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How to Make a Major Shift in a Redox Potential: Ligand Control of the Oxidation State of Dimolybdenum Units

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A compound reported earlier (*Polyhedron* **1989**, *8*, 2339) as $(Bu^n_4N)_2H_2\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}$ has been reexamined. We find that the hydrogen atoms in this formula are not present. Therefore, the complex must be considered as having a central triply bonded Mo_2^{6+} unit, instead of a quadruply bonded Mo_2^{4+} unit. Our conclusion is based on a variety of experimental evidence, including X-ray crystal structures of four crystal forms, as well as the neutron crystal structure of one. This explains the relatively long Mo–Mo bond lengths found in the range 2.1874(7)–2.2225(7) Å and the absence of a $\delta \rightarrow \delta^*$ transition in the visible spectrum. From electrochemistry we also find that the diphosphonate ligand has such an exceptional ability to stabilize higher oxidation states that even common solvents such as CH_2Cl_2 and C_2H_5OH readily oxidize the Mo_2^{4+} unit that is introduced from the $Mo_2(O_2CCH_3)_4$ or $[Mo_2(O_2CCH_3)_2(NCCH_3)_6](BF_4)_2$ employed in the preparation. The only chemically reversible wave at $E_{1/2} = -1.54$ V vs Ag/AgCl corresponds to the reduction process $Mo_2^{6+} \rightarrow Mo_2^{5+}$.

Introduction

Over a decade ago a compound was reported[1] to which an Mo_2^{4+} core was assigned. On this basis, it would have to contain a quadruple bond. However, the reported Mo−Mo bond length of 2.186(2) Å was described by the authors themselves as “slightly longer than any other Mo−Mo quadruple bond spanned by four bridging ligands”. Today, with over 470 structures of compounds having (or believed to have) quadruple bonds known,[2] this reservation is even more justifiable, given the fact that the bridging ligands are of the 3-atom type that do not impose any twist on the Mo_2X_8 core. Thus, on the basis that in any group of data, the genuineness of one point that is a distinct outlier should always be suspect, reexamination of this compound seemed worthwhile. Furthermore, recent preparation of authentically oxidized species[2,3] $Mo_2(carboxylate)_4^+$ and $Mo_2(hpp)_4^{+,2+}$ (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) has revealed that there is a smooth increase in the Mo−Mo distance as the bond order decreases from 4 to 3.5 to 3, with the metal−metal separation varying from 2.142(2) to 2.1722(9) Å for the $Mo_2(hpp)_4^{2+}$ units.

Moreover, the very formulation of the compound, $(Bu^n_4N)_2H_2\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}$, is also disquieting. The presence of the two hydrogen atoms is necessary to make the Mo_2 unit Mo_2^{4+} rather than Mo_2^{6+}, but where are these two hydrogen atoms located? The reported X-ray structure gave no hint and the point was not discussed. On the other hand, it was said that the ^1H NMR spectrum “revealed the presence of two protons (δ 2.79 in d_6-acetone)”. It should finally be noted that the compound in question was prepared by what appeared to be a simple metathesis from $Mo_2(O_2CCH_3)_4$, consistent with there being no oxidation. How then could oxidation have occurred? We have reinvestigated this chemistry and resolved all these, and other inconsistencies.

Experimental Section

Materials. All the solvents used were dried and distilled under N_2 by following standard procedures. All the chemicals were used

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Table 1. X-ray Crystallographic Data for **1**

