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A Pseudo-Jahn−Teller Distortion in an $Mo_2(\mu_2\text{-}O)_2$ Ring Having the Shortest $Mo^{IV}-Mo^{IV}$ Double Bond

F. Albert Cotton,*,† Lee M. Daniels,† Carlos A. Murillo,*,†,‡ and J. Garrett Slaton†

Department of Chemistry and the Laboratory for Molecular Structure and Bonding, P.O. Box 30012, Texas A&M University, College Station, Texas 77842-3012, and the Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

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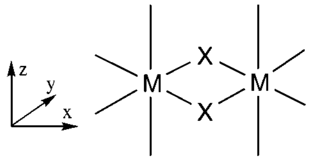
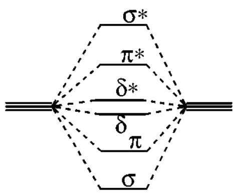
The literature on molecules with edge-sharing bioctahedral structures (ESBOs) (**I**) is vast. The metal-to-metal distances in such structures are governed in somewhat obvious ways by the size of the bridging atoms, X, and the oxidation states of the metal atoms, but in a more interesting way by the electron configurations of the metal atoms and their varying abilities to form metal−metal bonds.[1] The basic relationships were developed[2] and structural data reviewed[3] some years ago, mainly for molecules where X = Cl. Since that time there have been abundant new developments, but there is no more recent review.

It has previously been recognized that metal−metal bond formation may occur by overlap of d orbitals according to the general pattern shown as **II**. Thus, with two d^1 metal atoms, a single bond, σ^2, is formed and with d^2 metal atoms a double bond, $\sigma^2\pi^2$, is formed. With d^3 metal atoms, the simple picture **II** would incline one to believe that there would be a $\sigma^2\pi^2\delta^2$ triple bond. In fact, this is not a safe prediction because of the role that $p\pi$ orbitals on the X atoms may play.[2a,d] It is possible that the actual result may be a $\sigma^2\pi^2\delta^{*2}$ configuration, because of an interaction of the filled $p\pi$ orbitals of the X atoms on the $d\delta$ orbitals of the metal atoms. Numerous structural results for $M(\mu^2\text{-}Cl)_2M$ cases have confirmed this.[2,3]

I



II



We now report some important results concerning a new ESBO molecule, **1**, shown in Figure 1. The violet compound was easily prepared by air-oxidation of *cis*-$Mo_2(\mu_2\text{-}O_2CCH_3)_2(\mu_2\text{-}DXylF^{2,6})_2$ ($DXylF^{2,6}$ = *N,N′*-di(2,6-xylylformamidine)) according to eq 1:[4]

$$cis\text{-}Mo_2(\mu_2\text{-}O_2CCH_3)_2(\mu_2\text{-}DXylF^{2,6})_2 + O_2 \rightarrow Mo_2(\eta_2\text{-}O_2CCH_3)_2(\mu_2\text{-}DXylF^{2,6})_2(\mu_2\text{-}O)_2 \quad (1)$$

Crystals of **1a**, obtained by diffusion of hexanes into a dichloromethane solution of **1**, crystallized in space group $P\bar{1}$ with two chemically similar but crystallographically independent molecules (molecules 1 and 2). Alternatively, crystallization by slow evaporation of chloroform from solutions containing **1** afforded a monoclinic form of $\mathbf{1}\cdot 1.93CHCl_3$, **1b**. We therefore have three crystallographically independent structure determinations for molecule **1**; in each case the molecule lies on a crystallographic inversion center.[5] The first remarkable feature of this compound is that it contains the shortest bond between two molybdenum(IV) atoms ever reported. The range and the average of Mo−Mo distances in these three is 2.3048(4) to 2.3077(6) Å and 2.306[2] Å. As a result of the strong and short Mo═Mo bond, the O−Mo−O and Mo−O−Mo angles of the independent molecules in structures **1a**, **1b**, and **2** are all 107° ± 1° and 73° ± 1°, respectively. DFT calculations[6] have confirmed conclusively that, as expected from **II**, there is a $\sigma^2\pi^2$ double bond between the metal atoms. The exceptional shortness of this bond is presumably due to the combined effects of the smallness of the oxygen atoms, the high basicity and small bite of the bridging formamidinate ions, and the relatively weak binding of the acetate ions that are approximately trans to the μ_2-O atoms.[7]

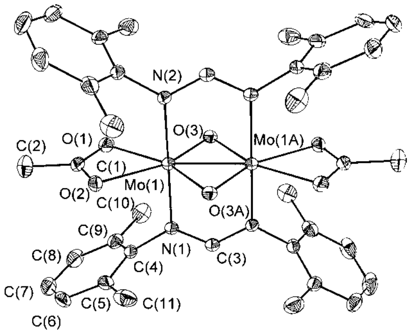


Figure 1. One of the two crystallographically independent and centrosymmetric molecules in $Mo_2(DXylF^{2,6})_2(O_2CCH_3)_2(\mu_2\text{-}O)_2$. **1a**, with displacement ellipsoids shown at the 50% probability level. The other molecule in **1a** and that in **1b** are similiar. In **2**, the two acetate anions are substituted by the chelating formamidinate anions DAniF (the anion of *N,N′*-di-*p*-anisylformamidine).

