	3·46	3·45
$Mo_2O_3[SP(OC_2H_5)_2]_4.2C_6H_4Cl_2$	9	1·617 (14) + 1·833 (12)	3·45	
$(MoO_2Cl_2OH_2)_3KCl$	2	1·68 (1) + 1·83 (1)	3·51	
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	1·697 (10) + 1·753 (10)	3·45	
$Mo_{18}O_{52}$	25	13 pairs of distances		3·45
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	1·713 (9) + 1·778 (8)		3·49
		q Mo–O_t + Mo–O_{br}		
Mo_8O_{23}	24	3 pairs of distances		3·511

(iii) '*Medium*' *long* Mo–O_{br} *from dative* O_t: So far we have considered only such bonds as are involved in the closer coordination (in brackets) of the studied characteristic types of CN 6, namely (2+2)+2, (3)+3 and (4)+2. These bonds might be (more or less) influenced by the π-bonding system using *d* orbitals of Mo.

Mo–O distances not belonging to the closer coordination are always Mo–O_{br}. However no accurate values are found between 1·95 and about 2·05 Å, except when the oxidation state of Mo is considerably lower than 6.

In $Mo_{18}O_{52}$ (Kihlborg, 1963/4*c*) four 2·00–2·03 Å (σ=0·03–0·04 Å) distances are found, while in Mo_8O_{23} 2·006(6) Å (CN of O=3) and in Mo_4O_{11} (Kihlborg, 1963/4*d*) 2·009(15) Å and two 1·990(15) Å were obtained. In these oxides they indicate special bonding situations, where the engaged Mo atoms must be considered to have a considerably lower oxidation state. Thus in MoO_2 we find a coordination of Mo and O with six distances between 1·972 and 2·073 Å.

The Mo–O_{br} distances greater than about 2·05 Å belong to chains in which a relatively short bonded

Table 7. *d*(Mo–O_{br}) *in* Å *from all known* Mo–O–Mo *double bridges*

(*f*) Each bridge is quasi-symmetric.

Compound	Ref.	*d*(Mo–O_{br}) exp.	Av. dist.	Red. av. dist.	Remarks
$Ba([MoO(C_2O_4)H_2O]_2O_2).3H_2O$	38	2 × 1·88 (3), 2 × 1·93 (3)	1·905	1·88	*f*
Mo_2O_4(*l*-histidine)$_2.3H_2O$	40	4 × 1·92	1·92	1·89	
$Mo_2O_4(SO_2NC_5H_{10})_2$	7	1·919 (18), 1·924 (15), 1·930 (14), 1·957 (18)	1·932	1·90	*f*, CN=5
$Na_2\{Mo_2O_4[SCH_2CH(NH_2)COO]_2.5H_2O\}$	39	1·907 (15), 1·915 (15), 1·946 (15), 1·954 (15)	1·930	1·90	*f*

Table 8. *d*(Mo–O) *in* Å *which can be derived from three* O_t

The distances Mo–O_t and Mo–O_{br} of the Mo^V compounds are 'reduced'.

Compound	Ref.	*d*(Mo–O) exp.	Sum of distances
$2O_t+1O_{br}$			
$K_2[(MoO_2(C_2O_4)H_2O)_2O]$	65	1·700 (20), 1·680 (19), 1·876 (2)	5·256
$(NH_4)_4Mo_8O_{26}.4H_2O$	21	1·67 (4), 1·71 (4), 1·88 (3)	5·26
		1·71 (4), 1·73 (4), 1·86 (3)	5·30
$[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)].3H_2O$	95	1·700 (4), 1·714 (4), 1·897 (3)	5·311
		1·709 (4), 1·709 (4), 1·898 (3)	5·316
		1·690 (4), 1·703 (4), 1·928 (3)	5·321
		1·712 (4), 1·714 (4), 1·910 (4)	5·336
		1·712 (4), 1·714 (4), 1·925 (3)	5·351
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	1·714 (7), 1·716 (7), 1·889 (7)	5·32
		1·707 (7), 1·725 (7), 1·883 (7)	5·32
		1·697 (7), 1·732 (7), 1·897 (7)	5·33
$(NH_4)_2[Mo_2O_5(O_2C_6H_4)_2]$	94	1·68, 1·68, 1·93	5·29
		1·71, 1·73, 1·91	5·35
$MoO_2(O_2N_2C_{17}H_{16})$	93	1·701 (4), 1·714 (4), 1·939 (5)	5·35
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	1·70 (1), 1·708 (9), 1·942 (8)	5·36
$NaNH_4[MoO_3(C_2O_4)].2H_2O$	66	1·815 (4), 1·850 (4), 1·878 (4)	5·543
$1O_t+2O_{br}$			
$MoO_3.2H_2O$	20	1·695 (2), 1·752 (1), 1·811 (1)	5·258
		1·693 (2), 1·761 (1), 1·821 (1)	5·275
		1·698 (2), 1·765 (1), 1·787 (1)	5·250
		1·695 (2), 1·768 (1), 1·792 (1)	5·255
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	1·697 (7), 1·753 (7), 1·874 (7)	5·32
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	1·713 (9), 1·778 (8), 1·826 (8)	5·32
		1·697 (9), 1·813 (9), 1·825 (8)	5·34
$Mo_2O_4(SO_2NC_5H_{10})_2$	7	1·627 (19), 1·927 (18), 1·900 (14)	5·45
		1·639 (16), 1·889 (18), 1·894 (15)	5·42
$Ba[(MoO(C_2O_4)H_2O)_2O_2].3H_2O$	38	1·67 (3), 1·88 (3), 1·90 (3)	5·45
Mo_2O_4(*l*-histidine)$_2.3H_2O$	40	1·68 (2), 1·89 (2), 1·89 (2)	5·46
$Mo_{18}O_{52}$	25	1·72 (3), 1·86 (3), 1·88 (3)	5·46
$Na_2\{Mo_2O_4[SCH_2CH(NH_2)CO_2]\}.5H_2O$	39	1·676 (18), 1·885 (15), 1·916 (15)	5·48
		1·682 (16), 1·877 (15), 1·924 (15)	5·48
3 quasi O_t (1,2,3)			
Mo_4O_{11}(rhom.)	80	1·708 (17), 1·708 (17), 1·760 (17)	5·176
		1·780 (17), 1·780 (17), 1·817 (17)	5·377
Mo_4O_{11}(monocl.)	80	1·742 (15), 1·770 (15), 1·751 (15)	5·263
		1·775 (15), 1·791 (15), 1·810 (15)	5·376
$Mo_{18}O_{52}$	25	1·78 (3), 1·83 (3), 1·89 (4)	5·50

O_{br} is involved in a second 'dative' bond to another Mo atom. These O_{br} atoms have almost exclusively a CN of 2. When the shorter bond decreases from 1·83 to 1·68–1·69 Å (qO_t) the longer bond increases consequently to about 2·36 Å. An O atom which shows such a distance to a Mo atom we have called a qO_t. The distances of this and the following group of Mo–O_{br} show greater deviations around their characteristic mean. The known values of such distances in this group are given in Table 10. The mean value of all 54 distances is $2{\cdot}22_6$ Å. Excluding the 12 indicated distances (greater than 2·30 Å) we obtain $2{\cdot}18_7$ Å.

(iv) $qO_t\cdots$Mo *from dative* O_t: The last characteristic Mo–O_{br} distance which has to be considered is that of O atoms with CN 3. The known distances are

Table 9. *d*(Mo–O) *in* Å *for* Mo–O–Mo *bridges* (*and chains*), *other than those listed in Tables* 5 *and* 7

br = bridge, k = chain.

