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The Lengths of Molybdenum to Molybdenum Quadruple Bonds: Correlations, Explanations, and Corrections

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A systematic search of the Cambridge Crystallographic Database has yielded structures of 467 molecules containing, or reported to contain, a molybdenum to molybdenum quadruple bond, $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$. We have arranged these data as a histogram, in order to determine the "normal" range of $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ lengths, 2.06–2.17 Å, as well as to examine molecules in which the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ length deviates from the norm. We discuss 24 molecules with exceptionally long $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ lengths. Another molecule, $Mo_2(pyNC(O)CH_3)_4$, was previously reported to have an unusually short $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond. However, the structure is highly disordered (probably twinned); thus we have prepared and determined the structure of an analogous molecule, $Mo_2(pyNC(O)CH_2CH_3)_4$, which displays a completely normal $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond length of over 2.08 Å.

Introduction

The first report of the length of a molybdenum to molybdenum quadruple bond, $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$, dealt with it in a bridged environment, Figure 1a. The compound was $Mo_2(O_2CCH_3)_4$, and the distance was reported[1] to be 2.11 Å; this was later redetermined[2] more accurately to be 2.0934(8) Å. The first report[3] of the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond length in a species with no bridging ligands, $[Mo_2Cl_8]^{4-}$, gave a value of 2.139(4) Å, Figure 1b. In the decades since, more than a thousand $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ compounds have been reported and structures have been determined by X-ray crystallography for at least 467 of them.

The purpose of this report is to examine the body of structural data now available and consider the probable causes of the more extreme deviations of some $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond lengths from the main body of the results. For $Mo_2(pyNC(O)CH_3)_4$, an outlying datum, the structure has been reinvestigated and shown to be in error. In others the probable reasons for their deviance from the majority of the results are discussed.

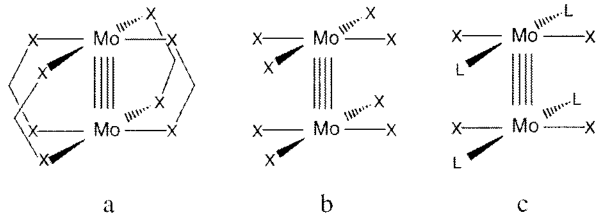

Figure 1. (a) $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ core bridged by four bidentate ligands. (b) $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ core coordinated by eight monodentate ligands. (c) $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ core coordinated by four neutral and four anionic monodentate ligands.

Experimental Section

Database Search. The Cambridge Crystallographic Database (version 5.21) was searched using two different diagrammatic queries in the program ConQuest (version 1.0). The first search included only compounds containing an $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond, while the second included any Mo−Mo bonds between 0 and 2.30 Å. When a structural feature (viz., Mo−Mo distance) was not used as a constraint in the search, as was the case in the first search, several hits were acquired for which the structure was not available. In these cases, the original papers were examined for structural information. Recommunications of structures previously reported were omitted from the histogram, but redeterminations have been included, as they often represent a different space group and/or Mo−Mo bond distance.

General Synthetic Procedures. All manipulations were carried out in an inert atmosphere utilizing standard Schlenk and drybox techniques. All reagents were obtained commercially and used as received. Dichloromethane was dried over P_2O_5, and hexanes and

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THF were dried over Na/K alloy, and these solvents were freshly distilled under N$_2$ prior to use.

Physical Measurements. Elemental analysis was performed by Canadian Microanalytical Service, Ltd., Delta, British Columbia. The ^{1}H NMR spectrum was recorded on a VXR-300 NMR spectrometer, with chemical shifts (δ) referenced to CHCl$_3$. The UV/vis spectrum was recorded on a Cary 17D spectrophotometer. The infrared spectrum was recorded on a Perkin-Elmer 14PC spectrophotometer.

