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Molybdenum–Oxygen Bond-Strength Bond-Length Relationships

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The performance of the bond-strength (s) *bond-distance* (d) *relationship* $s = (d/1.882)^{-6.0}$ *(Brown and Wu,* Acta Cryst., B32, *1957 (1976)) for oxomolybdenum(VI) configurations has been compared to other such non-linear expressions. The validity of the correlation has been extended from Mo(VI) to Mo(II) cations, including mixed valence states.*

Recent efforts towards rationalization and classification of inorganic structures and structure types has led to the development of bond-strength bond-length relationships. Element–oxygen bond-valence bond-distance correlations have been given by Brown and Shannon [1] for elements in the periodic table from H^+ to As^{5+}. The analytical expressions which have been derived to define these interdependencies are useful as an independent check on the validity of inorganic crystal structures, as a means of detecting secondary bonding effects and can profitably be applied to the examination of the valence distribution in mixed valency compounds. The latter aspect has not extensively been examined and yet provides a means for detecting trapping or mixing of valence states in specific sites in inorganic crystal structures. Particularly interesting is the case of molybdenum and other cations which exhibit a variety of valence states and severely distorted polyhedral oxo-configurations. Such elements are important as they are the main components in modern heterogeneous catalytic systems.

Various non-linear bond-strength bond-length relationships have been proposed for molybdenum in the last few years [2–8]. In most cases the analytical expressions have strictly been worked out and are valid only for Mo(VI) and differ mainly with regard to the low and high bond distances, *i.e.* in case of strong and weak bonding (Table I).

In recent studies on mixed valency compounds [9] we have found the variety of analytical expressions to be rather disturbing. Therefore, we have set out to compare the performance of the equations in a number of well determined oxomolybdenum(VI) structures (MoO_3, $MoO_3 \cdot 2H_2O$, $Bi_2(MoO_4)_3$, Bi_2MoO_6, α-Te_2MoO_7, $VOMoO_4$, $La_2(MoO_4)_3$), for a total of 16 independent polyhedra. Results of this analysis (Table II) indicate a fairly similar performance for these compounds for all but one parameter set ($\langle|s^{calc} - s^{theor}|\rangle$ = 0.34, 0.14, 0.16, 0.10 and

TABLE I. Bond Distances as a Function of Bond Strengths (s), Calculated According to Some Empirical Relationships.

Bond Length (A)	Bond Strength (v.u.)					Ref.
	2.0	1.5	1.0	0.5	0.25	
$1.872 - 0.668 \log s_{Mo-O}$	1.671	1.754	1.872	2.073	2.274 A	4
$1.874 - 0.600 \log s_{Mo-O}$	1.693	1.768	1.874	2.054	2.235	6
$1.906\, s_{Mo-O}^{-0.20}$	1.659	1.758	1.906	2.190	2.514	8
$1.90 - 0.76 \log s_{Mo-O}$	1.671	1.766	1.900	2.129	2.358	5
$1.882\, s_{Mo-O}^{-0.167}$	1.676	1.759	1.882	2.113	2.371	7
Mean	1.674	1.761	1.887	2.112	2.350	

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TABLE II. Average Bond Valence Values (in Valence Units), Calculated for Molybdenum According to Five Empirically Determined Non-linear Bond-strength (*s*) Bond-length (*d*) Relationships.