Compound	Ref.	*d*(Mo–O_{br}) exp.	Av. dist	Remark
Mo VI				
$K_2[(MoO_2(C_2O_4)H_2O)_2O]$	32	2 × 1·876 (2)	1·876	br
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	2 × 1·889 (7)	1·889	br
$Na_2Mo_2O_7$	45	2 × 1·900 (8)	1·90	k
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	1·886 (7), 1·942 (8)	1·91	k
$(pyH^+)_2\{[MoO(O_2)_2H_2O]_2O\}$	83	2 × 1·917 (7)	1·92	br
$K_4[Mo_4O_{12}(O_2)_2]$	35	2 × 1·89, 2 × 1·91, 2 × 1·93, 2 × 1·95	1·92	br
$Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$	86	10 values	1·922	br
$Na_6Mo_5P_2O_{23}(H_2O)_{13}$	88	6 values	1·924	br
$[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)].3H_2O$	95	10 values	1·925	k
$[HN_3P_3(NMe_2)_6^+]_2[Mo_6O_{19}^{2-}]$	23	12 × 1·855 (4) – 2·005 (4)	1·928	k
$Na_6Mo_7O_{24}(H_2O)_{14}$	87	14 values	1·93	br
$K_2[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	30	1·921 (10), 1·933 (10)	1·93	br
$CoMoO_4$	58	4 values	1·93	k
$HgMoO_4$	59	2 × 1·944 (4)	1·94	br
$(NH_4)_6[TeMo_6O_{24}].Te(OH)_6.7H_2O$	98	12 values	1·94	k
$(NH_4)_2[Mo_2O_5(O_2C_6H_4)_2]$	94	4 values	1·95	br
$K_6[Mo_7O_{22}(O_2)_2].8H_2O$	84	8 values	1·95	br
$K_2Mo_3O_{10}$	47	6 values	1·95	k
$K_2Mo_4O_{13}$	48	8 values	1·95	k
$Ag_6Mo_{10}O_{33}$	49	15 values	1·95	k
MoO_3	19	2 × 1·948 (8)	1·95	k
Mo < VI				
Mo_8O_{23}	24	7 values	1·91	k
$MoO_{2.4}F_{0.6}$	28	1·921 (3)	1·92	k
$Mo_4O_{11.2}F_{0.8}$	28	2 × 1·947 (2), 2 × 1·963 (3)	1·955	k
$Mo_{17}O_{47}$	81	30 values	$1{\cdot}94_7$	k
$Mo_4O_{10}(OH)_2$	27	2 × 1·959 (30), 2 × 1·956 (30)	1·96	k
$Mo_{18}O_{52}$	25	26 values	1·96	k

Table 10. *d*(Mo···O) *in* Å *of asymmetric bridges and chains*

Values with asterisk, see text.

Compound	Ref.	*d*(Mo–O) exp.	Av. distance
$MoO_2Cl_2.H_2O$	1	2·09 (5), 2·12 (6)	2·10
$Na_2Mo_2O_7$	45	2·267 (18)	
$K_2Mo_2O_7$	46	2·17, 2·27	2·22
$K_2Mo_3O_{10}$	47	2·14 (3)	
$K_2Mo_4O_{13}$	48	2·23 (3), 2·34 (3),* 2·39 (3),* 2·35 (3)*	2·36*
MoO_3	19	2·251 (8)	
$Mo_{18}O_{52}$	25	2·210, 2·140, 2·170, 2·060, 2·190, 2·160, 2·290, 2·160, 2·210, 2·090, 2·210, 2·110, 2·120 (all $\sigma = 0{\cdot}025$)	2·16
Mo_8O_{23}	24	2·369 (6),* 2·362 (6),* 2·360 (6),* 2·356 (6)*	2·36
$K_6[Mo_7O_{22}(O_2)_2].8H_2O$	35	2·08 (7), 2·16 (2), 2·20 (2), 2·28 (2), 2 × 2·33 (2),* 2·34 (3),* 2·49 (3)*	2·18 2·37*
$Mo_{17}O_{47}$	81	2·10, 2·12, 2·16, 2 × 2·20, 2 × 2·21, 2·29, 2·30* (all $\sigma = 0{\cdot}03$ Å)	2·19
Bi_2MoO_6	82	2 × 2·24 (2)	
$(NH_4)_6Mo_8O_{27}.4H_2O$	22	2·046 (7)	2·05
$Mo_2O_2S_2$-(*l*-histidine.1·5H_2O)	47	2·213 (6), 2·204 (6)	2·208
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	92	2·075 (8), 2·080 (7), 2·258 (9)	2·14
$MoO_2(O_2N_2C_{17}H_{16})$	93	2·074 (4)	

shown in Table 11. The mean value of all 76 distances is 2·29 Å; omitting ten indicated values (less than 2·20 Å) gives 2·32 Å. It is remarkable that in $\{HN_3P_3[N(CH_3)_2]_6^+\}_2[Mo_6O_{19}^{2-}]$, where one O is at a centre of an (O-bridged) octahedron of six Mo atoms, this O has six distances between 2·312 and 2·324 Å (average 2·319) (Allcock, Bissel & Shawl, 1972).

(II) *Assignment of the characteristic distances to bond orders* (BO)

From the characteristic distances we obtain the influence of the two types of additional ligand atoms upon the bond length of one $Mo–O_t$ and two *cis* $Mo–O_t$, expressed in differences of these distances. For one $Mo–O_t$ the change is $1{\cdot}67-1{\cdot}62=\Delta d_1=0{\cdot}05$ Å, for two *cis* $Mo–O_t$ the change is $1{\cdot}70_5-1{\cdot}68_3=\Delta d_2=0{\cdot}02_2$ Å. The differences are correlated with the total influence of the two types of additional ligands being the same in both arrangements. We expect a relation $2\Delta d_1=5\Delta d_2$, which is satisfactorily fulfilled.

For the differences between the characteristic $Mo–O_t$ distances of a single $Mo–O_t$, two *cis* $Mo–O_t$, three $Mo–O_t$ and the MoO_4^{2-} tetrahedron we obtain: $1{\cdot}70_5-1{\cdot}67=0{\cdot}03$ Å, $1{\cdot}73_8-1{\cdot}70_5=0{\cdot}03_3$ Å and $1{\cdot}77-1{\cdot}73_8=0{\cdot}03_2$ Å. From these, within the limits of error, equal differences we assume a correlation between these four types of arrangements. We attribute the change of π-bond order to be mainly responsible for these changes in distances.

We follow the ideas of Cotton & Wing (1965*a*) that a single $Mo–O_t$ bond (placed along the z axis) has access to two $d\pi$ orbitals, namely the d_{xz} and d_{yz} orbitals of Mo. We call this type of interaction π_1. Two *cis* $Mo–O_t$ bonds (placed along the x and z axes)

Table 11. $d(Mo\cdots O)$ *in* Å *of asymmetric bridges and chains with* $CN=3$ *for the* O *atom*

Values with asterisk, see text.