	1a	**1b**	**1c** (=**1**·2CH$_2$Cl$_2$)	**1d** (=**1**·3.43THF)
empirical formula	$C_{64}H_{92}Mo_4N_2O_{16}P_4$	$C_{64}H_{92}Mo_4N_2O_{16}P_4$	$C_{66}H_{96}Cl_4Mo_4N_2O_{16}P_4$	$C_{77.72}H_{119.44}Mo_4N_2O_{19.43}P_4$
fw	1653.04	1653.04	1822.89	1900.35
space group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No.14)
a, Å	12.9530(8)	16.865(1)	12.181(1)	14.214(1)
b, Å	15.785(1)	20.861(1)	12.332(1)	14.871(1)
c, Å	18.086(1)	20.882(1)	14.399(1)	22.103(2)
α, deg	90	90	86.699(2)	90
β, deg	98.782(1)	90	72.836(2)	92.879(1)
γ, deg	90	90	81.031(2)	90
V, Å^3	3654.6(4)	7346.7(9)	2041.3(3)	4666(2)
Z	2	4	1	2
T, K	213	213	213	213
λ, Å	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g/cm^3	1.502	1.495	1.483	1.353
μ, mm^{-1}	0.820	0.816	0.869	0.655
R1^a (wR2^b)	0.033 (0.062)	0.062 (0.13)	0.087 (0.246)	0.079 (0.167)

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

as purchased; *cis*-tetracarbonylbis(piperidine)molybdenum[4] and *cis*-diacetatohexaacetonitriledimolybdenum tetrafluoroborate[5] were prepared according to literature methods.

Physical Measurements. The infrared spectrum was recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Varian Unity 300 NMR spectrometer; for ^{1}H NMR, chemical shifts were referenced to TMS ($\delta = 0.00$ ppm) or the signals of the deuterium solvents; for ^{31}P NMR, chemical shifts were referenced to 85% H_3PO_4. The electronic spectrum of an acetonitrile solution of the complex (0.05 mM) was measured on a Cary 17 spectrophotometer. The cyclic voltammogram of the complex (1.0 mM in THF) was recorded on a BAS 100 electrochemical analyzer with $Bu^n_4NPF_6$ (0.1 M) electrolyte, Pt working and auxiliary electrodes, a Ag/AgCl reference electrode, and a scan rate of 100 mV/s.

X-ray Structure Determinations. Suitable single crystals were mounted on the tips of quartz fibers and then attached to a goniometer head. X-ray diffraction data were collected on a Bruker-SMART 1000 CCD area detector system at 213 K. All of the structures were determined by direct methods and refined with SHELXS[6] and SHELXL-97[7] software programs, respectively. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were added in the calculated positions and refined isotropically. A summary of crystallographic data for the X-ray structures is given in Table 1.

Neutron Structure Determination. Neutron diffraction data were collected from a single crystal of **1a** at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. Data collection and analysis were performed according to published procedures.[8-10] The sample temperature was controlled at 20 K by a Displex closed-cycle helium refrigerator (Air Products and Chemicals, Inc., Model CS-202). An autoindexing algorithm[11] was used to obtain an initial orientation matrix from the peaks in one histogram. For intensity data collection, a total of 32 histograms were measured—each with a different diffractometer χ and ϕ angle—in order to cover a quadrant of reciprocal space. The counting time for each histogram was 6 h and a total of 192 h (8 d) were used for data collection. Bragg peaks were integrated in three dimensions about their predicted locations and were corrected for the incident neutron spectrum and the detector efficiency. Lorentz and wavelength-dependent spherical absorption corrections were applied but symmetry-related reflections were not averaged (because of the wavelength dependence of extinction). Non-hydrogen atomic coordinates from the X-ray analysis were used as the starting solution for the neutron structure. The GSAS software package[12] was used for structural analysis. The refinement was based on *F* using 5261 reflections with $|F_o| > 2\sigma(F_o)$ and a minimum *d*-spacing of 0.60 Å. Weights were assigned as $w(F_o) = [2F_o/(\sigma(F_o^2) + (0.002F_o^2)^2)]^2$, where $\sigma(F_o^2)$ is the variance based on counting statistics. Non-hydrogen atoms were refined isotropically. All hydrogen atoms were refined with anisotropic atomic displacement parameters at the final stage. A summary of parameters related to the neutron diffraction analysis is presented in Table 2.

