

## Molecular Modeling of Dimetal Systems. Part 2. Low-Order Dimolybdenum

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Through molecular modeling of the available structures containing dimolybdenum bonds of orders 3.5 and 3, solution pairs of harmonic force constant ( $k_r$ ) and bond length ( $r_o$ ) have been obtained as (3.63 mdyne/Å, 2.07 Å) and (3.37 mdyne/Å, 2.10 Å), respectively. Together with the known solution pair for Mo<sup>4</sup>-Mo, this sufficed to establish a general relationship between  $k_r$ ,  $r_o$  and bond order,  $N$ , as  $N = 0.9537k_r = 131.8r_o^{-5}$ . Using this relationship as a sampling curve, we extended the analysis to include Mo<sub>2</sub> bonds of orders 2 and 1. The relationship was accordingly shown to apply to the entire  $\{N, k_r\}$  space.

The simulation of molecular structure and conformation by molecular mechanics is a well-established procedure, but it is not always appreciated that in the process it is possible to also obtain bonding parameters of fundamental importance, provided the force field is selected with care. It is important to note that all empirical parameters have characteristic values that represent the gross effects of more subtle factors that determine the nature of chemical bonds at a more fundamental level. It is argued that, environmental factors aside, a well-adapted force field should therefore be able to reproduce crystallographically observed molecular structures precisely by energy minimization unless some fundamental interaction has been overlooked. For example, if a dimetal bond is assumed to be of order 3, no provision will be made to introduce any parameter that simulates torsional interactions. Failure to reproduce the observed conformation at the dimetal center would then indicate that an incorrect bond order was assumed. In this ongoing study of dimetal bonds it is assumed that all interactions within the ligand moieties are correctly described in terms of standard force fields, developed in the course of many analyses of organic structures. The only unknown is therefore the metal–metal bond to be characterized by three parameters related to the bond length, the bond strength and the conformation dictated by electronic factors. These three parameters are the characteristic undistorted bond length  $r_o$ , the harmonic force constant  $k_r$ , and a torsional parameter that depends on bond order. The analysis is initiated by minimizing the strain energy calculated for the crystallographically observed structure in terms of the organic part of the force field and trial values of  $r_o$ ,  $k_r$ , and the torsional parameter of the dimetal bond. If the wrong conformation is obtained, the torsional parameter needs adjustment, and this only happens when steric factors are so powerful that they affect the bond order. This happens very rarely, and as a rule the only degrees of freedom available are  $r_o$  and  $k_r$ . Both of these affect the observed bond length and therefore are not independent.

The standard procedure is to minimize the strain energy starting from crystal coordinates and a guesstimate of  $k_r$  and  $r_o$ . It is important to select only the highest quality crystallographic structures for study, to avoid, as far as possible any artifacts due to data errors. To match calculated to observed bond length either  $k_r$  or  $r_o$  can be adjusted until the measured value is reproduced exactly. The final values ( $k_r, r_o$ ) constitute what is

called a solution pair. For any given bond, solution pairs are possible within an extended range of both  $k_r$  and  $r_o$  values. By changing  $k_r$  (say) according to some regular procedure and finding the matching value of  $r_o$  at each chosen value of  $k_r$ , a family of solution pairs are obtained by minimization of the structure at each point. The set of solution pairs  $\{k_r, r_o\}$  constitutes a solution curve in  $k_r$ - $r_o$  space.

The slope of a solution curve depends on the steric environment of the bond. In general it differs between bonds that are bridged by ligands and those that are unbridged. In one case the bond may be compressed, and in the other it is stretched in the steric environment. Two bonds of the same order and different steric environment therefore have solution curves that intersect at a point which defines the unique values of  $k_r$  and  $r_o$  for that bond order.

Finally the solution pairs obtained for bonds of different order should follow some functional relationship that links characteristic bond lengths, force constants, and bond orders in a single equation. This relationship represents a sampling curve in the sense that it intersects the solution curve of any given bond at a point that uniquely fixes all three variables.