Compound	Ref.	d(Mo–O) exp.	Av. distance
$HgMoO_4$	59	2·228 (4)	
$CoMoO_4$	58	2·313 (8), 2·328 (8)	2·32
$K_2Mo_4O_{13}$	48	2·30 (3), 2·23 (3), 2·30 (3), 2·11 (3)*	2·28
$Mo_{18}O_{52}$	25	2·240, 2·260, 2·270, 2 × 2·300, 2·320,	
		2·330, 2·350, 2·380, 3 × 2·390, 2 × 2·400,	
		2·450, 2·470,	2·35
		2·020,* 2 × 2·090,* 2·130,* 2·150,*	
		2·160,* 2·190*	2·12*
		(all $\sigma=0{\cdot}025$ Å)	
$K_4[Mo_4O_{12}(O_2)_2]$	35	2·30, 2·21, 2·22, 2·25	2·24
$[HN_3P_3(N(CH_3)_2)_6^+]_2[Mo_6O_{19}^{2-}]$	23	6 × 2·312 (4) – 2·324 (4)	2·319
$(NH_4)_4Mo_8O_{26}.4H_2O$	21	2·23 (3), 2 × 2·28 (3), 2·31 (3), 2·32 (3),	
		2·41 (4), 2·46 (4)	2·33
$(NH_4)_4Mo_8O_{27}.4H_2O$	22	2·348 (7), 2·370 (7), 2·401 (7)	2·37
$(NH_4)_2[Mo_2O_5(O_2C_6H_4)_2]$	94	2·15,* 2·17*	2·16*
		2·35, 2·37	2·36
$[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)].3H_2O$	95	2·172,* 2·205, 2·269,	
		2·270, 2·307, 2 × 2·338,	
		2·345, 2·367, 2·427	
		(all $\sigma=0{\cdot}003$ Å)	2·303
(NH_4) $[TeMo_6O_{24}].Te(OH)_6.7H_2O$	98	12 × 2·299 (32)	2·30
α-$MoO_3.H_2O$	50	2·277 (7)	

Table 12. $d(Mo\cdots O)$ *in* Å *of coordinated water molecules*

Compound	Ref.	d(Mo–O) exp.	Average distances
Mo VI			
$MoO_2Cl_2.H_2O$	1	2·23 (3), 2·25 (3)	2·24
$(MoO_2Cl_2H_2O)_3.KCl$	2	2·25 (2)	
$KMoOCl_4.H_2O$	10	2·27 (5)	
$[(C_6H_5)_4As]$ $[MoOBr_4(H_2O)]$	12	2·39 (3)	
$MoO_3.2H_2O$	20	2·274 (2), 2·276 (2), 2·290 (2), 2·294 (2)	2·284
$K_2([MoO_2(C_2O_4)H_2O]_2O)$	65	2·330 (18)	
$H[MoO_2(OCH_2CH_2)_3N]$	64	2·34 (3), 2·35 (3)	
$MoO_2(OC_2H_4OH)_2$	61	2·236 (9), 2·271 (10),	2·254
		2·372 (9), 2·351 (9)	2·361
$MoO(O_2)_2PO[N(CH_3)_2]_3.H_2O$	31	2·347 (5)	
$(pyH^+)_2([MoO(O_2)_2H_2O]_2O)$	83	2·445 (7)	
$K_2[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	30	2·420 (9), 2·470 (9)	2·445
α-$MoO_3.H_2O$	50	2·346 (7)	
Mo V			
Mo_2O_4(*l*-histidine)$.3H_2O$	40	2·21 (4)	
$Ba([MoO(C_2O_4)H_2O]_2O_2).3H_2O$	38	2·22 (4)	

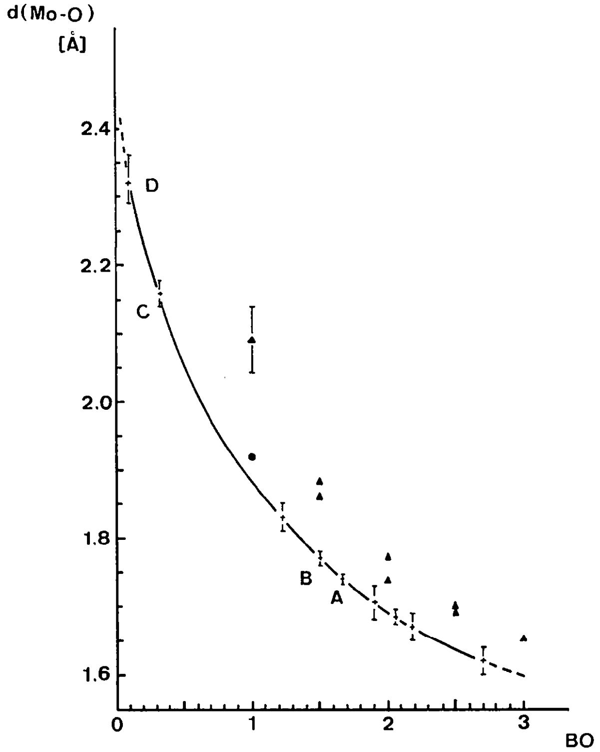

Fig. 2. *d*(Mo–O)/BO$_{\mathrm{Mo-O}}$ diagram on a linear scale. + This work with estimated errors (vertical lines). *A*, *B*, *C*, *D* are the points of definition. ▲ Values of Cotton & Wing (1965*a*). ● Value of Le Carpentier, Mitschler & Weiss (1972).

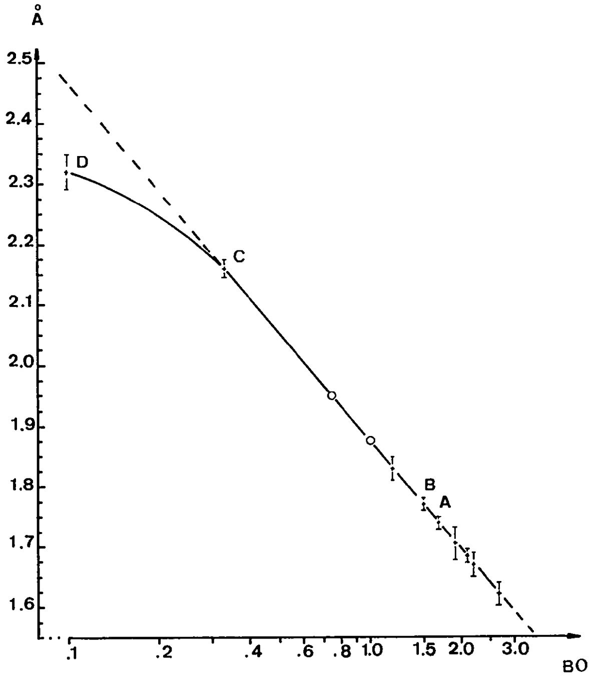

Fig. 3. *d*(Mo–O)/BO$_{\mathrm{Mo-O}}$ diagram on a half-logarithmic scale. *A*, *B*, *C*, *D* are the points of definition. Vertical lines give the estimated errors, circles mark the points with BO = 1 and with a distance equal to the sum of the ionic radii.

may also have together two interactions of type π_1 plus one using the d_{xz} orbital of Mo, which we call π_2. For the difference in π-bond order we expect per one Mo–O$_t$ bond: $2\pi_1-(2\pi_1+1\pi_2)/2=\pi_1-0{\cdot}5\pi_2$. Including the arrangement of three O$_t$ we attribute to it three additional bonds of type π_2. The difference in π-bond order between three Mo–O$_t$ and two *cis* Mo–O$_t$ is obtained by $(2\pi_1+1\pi_2)/2-3\pi_2/3=\pi_1-0{\cdot}5\pi_2$. As the geometry of the structures of the 'three Mo–O$_t$' compounds shows (angles O$_t$–Mo–O$_t$ all about 106°), the description through the π bonding of octahedral compounds (three metal *d* orbitals) is less favourable, than through the π bonding of tetrahedral compounds (two metal *d* orbitals). We call this type of interaction π_3. The Mo–O$_t$ in the $\mathrm{MoO_4^{2-}}$ tetrahedron are assigned 0·5 π_3 bonds each; each Mo–O$_t$ of the three Mo–O$_t$ arrangement is assigned 0·67 π_3 bonds. For the difference in π bonding we obtain $2\pi_3/3-2\pi_3/4=\pi_3/6$. From this, we can correlate the octahedral π bonding to the tetrahedral π bonding which results in $\pi_2\approx\frac{1}{3}\pi_3$.