Preparation of Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$, 1. The ligand 2-propionamidopyridine was prepared according to a literature method[4] for 2-acetamidopyridine, except that a stoichiometric amount of propionic anhydride was used in place of acetic anhydride. The anion of 2-propionamidopyridine was prepared by reacting the ligand (0.75 g, 5.4 mmol) with 3.4 mL of 1.6 M hexane solution of *n*-butyllithium in 50 mL of THF. Dimolybdenum tetraacetate (0.44 g, 1.0 mmol), prepared by a literature method,[5] was added, and a red solution immediately developed. The solution was stirred for 24 h, at which time copious red precipitate had formed. The suspension was filtered, and the filtrate was allowed to evaporate under a slow stream of N$_2$. This method yielded red blocks, Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$·2THF, **1**·2THF. The red precipitate was dried under vacuum, and approximately 100 mg was transferred to a Schlenk tube, dissolved in 20 mL of CH$_2$Cl$_2$, and layered with hexanes. This process yielded several large red blocks, Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$·$^1/_2$CH$_2$Cl$_2$, **1**·$^1/_2$CH$_2$Cl$_2$. Dichloromethane and THF solutions of **1** are only moderately air-sensitive; a brown decomposition product precipitated after several hours in air. No evidence of decomposition was observed when the powder or crystalline phases of **1** were exposed to air over the course of 2 weeks.

The overall yield of the reaction was approximately 80%. After elimination of interstitial solvent molecules under vacuum: Anal. for C$_{32}$H$_{36}$Mo$_2$O$_4$N$_8$. Calcd (found): C, 48.74 (49.20); H, 4.60 (4.89). ^{1}H NMR δ (ppm, in CDCl$_3$): 7.967 (d, 1 H, aromatic), 7.927 (d, 1 H, aromatic), 7.538 (t, 1 H, aromatic), 6.769 (t, 1 H, aromatic), 1.915 (q, 2 H, methylene), 1.062 (t, 3H, methyl). IR (KBr): 3080, 2971, 2936, 1648, 1587, 1546, 1467, 1439, 1399, 1376, 1351, 1321, 1300, 1285, 1256, 1222, 1195, 1167, 1112, 1068, 1049 cm^{-1}. UV/vis $\lambda(\epsilon)$, nm (M^{-1}cm^{-1}) in CH$_2$Cl$_2$: 555 (3060), 450 (11510), 380 (3980), 325 (12260), 293 (18560), 260 (32030).

X-ray Crystallography. Single crystals of **1**·2THF and **1**·$^1/_2$CH$_2$Cl$_2$ were attached to glass fibers with a small amount of silicon grease and mounted on the Bruker SMART system for data collection using Mo Kα radiation at 213(2) K. Cell parameters were obtained from an autoindexing routine. For **1**·2THF, cell parameters were refined with 6942 reflections within a 2θ range of 4.813−55.014°. For **1**·$^1/_2$CH$_2$Cl$_2$, cell parameters were refined with 7492 reflections within a 2θ range of 4.573−55.046°.

The coordinates of many of the non-hydrogen atoms were found via direct methods using the structure solution program SHELXS.[6] The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-93 program[7] (for **1**·$^1/_2$CH$_2$Cl$_2$) and the SHELXL-97 program[8] (for **1**·2THF). Non-hydrogen atoms were refined with anisotropic displacement parameters, except for disordered portions of the structures. In **1**·2THF, one ethylamido group and one THF molecule were each disordered over two positions. The second THF molecule was highly disordered and was modeled by allowing three different oxygen atom positions and eleven carbon atom positions to sum to an occupancy of one and four, respectively. The hydrogen atoms were included in the structure factor calculations at idealized positions. Cell parameters and refinement results for both crystals are summarized in Table 1. Selected bond distances and angles are given in Table 2.