Molecular modeling of dimolybdenum systems with quadruple bonds has shown<sup>1</sup> that a characteristic pair of stretching force constant and undistorted bond length, ( $k_r, r_o$ ) = (4.07 mdyne/Å, 2.02 Å), correctly describes the behavior of the bond in molecular mechanics. Finding comparable solutions for lower-order bonds of well-defined bond order ( $N$ ) would clearly establish a general relationship between  $k_r$ ,  $r_o$  and  $N$ , in terms of which the nature of any dimolybdenum bond can be determined directly, by computing a solution curve  $\{k_r, r_o\}$  over a suitable range. The ultimate aim is to obtain a relationship that can be transferred to dichromium systems to account for the unusual variability of these dimetal bonds. Mo<sup>*n*</sup>-Mo bonds with  $n = 3.5, 3.0, 2.0$ , and 1.0 are considered in this paper. The methodology has been described fully in part 1 of this series.<sup>1</sup> The force fields are exactly as described before, except for some parameters that now appear for the first time.

### Mo<sup>3.5</sup>-Mo Bonds

In the process of crystallizing pink K<sub>4</sub>Mo<sub>2</sub>(SO<sub>4</sub>)·2H<sub>2</sub>O slowly, so as to obtain useful crystals, it was found that lavender crystals

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also formed.<sup>2,3</sup> X-ray crystallography showed them to have the composition  $K_3Mo_2(SO_4)_4 \cdot 3.5 H_2O$  and contain the ion  $[Mo_2(SO_4)_4]^{3-}$  with a structure very close to that of the well-known paddle-wheel structure of  $[Mo_2(SO_4)_4]^{4-}$ , except for the presence of coaxial water molecules here, as opposed to sulfato O atoms of neighboring units in the 4- ion.

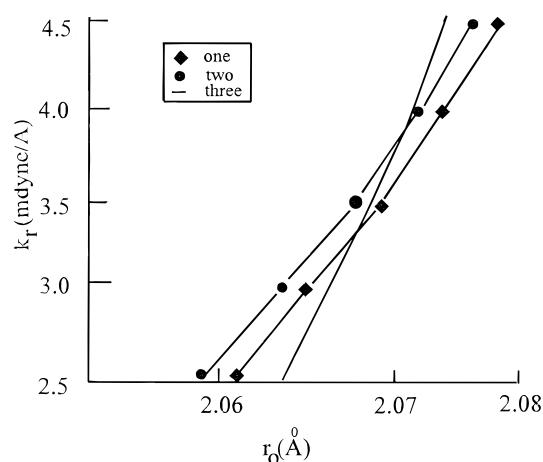
According to the accepted description of the quadruple bond, the electrons lost from the 4- ion to give the 3- ion should come from the  $\delta$ -bonding orbital, thereby giving the latter species a  $\sigma^2\pi^4\delta^1$  configuration. The 3- ion is paramagnetic, and EPR shows that the unpaired electron is evenly distributed over two magnetically equivalent Mo atoms. Loss of the  $\delta$  electron causes a lengthening of the dimolybdenum bond by about 0.05 Å and a shortening of the Mo-O (bridge) distance by about 0.07 Å.

Each  $(MoO)_2S$  ring is folded along the O-O line with a dihedral angle of 20°. Each molybdenum atom is approached by the O atom of a water molecule, approximately along the extension of the  $Mo_2$  bond, but only at a distance of 2.55 Å. There are two crystallographically distinct  $[Mo_2(SO_4)_4]^{3-}$  ions in the unit cell, with very little difference between chemically equivalent bond parameters. The major structure difference consists of coordinated water, which is shared between neighboring units of one type, but not the other. The  $Mo_2$  bond length in the chains sharing water is 0.005 Å shorter than the bond in molecules occurring as isolated units. In another modification the same anion is found, linked together through either  $Cl^4$  or  $Br^5$  atoms into linear continuous chains of the type  $(-Mo-Mo-X-Mo-Mo-)$ .

The other known  $Mo^{3.5}Mo$  bond occurs<sup>6</sup> in  $[Mo_2(DFM)_4]^+$ , which derives from the quadruple-bond molecule  $Mo_2(DFM)_4$  (DFM = di-*p*-tolylformamide anion). The central bond in the cation is once more somewhat (0.037 Å) longer than in the neutral molecule.

Molecular modeling of these structures proceeded as described before.<sup>1</sup> Additional parameters needed to complete the force field for all interactions in the new situation are in Table 1. There was no need to include Coulombic interactions or an attractive torsional term in order to reproduce the observed molecular geometries. Solution curves,  $\{k_r, r_o\}_{Mo-Mo}$ , for the compounds of Table 2 were calculated as described before and requiring calculated bond lengths to match the observed values within 0.001 Å. The solution curves are shown in Figure 1.