For a definition of a Mo–O bond distance/bond order relation we state:

(1) The characteristic Mo–O distances of three O$_t$, 1·738 Å, have a bond order of 1·67 (one σ and $\frac{2}{3}\pi_3$ bonds) each. (Point *A*.)

(2) The characteristic Mo–O$_t$ distance of the $\mathrm{MoO_4^{2-}}$ tetrahedra, 1·77 Å, has a bond order of 1·5 (one σ and $\frac{1}{2}\pi_3$ bonds) each. (Point *B*.)

(3) A bond order of 0·33 is assigned to the value of the Mo–O$_{\mathrm{br}}$ distance of 2·16 Å. (Point *C*).

(4) A bond order of 0·1 is assigned to the value of the Mo–O$_{\mathrm{br}}$ distance of 2·32 Å. (Point *D*.)

For statement (3) we consider in particular the two compounds $\mathrm{MoO_3.dien}$ and $\mathrm{Na_4(O_3MoAMoO_3).8H_2O}$ (A = ethylenediaminetetraacetato-). Both compounds contain Mo in oxidation state 6 and both also have three equal Mo–O$_t$ distances. While $\mathrm{MoO_3.dien}$ contains as further ligands three N atoms with equal distances [2 × 2·320(6) Å, 2·332(9) Å, average 2·324 Å], $\mathrm{Na_4(O_3MoAMoO_3).8H_2O}$ has one further N atom [2·399(5) Å] and two more O atoms [2·176(6) Å and 2·213(6) Å, average 2·195 Å]. Assuming that the bond strength to these more distant ligand atoms is very similar in both compounds and also equal for O and N, we obtain the relation that a Mo–N distance of 2·399 Å is equivalent to a Mo–O distance of 2·195 Å. This difference of 0·204 Å allows a transformation of the 2·324 Å Mo–N distances in $\mathrm{MoO_3.dien}$ into 'corresponding Mo–O distances' of 2·12 Å. The average of 2·12 and 1·295 Å is 2·17 Å which is regarded as the characteristic Mo–O$_{\mathrm{br}}$ bond for these situations. This value is close to the average value of 2·18 Å in Table 10. The sums of the bond order from the three Mo–O$_t$ bonds in both these compounds is 3 × 1·67 = 5·01, leaving a difference of BO = 0·99 for the residual three ligands, 0·33 for each bond.

The BO of 0·1 in statement (4) has been taken from a SCMO calculation of Brown, Perkins & Stewart (1972). These authors calculated bond-order values

Table 13. *Results of the application of Fig.* 3 *to all* Mo–O *coordination polyhedra from sufficiently accurate crystal structures*

The listing follows the given e.s.d.'s of the Mo–O distances from the structure determination. The distances of $[Zn(NH_3)_4]\,[Mo(O_2)_4]$ are given by Stomberg (1969).

Compound	Average σ (Å) of d_{Mo-O}	Average d_{Mo-O}	Sum of BO	Av. sum BO in one compound	Formal oxidation state	CN (pseudo CN)
$MoO_3.2H_2O$	0·001–2	1·960	5·898 (~15)		6	6
MoO_2	0·003	2·011	3·719 (48)		4	6
$(NH_4)_5[(MoO_3)_5(PO_4)(HPO_4)].3H_2O$	0·003	1·97	5·740 (70)	5·721	6	6
	0·003	1·976	5·723 (70)			6
	0·003	1·981	5·720 (70)			6
	0·003	1·974	5·720 (70)			6
	0·003	1·991	5·705 (70)			6
$MoOPO_4$	0·003	1·914	5·030 (80)		5	5 (6)
$HgMoO_4$	< 0·004	1·965	5·58 (< 12)		6	6
$[HN_3P_3(NMe_2)_6^+]_2[Mo_6O_{19}^{2-}]$	0·004	1·950	5·58 (10)	5·56	6	6
	0·004	1·950	5·56 (10)			6
	0·004	1·953	5·54 (10)			6
$NaNH_4[MoO_3C_2O_4].2H_2O$	0·004	2·042	3·985 (50)		6	6
$MoO(O_2)_2OP[N(CH_3)_2]_3.H_2O$	0·005	1·976	6·02 (10)		6	7 (5)
$MoO(O_2)_2OP[N(CH_3)_2]_3.C_5H_5N$	0·005	1·978	6·25 (10)		6	7 (5)
α-$MnMoO_4$	0·005	1·759	6·37 (8)	6·30	6	4
	0·005	1·763	6·24 (8)			4
$PbMoO_4$	0·006	1·772	6·00 (9)		6	4
Mo_8O_{23}	0·006	1·958	5·90 (10)	5·77	5·75	6
	0·006	1·956	5·83 (10)			6
	0·006	1·955	5·70 (10)			6
	0·006	1·954	5·65 (10)			6
$(pyH^+)_2[MoO(O_2)_2OOH]_2$	0·006	1·979	6·01 (10)		6	7 (5)
$(NH_4)_6Mo_8O_{27}.4H_2O$	0·007	1·960	5·74 (10)	5·66	6	6
	0·007	1·972	5·73 (10)			6
	0·007	1·976	5·59 (10)			6
	0·007	1·974	5·58 (10)			6
$(pyH^+)_2([MoO(O_2)H_2O]_2O)$	0·007	1·984	5·96 (10)		6	7 (5)
MoO_3	0·008	1·981	5·74 (20)		6	6
$CoMoO_4$	0·008	1·991	5·50 (13)	5·44	6	6
	0·008	1·992	5·37 (13)			6
$Na_4H_2Mo_5P_2O_{23}.10H_2O$	0·008	1·974	5·826 (15)	5·743	6	6
	0·008	1·979	5·819 (15)			6
	0·008	1·984	5·727 (15)			6
	0·008	1·979	5·686 (15)			6
	0·008	1·989	5·657 (15)			6
$MoO_2(C_{15}H_{11}O_2)_2$	0·008	1·952	5·885 (15)		6	6
$MoO_2(OCH_2CH_2OH)_2$	0·009	2·001	5·16 (16)	5·16	6	6
	0·009	2·003	5·18 (16)			6
$Na_3H_6Mo_9PO_{34}(H_2O)_x$	0·009	1·968	5·67 (16)	5·57	6	6
	0·009	1·982	5·61 (16)			6
	0·009	1·982	5·43 (16)			6
$Na_6Mo_5P_2O_{23}.13H_2O$	0·009	1·965	5·658 (17)	5·59	6	6
	0·009	1·984	5·60 (17)			6
	0·009	1·979	5·512 (17)			6
α-$ZnMoO_4$	0·009	1·761	6·36 (15)	6·25	6	4
	0·009	1·762	6·29 (15)			4
	0·009	1·768	6·10 (15)			4
$CuMoO_4$	0·009	1·766	6·17 (15)	6·09	6	4
	0·009	1·776	6·12 (15)			4
	0·009	1·775	5·98 (15)			4
$Gd_2(MoO_4)_3$	0·01	1·732	6·96 (< 17)	6·77	6	4
	0·01	1·749	6·58 (< 17)			4
	0·01	1·752	6·50 (< 17)	6·40		4
	0·01	1·758	6·35 (< 17)			4
	0·01	1·758	6·35 (< 17)			4
$NaCo_{2.31}(MoO_4)_3$	0·01	1·765	6·18 (20)	6·08	6?	4
	0·01	1·774	5·97 (20)			4
$K_2[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	0·01	1·986	6·07 (22)	6·02	6	7 (5)
	0·01	1·983	5·98 (22)			7 (5)
K_2MoO_4	0·01	1·76	6·30 (20)		6	4
$LiMoO_2AsO_4$	0·011	1·967	5·70 (25)		6	6
$VOMoO_4$	0·012	1·764	6·16 (28)		6	4