Compound	Bond-strength Bond-length Relationship[a]						Formal Valence State	σ_d (Å)	σ_s (v.u.)	Ref.
	Eq. (*1*)	Eq. (*2*)	Eq. (*3*)	Eq. (*4*)	Eq. (*5*)	Mean				
MoO_3	5.62	5.80	6.13	6.00	5.92	5.90	6.00	0.008	0.06	b
$MoO_3 \cdot 2H_2O$	5.74	5.90	6.25	6.14	6.02	6.01	6.00	0.003	0.03	c
$Bi_2(MoO_4)_3$	5.70	5.92	6.01	6.02	5.89	5.91	6.00	0.01	0.07	d
Bi_2MoO_6	5.42	5.51	5.98	5.86	5.68	5.69	6.00	0.03	0.17	e
α-Te_2MoO_7	5.49	5.63	6.00	5.88	5.75	5.75	6.00	0.006	0.04	f
$VOMoO_4$	5.80	6.10	5.89	6.04	5.90	5.95	6.00	0.012	0.06	g
$La_2(MoO_4)_3$	5.65	5.93	5.76	5.90	5.75	5.80	6.00	0.013	0.08	h
Mo_4O_{11} orthorh.	5.71	5.86	6.15	6.10	5.93	5.95	5.50	0.017	0.12	i
Mo_4O_{11} monocl.	5.47	5.58	5.95	5.88	5.68	5.71	5.50	0.015	0.08	i
Mo_5O_{14}	5.55	5.67	6.14	5.99	5.85	5.84	5.60	n.d.	n.d.	j
Mo_8O_{23}	5.65	5.78	6.18	6.07	5.91	5.92	5.75	0.006	0.07	k
$Mo_{17}O_{47}$	5.22	5.26	5.86	5.70	5.50	5.51	5.53	0.09	0.60	l
$Mo_{18}O_{52}$[o]	5.44	5.58	5.96	5.84	5.72	5.71	5.78	0.035	0.40	m
$TeMo_5O_{16}$	5.39	5.48	5.96	5.83	5.66	5.66	5.60	0.007	0.06	n

[a] Eq. (*1*): $s = 10^{\{(1.872-d)/0.668\}}$ Ref. 4. Eq. (*2*): $s = 10^{\{(1.874-d)/0.600\}}$ Ref. 6. Eq. (*3*): $s = (d/1.906)^{-5.0}$ Ref. 8. Eq. (*4*): $s = 10^{\{(1.90-d)/0.76\}}$ Ref. 5. Eq. (*5*): $s = (d/1.882)^{-6.0}$ Ref. 7. [b] L. Kihlborg, *Arkiv Kemi, 21,* 357 (1963). [c] S. Asbrink and G. Brandt, *Chem. Scripta, 1,* 169 (1971). [d] A. F. Van den Elzen and G. D. Rieck, *Acta Cryts. B29*, 2433 (1973). [e] A. F. Van den Elzen and G. D. Rieck, *Acta Cryst., B29,* 2436 (1973). [f] J. C. J. Bart and N. Giordano, *Gazz. Chim. Ital. 109,* 73 (1979). [g] H. A. Eick and L. Kihlborg, *Acta Chem. Scand., 20,* 722 (1966). [h] W. Jeitschko, *Acta Cryst., B29,* 2074 (1973). [i] L. Kihlborg, *Arkiv Kemi, 21,* 365 (1963). [j] L. Kihlborg, *Arkiv Kemi, 21,* 427 (1963). [k] L. Kihlborg, *Arkiv Kemi, 21,* 461 (1963). [l] L. Kihlborg, *Acta Chem. Scand., 14,* 1612 (1960). [m] L. Kihlborg, *Arkiv Kemi, 21,* 443 (1963). [n] Y. Arnaud and J. Guidot, *Acta Cryst., B33,* 2151 (1977). [o] Excluding octahedron with terminal Mo–O bond of 1.54 Å.