Table 2. Neutron Crystal Data and Structure Refinement Parameters for **1a**

empirical formula	$C_{64}H_{92}Mo_4N_2O_{16}P_4$
fw	1653.04
space group	$P2_1/n$
a, Å	12.952(2)
b, Å	15.706(2)
c, Å	17.948(3)
α, deg	90
β, deg	98.78(1)
γ, deg	90
V, Å^3	3608.3(9)
Z	2
T, K	20.0(1)
d_{calcd}, g/cm^3	1.522
size, mm^3	1.7 × 1.4 ×1.2
radiation	neutrons
data collection technique	time-of-flight Laue
$\mu(\lambda)$, cm^{-1}	$1.306 + 0.885\,\lambda$
R(*F*)^a	0.109
Rw(*F*)^b	0.070
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.240, −0.257

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $Rw(F) = \{\Sigma[w(F_o - F_c)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

Preparation of *cis*-(CO)$_4$Mo(PhPCl$_2$)$_2$. The ligand precursor was prepared by modifying a published procedure[4] as follows: To

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(11) Jacobson, R. A. *J. Appl. Crystallogr*. **1986**, *19*, 283.

(12) Larson, A. C.; Von Dreele R. B. *GSAS General Structural Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 2000.

a suspension of *cis*-tetracarbonylbis(piperidine)molybdenum (1.52 g, 4.02 mmol) in 20 mL of CH_2Cl_2 was added dropwise dichlorophenylphosphine (1.63 g, 9.11 mmol) with vigorous stirring. A yellow solution developed as the yellow solid of the starting material disappeared. The solution was then heated to reflux for about 15 min until the color turned to orange red. After removal of the solvent under reduced pressure, 5 mL of tetrahydrofuran was added by syringe. The mixture was stirred for 10 min, then filtered to remove a white crystalline solid. Removal of the solvent from the filtrate under vacuum afforded an oily, orange, crude product, *cis*-$(CO)_4Mo(PhPCl_2)_2$, which was used for the next reaction step without further purification.

Preparation of $(Bu^n{}_4N)H_3[(CO)_4Mo(PhPO_2)_2]$. The ligand was prepared by modifying a published procedure[13] as follows: The material prepared above was dissolved in 15 mL of $CHCl_3$. With vigorous stirring, an aqueous solution of NaOH (1.50 g, 37.6 mmol, in 50 mL of H_2O) was added dropwise over a period of 1 h. The layers were separated. After the acidity of the aqueous solution was adjusted to a pH of 8, the mixture was filtered; the pH was readjusted to 7. Again with vigorous stirring, tetrabutylammonium bromide (12.0 g, 37.2 mmol) was added in small portions. A white precipitate formed immediately. The solid was separated by filtration, washed with water and ether, and then dried under vacuum. Yield: 1.25 g (42.6%). ^1H NMR δ (ppm in acetone-d_6): 7.80 (m, 4H, phenyl), 7.32 (t, 6H, phenyl), 3.48 (t, 8H, $-CH_2-$), 1.85 (p, 8H, $-CH_2-$), 1.47 (h, 8H, $-CH_2-$), 1.01 (t, 12H, $-CH_3$).

Preparation of $(Bu^n{}_4N)_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$, 1. Method A. Purple $[Mo_2(O_2CCH_3)_2(NCCH_3)_6](BF_4)_2$ (0.146 g, 0.200 mmol) was mixed with colorless $(Bu^n{}_4N)H_3[(CO)_4Mo(PhPO_2)_2]$ (0.312 g, 0.425 mmol) in 20 mL of acetonitrile and the mixture was stirred for 30 min. The resulting dark brown solution was transferred to another flask containing 0.450 g of anhydrous K_2CO_3. After 4 h the color of the solution had turned to brown. The solvent was then removed under vacuum, giving a red-brown residue. The residue was extracted with 15 mL of dichloromethane. After filtration, the solution was layered with hexanes, affording 0.178 g (53.8%, based on the ligand) of red-brown crystals after 4 days.