The mean of all the (μ_2-O)−Mo distances is 1.938[4] Å, but this average is far less important than the fact that there are systematic inequalities within each set of four. Instead of D_{2h} symmetry, the $Mo(\mu_2\text{-}O)_2Mo$ units have only C_{2h} symmetry, as shown in Table 1.[8] While packing distortions can occur in crystals, it seems very unlikely that the same distortion would occur four times in crystallographically independent molecules. We propose that these results, which are summarized in **III**, are the systematic result of a pseudo-Jahn−Teller effect,[9,10] as will now be explained.

We employ as the local coordinate system for each M and X atom that shown in **I**. For a rigorously rhomboidal $M_2(\mu_2\text{-}O)_2$ group (D_{2h}) the pair of p_z orbitals on the oxygen atoms can be combined into linear combinations b_{1u} ($p_1 + p_2$) and b_{3g} ($p_1 - p_2$). The d_{xz}

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* To whom correspondence should be addressed. E-mail: cotton@tamu.edu (F.A.C.). murillo@tamu.edu (C.A.M.).
† Texas A&M University.
‡ University of Costa Rica.

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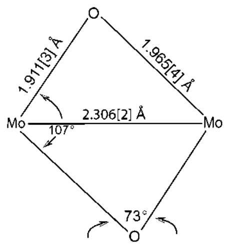
Table 1. Mo$-$(μ_2-O) Distances, Å

compd	longer	shorter	difference
1a, molecule 1	1.960(2)	1.913(2)	0.047(3)
1a, molecule 2	1.965(2)	1.907(2)	0.058(3)
1b	1.970(3)	1.913(2)	0.057(4)
2	1.996(2)	1.948(2)	0.048(3)
average	1.965[a]	1.911[a]	0.053[b]

[a] Values for **2** not included. [b] Value for **2** included.

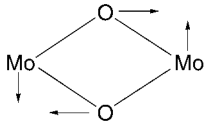
orbitals form the combinations b_{2g} ($d_1 + d_2$) and b_{1u} ($d_1 - d_2$). The latter, by itself, provides the essential part of the $d\pi-d\pi$ bond between the metal atoms, if an electron pair is available to fill it. When it is recalled that the interaction of the b_{3g} combination of the Xp_z orbitals with the b_{3g} combination of the d_{yz} orbitals leads to the inversion of the δ and δ^* orbitals,[2a,d] it is clear that we have the π-bonding orbital as the HOMO, of b_{1u} symmetry, and the δ^* (a_u) orbital consisting largely of metal d_{yz} orbitals as the LUMO.

III



A necessary condition for the occurrence of a pseudo-Jahn$-$Teller effect to carry a more symmetrical structure into a less symmetrical one (while preserving a center of inversion) is that the HOMO and the LUMO be coupled by a normal vibration.[11] This will cause a lowering of the energy of the HOMO thereby stabilizing the molecule in the structure of lower symmetry. In this case the b_{1u} HOMO and the a_u LUMO can interact via the b_{1g} in-plane vibration of the Mo(μ_2-O)Mo rhombus ($b_{1u} \times a_u \times b_{1g} = a_g$ in D_{2h}). This vibration is depicted schematically as **IV**, and it is evident that it corresponds to exactly the type of ($D_{2h} \rightarrow C_{2h}$) distortion observed in the $Mo^{IV}-(\mu_2\text{-}O)_2Mo^{IV}$ molecules reported here.

IV



It is logical to ask whether the pseudo-Jahn$-$Teller effect reported here has previously been seen. It appears that it has not, but that, of course, raises the question of why not. First, it must be recognized that the prediction that a certain stereoelectronic system is *susceptible* to a pseudo-Jahn$-$Teller effect (or even a first-order one, for that matter) is not a prediction that it *will be observed*. Observability depends on the related questions of how large the distortion is and whether experimental data are precise enough to see it.[12] In practically all previously determined ESBO structures such as those with halide bridges the M$-$M, X$-$X, and M$-$X distances are long, thus lowering the magnitude of the effect. Moreover, few ESBO structure determinations have replicated with the exactitude of those reported here.