All solution curves have positive slopes, but the solution curve for  $[Mo_2(DFM)_4]^+$  slopes more steeply than those of the sulfato molecules with axial ligands, which assist in stretching the central bond to the observed bite distance. The curves do not intersect at a single point, but the region of overlap is sufficiently narrow to identify an average position as the unique solution pair,  $(k_r, r_o)_{Mo-Mo} = (3.63 \text{ mdyne/Å}, 2.07 \text{ Å})$  for the 3.5 bond order. Compared to the quadruple bonds a significant lengthening of the bond by 0.05 Å therefore occurs. Because of the confusing role of steric effects such a clear difference does not emerge on comparison of observed bond lengths, demonstrating the advantage of comparing intrinsic  $r_o$  values rather than actual bond lengths. As in the case of  $Mo^4-Mo$  bonds neither the



**Figure 1.** Molecular mechanics solution curves  $\{k_r, r_o\}$  for the dimolybdenum bond of order 3.5.

**Table 1.** Force Field Parameters ( $k_r/\text{Mdyne } \text{Å}^{-1}$ ,  $k_\theta/\text{mdyne } \text{Å}$ ), Intrinsic Bond Length ( $\text{Å}$ ), and Angle ( $\text{rad}$ ) Used To Model Dimolybdenum Bonds of Various Orders

bond or angle	parameters					
	$Mo^{3.5}Mo$		$Mo^3Mo$		$Mo^2Mo$	
	$k$	$p_o$	$k$	$p_o$	$k$	$p_o$
$Mo-O_{eq}$					2.00	1.88
$Mo-N_{hr}$	0.84	2.08	0.84	1.96		
$Mo=N$			0.84	1.90		
$Mo-O_{hr}$	0.90	2.05				
$Mo-O_{base}$					1.50	1.88
$Mo-O_{ax}$	0.80	2.53	0.84	1.85	2.05	1.98
$Mo-C$			2.00	2.13	2.00	2.00
$Mo-Cl_{ax}$	0.50	2.86	0.70	2.34		
$Mo-Br_{ax}$	0.50	2.90				
$Mo-O_{ax}-H(Lp)$	0.40	1.911	0.40	2.094		
$Mo-Mo-L$			0.20	1.571		
$L-Mo-L$			0.10	2.094		
$Mo-O-C$			0.20	2.094	0.10	2.094
$Mo-N-C$			0.20	2.094		
$Mo-C-H$			0.10	1.911		
$Mo-C-C$			0.10	1.911		
$Mo-C_{hr}=O$					0.10	2.094
$O_{ax}-Mo-O_{ax}$					0.20	3.1416
$O_{ax}-Mo-O_{eq}$					0.80	1.571
$O_{eq}-Mo-O_{eq}$					1.00	2.094
$C_{apex}-Mo-O_{base}$					0.80	1.780
$O_{base}-Mo-O_{base}$					0.80	2.723
$O_{base}-Mo-O_{base}$					0.80	1.524

**Table 2.** Calculated and Observed Bond Lengths in Compounds with  $Mo^{3.5}Mo$  Bonds

molecule	$(L_{ax})_2$	calcd/Å	obsd/Å	figure label	ref
$[Mo_2(DFM)_4]^+$	—	2.120	2.122(3)	three	6
$[Mo_2(SO_4)_4]^{3-}$	$H_2O$	2.166	2.167(1)	two	2
	(isolated)				
$[Mo_2(SO_4)_4]^{3-}$	$H_2O$	2.162	2.162(1)	one	3
	(chains)				
$[Mo_2(SO_4)_4]^{3-}$	Cl	2.166	2.167(2)	two	4
	(chains)				
$[Mo_2(SO_4)_4]^{3-}$	Br	2.166	2.169(3)	two	5
	(chains)				

inductive nature of the bridging group nor the presence of axial ligands alters the  $Mo-Mo$  bonding parameters.

The calculated force constant is not unequivocally confirmed by spectroscopic measurements, but also not refuted. Solid-state Raman spectra for the sulfate compounds have been recorded.<sup>4,5,7</sup> The complexity of the  $[Mo_2(SO_4)_4(H_2O)_2]^{3-}$  spectrum relates to the presence of crystallographically distinct

(2) Cotton, F. A.; Frenz, B. A.; Pederson, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391.