Method B. To a mixture of $(Bu^n{}_4N)H_3[(CO)_4Mo(PhPO_2)_2]$ (0.240 g, 0.327 mmol), $Mo_2(O_2CCH_3)_4$ (0.065 g, 0.152 mmol), and $Bu^n{}_4NBH_4$ (0.620 g, 2.41 mmol) was added 15 mL of tetrahydrofuran. The resulting solution was stirred overnight. Addition of 30 mL of toluene to the reaction solution produced a brown precipitate that was washed with 5 mL of hexanes. After addition of 5 mL of ethanol, the solid dissolved and then a brick-red crystalline solid formed very quickly. The product was separated by filtration, washed with a small amount of ethanol, and dried under vacuum, yielding 0.120 g (47.8%).

Spectroscopic Characterization of 1. IR (cm^{-1}, KBr): 3055 (m, sharp, H−C stretching, phenyl), 2968 (H−C stretching, methylene), 2869.5 (H−C stretching, methyl), 2000, 1881, 1846 (s, broad, C−O stretching, carbonyl). ^1H NMR δ (ppm in acetone-d_6): 8.12 (d, 8H, phenyl), 7.35 (t, 12H, phenyl), 3.34 (t, 16H, $-CH_2-$), 1.73 (p, 16H, $-CH_2-$), 1.35 (h, 16H, $-CH_2-$), 0.94 (t, 24H, $-CH_3$). ^1H NMR δ (ppm in CD_2Cl_2): 8.06 (d, 8H, phenyl), 7.43 (t, 12H, phenyl), 2.81 (t, 16H, $-CH_2-$), 1.38 (p, 16H, $-CH_2-$), 1.21 (h, 16H, $-CH_2-$), 0.90(t, 24H, $-CH_3$). ^{31}P NMR δ (ppm in acetone-d_6): 219.3 (s). ^{31}P NMR δ (ppm in CD_2Cl_2): 222.73 (s). UV−visible spectrum λ_{max} (nm, in acetonitrile): 373 ($\epsilon = 4.8 \times 10^3$ M^{-1} cm^{-1}).

Growth of Crystals for Structural Analysis. Three crystal forms, **1a**, **1b**, and **1c**, were obtained from the same Schlenk tube by layering a CH_2Cl_2 solution of **1** with hexanes. These were separated manually. The crystals were mainly **1a** (red brown), some **1b** (brown), and a few **1c** (pale brown). Orange-red crystals of **1d** were obtained by slow diffusion of hexanes into a THF solution of **1**. Crystals of **1a** and **1b** contained unsolvated molecules while **1c** contained two interstitial CH_2Cl_2 molecules per formula weight (**1c** ≈ **1**·$2CH_2Cl_2$). **1d** crystallized with 3.43 THF molecules per formula weight (**1d** ≈ **1**·3.43THF); two of these are weakly coordinated in axial positions and the remaining 1.43 are disordered and occupying crystal interstices. Large crystals of **1a**, used for neutron diffraction, crystallized after slow diffusion of ethyl ether into an CH_3CH_2OH/CH_3CN (5:1, v:v) solution of **1**.

Results and Discussion

As noted in the Introduction, the Mo−Mo distance of 2.186(2) Å in the anion of **1** was recognized from the beginning to be surprisingly long for a quadruple bond.[1] A recent survey of all $Mo\overset{4}{-}Mo$ bond lengths reinforced that perception,[2] especially since there was bridging by three-atom groups, which usually tends to shorten rather than lengthen metal-to-metal bonds. In view of the fact that the reported Mo−Mo distance of 2.186(2) Å would not be surprising for a triple bond,[3] we set out to see whether that might be the case. To accomplish this, there were three major tasks:

(1) To show that there is no structural basis for postulating the presence of two hydrogen atoms per formula unit. To prove a negative is always difficult, though not always impossible. One approach is to make the positive so difficult to accept that it is, effectively, disproved.

(2) To examine other types of physical data to show that they are consistent with the presence of a triple bond, but not with the presence of a quadruple bond.

(3) To explain how the postulated quadruple bond became a triple bond.