Table 13 (*cont.*)

Compound	Average σ (Å) of $d_{\mathrm{Mo-O}}$	Average $d_{\mathrm{Mo-O}}$	Sum of BO	Av. sum BO in one compound	Formal oxidation state	CN (pseudo CN)
$K_2[MoO(O_2)_2C_2O_4]$	0·015	1·971	5·95 (16)		6	7 (5)
Mo_4O_{11} (monoclinic)	0·017	1·756	6·37 (40)	5·68	5·50	4
	0·017	1·945	5·95 (40)			6
	0·017	1·937	5·58 (40)			6
	0·017	1·946	4·81 (40)			6
Mo_4O_{11} (orthorhombic)	0·017	1·758	6·34 (40)	5·61	5·50	4
	0·017	1·936	5·96 (40)			6
	0·017	1·951	5·30 (40)			6
	0·017	1·942	4·85 (40)			6
$Na_2Mo_2O_7$	0·018	1·757	6·47 (51)	6·43	6	4
	0·018	1·950	6·39 (54)			6
$K_2([MoO_2(C_2O_4)H_2O]_2O)$	0·019	1·976	6·12 (46)		6	6
$Na_6Mo_7O_{24}(H_2O)_{14}$	0·02	1·997	5·99 (50)	5·63	6	6
	0·02	1·958	5·85 (50)			6
	0·02	1·953	5·83 (50)			6
	0·02	1·997	5·52 (50)			6
	0·02	1·977	5·48 (50)			6
	0·02	1·967	5·45 (50)			6
	0·02	1·977	5·32 (50)			6
$Mo_{18}O_{52}$	0·025	1·92	6·69 (55)	5·63	5·78	6
	0·025	1·99	6·62 (55)			6
	0·025	1·76	6·53 (55)			4
	0·025	1·97	6·00 (55)			6
	0·025	1·93	5·98 (55)			6
	0·025	1·97	5·76 (55)			6
	0·025	1·97	5·74 (55)			6
	0·025	1·97	5·72 (55)			6
	0·025	1·99	5·48 (55)			6
	0·025	1·97	5·46 (55)			6
	0·025	1·99	5·43 (55)			6
	0·025	1·97	5·41 (55)			6
	0·025	2·00	5·38 (55)			6
	0·025	2·00	5·34 (55)			6
	0·025	1·98	5·27 (55)			6
	0·025	2·00	5·14 (55)			6
	0·025	1·99	5·01 (58)			4
	0·025	2·03	4·30 (55)			6
$[Zn(NH_3)_4]\,[Mo(O_2)_4]$	0·025	1·965	5·84 (52)		6	8 (4)
$H_2Mo_4O_{12}$	0·03	1·98	5·15 (62)		5·5	6
$K_2Mo_3O_{10}$	0·03	1·85	6·60 (61)	6·20	6	5
	0·03	1·95	5·81 (60)			6
$K_2Mo_4O_{13}$	0·03	1·96	5·97 (61)	5·77	6	6
	0·03	1·98	5·94 (62)			6
	0·03	1·99	5·64 (61)			6
	0·03	1·99	5·54 (62)			6
$Ag_6Mo_{10}O_{33}$	0·03	1·99	5·78 (61)	5·50	6	6
	0·03	1·99	5·58 (61)			6
	0·03	1·98	5·42 (61)			6
	0·03	2·02	5·38 (61)			6
	0·03	1·97	5·36 (61)			6
$Ba\{[MoO(C_2O_4)H_2O]_2O_2\}.3H_2O$	0·03	2·00	4·83 (61)		5	6
$K_6[Mo_7O_{22}(O_2)_2].8H_2O$	0·03	1·997	6·06 (70)	5·69	6	7 (5)
	0·03	1·965	5·81 (70)			6
	0·03	1·975	5·74 (70)			6
	0·03	1·995	5·16 (70)			6
$KEu(MoO_4)_2$	0·03	1·78	5·985 (60)	5·80	6	4
	0·03	1·79	5·625 (65)			4
$Cu_3Mo_2O_9$	0·03	1·755	6·41 (65)	6·27	6	4
	0·03	1·77	6·13 (65)			4
$(NH_4)_6[TeMo_6O_{24}].TeOH_6.7H_2O$	0·035	1·985	5·52 (70)		6	6
$(NH_4)_4Mo_8O_{26}.4H_2O$	0·04	1·992	6·80 (75)	6·02	6	6
	0·04	1·988	5·94 (75)			6
	0·04	1·967	5·81 (75)			6
	0·04	2·008	5·51 (75)			6

Table 13 (*cont.*)

Compound	Average σ (Å) of $d_{\text{Mo-O}}$	Average $d_{\text{Mo-O}}$	Sum of BO	Av. sum BO in one compound	Formal oxidation state	CN (pseudo CN)
$Mo_{17}O_{47}$	0·04	1·94	6·20 (75)	5·22	5·53	6
	0·04	1·95	5·84 (75)			6
	0·04	1·97	5·36 (75)			6
	0·04	1·95	5·27 (75)			6
	0·04	1·94	5·22 (75)			6
	0·04	1·96	5·16 (75)			6
	0·04	1·99	5·08 (75)			7
	0·04	1·94	4·88 (75)			6
	0·04	2·02	4·01 (75)			6
$AgMoO_2PO_4$	~0·06	1·98	4·79		6	6
$K_2Mo_2O_7$	–	1·78	5·96	5·64	6	4
	–	1·98	5·33			6
$K_4[Mo_4O_{12}(O_2)_2]$	–	1·94	6·18	6·03	6	6
	–	1·96	6·06			6
	–	1·96	5·83			6
$UO_2[MoO_2(H_2O)O_{3/2}]_2$	–	1·96	6·40	5·87	6	6
	–	2·02	5·14			6
$(NH_4)_2[Mo_2O_5(O_2C_6H_4)_2]$		1·97	5·93	5·76	6	6
		1·97	5·58			6

('defined so that they afford a measure of the covalent character of the bond') in a model compound $[MoO_2(OH)_2H_2O]_2O$ for which the geometrical values were taken from $K_2[\{MoO_2(C_2O_4)H_2O\}_2O]$ according to Cotton, Morehouse & Wood (1964). The coordinated H_2O molecule in this compound shows a Mo–O distance of 2·330(18) Å. Table 12 shows all known Mo–O distances of coordinated water and in two cases of coordinated C–O–H groups. The average value of these distances is 2·317 Å, practically equal to the distance of 2·32 Å according to statement (4) and also equal to the average of Mo–O–Mo bridges, having O with a CN of 3 (Table 11).