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molecules in the unit cell and both a singlet at  $371\text{ cm}^{-1}$  and a doublet at  $373$  and  $386\text{ cm}^{-1}$  were assigned to Mo–Mo stretching. The two  $[\text{Mo}_2(\text{SO}_4)_4\text{X}]^{4-}$  ions both have strong Raman bands at  $370\text{ cm}^{-1}$ , which by isotopic studies were confirmed to be virtually pure  $\nu_{\text{Mo-Mo}}$  modes. Accepting this as the most reliable estimate the corresponding harmonic force constant of  $3.85\text{ mdyne \AA}^{-1}$  is still significantly higher than the value obtained here but is acceptable in view of anharmonicity and other effects not corrected for.

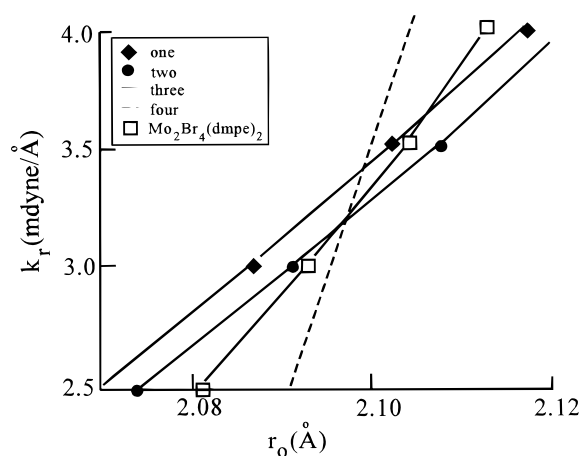
### Mo<sup>3</sup>-Mo Bonds

Two distinct types of molecule with Mo–Mo triple bonds have been identified, i.e., with and without bridging ligands. As for the Mo<sup>4</sup>-Mo and Mo<sup>3.5</sup>-Mo structures, molecular mechanics solution curves, intersecting at a unique point, are expected and observed.

Most of the structures not supported by a bridging framework are of the type  $\text{Mo}_2\text{X}_6$ , related to substituted ethanes, by composition, and therefore expected to adopt related geometries, depending on the size of X. Like the C–C single bond the Mo<sup>3.5</sup>-Mo bond has cylindrical symmetry and therefore is expected to have a small torsional barrier to rotation. Modeling of the molecular conformations should therefore proceed only in terms of steric interactions. All the known structures<sup>8,9</sup> have bulky ligands such as  $\text{Mo}_2(\text{NMe}_2)_6$  and are so sterically crowded that the disposition of the methyl groups with respect to the dimetal bond is not identical for all ligands. These special features were faithfully reproduced in the modeling analysis, according to our stated criteria.

A number of closely related derivatives of general formula  $\text{Mo}_2\text{X}_2(\text{NR}_2)_4$ , where X = Cl,<sup>12</sup> Me,<sup>14</sup> and Et,<sup>15</sup> are also of interest and adopt 1,2-disubstituted ethane-like geometries. A special feature of these structures is the surprisingly short Mo–X bonds, observed for X = OR and  $\text{NR}_2$  and commonly ascribed to multiple Mo–X bonds, because of  $\pi$  contributions. This is consistent with the observed planarity of Mo–NC<sub>2</sub> fragments and the arrangement of methylene carbons in the Mo–Mo–O planes. The force field parameters required for the correct simulation of these structures (Table 1) support this interpretation.

The numerical results are in Table 3. All of the equilibrium structures achieve a minimum strain energy at essentially the same Mo–Mo separation. Steric factors impede rotation about the Mo<sup>3</sup>-Mo bond, leading to the isolation of either anti or gauche rotamers. All structures, except  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ , adopt the anti conformation. The steric bulk of the Et groups favors the gauche rotamer, with little effect on the distances and angles associated with the  $\text{Mo}_2\text{N}_4\text{C}_2$  skeleton. The methyl groups of the Et ligands are distal from the Mo<sup>3</sup>-Mo bond, minimizing intramolecular crowding. In short, steric congestion is successfully minimized within the electronically favored arrangement of NC<sub>2</sub> and  $\text{OCH}_2\text{CMe}_3$  units. In other words no special