Table 1. Crystallographic Data for Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$ Complexes

	1·2THF	**1**·$^1/_2$CH$_2$Cl$_2$
empirical formula	C$_{40}$H$_{52}$Mo$_2$N$_8$O$_6$	C$_{32.5}$H$_{37}$ClMo$_2$N$_8$O$_4$
fw	932.78	831.03
space group	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*n* (No. 14)
a, Å	11.062(1)	20.085(2)
b, Å	26.886(2)	15.563(1)
c, Å	13.704(1)	21.863(2)
α, deg	90	90
β, deg	94.311(2)	96.844(2)
γ, deg	90	90
V, Å^3	4064.2(6)	6785(1)
Z	4	8
T, °C	−60	−60
λ, Å	0.71073	0.71073
d_{calcd}, g/cm^3	1.524	1.627
μ, mm^{-1}	0.674	0.868
R1,^{a} wR2^b	0.0980, 0.1514	0.0449, 0.0809

^{a} $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $\mathrm{wR2} = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2 \text{ or } 0) + 2(F_c{}^2)]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$ Complexes

	1·2THF	**1**·$^1/_2$CH$_2$Cl$_2$
Mo−Mo	2.0826(6)	2.0869(4) 2.0806(4)
Mo−N (av)	2.177[5]	2.177[3] 2.171[3]
Mo−Mo−N (av)	92.7[1]	92.56[7] 92.83[7]
cis-N−Mo−N (av)	89.9[2]	89.93[9] 89.9[1]
trans-N−Mo−N (av)	173.8[2]	174.77[9] 173.68[9]

Results and Discussion

As a result of our database search, we have a list of all compounds that contain an Mo$_2{}^{4+}$ core for which X-ray crystal structures have been reported in the refereed literature. A few that turned up were discarded summarily because they did not meet the minimal criterion of having each molybdenum atom bound to four ligand atoms that define, at least approximately, a square. No restriction has been placed on the types or relative numbers of different ligand atoms, nor on whether they are a monodentate or some type of polydentate ligand. Also, no restrictions were placed on the presence or absence of axial ligands, on the overall charge of the species, or on the internal twist angle. A histogram of the data is presented in Figure 2. Of the 467 distances, all but 25 are within the narrow (0.12 Å) span of 2.06−2.17 Å, using numbers rounded off to 0.01 Å. We will, somewhat arbitrarily, define this as the “normal” range. The bimodal

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Table 3. Compounds Containing Long Mo$\overset{4}{-}$Mo Bonds

group I			group II		miscellaneous	
compound	Mo−Mo, Å	twist, deg	compound	Mo−Mo, Å	compound	Mo−Mo, Å
β-$Mo_2Cl_4(dmpe)_2$[a]	2.183(3)	40.0	$Mo_2(OCH_2Bu^t)_4(PMe_3)_4$[g]	2.218(2)	$[Mo_2(NCCH_3)_8(\textit{ax}\text{-}NCCH_3)_2](BF_4)_4 \cdot 2CH_3CN$[l]	2.187(1)
β-$Mo_2Cl_4(dppe)_2$[b]	2.183(3)	30.5	$Mo_2(OPr^i)_4(py)_4$[g]	2.195(1)	$[Mo_2(NCCH_3)_8(\textit{ax}\text{-}NCCH_3)](BF_4)_4$[m]	2.180(1)
β-$Mo_2Br_4(dppe)_2$[c]	2.177(8)	31.1	$Mo_2(OPr^i)_4(dmpe)_2$[h]	2.236(1)	$Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF \cdot 2C_7H_8$[n]	2.191(1)
β-$Mo_2I_4(dppe)_2 \cdot {}^2/_3CH_2Cl_2$[d]	2.180(4)	27.9			*trans*-$Mo_2(OAc)_2Cl_2(Ph_2Ppy)_2 \cdot 2CH_2Cl_2$[o]	2.1900(3)
β-$Mo_2I_4(dppe)_2 \cdot C_7H_8$[d]	2.179(3)	25.7	group III		$Mo_2(\mu^2\text{-}O_2CCF_3)_2(2,2\text{-}bpy)_2(O_2CCF_3)_2$[p]	2.181(2)
meso-$Mo_2Cl_4(tetraphos)$[e]	2.186(1)	30.9	$Mo_2(TPP)_2 \cdot C_6H_6 \cdot C_{10}H_{18}$[i]	2.239(1)	$(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$[q]	2.177(1)
meso-$Mo_2\ Br_4(tetraphos) \cdot CH_2Cl_2$[e]	2.195(3)	30.5	$Mo_2(tmtaa)_2$[j]	2.175(1)	$Mo_2(OAc)_2(dppa)_2Br_2$[r]	2.176(1)
	2.183(3)	30.9				
meso-$Mo_2\ Br_4(tetraphos) \cdot 1.5THF$[e]	2.195(1)	28.6	$[(Bu^t\text{-}salophen)\text{-}Mo]_2$[k]	2.2057(8)	$(Bu_4N)_2H_2(Mo_2((O_2PPh)_2Mo(CO)_4)_2)$[s]	2.186(2)
$Mo_2I_4(dppm)_2$[f]	2.178(3)	0				