(III) *Bond-distance bond-order correlation diagram*

The expected shape of such a diagram is known from the first attempts to derive one for the Mo–C and Mo–O bonds by Cotton & Wing (1965*a*, *b*). The recent most general treatment of element–oxygen bonds for elements in the periodic table from H^+ to As^{5+} (Brown & Shannon, 1973) resulted in similar curves.

Fig. 2 shows the curve through our four points of definition. On this curve, the points of the characteristic distances are marked. Estimated errors are indicated by vertical bars. The diagram also contains the values used by Cotton & Wing (1965*a*), and the one given by Le Carpentier, Mitschler & Weiss (1972). The curve of Fig. 2 is transformed to a half-logarithmic scale in Fig. 3.

A least-squares calculation with the values of points *A*, *B* and *C* gave the equation

$$d_{\text{Mo-O}} = 1{\cdot}87_4 - 0{\cdot}60_0 \log \text{BO}_{\text{Mo-O}} . \qquad (1)$$

What information does this curve provide?

(1) For higher bond order the curve leads to a bond order of 2·9 for a Mo–O distance of 1·60 Å. As Table 1 shows, this value is obviously a limiting value and is reached in some structures, although associated with considerable e.s.d.'s.

(2) If point *D* is also included in the least-squares calculation the resulting equation is

$$d_{\text{Mo-O}} = 1{\cdot}86_6 - 0{\cdot}49_1 \log \text{BO} . \qquad (2)$$

According to equation (2) a distance of 1·62 Å would correspond to a BO of 3·17 which is unreasonable. With equation (1) this distance gives a reasonable BO of 2·66.

(3) We find from Fig. 3 that the characteristic $Mo\text{–}O_t$ bond distances of 1·67, 1·683 and 1·705 Å described in §(I), correspond to bond orders of about 2·2, 2·1 and 1·9, respectively.

(4) The distance, corresponding to a bond order of one, is of special interest. According to equation (1) it corresponds to a distance of $1{\cdot}87_4$ Å. This value has been found in $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ (Cotton, Morehouse & Wood, 1964) in a symmetrical, straight Mo–O–Mo bridge with Mo–O distances of 1·876(2) Å. This anion is a $2O_t + 1O_{br}$ case with a sum of 1·68 + 1·70 + 1·876 = 5·25 Å for these three distances. This is fairly close to the value of 5·21 Å for three O_t. As the anion is a dinuclear, single bridged complex anion with Mo^{VI}, the existence of a $Mo\text{–}O_{br}$ (σ) single bond in this compound looks extremely reasonable.

For shorter distances than this we find, according to Table 5, symmetrical Mo–O bridges with bridge bond angles close to 180° in Mo^{V} compounds. For bridging distances corresponding to a bond order smaller than one we do not find any example with a 180° Mo–O–Mo bridge. In the accurately determined structure of $Na_2Mo_2O_7$ (Seleborg, 1967) in the octahedron a $Mo\text{–}O_{br}$ distance is found to be 1·900(8) Å which is the next closest distance to the above 1·876 Å. There exist endless, symmetrical chains, exhibiting a typical bridge angle of about 150°, provided that the Mo–O_{br} distance is larger than about 1·88 Å. This is also true for $(pyH^+)_2\{[MoO(O_2)_2H_2O]_2O\}$ (Le Carpentier, Mitschler & Weiss, 1972) with a symmetrical bridge distance of 1·917(7) Å and an angle of 148·6(2)°.

(IV) *Sums of bond order*

The established diagram according to Fig. 3 makes it possible to calculate the sum of the bond orders for any Mo–O coordination polyhydron whose bond distances are known. The results for all known examples are shown in Table 13. We find, that all bond-order sums for tetrahedrally coordinated Mo lie in the range 5·97 to 6·53 with one exception in $Mo_{18}O_{52}$. The deviation from 6·0 is often within one σ_{BO}, in some cases within two σ_{BO}. Only in $MnMoO_4$ and $Gd_2(MoO_4)_3$ are the deviations higher. The sums of bond orders in peroxo compounds are in all cases extremely close to six. For accurately determined structures with Mo obviously in a well defined oxidation state, *e.g.* $MoO_3.2H_2O$, MoO_3, the sums of bond orders are slightly below six. In compounds with a non-integer overall oxidation number, the bond sums vary considerably between the different coordination polyhedra and give average values fairly close to the formal (overall) oxidation number of the compound. This is the first proof of Kihlborg's earlier suggestion (Kihlborg, 1963/4*e*) that small changes of the oxidation state of Mo might be indicated by the change of the size of the distortion of the Mo–O coordination polyhedron.

Conclusion

A systematic description of the geometrical aspects of all Mo–O bonds has been developed. This could be done, because it has been possible to show that:

(*a*) All isolated and polymeric structural arrangements of Mo–O coordination can be expressed in terms of the fundamental coordination polyhedra of Fig. 1.

(*b*) All hexacoordinated Mo–O and partly Mo–O coordinated systems could be described by regarding parts of the total sets of ligands, especially the Mo–O_t and those Mo–O_{br} bonds whose distances are strongly determined by contributions from π bonding.

All combinations of Mo–O distances around one central Mo atom can now be understood as a consequence of the following.

(i) All ligands are O which are in part $d\pi$–$p\pi$ interacting (Mo–O_t), or else the $d\pi$–$p\pi$ interacting ligand O has neighbouring non-π-interacting ligands (or $d\pi$–$d\pi$ interacting ligands) P, S, Cl, Br and the π-bonding of the Mo–O_t is thus strengthened.

(ii) Constraints are imposed by the types of ligand O atoms. Isolated O atoms give O_t or O_{br}, the latter possibly also containing π bonding, while O atoms belonging to ligand molecules give O_{br}(Mo–$O_{br} > \sim$ 2·05 Å) which do not contain π bonding.

These two aspects determine the way in which the π-bonding system is distributed in detail over a maximum of four ligand atoms and, as a consequence, how far the actual Mo–O distances deviate from their 'characteristic' values as derived above.

As the results show, an understanding of Mo–O coordination including CN 4, 5, 6 and 7 has been gained.

The application of the curve of Fig. 3 to the lower oxides of Mo offers a differentiation between the differently distorted octahedra (*cf.* Table 13) according to the different states of oxidation of the central Mo atom.

Note: The referee has informed the author that a Mo^{VI}–O distance/BO relation of the form $s = 1{\cdot}5(R/1{\cdot}761)^{-5{\cdot}45}$ has been derived (I. D. Brown & K. K. Wu, private communication). This function would give a curve in Fig. 2 which would meet our curve at approximately point *B*, and decrease more at higher and less at lower BO's. We have tried to check the curve in the last region by calculating the sum of the BO in MoO_2 (although Brown & Wu do not claim that their curve is valid for Mo^{IV} compounds) for which all the distances occur in this region. With the Brown & Wu curve we obtain a value of 4·40 while for this work (*cf.* Table 13) the value is 3·72. Thus it seems that our curve might underestimate the BO at longer distances and overestimate it at shorter distances, while the curve of Brown & Wu might do the reverse.

References

ABRAHAMS, S. C. (1967). *J. Chem. Phys.* **46**, 2052–2063.

ABRAHAMS, S. C., BERNSTEIN, J. L. & JAMIESON, P. B. (1968). *J. Chem. Phys.* **48**, 2619–2629.

ABRAHAMS, S. C. & REDDY, J. M. (1965). *J. Chem. Phys.* **43**, 2533–2543.

ADAM, V. C., GREGORY, U. A. & KILBOURN, B. T. (1970). *Chem. Commun.* pp. 1400–1401.