**Figure 2.** Molecular mechanics solution curves  $\{k_r, r_0\}$  for the triple bond  $\text{Mo}_2^{6+}$  center.

**Table 3.** Calculated and Observed Dimetal Bond Lengths in Compounds with Mo<sup>3</sup>-Mo Bonds

molecule	(L <sub>ax</sub> ) <sub>2</sub>	calcd/Å	obsd/Å	figure label	ref
$\text{Mo}_2(\text{NMe}_2)_6$	—	2.214	2.211(2)	two	8
		2.218	2.217(2)		
$\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$	—	2.219	2.222(2)	two	9
$\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4$	—	2.200	2.201(2)	one	10
$\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$	—	2.200	2.201(1)	one	11
$\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$	—	2.201	2.203(1)	one	12
$[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$	$\text{H}_2\text{O}$	2.226	2.223(2)	four	13
$[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$	Cl	2.230	2.232(1)	four	14
$[\text{Mo}_2(\text{O}_2\text{CMe})_4]$	$\text{CH}_2\text{Bu}^t$	2.130	2.1302(6)	three	15
$\text{Mo}_2\text{Br}_4(\text{dmpe})_2$	—	2.169	2.169(2)	—	16

torsional parameters are required to reproduce the observed structure. The influence of suggested<sup>9</sup> crystal packing forces on the equilibrium structure is clearly not required in order to match the observed arrangement against the force field.

Three families of compound with Mo<sup>3</sup>-Mo bonds supported by bridging ligands are known. In the phosphate group two structures have been determined, i.e.,  $\text{Cs}_2[\text{Mo}_2(\text{HPO}_4)_4(\text{H}_2\text{O})_2]$ , with axial water molecules,<sup>13</sup> and  $(\text{pyH}_3)_3[\text{Mo}_2(\text{HPO}_4)_4\text{Cl}]$ , in which there are infinite chains with shared  $\text{Cl}^-$  ions in axial positions.<sup>14</sup> While the H atoms of the  $\text{HPO}_4$  ligands had not been located, it was easy to infer their presence from the outer P–O distances of  $1.48\text{ \AA}$  (P=O) and  $1.54\text{ \AA}$  (P–OH).

The second type is a carboxylate, represented<sup>15</sup> by  $\text{Mo}_2(\text{CH}_2\text{Bu}^t)_2(\text{O}_2\text{CMe}_4)_4$ , which is of the same structure type as the quadruple-bond carboxylates, and with neopentyl groups in axial position. The surprisingly short Mo–Mo distance of  $2.130(6)\text{ \AA}$ , compared to  $2.093(1)\text{ \AA}$  in the parent compound without axial ligands, has been suggested<sup>15</sup> to arise from a  $\pi^4\delta^2$  configuration. Significantly though, molecular modeling of the structure does not require an attractive torsional term, which could have confirmed the conjecture. Essential details of the modeling are also in Table 3.

As explained in part 1 of this series,<sup>1</sup>  $\text{Mo}_2\text{Br}_4(\text{dmpe})_2$ ,<sup>16</sup> with only 29%  $\delta$  character properly belongs with the triple bonds. It was found<sup>1</sup> that steric distortion of planar bridging ligands across the dimetal center prevents effective  $\delta$  interaction to the point where it no longer contributes to the bonding.

The  $\{k_r, r_0\}$  solution curves for all these formally triple-bond compounds are shown in Figure 2. As expected, the curves separate into two groups that intersect in a narrow range, and that are removed from the corresponding curves for Mo<sup>4</sup>-Mo

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(16) Campbell, F. L.; Cotton, F. A.; Pavell, G. L. *Inorg. Chem.* **1985**, *24*, 177.

and  $\text{Mo}^{3.5}\text{Mo}$  compounds. This is interpreted as distinguishing these compounds as a separate class with bond order of 3. The average  $(k_r, r_o)_{\text{Mo-Mo}} = (3.37 \text{ mdyne/\AA}, 2.10 \text{ \AA})$  of the overlap region is accepted as the most likely solution pair for  $\text{Mo}^3\text{Mo}$ . The elimination of the  $\delta^2$  contribution therefore results in lengthening of the intrinsic Mo–Mo separation from 2.02 to 2.10  $\text{\AA}$ .

The assignment of vibrational spectra for this group is somewhat problematic since the Mo–Mo stretching mode appears to be extensively mixed with other modes such as the Mo–N(O) stretch or the Mo–NC<sub>2</sub> rocking mode. However, a prominent feature in each solid-state Raman spectrum of the  $[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$  ions<sup>17</sup> is a line at 358  $\text{cm}^{-1}$  for  $L_{\text{ax}} = \text{H}_2\text{O}$  and at 361  $\text{cm}^{-1}$  for  $L_{\text{ax}} = \text{Cl}$ . This would correspond to a harmonic Mo–Mo stretching force constant of about 3.65  $\text{mdyne \AA}^{-1}$ . The value of 3.37  $\text{mdyne \AA}^{-1}$  derived here is therefore not totally unreasonable.