[a] Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507. [b] Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1984**, *23*, 3383. [c] Agaskar, P. A.; Cotton, F. A. *Rev. Chim. Miner.* **1985**, *22*, 302. [d] Cotton, F. A.; Dunbar, K. R.; Matusz, M. *Inorg. Chem.* **1986**, *25*, 3641. [e] Chen, J.-D.; Cotton, F. A.; Hong, B. *Inorg. Chem.* **1993**, *32*, 2343. [f] Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7. [g] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Putilina, E. F.; Streib, W. E.; Tatz, R. J. *Inorg. Chem.* **1993**, *32*, 3771. [h] Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 2514. [i] Yang, C.-H.; Dzugan, S. J.; Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1313. [j] Cotton, F. A.; Czuchajowska, J.; Feng, X. *Inorg. Chem.* **1990**, *29*, 4329. [k] Floriani, C.; Solari, E.; Franceschi, F.; Scopelliti, R.; Belanzoni, P.; Rosi, M. *Chem. Eur. J.* **2001**, *7*, 3052. [l] Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1991**, *30*, 871. [m] Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Polyhedron* **1998**, *17*, 2781. [n] Cotton, F. A.; Matusz, M. *Inorg. Chim. Acta* **1989**, *157*, 223. [o] Cotton, F. A.; Matusz, M. *Polyhedron* **1988**, *7*, 2201. [p] Matonic, J. H.; Chen, S.-J.; Perlepes, S. P.; Dunbar, K. R.; Christou, G. *J. Am. Chem. Soc.* **1991**, *113*, 8169. [q] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. [r] Arnold, D. I.; Cotton, F. A.; Kühn, F. E. *Inorg. Chem.* **1996**, *35*, 4733. [s] Wong, E. H.; Valdez, C.; Gabe, E. J.; Lee, F. L. *Polyhedron* **1989**, *8*, 2339.

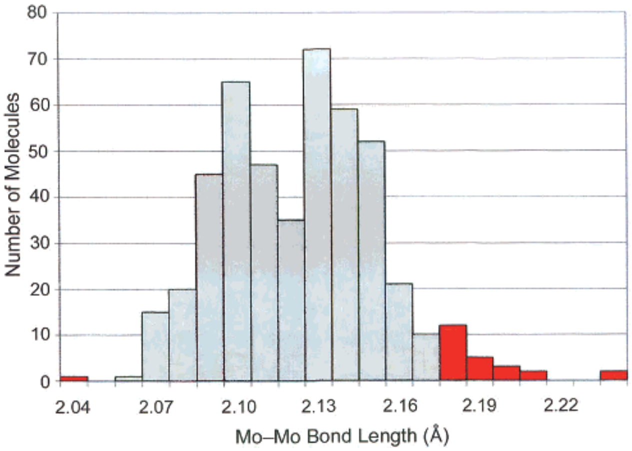

Figure 2. Histogram representing all molecules with an Mo$\overset{4}{-}$Mo core, where each molybdenum atom is bound to four ligands defining a square. All bond lengths have been rounded to the nearest 0.01 Å.

distribution within it is correlated with the type of structure, in the sense of Figure 1, that is involved. Most compounds of the type (a) have distances in the lower range 2.06−2.13 Å, with a median of about 2.09 Å, while most of those of type (b) or (c) have distances in the higher range of 2.11−2.17 Å, with a median of about 2.14 Å.