ALLCOCK, H. R., BISSELL, E. C. & SHAWL, E. T. (1973). *Inorg. Chem.* **12**, 2963–2968.

ATOVMYAN, L. O. & BOKII, G. B. (1963). *Russ. J. Struct. Chem.* **4**, 524–530.

ATOVMYAN, L. O., D'YACHENKO, O. A. & LOBKOVSKII, E. B. (1970). *Russ. J. Struct. Chem.* **11**, 429–431.

ATOVMYAN, L. O. & KRASOCHKA, O. N. (1970). *Chem. Commun.* pp. 1670–1671.

ATOVMYAN, L. O. & KRASOCHKA, O. N. (1971). *Sov. Phys. Dokl.* **16**, 7–8.

ATOVMYAN, L. O. & KRASOCHKA, O. N. (1972). *Russ. J. Struct. Chem.* **13**, 319–320.

ATOVMYAN, L. O., KRASOCHKA, O. N. & RAHLIN, M. YA. (1971). *Chem. Commun.* pp. 610–611.

ATOVMYAN, L. O. & SOKOLOVA, YU. A. (1969). *Chem. Commun.* p. 649.

ATOVMYAN, L. O., SOKOLOVA, YU. A. & TKACHEV, V. V. (1970). *Dokl. Phys. Chem. Sect.* **193/5**, 968–969.

ATOVMYAN, L. O., TKACHEV, V. V. & SHISHOVA, T. G. (1972). *Dokl. Phys. Chem. Sect.* **205/7**, 622–623.

Beaver, J. A. & Drew, M. G. B. (1973). *J. Chem. Soc. Dalton*, pp. 1376–1380.

Blake, A. B., Cotton, F. A. & Wood, J. S. (1964). *J. Amer. Chem. Soc.* **86**, 3024–3031.

Boorman, P. M., Garner, C. D. & Mabbs, F. E. (1974). *Chem Commun.* pp. 663–664.

Böschen, J., Buss, B. & Krebs, B. (1974). *Acta Cryst.* B**30**, 48–56.

Böschen, J. & Krebs, B. (1974). *Acta Cryst.* B**30**, 1795–1800.

Brown, D. H. & Jeffreys, J. A. D. (1973). *J. Chem. Soc. Dalton*, pp. 732–735.

Brown, D. H., Perkins, P. G. & Stewart, J. J. (1972). *J. Chem. Soc. Dalton*, pp. 2243–2246.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Chatt, J., Kubota, M., Leigh, G. J., March, F. C., Mason, R. & Yarrow, D. J. (1974). *Chem. Commun.* pp. 1033–1034.

Cotton, F. A. & Elder, R. C. (1964). *Inorg. Chem.* **3**, 397–401.

Cotton, F. A. & Morehouse, S. A. (1965). *Inorg. Chem.* **4**, 1377–1381.

Cotton, F. A., Morehouse, S. M. & Wood, J. S. (1964). *Inorg. Chem.* **3**, 1603–1608.

Cotton, F. A. & Wing, R. M. (1965*a*). *Inorg. Chem.* **4**, 867–873.

Cotton, F. A. & Wing, R. M. (1965*b*). *Inorg. Chem.* **4**, 314–317.

Darriet, B. & Galy, J. (1973). *J. Solid State Chem.* **8**, 189–194.

Day, V. W. & Hoard, J. L. (1968). *J. Amer. Chem. Soc.* **90**, 3374–3379.

Delbaere, L. T. J. & Prout, C. K. (1971). *Chem. Commun.* p. 162.

Dexter, D. D. & Silverton, J. V. (1968). *J. Amer. Chem. Soc.* **90**, 3589–3590.

Drew, M. G. B. & Kay, A. (1971*a*). *J. Chem. Soc.* (*A*), pp. 1846–1850.

Drew, M. G. B. & Kay, A. (1971*b*). *J. Chem. Soc.* (*A*), pp. 1851–1854.

Drew, M. G. B. & Tomkins, I. B. (1970*a*). *J. Chem. Soc.* (*A*), pp. 22–25.

Drew, M. G. B. & Tomkins, I. B., (1970*b*). *Acta Cryst.* B**26**, 1161–1165.

Edwards, A. J. & Steventon, B. R. (1968). *J. Chem. Soc.* (*A*), pp. 2503–2510.

Efremov, V. A. & Trunov, V. K. (1975). *Sov. Phys. Crystallogr.* **19**, 613–615.

Eick, H. A. & Kihlborg, L. (1966). *Acta Chem. Scand.* **20**, 722–729.

Elzen, A. F. van der & Rieck, G. D. (1973*a*). *Acta Cryst.* B**29**, 2433–2436.

Elzen, A. F. van der & Rieck, G. D. (1973*b*). *Acta Cryst.* B**29**, 2436–2438.

Evans, H. T. (1968). *J. Amer. Chem. Soc.* **90**, 3275–3276.

Fenn, R. H. (1969). *J. Chem. Soc.* (*A*), pp. 1764–1769.

Ferguson, G., Mercer, M. & Sharp, D. W. A. (1969). *J. Chem. Soc.* (*A*), pp. 2415–2418.

Fischer, J., Ricard, L. & Toledano, P. (1974). *J. Chem. Soc. Dalton*, pp. 941–946.

Florian, L. R. & Corey, E. R. (1968). *Inorg. Chem.* **7**, 722–725.

Gatehouse, B. M. & Leverett, P. (1968). *Chem. Commun.* pp. 901–902.

Gatehouse, B. M. & Leverett, P. (1969). *J. Chem. Soc.* (*A*), pp. 849–854.

Gatehouse, B. M. & Leverett, P. (1970). *J. Solid State Chem.* **1**, 484–496.

Gatehouse, B. M. & Leverett, P. (1971). *J. Chem. Soc.* (*A*), pp. 2107–2112.

Gloviak, T. (1967). Thesis, Wrozlaw, cited by Atovmyan, D'yachenko & Lobkovskii (1970).

Gonschorek, W. & Hahn, T. (1973). *Z. Kristallogr.* **138**, 167–176.

Graham, J. & Wadsley, A. D. (1966). *Acta Cryst.* **20**, 93–100.

Grandjean, D. & Weiss, R. (1967*a*). *Bull. Soc. Chim. Fr.* pp. 3044–3049.

Grandjean, D. & Weiss, R. (1967*b*). *Bull. Soc. Chim. Fr.* pp. 3054–3059.

Grandjean, D. & Weiss, R. (1967*c*). *Bull. Soc. Chim. Fr.* pp. 3049–3054.

Hedman, B. (1973). *Acta Chem. Scand.* **27**, 3335–3354.

Hedman, B. (1974). *Acta Chem. Scand.* A**28**, 591–592.

Ibers, J. A. & Smith, G. W. (1964). *Acta Cryst.* **17**, 190–197.

Jeitschko, W. (1972). *Acta Cryst.* B**28**, 60–76.

Jeitschko, W. (1973). *Acta Cryst.* B**29**, 2074–2081.

Jeitschko, W. & Sleight, A. W. (1973). *Acta Cryst.* B**29**, 869–875.

Kamenar, B., Penavić, M. & Prout, C. K. (1973). *Cryst. Struct. Commun.* **2**, 41–44.

Kierkegaard, P. (1961*a*). *Ark. Kem.* **18**, 553–575.

Kierkegaard, P. (1961*b*). *Ark. Kem.* **18**, 521–532.

Kierkegaard, P. & Holmen, S. (1964). *Ark. Kem.* **23**, 213–221.