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Supporting Information Available: Synthetic and crystallographic procedures, fully labeled drawings of each independent molecule, and mass spectroscopic data for **1a** (simulation and actual data) (PDF) and crystal data for **1a**, **1b**, and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) $Mo_2^{IV}(\eta^2\text{-}O_2CCH_3)_2(\mu_2\text{-DXylF}^{2,6})_2(\mu_2\text{-}O)_2$, **la**, was prepared by dissolving 0.080 g (0.10 mmol) of *trans*-$Mo_2(O_2CCH_3)_2(\text{DXylF}^{2,6})_2$ in 70 mL of distilled, degassed acetone and sparging with *dry* dioxygen. The oxygen was added via cannula until no further color change from the initial yellow to a deep red occurred. Upon standing, a violet solid developed. After isolation by filtration; this solid was rinsed with 3 × 10 mL of acetone until the washings became colorless. The solid was then washed with 3 × 10 mL portions each of methanol and hexanes, dried under vacuum, and then extracted with 5 × 30 mL of dichloromethane. The saturated solution was layered with hexanes and after a few days crystals suitable for X-ray structural analysis developed. ^{1}H NMR (δ, ppm in $CDCl_3$) 7.41 (s, 2 H, N$-$C*H*$-$N), 6.94 (s, 12 H, aromatic C$-$*H*), 2.21 (s, 24 H, $-CH_3$), 1.03 (s, 6 H, $-CH_3$). ESI MS (monoisotopic *m/z*): 849.2 $[M + 1]^+$. Absorption spectrum (CH_2Cl_2): λ/nm (ϵ_M) 394 (13 300). IR (KBr): 3468 (s), 2960 (s), 1946 (w), 1515 (s), 1492 (s), 1464 (s), 1303 (s), 1260 (s), 1191 (m), 819 (s). The yield was 0.051 g (61%)

(5) Crystal data for the following: (a) $Mo_2^{IV}(\eta^2\text{-}O_2CCH_3)_2(\mu_2\text{-DXylF}^{2,6})_2(\mu_2\text{-}O)_2$, **1a**, violet crystal, $C_{38}H_{44}Mo_2N_4O_6$, $M = 844.7$, triclinic, space group *P*1, $a = 10.9617(6)$ Å, $b = 11.7084(7)$ Å, $c = 15.7064(9)$ Å, $\alpha = 90.159(1)°$, $\beta = 109.117(1)°$ $\gamma = 98.745(1)°$, $V = 1878.8(2)$ Å^3, Z = 2, $D_c = 1.495$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) 0.717 mm^{-1}. $R1 = 0.034$, $wR2 = 0.072$ for all data. (b) $Mo_2^{IV}(\eta^2\text{-}O_2CCH_3)_2(\mu_2\text{-DXylF}^{2,6})_2(\mu_2\text{-}O)_2 \cdot 1.93CHCl_3$, **1b**, violet crystal, $C_{39.93}H_{45.93}Cl_{5.79}Mo_2N_4O_6$, $M = 1075.24$, monoclinic, space group *C*2/c, $a = 16.823(l)$ Å, $b = 14.517(l)$ Å, $c = 20.321(2)$ Å, $\beta = 110.245(l)°$, $V = 4656.2(7)$ Å^3, Z = 4, $D_c = 1.534$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) 0.918 mm^{-1}, $R1 = 0.062$, $wR2 = 0.127$ for all data.

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(7) We have also prepared and obtained the structure of **2**, an analogous molecule in which there are μ_2-DAniF (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) ligands and η^2-DAniF ligands (instead of acetate ions) in the central plane. Here, because of the stronger bonding of the latter ligands, the Mo═Mo bond length increases by 0.04 Å to 2.345(5) Å. In this centrosymmetric molecule the Mo$-$(μ_2-O) distances are 1.996(2) and 1.948(2) Å, the difference being 0.048(3) Å.

(8) Here we have also included data for $Mo_2^{IV}(\eta^2\text{-DAniF})_2(\mu_2\text{-DAniF})_2(\mu_2\text{-}O)_2 \cdot 4CH_2Cl_2$, **2**. Compound **2** was prepared by oxidation of $Mo_2(\text{DAniF})_4$ and crystallized analogously to **1a**. The core is similar to that in **1**, but the chelating acetate groups have been substituted by formamidinate ligands. Crystal data are the following: black crystal, $C_{62}H_{64}Cl_4Mo_2N_8O_{10}$, $M = 1414.89$, monoclinic, space group $P2_1/n$, $a = 13.208(7)$ Å, $b = 10.3291(5)$ Å, $c = 22.958(1)$ Å, $\gamma = 92.136(1)°$, $V = 3147.1(3)$ Å^3, $Z = 2$, $D_c = 1.493$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo Kα) 0.632 mm^{-1}, $R1 = 0.062$, $wR2 = 0.126$ for all data.

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(10) Most of the Jahn$-$Teller effects discussed in ref 9 are centered at a single metal atom, but there is a precedent for a pseudo-Jahn$-$Teller effect in a metal atom cluster compound, namely, $W_4(OC_2H_5)_{16}$. See: Cotton, F. A.; Fang, A. *J. Am. Chem. Soc.* **1982**, *104*, 113.

(11) In principle, coupling of the HOMO with any higher empty orbital of approximate symmetry can cause a distortion. However, because of an inverse dependence on the square of the energy difference, the LUMO is by far the most important.

(12) The difficulty in observing expected Jahn$-$Teller distortions has been encountered earlier. An example is the series of face-sharing bioctahedral anions of the type $W_2X_9^{3-}$. These typically have nondistorted D_{3h} symmetry. Only once a slight canting of two planes that lowered the symmetry to C_{2v} was measured in the $W_2Br_9^{3-}$ anion. See: Templeton, J. L.; Jacobson, R. A.; McCarley, R. E. *Inorg. Chem.* **1977**, *16*, 3320.

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