Table 3 lists, with references, those compounds for which the reported Mo$\overset{4}{-}$Mo distances exceed 2.17 Å. There are 24 of these, and they will now be discussed.

"Long" Bonds: Group I. There are 10 molecules in this group, and all but one are of the $Mo_2X_4(LL)_2$ type, where X is Cl or Br, and LL is a diphosphine, with two carbon atoms between the coordinated phosphorus atoms. In all of these cases the Mo$\overset{4}{-}$Mo distance is between 2.177 and 2.195 Å, that is, only slightly above the cutoff value of 2.17 Å. They are considered to be "long" mainly because there is a reason why they should be long. In all but one case, the internal twist angle is 26−40°. Since this means that the $\delta-\delta$ overlap is reduced to only 62−17% of its maximum possible value, it is not surprising that the δ component of the bond is weaker and the Mo$\overset{4}{-}$Mo distance increased. In the remaining group I case the ligand, LL, is a diphosphinomethane, but the results are very ambiguous, as explained in the original publication. It should also be noted that there are a few $Mo_2X_4(LL)_2$ molecules that are close to the 2.17 Å limit but not beyond it. It is likely that, because of constraints in the solid state (often referred to as packing forces), variations of up to 0.02 Å cannot be taken too seriously. On the other hand, the existence of an approximate dependence of Mo$\overset{4}{-}$Mo distance on internal twist angle was established some time ago.[9]

"Long" Bonds: Group II. There are three molecules containing alkoxide ligands that have Mo$\overset{4}{-}$Mo distances of 2.20, 2.22, and 2.24 Å. Since it is well known that RO ligands can be π-donors,[10] it seems likely that they weaken the Mo$\overset{4}{-}$Mo bond by donating electron density to the π^* and/or δ^* orbitals. In one case the disposition of ligands is also quite unusual, with all four RO groups on one molybdenum atom and four phosphorus atoms on the other, which may also contribute to making this bond one of the two longest reported.

"Long" Bonds: Group III. Four compounds have been reported in which each molybdenum atom is clasped by a tetradentate ligand, either chelating or macrocyclic. In three cases, the Mo$\overset{4}{-}$Mo bond is >2.17 Å (and in the fourth, not listed in Table 3, it is 2.17 Å). The elongation of these bonds seems very likely to be no more than the expected result of ligand−ligand repulsion.

"Long" Bonds: Eight Miscellaneous Cases. These have no clear commonality. There are two crystal compositions containing the $[Mo_2(NCCH_3)_8(\textit{ax}\text{-}NCCH_3)]^{4+}$ ion, and the Mo$\overset{4}{-}$Mo distances are 2.187(1) and 2.180(1) Å. The explanation for this long bond could be that none of the ligands is negative and thus repulsion between the two formally

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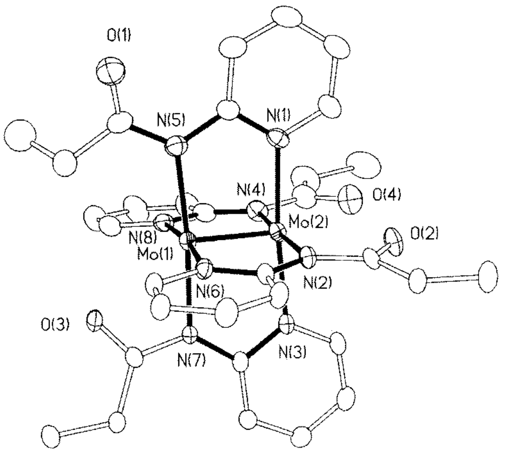