0.15 for eqns. (*1*) to (*5*) of Table II). Although essentially not devised for application to lower oxidation states, the five analytical expressions were then used to calculate bond orders in reduced molybdenum oxides (Mo_4O_{11}, Mo_5O_{14}, Mo_8O_{23}, $Mo_{17}O_{47}$, $Mo_{18}O_{52}$, $TeMo_5O_{16}$), with average formal valences of molybdenum ranging from 5.50 to 5.78 v.u. Differences in the performance of the parameter sets were again found to be quite pronounced. However, it turned out that the analytical expression $s = (d/1.882)^{-6.0}$ (eqn. (*5*)) of Brown and Wu [7] very closely agreed with the mean value calculated by application of the five equations to all molybdenum oxides and molybdates cited above. This was taken as an indication that eqn. (*5*) best describes the average performance of the set. This is confirmed by the data collected in Table I. It is noticed that eqn. (*5*) was originally derived from data based on 50 oxomolybdenum(VI) structures. The result suggests a 1.882 Å Mo(VI)–O bond distance in the ideal octahedron. Unfortunately, it is not possible to verify this value as no regular octahedral oxomolybdenum(VI) co-ordination has been observed experimentally, as opposed to regular tetrahedra (*cf.* $VOMoO_4$). The most regular octahedron has been found in $Mo_2(O_2C_6Cl_4)_6 \cdot 3C_6H_6$ with an average Mo–O bond length of 1.919 Å (range 1.853–1.959(7) Å) [10]. An even more regular MoO_6 coordination, albeit trigonal prismatic, occurs in $Mo(PQ)_3$ [11] with corresponding values of 1.961 Å and 1.939–1.988(5) Å, respectively. In compounds of this kind, as well as in the related trigonal prismatic 1,2-dithiolene complexes $Mo(S_2C_2H_2)_3$ [12] and $Mo(S_2C_6H_4)_3$ [13], the metal–ligand charge distribution depends on the electron withdrawing ability of the ligand and the metal oxidation states are reported to be intermediate between the formal charges of zero and +6 [14]. Using $s = (d/1.882)^{-6.0}$ bond-strength sums of 5.39, 4.70 and 5.93–6.02 v.u. are calculated for $Mo_2(O_2C_6Cl_4)_6$ [10], $Mo(PQ)_3$ [11] and $Mo_2O_5(PQ)_2 \cdot CH_2Cl_2$ [15], respectively, indicating a much less strongly oxidized metal in $Mo(PQ)_3$ than in $Mo_2(O_2C_6Cl_4)_6$. Apparently, $Mo_2O_5(PQ)_2$ is a typical Mo(VI) complex with semiquinone ligands. It is of interest to notice that the short Mo–O distances of 1.853(7) and 1.869(6) Å for the bridging ligand in $Mo_2(O_2C_6Cl_4)_6$ are in the range of Mo–O distances observed for bridging oxo-ligands in Mo(V) and Mo(VI) structures.

It is not unusual that the more regular coordinations are found for molybdenum in a lower than maximum valence state, as may be seen from Table

TABLE III. Bond Strengths and Bond Lengths in Molybdenum-Oxygen Coordination Spheres.