### Bond-Order Function

It will be shown below that, although solution curves for compounds with double or single dimolybdenum bonds can be obtained, there are no intersecting curves among these. Only the solutions for bond orders 4, 3.5, and 3 can therefore be used in the first instance to derive a relationship between  $N$ ,  $k_r$  and  $r_o$ . Relationships of this kind have been proposed before by Badger<sup>18</sup>

$$kr_o^3 = \text{constant}$$

and by Gordy<sup>19</sup>

$$kr_o^{3/2}N^{-1} = \text{constant}$$

but neither of these could interpret our results correctly, i.e.

$$\{k, r_o\}_{N=4} = \{4.07, 2.02\}$$

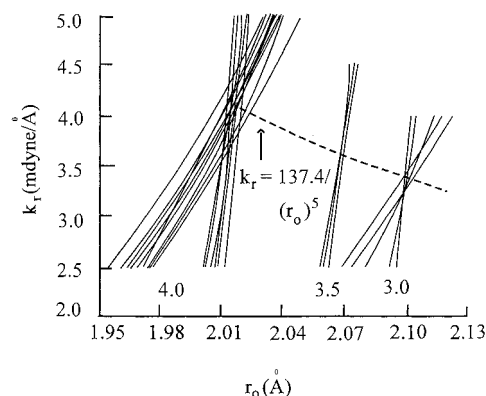
$$\{k, r_o\}_{N=3.5} = \{3.63, 2.07\}$$

$$\{k, r_o\}_{N=3} = \{3.37, 2.10\}$$

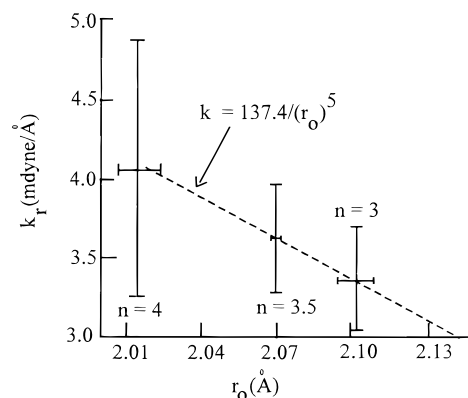
in units of  $\text{mdyne \AA}^{-1}$  and  $\text{\AA}$ , respectively. It is noted that the values obtained here refer specifically to harmonic force fields and should not be applied beyond that.

A curve was therefore fitted to the observed values by an iterative least-squares procedure, using the Marquart–Levenberg algorithm. As a guide, the value of 1.05  $\text{mdyne \AA}^{-1}$  for  $k_r$  ( $N = 1$ ) calculated from the observed Raman band<sup>20</sup> at 193  $\text{cm}^{-1}$  was available. Because of this constraint a linear relationship like  $k_r = -ar_o + c$ , could not be fitted, but the nonlinear form,  $k_r = cr_o - a$  could accommodate all evidence, with  $c = 137.4$  and  $a = 5$ . This solution, superimposed on the calculated solution curves is shown in Figure 3. The ranges of  $k_r$  and  $r_o$  in the form of error bars are shown with the general curve in Figure 4. The relationship involving  $N$ , based on the same analysis, is

$$N = 0.9537k_r = 131.8r_o^{-5}$$



**Figure 3.** Sampling curve  $k_r = 137.4r_o^{-5}$  shown in relation to the molecular mechanics solution curves for dimolybdenum centers with bond orders 4, 3.5, and 3.



**Figure 4.** Error bars showing the range of  $k_r$  and  $r_o$  for  $\text{Mo}_2$  bonds of order 4, 3.5, and 3.

It is now proposed that this result be tested against the available data for  $\text{Mo}^2\text{Mo}$  and  $\text{Mo-Mo}$  bonds.

### $\text{Mo}^2\text{Mo}$ Bonds

There is no unassailable evidence as yet as to the formation of double bonds in dimolybdenum, mainly because no such form, unsupported by bridging ligands, has been obtained. However, on the basis of electron counts there are some good candidates with bond lengths within the expected range between triple and single bonds. One of these<sup>21</sup> is the diamagnetic compound  $\text{Mo}_2(\text{O}^i\text{Bu})_6(\mu\text{-CO})$ , with  $d(\text{Mo-Mo}) = 2.498 \text{ \AA}$ , and four electrons for the dimetal bond, i.e.,  $\sigma(d_{yz})\pi(d_{xz})$ . The other<sup>22</sup> is  $\text{Mo}_2(\text{OPr}^i)_8$ , an alkoxy-bridged dimer with  $d(\text{Mo-Mo}) = 2.523(1) \text{ \AA}$  and the same electronic structure as the former. The compound<sup>21</sup>  $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$  has the same coordination geometry, but  $d(\text{Mo-Mo}) = 3.335(2) \text{ \AA}$ , and clearly it has no dimetal bond.