Figure 3. Thermal ellipsoid plot of the Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$ molecule in **1**·2THF. Probability ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

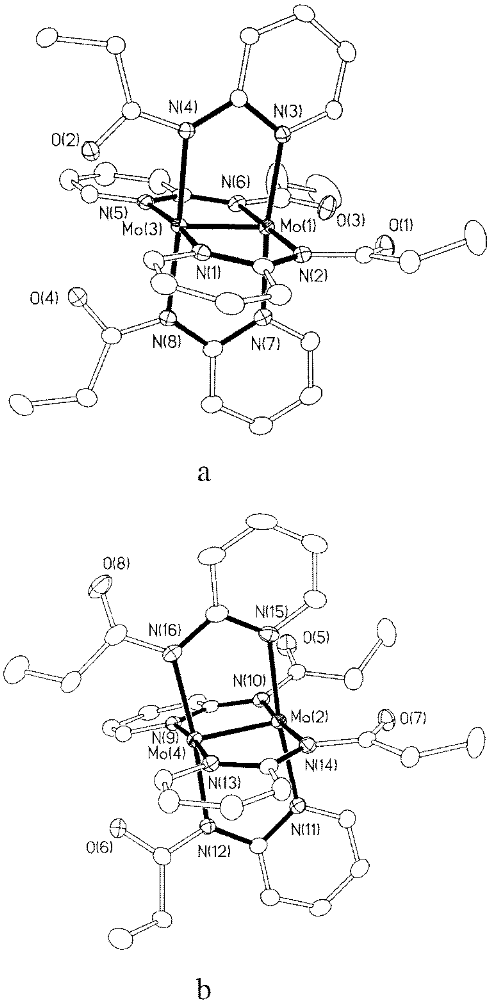
+2 metal atoms is greater than in all other molecules where some negatively charged ligands are present.

There are two compounds in which the Mo$\overset{4}{-}$Mo unit is bridged by two *o*-(Ph$_2$P)py ligands, and in these the Mo$\overset{4}{-}$Mo distances are 2.19 Å. Since there is no other apparent reason for these long bonds, we suggest that they be attributed to the long "bite" of the *o*-(Ph$_2$P)py ligands.

There is one case in which each molybdenum atom is ligated by a chelating bpy ligand. Here repulsion between the face-to-face bpy ligands could be the cause of elongation to 2.181(2) Å.

In two cases, there are Mo$\overset{4}{-}$Mo distances of 2.177(1) and 2.176(1) Å, which, it is true, round off to 2.18 Å. However, in the former there are two [Mo$_2$(NCS)$_8$]$^{4-}$ ions in the asymmetric unit, and the other one has a distance of 2.174(1) Å. Thus, the Mo$\overset{4}{-}$Mo distance in this ion lies right on the borderline. It shows that NCS ligands tend to give long Mo$\overset{4}{-}$Mo bonds, for obscure reasons, but the structure or identity of the species is not in doubt. The bond length of 2.176(1) Å is found in the molecule Mo$_2$(O$_2$CCH$_3$)$_2$(dppa)$_2$Br$_2$, where dppa is the analogue of dppm in which the bridging CH$_2$ is replaced by NH. Since the distance here, 2.176(1) Å, is not significantly beyond our upper limit on "normal", namely, 2.174 Å rounding down to 2.17 Å, there is no reason to be concerned as to the identity of this compound.

We turn now to the remaining compound that has a "long" Mo−Mo bond, (Bu$_4$N)$_2$H$_2$[Mo$_2$((O$_2$PPh)$_2$Mo(CO)$_4$)$_2$]. In fact, this is not a quadruply bonded Mo$_2$$^{4+}$ compound, but a triply bonded Mo$_2$$^{6+}$ compound. The reinvestigation of this compound was motivated by its inexplicably long Mo−Mo distance and will be reported in detail in a forthcoming paper.[11]



a

b

Figure 4. Thermal ellipsoid plot of the Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$ molecule in **1**·$^1/_2$CH$_2$Cl$_2$. Probability ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. There are two independent molecules in the asymmetric unit, (a) and (b).