Compound[a]	Bond distances (Å) Mo–O	Mo–Mo	Σs_{Mo-O}[b,c]	Formal valence state[b]	σ_s[c]	σ_d[d]	Structural unit	Ref.
$Mo_2O_5(PQ)_2.CH_2Cl_2$	1.683,1.691,1.904,2.044,2.247,2.478	3.160(2)	5.93	6.0	0.04	0.005	Mo_2O_9[l]	u
	1.678,1.690,1.892,2.038,2.236,2.511	3.160(2)	6.02	6.0	0.04	0.005		
$Mo_4O_{10}(OH)_2$	1.687,1.956(2x),1.959(2x),2.332	-	5.36	5.5	0.22	0.03	MoO_6[m]	v
$Mo_2(O_2C_6Cl_4)_6.3C_6H_6$	1.853,1.869,1.938,1.942,1.955,1.959	-	5.39	n.d.	0.03	0.007	MoO_6[n]	w
$MoOPO_4$	1.652,1.979(4x),2.641	-	5.15+0.13	5.0	0.04	0.005	MoO_6[o]	x
$[Mo_2O_3Cl(CH_3COO)_3]_2$	1.659,1.951,1.954,2.083,2.120,2.215	2.601(2)	5.14	5.0	0.03	0.004	MoO_6[p]	y
$BaMo_2O_4(C_2O_4)_2.5H_2O$	1.70,1.88,1.93,2.11,2.14,2.22	2.541(4)	5.04	5.0	0.28	0.04	MoO_6[p]	z
$Mo(PQ)_3$	1.939,1.947,1.953,1.969(2x),1.988	-	4.70	n.d.	0.02	0.005	MoO_6[q]	aa
$NaNH_4(MoO_3C_2O_4).2H_2O$	1.815,1.850,1.878,2.230,2.235,2.242	-	4.43	4.0 ?	0.02	0.004	MoO_6[r]	bb
MoO_2	1.972,1.978,1.984,1.995,2.064,2.073	2.511,3.112(1)	4.07	4.0	0.01	0.003	MoO_6	cc
$Zn_2Mo_3O_8$[e,f]	1.928(2x),2.002,2.058(2x),2.128	2.524,3.235(2)[i]	4.07	4.0	0.08	0.03	MoO_6	dd
$Mo_2(OCH_2CMe_3)_6$	1.855,1.867,1.905	2.222(2)	3.07	3.0	0.02	0.006	Mo_2O_6[s]	ee
$Mo_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$	1.860,1.903,2.111,2.136	(2.241(1)	2.98	3.0	0.02	0.006	(Mo_2O_8	ff
	1.869,1.908,2.117,2.142	(	2.92				(	
$K_3[Mo_2(SO_4)_4].3.5H_2O$	2.046,2.069,2.070,2.084,2.550	2.167(1)	2.44	2.5	0.01	0.004	(Mo_2O_{10}	gg
	2.051,2.055,2.066,2.076,2.545	2.162(1)	2.48	2.5	0.01	0.004	(	
$K_4[Mo_2(SO_4)_4].2H_2O$	2.127,2.139,2.143,2.148,2.591	2.111(1)	2.00	2.0	0.01	0.004	Mo_2O_{10}	gg
$Mo_2(O_2CCH_3)_4$	2.107,2.110,2.121,2.137,2.645[g]	2.093(1)	1.96+0.13[j]	2.0	0.01	0.005	Mo_2O_8[t]	hh
$Mo_2(O_2CCF_3)_4$	1.97,2.01,2.11,2.14,2.72[g]	2.090(4)	2.40+0.11[j]	2.0	0.05	0.02	Mo_2O_8[t]	ii
$Mo_2(O_2CH)_4$	2.100,2.112,2.122,2.125,2.643[g]	(2.091(2)	1.99+0.13[j]	2.0	0.02	0.014	(Mo_2O_8[t]	jj
	2.072,2.087,2.112,2.140,2.646[g]	(	2.06+0.13[j]	2.0			(	
$Mo_2(O_2CCH_2NH_3)_4(SO_4)_2.4H_2O$	2.120(2x),2.130(2x),2.93(2x)[h]	2.115(1)	1.93+0.14[k]	2.0	0.01	0.004	Mo_2O_8	kk
$Mo_2(O_2CCMe_3)_4$	2.098,2.109,2.111,2.126,2.870[g]	(2.088(1)	2.01+0.08[j]	2.0	0.01	0.005	(Mo_2O_8[t]	ll
	2.100,2.103,2.110,2.135,2.926[g]	(	2.00+0.07[j]	2.0	0.01	0.005	(	
$Mo_2(O_2CC_6H_5)_4$	2.092,2.099,2.104,2.131,2.876[g]	2.096(1)	2.03+0.08[j]	2.0	0.01	0.003	Mo_2O_8[t]	ll
$Mo_2(O_2CC_6H_5)_4.2(diglyme)$	2.100,2.106,2.110,2.112,2.663[g]	2.100(1)	2.04+0.12[j]	2.0	0.01	0.006	Mo_2O_8[t]	mm
$Mo_2(O_2CMe)_2(MeCOCHCOMe)_2$	2.09(2x),2.10(2x),2.709[g]	2.129(1)	2.10+0.11[j]	2.0	0.01	0.02	Mo_2O_8[t]	nn