Force field parameters, based on the observed structures of the two compounds are listed in Table 1. Both molecules could be simulated well without special torsional parameters, and their geometries were reproduced with the same detail as before. The solution curves are virtually coincident, as shown in Figure 5. Also shown is the sampling curve,  $k = 137.4r_o^{-5}$ , derived for the high-order bonds. The average intersection is at  $\{k_r, r_o\} = \{2.04 \text{ mdyne/\AA}, 2.32 \text{ \AA}\}$ , which should be the solution pair for

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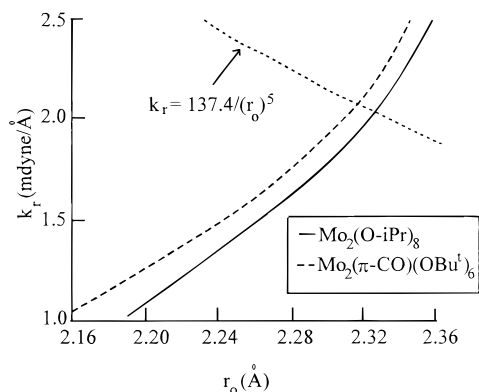
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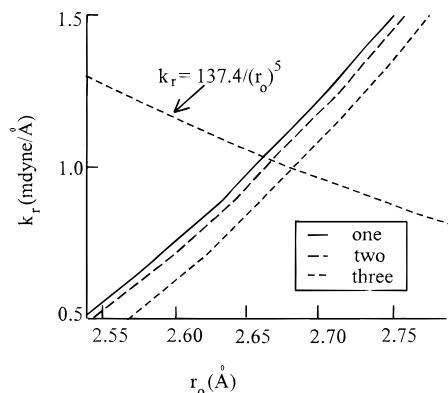
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**Figure 5.** Molecular mechanics solution curves  $\{k_r, r_o\}$  for  $\text{Mo}_2$  double bonds.



**Figure 6.** Molecular mechanics solution curves  $\{k_r, r_o\}$  for  $\text{Mo}_2$  single bonds.

**Table 4.** Calculated and Observed Dimetal Bond Lengths in Compounds with  $\text{Mo}^I\text{-Mo}$  Bonds

molecule	calcd/Å	obsd/Å	figure label	ref
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$	3.233	3.235(1)	two	20
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\text{CO})_6$	3.280	3.281(1)	three	23
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_5(\text{CNMe})$	3.231	3.230(1)	two	24
$\{[\eta^5\text{-C}_5\text{H}_4((\text{CH}_2)_2\text{CH}_2\text{OH})]\text{Mo}(\text{CO})_3\}_2$	3.22	3.213	one	25

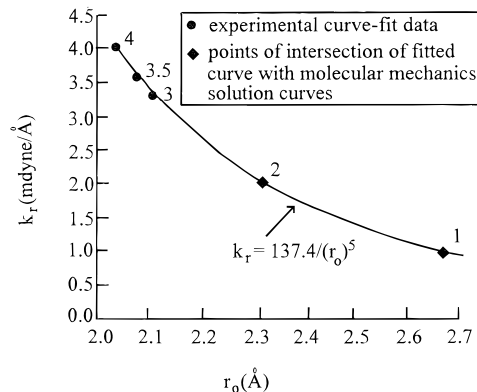
$\text{Mo}^2\text{-Mo}$ . Supporting spectroscopic evidence could not be found.

### $\text{Mo-Mo}$ Single Bond

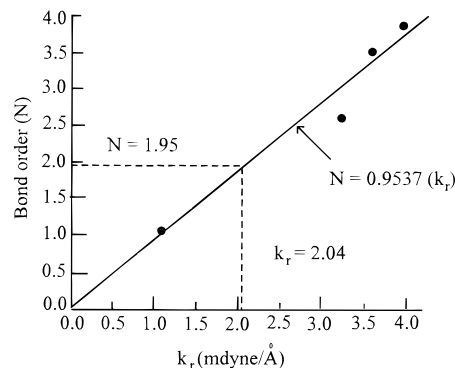
A number of related substituted dimolybdenum cyclopentadienyl carbonyl molecules<sup>20,22–25</sup> have in common an unsupported  $\text{Mo}_2$  bond, which by the 18-electron rule, and confirmed by extended HMO calculations,<sup>26</sup> is of order 1. The bond length ranges from 3.213 to 3.281 Å, probably because of steric strain.