A "Short" Bond. Having disposed of the "tail" at the high end of the histogram in Figure 2, we turn now to the one "outlier" at the low end.[12] There are many factors that may come into play to make a bond longer than "normal", as we have seen. It is not so easy to see, however, why the bond in one molecule, which seems to be entirely typical of its class in every other way, should be shorter than all the others. We therefore decided to redetermine the structure of Mo$_2$(pyNC(O)CH$_3$)$_4$. This was done, beginning with a new, freshly grown crystal, and taking advantage of a present-day instrument for the collection of a larger, more precise data set, and employing the superior computer codes for data processing and structure refinement available today. The result was exactly the same structure as previously found, including large crystallographic disorder and an Mo$\overset{4}{-}$Mo bond length that was not significantly different.[13]

Because we cannot justify this extremely short (2.037(3) Å) bond length in a molecule with apparently "normal" bridging ligands, we have determined the Mo$\overset{4}{-}$Mo distance in a very similar compound. Thus, we synthesized a compound in which the bridging ligand was modified by the addition of a methylene group, Mo$_2$(pyNC(O)CH$_2$CH$_3$)$_4$,

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(13) As previously reported, the crystal shows considerable disorder and there are some indications that it may be a merohedral twin. We believe it is legitimate to consider the Mo−Mo distance, and probably other dimensions of the molecule, obtained from this structure to be unreliable.

which should not change the electronic structure significantly, but may perhaps solve the crystallographic disorder. We crystallized this compound using two different methods, which has allowed us to determine the molecular structure three times, independently. The structure found in **1**$\cdot$2THF is shown in Figure 3, and the structures of the two perfectly ordered, crystallographically independent, molecules in **1**$\cdot{}^1/_2CH_2Cl_2$ are depicted in Figure 4. The Mo−Mo distances in all three are within the range 2.0806(4)−2.0869(4) Å, and therefore not at all anomalous compared to the hundreds of others represented in Figure 2. This supports the idea that the anomalously short Mo−Mo distance in $Mo_2(pyNC(O)CH_3)_4$ is indeed an artifact.

It is interesting to note that small variations in the Mo−Mo distances among the three independent molecules correlate with a qualitative variation among the conformations of the amido groups. The orientation of the amido oxygen atom in each ligand is either toward the axial position of the Mo_2 unit (in) or away from that position (out). In each of the three molecules, there is a different arrangement. These arrangements, along with the pertinent Mo−Mo distances, are as follows:

in, in, in, in	2.0869(4) Å
in, in, in, out	2.0826(6) Å
in, in, out, out	2.0806(4) Å

It is clear that the Mo−Mo distances vary systematically with the arrangement of the amido oxygen atoms in just the way that would be expected if an “in” oxygen atom provides a modicum of axial electron density to the $Mo\overset{4}{-}Mo$ unit. It is well established that the lengths of M−M multiple bonds are all more or less sensitive to the presence of electron density in the axial positions. Some, such as the $Cr\overset{4}{-}Cr$ bond, are extremely sensitive.[14,15] The $Mo\overset{4}{-}Mo$ bond is much less so, but such a sensitivity has been established in numerous instances, of which the first was the comparison of $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4\cdot 2py$, where the Mo−Mo distance is increased from 2.090(4) to 2.129(2) Å by the coordination of the pyridine molecules.[16] The same effect is being observed in the three variations of the molecular structure of **1**.

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Supporting Information Available: An X-ray crystallographic file in CIF format for compounds **1**$\cdot$2THF and **1**$\cdot{}^1/_2CH_2Cl_2$ and IR, NMR, and electronic spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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