[a] Bu-*t*, *t*-butyl; Me, methyl; PQ, 9, 10-phenanthrenequinone. [b] Calculated according to $s_{Mo-O} = (d_{Mo-O}/1.882)^{-6.0}$. [c] In valence units. Standard deviations were estimated for the shortest *d*-value of the set. [d] In Angstrom units. [e] Isostructural with $A_2Mo_3O_8$, where A = Mg, Mn, Fe, Co, Ni, Cd (ref. 50) and related to $LiScMo_3O_8$ (ref. 51). [f] The compounds $AMo^{IV}O_3$ and $A(Mo^{V}O_3)_2$ with A = Mg, Ca, Sr, Ba have been synthesized [52], but no structural data are available. [g] The longest d_{Mo-O} is the shortest axial intermolecular contact. [h] The longest d_{Mo-O} are due to sulphate counter-ions. [i] Arrangement of molybdenum ions in equilateral triangles. [j] Contribution of the axial intermolecular Mo–O bond to the bond valence sum. [k] Contribution of sulphate counter-ions to total bond valence sum. [l] Confacial bioctahedron. [m] Octahedron with [1 + 4 + 1] distortion. [n] Almost regular octahedron. [o] Highly distorted [1 + 4 + 1] octahedron; square pyramid. [p] Octahedron with [1 + 2 + 2 + 1] distortion. [q] Trigonal prism. [r] Octahedron with [3 + 3] distortion. [s] D_{3d} symmetry. [t] The Mo_2^{4+} binuclear unit is always co-ordinated at eight sites. These may be considered to be at the corners of eclipsed squares whose centers are occupied by the metal ions. Additionally, two sites co-axial to the metal–metal bond are available and are sometimes co-ordinated. [u] Ref. 15. [v] K. A. Wilhelmi, *Acta Chem. Scand.*, *23*, 419 (1969). [w] Ref. 10. [x] P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.*, *24*, 427 (1970). [y] B. Kamenar, M. Penavić and B. Korpor-Čolig, *Proc. Eleventh International Congress of Crystallography*, Warszawa (1978). Paper 0.5.5-21. [z] F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, *4*, 1377 (1965). [aa] Ref. 11. [bb] L. O. Atovmyan and G. B. Bokii, *Zh. Strukt. Khim.*, *4*, 576 (1963). [cc] B. J. Brandt and A. C. Skapski, *Acta Chem. Scand.*, *21*, 661 (1967). [dd] G. B. Ansell and L. Katz, *Acta Cryst.*, *21*, 482 (1966). [ee] M. H. Chisholm, W. R. Reichert, F. A. Cotton and C. A. Murillo, *J. Am. Chem. Soc.*, *99*, 1652 (1977). [ff] M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, *J. Am. Chem. Soc.*, *100*, 1727 (1978). [gg] F. A. Cotton, B. A. Frenz, E. Pedersen and T. R. Webb, *Inorg. Chem.*, *14*, 391 (1975). [hh] Ref. 37. [ii] Ref. 39. [jj] F. A. Cotton, J. G. Norman, B. R. Stults and T. R. Webb, *J. Coord. Chem.*, *5*, 217 (1976). [kk] F. A. Cotton and T. R. Webb, *Inorg. Chem.*, *15*, 68 (1976). [ll] F. A. Cotton, M. Extine and L. D. Gage, *Inorg. Chem.*, *17*, 172 (1978). [mm] D. M. Collins, F. A. Cotton and C. A. Murillo, *Inorg. Chem.*, *15*, 2950 (1976). [nn] C. D. Garner, S. Parkes, I. B. Walton and W. Clegg, *Inorg. Chim. Acta*, *31*, L451 (1978).

III. Further examples are the square antiprismatic $Mo(S_2CNEt_2)_4$ (Mo(IV)–S, 2.520–2.537 Å) [16], tetrahedral $Mo(NMe_2)_4$ (Mo(IV)–N, 1.917–1.934 Å) [17] and octahedral $K_3Mo(NCS)_6{\cdot}H_2O{\cdot}CH_3COOH$ (Mo(III)–N, 2.034–2.119 Å) [18].

A fairly accurate bond-length value corresponding to a bond-strength of 1.0 v.u. should be obtained from symmetric Mo–O–Mo bridges. A linear Mo(VI)–O–Mo(VI) bridge has been found in $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ [19] with an Mo(VI)–O bond length of 1.876(2) Å, in good agreement with the dimensions of the ideal octahedron according to eqn. (*5*). The result implies that the mean Mo(VI)–O bond length and the octahedral distortion, expressed as $\langle(\Delta d/d)^2\rangle$, are not linearly dependent, as opposed to a previous suggestion [20].