The molecular modeling, which is complicated by the presence of the cyclopentadienyl ring, was achieved by a procedure<sup>27</sup> using a virtual bond to the centroid of the ring and restricting all  $\text{Mo-cen-C}$  angles to  $90^\circ$ . Ring substituents are kept in the plane by restricting out-of-plane bending with the

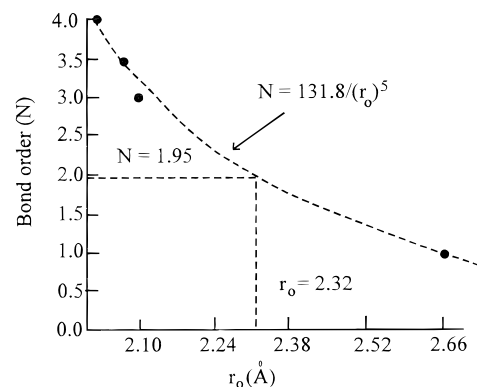
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**Figure 7.** Sampling curve representing the relationship between  $k_r$  and  $r_o$  for  $\text{Mo}_2$  bonds of all orders.



**Figure 8.** Relationship between  $N$  and  $k_r$  for  $\text{Mo}_2$  bonds, used here to derive the order of presumed double bonds from experimental force constant.



**Figure 9.** Same as Figure 8, but obtaining the bond order from the calculated value of  $r_o$ .

parameter,  $\delta = 0.80$  and  $1.20$   $\text{mdyne } \text{Å}^{-1}$  for hydrogen and carbon atoms, respectively. This was sufficient to reproduce the observed structures with the required accuracy, as shown in Table 4.

The  $\{k_r, r_o\}_{\text{Mo-Mo}}$  solution curves, shown in Figure 6, are clustered together and well separated from the curves for all other bond orders. However, the curves are nonintersecting and hence not suitable for the independent fixing of a unique solution pair. This follows from the intersection with the  $k_r$  vs  $r_o$  sampling curve, to yield  $(k_r, r_o)_{\text{Mo-Mo}} = (1.01 \text{ mdyne } \text{Å}^{-1}, 2.67 \text{ Å})$ . The assignment of the strong  $\text{Mo-Mo}$  Raman stretch at  $193 \text{ cm}^{-1}$  requires a harmonic force constant of  $1.05 \text{ mdyne } \text{Å}^{-1}$  and is interpreted as supporting the validity of the sampling curve. Because of the low force constant the bond is stretched considerably by steric repulsions, contrary to the suggestion<sup>26</sup> that the bond length depends on electronic factors only.

**Sampling Curve**

As a final test of the sampling curve (Figure 7), the relationships  $N = 0.9537k_r = 131.8r_o^{-5}$ , are plotted in Figures 8 and 9, together with the fixed points already derived for the bond orders 4, 3.5, 3, and 1. This yields a bond order of 1.95 for the presumed dimolybdenum double bond, safely interpreted as 2. The final  $k_r$ - $r_o$  sampling curve, shown in Figure 7, shows that all available data pertaining to dimolybdenum bonds have now been synthesized into a set of simple equations relating  $N$ ,  $k_r$ , and  $r_o$ . All solution curves  $\{k_r, r_o\}$  intersect the sampling curve sufficiently close to the points indicated by simple electron counts that we may conclude that steric factors have no or little influence on the bond order. This vindicates the initial assumption<sup>1</sup> which enabled this analysis.

To apply this result to other systems further assumptions are needed. As a first step it can be assumed that the equations relating  $k_r$ ,  $r_o$ , and  $N$  have the same general form, at least within the same periodic family, i.e.,  $k_r = cr_o^{-5}$ ,  $N = bk_r = bcr_o^{-5}$ . The aim is to extend the analysis to dichromium and gain insight into the extreme flexibility of this dimetal bond. To establish the required coefficient for dichromium, at least one fixed point in the  $\{N, k_r, r_o\}$  space is needed and is provided by the supershort Cr<sup>4</sup>-Cr bonds. This work appears in the following paper in this issue.

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