Kierkegaard, P. & Longo, J. M. (1970). *Acta. Chem. Scand.* **24**, 427–432.

Kihlborg, L. (1963). *Acta Chem. Scand.* **17**, 1485–1487.

Kihlborg, L. (1963/4*a*). *Ark. Kem.* **21**, 357–364.

Kihlborg, L. (1963/4*b*). *Ark. Kem.* **21**, 461–469.

Kihlborg, L. (1963/4*c*). *Ark. Kem.* **21**, 443–460.

Kihlborg, L. (1963/4*d*). *Ark. Kem.* **21**, 365–377.

Kihlborg, L. (1963/4*e*). *Ark. Kem.* **21**, 471–495.

Kihlborg, L., Norrestam, R. & Olivecrona, B. (1971). *Acta Cryst.* B**27**, 2066–2070.

Klevtsova, R. F. & Klevtsov, P. V. (1971). *Sov. Phys. Crystallogr.* **15**, 829–834; **16**, 241–245.

Klevtsova, R. F., Kozeeva, L. P. & Klevtsov, P. V. (1974). *Sov. Phys. Crystallogr.* **19**, 50–53.

Knöpnadel, I., Hartl, H., Hunnius, W. D. & Fuchs, J. (1974). *Angew. Chem.* **86**, 894–895.

Knox, J. R. & Prout, C. K. (1969*a*). *Acta Cryst.* B**25**, 1857–1866.

Knox, J. R. & Prout, C. K. (1969*b*). *Acta Cryst.* B**25**, 2281–2285.

Kobtsev, B. M., Kharitonov, Yu. A., Pobedimskaya, E. A. & Belov, N. V. (1968). *Sov. Phys. Dokl.* **13**, 193–195.

Kojić-Prodić, B. Ružić-Toroš, Ž., Grdenić, D. & Golič, L. (1974). *Acta Cryst.* B**30**, 300–305.

Kopwillem, A. & Kierkegaard, P. (1969). *Acta Chem. Scand.* **23**, 2184–2186.

Krebs, B. (1972). *Acta Cryst.* B**28**, 2222–2231.

Larking, I. & Stomberg, R. (1970). *Acta Chem. Scand.* **24**, 2043–2054.

Larking, I. & Stomberg, R. (1972). *Acta Chem. Scand.* **26**. 3708–3722.

Le Carpentier, J. M., Mitschler, A. & Weiss, R. (1972). *Acta Cryst.* B**28**, 1288–1298.

Le Carpentier, J. M., Schlupp, R. & Weiss, R. (1972). *Acta Cryst.* B**28**, 1278–1288.

Leciejewicz, J. (1965). *Z. Kristallogr.* **121**, 158–164.

Linnros, B. (1970). *Acta Chem. Scand.* **24**, 3711–3722.

Magarill, S. A. & Klevtsova, R. F. (1972). *Sov. Phys. Crystallogr.* **16**, 645–648.

Magarill, S. A., Klevtsova, R. F. & Bakakin, V. V. (1975). *Sov. Phys. Crystallogr.* **19**, 539–540.

Manojlović-Muir, L. (1971). *J. Chem. Soc.* (*A*), pp. 2796–2800.

Manojlović-Muir, L. & Muir, K. W. (1972). *J. Chem. Soc.* (*A*), pp. 686–690.

Mattes, R. & Müller, G. (1973). *Naturwissenschaften*, **60**, 550.

Mattes, R., Müller, G. & Becher, H. J. (1972). *Z. anorg. allgem. Chem.* **389**, 177–187.

Mumme, W. G. & Watts, J. A. (1970). *J. Solid State Chem.* **2**, 16–23.

Park, J. J., Glick, M. D. & Hoard, J. L. (1969). *J. Amer. Chem. Soc.* **91**, 301–307.

Perloff, A. (1970). *Inorg. Chem.* **9**, 2228–2239.

Peytavin, S. & Philippot, E. (1973). *Cryst. Struct. Commun.* **2**, 355–357.

Pierce, J. W., McKenzie, H. L., Vlasse, M. & Wold, A. (1970). *J. Solid State Chem.* **1**, 332–338.

Pierce, J. W. & Vlasse, M. (1971). *Acta Cryst.* B**27**, 158–163.

Porai-Koshits, M. A., Aslanov, L. A., Ivanova, G. V. & Polynova, T. N. (1968). *J. Strukt. Chem.* **9**, 401–405.

Scane, J. G. (1967). *Acta Cryst.* **23**, 85–89.

Schröder, F. A. (1973). Habilitationsschrift, Universität Freiburg i Br.

Schröder, F. A., Scherle, J. & Hazell, R. (1975). *Acta Cryst.* B**31**, 531–536.

Schulz, H. & Schröder, F. A. (1973). *Acta Cryst.* A**29**, 322–333.

Seleborg, M. (1966). *Acta Chem. Scand.* **20**, 2195–2201.

Seleborg, M. (1967). *Acta Chem. Scand.* **21**, 499–504.

Serezhkin, V. N., Chuvaev, V. F., Kovba, L. M. & Trunov, V. K. (1973). *Dokl. Chem.* **210**, 476–479.

Serezhkin, V. N., Kovba, L. M. & Trunov, V. K. (1973*a*). *Sov. Phys. Crystallogr.* **18**, 323–325.

Serezhkin, V. N., Kovba, L. M. & Trunov, V. K. (1973*b*). *Sov. Phys. Crystallogr.* **18**, 603–605.

Serezhkin, V. N., Kovba, L. M. & Trunov, V. K. (1973*c*). *Sov. Phys. Crystallogr.* **18**, 689–691.

Serezhkin, V. N., Kovba, L. M. & Trunov, V. K. (1974). *Sov. Phys. Crystallogr.* **19**, 231–233.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

Shimao, E. (1967). *Bull. Chem. Soc. Japan*, **40**, 1609–1613.

Smith, G. W. & Ibers, J. A. (1965). *Acta Cryst.* **19**, 269–275.

Sjöbom, K. & Hedman. B. (1973), *Acta Chem. Scand.* **27**, 3673–3691.

Spivack, B. & Dori, Z. (1973). *J. Chem. Soc. Dalton*, pp. 1173–1177.

Spivack, B. & Dori, Z. (1974). *J. Less-Common Met.* **36**, 249–254.

Stephenson, N. C. (1966). *Acta Cryst.* **20**, 59–66.

Stephenson, N. C. & Wadsley, A. D. (1965). *Acta Cryst.* **18**, 241–247.

Stevenson, D. L. & Dahl, L. F. (1967). *J. Amer. Chem. Soc.* **89**, 3721–3726.

Stomberg, R. (1968). *Acta Chem. Scand.* **22**, 1076–1090.

Stomberg, R. (1969). *Acta Chem. Scand.* **23**, 2755–2763.

Stomberg, R. (1970). *Acta Chem. Scand.* **24**, 2024–2036.

Stomberg, R., Trysberg, L. & Larking, I. (1970). *Acta Chem. Scand.* **24**, 2678–2679.

Strandberg, R. (1973). *Acta Chem. Scand.* **27**, 1004–1018.

Strandberg, R. (1974). *Acta Chem. Scand.* A**28**, 217–225.

Villa, A. C., Coghi, L., Manfredotti, A. G. & Guastini, C. (1974). *Cryst. Struct. Commun.* **3**, 551–554.

Wilhelmi, K. A. (1969). *Acta Chem. Scand.* **23**, 419–428.

Åsbrink, S. & Brandt, B. G. (1971). *Chem. Script.* **1**, 169–181.