For the purpose of studies of mixed valency effects it is of interest to dispose of bond-strength bond-length equations for lower valent molybdenum. Tables I–III indicate a scarcity of reliable reference points for the derivation of such parameter sets. Linear Mo(V)–O–Mo(V) bridges in $[(C_2H_5OCS_2)_2MoO]_2O$ [21], $\{MoO[S_2P(iso\text{-}C_8H_7O)_2]_2\}_2O$ [22], $Mo_2O_3[S_2P(OC_2H_5)_2]_4 \cdot 2C_6H_4Cl_2$ [23], $Mo_2O_3(S_2CNPr^n_2)_4$ [24], $Mo_2O_3(S_2CSPr^i)_4$ [25], $Mo_2O_3(C_5H_4NS)_4$ [26], $(pyH)_4\{Mo_2O_3(NCS)_4(C_2O_4)_2\}$ and $(pyH)_4\{Mo_2O_3(NCS)_6(HCO_2)_2\}$ [27] with an average Mo(V)–O bond distance of 1.859 Å suggest slightly different bond-strength bond-length curves for Mo(VI)–O and Mo(V)–O bonds. The considerably longer Mo(V)–O bridging bond distance of 1.936(3) Å in the linear grouping O=MoOMo=O in the complex $[Mo_2O_3(TPP)_2]$, where TPP is the dianion of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin [28], is clearly the result of the *trans* influence of the terminal oxo ligands.

As may be seen from Table III, application of eqn. (*5*) gives results for the cation bond valence sums which are in good accordance with the formal oxidation states. Present information then suggests the use of this parameter set over a wider range of valence states than supposed so far, namely from Mo(II) to Mo(VI). There is essentially only one serious discrepancy between calculated and formal valence states of molybdenum in the compounds listed in Table III, namely for $Mo_2(O_2CCF_3)_4$. This is at variance to the result of the corresponding bispyridine adduct (1.98 v.u.) [29]. As a reasonable explanation is lacking, it appears that a redetermination of $Mo_2(O_2CCF_3)_4$ is warranted. It is noticed that in the binuclear $Mo_2(O_2CR)_4L_2$ complexes the calculated valence sums are best in accordance with the formal valence if no account is taken of the axial intermolecular Mo–O bonds. Comparison with the results for $MoOPO_4$ then suggests either that the limit of the Mo–O co-ordination sphere should be placed at about 2.6 Å or that the use of the analytical expressions for very low bond-strengths is not appropriate.

It is surprising to find that the parameters d_1 and N in the bond-strength bond-length expression $s = (d/d_1)^{-N}$ are constant over a wide range of molybdenum valence states, as usually such values vary with valency [7]. However, the variations are often very small, at least in the few cases where reliable data have been reported (Mn(II, III), Fe(II, III), Se(IV, VI)), although occasionally large (Sn(II, IV)) [7]. Also in case of V–O bonds one parameter set appears to apply to the metal in various valency states [30].

It should be mentioned that in the calculation of the bond valence sums of Table III no explicit account has been taken of the fact that molybdenum in its lower valence states has an extraordinary tendency to form multiple Mo–Mo bonds, of various orders (*cf.* Table III and refs. 29, 31–49). As a matter of fact, there exists no relation between $|\Sigma s^{obs}_{Mo-O} - \Sigma s^{calc}_{Mo-O}|$ and Mo–Mo bond distances. Therefore, cation-cation interaction apparently has not seriously influenced our results. We still notice that the strength of the metal-to-metal bonding is not a direct function of the oxidation number [31], even though the stronger bonds are found for the lower Mo valence states (Table III). These metal-to-metal distances and their bond orders are correlated, as has been shown by Cotton for halo metal atom cluster systems [32]. Similar correlations do not apply to dimeric metal carboxylates and metal dioxides with distorted rutile structure [49].

Finally, it is apparent from the data in Table III that π-donation from oxygen to the metal giving a multiple bond occurs less readily as the formal oxidation state of molybdenum decreases.

All calculations were performed at the local UNIVAC 1100/20 computer.

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