

Dependence of metal-to-metal distances on Mo–Mo multiple bond orders; a new triple bond

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A paddlewheel compound with a triply bonded Mo₂⁶⁺ core is reported and used to reexamine and correct a previously reported Mo₂⁵⁺ distance that was too long.

The question of how the Mo–Mo distance will change when the formal Mo–Mo bond order changes in the range of three to four is not quite as simple as might naively be expected.¹ The reason is that the usual way of changing bond order also changes the average oxidation state of the metal atoms in the Mo₂ⁿ⁺ core, and this in itself also affects the strength of the Mo–Mo bond. Specifically, in going through the series Mo₂⁴⁺, Mo₂⁵⁺, Mo₂⁶⁺, the bonding electron configuration changes in the order $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta$, $\sigma^2\pi^4$, which should progressively weaken the bond. However, in the same series, the increased charge should contract the σ and π orbitals of the metal atoms, thus also weakening the bond.[†] The two effects act in the same direction, so the net effect can be qualitatively predicted, namely, bond length will increase in the order Mo₂⁴⁺, Mo₂⁵⁺, Mo₂⁶⁺. But by how much?

To approach the problem quantitatively, it is necessary to prepare compounds in which the core changes but the surrounding ligands do not. There has not heretofore been any such series for Mo₂ⁿ⁺ although the series [Mo₂(SO₄)₄]^{4–}, [Mo₂(SO₄)₄]^{3–}, [Mo₂(HPO₄)₄]^{2–} comes close.² The Mo–Mo distances in that case are 2.11, 2.17, 2.22 Å, respectively. The SO₄^{2–} and HPO₄^{2–} ligands are rather hard and would not tend to compensate very much for the effect of increasing charge, and thus the charge effect might be contributing as much (or more) than the bond order effect in this series.

One would predict that in a similar series where the ligands are much softer (more basic and/or more polarizable) the charge effect would be mitigated and the net changes would be smaller and due more to the bond order changes. We have now obtained a compound that allows us to test this prediction and correct a recently published report. This compound is [Mo₂(hpp)₄(BF₄)₂]·4CH₂Cl₂,^{‡,§} 1·4CH₂Cl₂, and its structure[¶] is presented in Fig. 1.

We have previously³ prepared and structurally characterized the neutral molecule [Mo₂(hpp)₄] and found the Mo–Mo bond

(of order 4) to have a length of 2.067(1) Å. Thus, as shown in Table 1, the change in going from bond order 4 to bond order 3 is +0.075 Å. Similarly, earlier work in this laboratory⁴ showed that with the very similar ligand, [(*p*-C₆H₄Me)NC(H)N(*p*-C₆H₄Me)][–], the change in going from the neutral (quadruply bonded) compound to the +1 cation is 0.037 Å (see Table 1). Thus, the changes found on going from the Mo₂⁴⁺ to Mo₂⁵⁺ to Mo₂⁶⁺ species with soft, basic ligands are only about 60% of those with the hard ligands.

However, Table 1 also shows a disturbing observation: the difference in the Mo–Mo distance in a recently reported guanidinate derivative is 0.206 Å in changing from Mo₂⁴⁺ to Mo₂⁵⁺.⁵ Is our prediction incorrect?

A careful analysis of the supporting information provided with the structural report of the cationic guanidinate complex

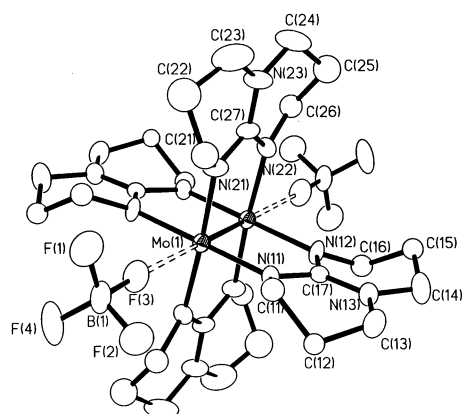


Fig. 1 A drawing of the centrosymmetric ionic compound **1** showing the atom labelling scheme and displacement ellipsoids at the 30% probability level. The hpp ligands are conformationally disordered; only one orientation is shown. Selected bond distances (Å) are Mo(1)–Mo(1') 2.142(2), Mo–N(11) 2.075(7), Mo(1)–N(21) 2.088(8), Mo(1')–N(22) 2.073(8), Mo(1')–N(12) 2.083(7), Mo(1)–F(3) 2.768(6).

Table 1 Variations of the Mo–Mo and Mo–N distances (Å) for dimolybdenum species bridged by amidinate ligands and differences in the metal–metal distance between the corresponding cationic and neutral species

Compound	Mo–Mo	$\Delta(\text{Mo–Mo})$ cationic–neutral species	Mo–N (av.)	Charge of Mo ₂ ⁿ⁺ unit	Ref.
[Mo ₂ (DTolF) ₄] ^a	2.085(4)	0.037	2.17	4	4
[Mo ₂ (DTolF) ₄]PF ₆	2.122(3)		2.15	5	4
[Mo ₂ { μ - η^2 -(NPh) ₂ CNHPPh} ₄]	2.0839(9)	0.206	2.17	4	5
[Mo ₂ { μ - η^2 -(NPh) ₂ CNHPPh} ₄]BF ₄ ^b	2.290(1)		2.14	5	5
[Mo ₂ { μ - η^2 -(NPh) ₂ CNHPPh} ₄]BF ₄ ^c	2.121(1)		2.14	5	^d
[Mo ₂ (hpp) ₄]	2.067(1)	0.075	2.16	4	3
[Mo ₂ (hpp) ₄ (BF ₄) ₂]	2.142(2)		2.08	6	^d

^a DTolF = N,N'-di-*p*-tolylformamidinate anion. ^b Uncorrected. ^c Corrected. ^d This work.

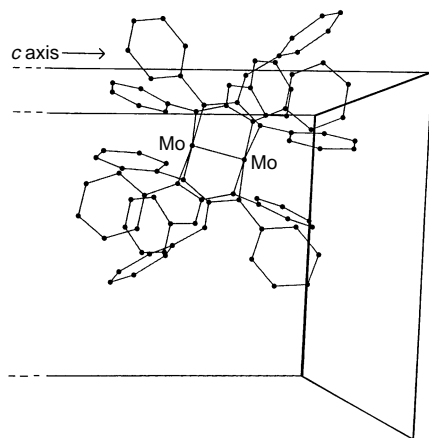


Fig. 2 A drawing of one cation of the molecule $[\text{Mo}_2\{\mu\text{-}\eta^2\text{-(NPh)}_2\text{CNHPh}\}]\text{BF}_4$ (from ref. 5) in a box representing the unit cell, showing that the Mo–Mo unit is more or less aligned along the c axis

showed that the geometry of the phenyl groups in the ligands had significant distortions. In many cases the C–C distances were as long as 1.50 Å; the internal C–C–C angles varied from 115 to 125°. Furthermore, a plot of the unit cell for this compound (Fig. 2) shows that the Mo–Mo units are nearly aligned parallel to the c axis. Significantly, most of the long C–C bonds of the phenyl groups were more or less along the same direction. We therefore suspected that an error had been made in the input data^{||} of the c axis used for the calculation of the bond distances and angles. Indeed, when the length of 23.573(7) Å for the c axis reported in the abstract given in ref. 5 is used for the calculation of the bond distances and angles, as opposed to 25.573(7) Å given in their crystallographic data and subsequently used by Bailey *et al.* for their calculations, the phenyl rings are found to be very regular. The internal bond angles vary from 119 to 121° and the C–C distances are found in the normal range 1.36–1.41 Å. Such calculation gives a Mo–Mo distance of 2.121 Å which is entirely consistent with our prediction. We are currently working on the preparation of a compound containing the $[\text{Mo}_2(\text{hpp})_4]^+$ species which we expect to have a Mo–Mo distance similar to that of the $[\text{Mo}_2(\text{DTolF})_4]^+$ analog.

Support from the National Science Foundation and the University of Costa Rica is gratefully appreciated.

Footnotes

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† An equivalent explanation is that an increase in the metal charge also increases intermetal repulsions, an opposite effect to that observed for the metal-to-ligand interactions.

‡ hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinate.

§ *Preparation:* Under a nitrogen atmosphere, a solution of $[\text{Mo}_2(\text{hpp})_4]^3$ (0.74 g 1.0 mmol) in 15 ml CH_2Cl_2 was added to AgBF_4^- (0.20 g 1.0 mmol). The reaction mixture was stirred for 30 min at room temp. and filtered. The resulting dark brown solution was carefully layered with hexanes. Within a few days, the slow diffusion of the layers afforded dark brown crystals of $1\cdot4\text{CH}_2\text{Cl}_2$. Yield: 22% (based on $[\text{Mo}_2(\text{hpp})_4]$); 44% (based on AgBF_4). Elemental analysis was satisfactory.

¶ *Crystal data for $1\cdot4\text{CH}_2\text{Cl}_2$:* crystal dimensions $0.3 \times 0.2 \times 0.05$ mm, $\text{C}_{32}\text{H}_{56}\text{N}_{12}\text{B}_2\text{Cl}_8\text{F}_8\text{Mo}_2$, $M = 1257.99$, orthorhombic, space group $Pbca$, $a = 15.783(8)$, $b = 15.456(8)$, $c = 20.657(6)$ Å, $Z = 4$, $D_c = 1.658$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 0.991$ mm $^{-1}$. Data were obtained at 213(2) K on a Nonius FAST diffractometer. A total of 3306 unique reflections were collected using ellipsoid-mask fitting within a 2θ range of 4.72–45.1°. The structure was solved by direct methods and refined by full-matrix least squares using all 3301 reflections for 288 parameters. The hpp ligands are conformationally disordered and adjacent CH_2 groups deviate in opposite directions. Disordered atoms were refined isotropically. Chemically identical bonds were constrained to have identical distances. The final refinement converged to $R_1(F_o) = 0.081$ and $wR_2(F_o^2) = 0.152$. CCDC 186/528.

|| Similar errors have been made before. See for example our earlier report: F. A. Cotton, L. M. Daniels, C. A. Murillo and X. Wang, *J. Am. Chem. Soc.*, 1996, **118**, 12449.

Note added in proof: We have been informed by the authors of ref. 5 that they concur with our discussion of the error in the bond length in their compound.

References

- 1 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Oxford University Press, 1993.
- 2 Ref 1, p. 632.
- 3 F. A. Cotton and D. J. Timmons, *Polyhedron*, in the press.
- 4 F. A. Cotton, X. Feng and M. Matusz, *Inorg. Chem.*, 1989, **28**, 594.
- 5 P. J. Bailey, S. F. Bone, L. A. Mitchell, S. Parsons, K. J. Taylor and L. J. Yellowlees, *Inorg. Chem.*, 1997, **36**, 867.

Received in Bloomington, IN, USA; 8th April 1997; 7/02384G