1. Structural Results. The compound originally reported has been prepared in the same crystalline form (**1b**) and in two others, **1a** and **1c**. Also we have prepared a fourth crystalline variant, **1d**, in which there are two axially coordinated THF molecules. All four structures have been solved and refined with X-ray diffraction data, the structures being shown in Figures 1, 2, 3, and 4, respectively, and the structure of **1a** has also been refined with neutron diffraction data (Figure 5). The salient feature of all these results is that all of them are very similar to that reported earlier. For example, bond distances and angles in the forms **1a**, **1b**, and **1c** are the same within three standard deviations. For **1d** there are differences due to the presence of axial THF molecules. This strongly supports that idea that we are dealing with the same compound as that originally reported.

Since hydrogen atoms cannot be reliably determined from X-ray diffraction data we turned to neutron diffraction, checking very carefully for possible signs of such atoms. Special attention was given to the region around the oxygen atoms of the *cis*-$Mo(CO)_4(PhPO_2)_2{}^{n-}$ entity. Chemically this would be the most likely place for them to be. Due to the negative neutron scattering length of ^1H, hydrogen atoms appear as negative troughs in neutron Fourier maps. For **1a**, we found that the largest negative residual in the difference

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[13] Wong, E. H.; Turnbull, M. M.; Hutchinson, K. D.; Valdez, C.; Gabe, E. J.; Lee, F. L.; Le Page, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8422.

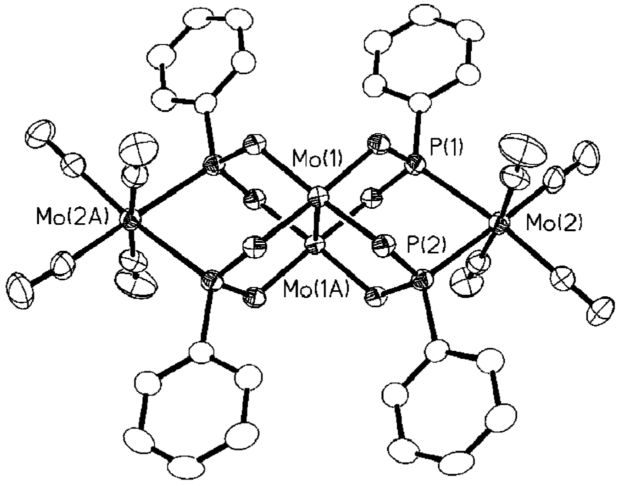

Figure 1. The dianion in $(Bu^n{}_4N)_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$, **1a**, drawn with displacement ellipsoids at the 50% probability level. There is an inversion center at the midpoint of the triply bonded Mo_2 unit. The Mo(1)−Mo(1A) distance is 2.1902(3) Å and the four independent Mo−$O_{phosphonate}$ distances are 1.993(1), 1.998(1), 2.002(1), and 2.014(1) Å.

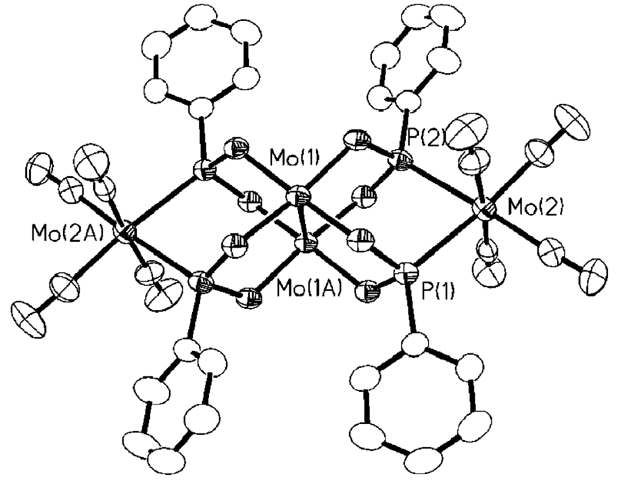

Figure 2. The dianion $\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}^{2-}$ in **1b**. An inversion center is located at the midpoint of the triply bonded dimetal unit. Displacement ellipsoids are shown at the 50% probability level. The Mo(1)−Mo(1A) distance is 2.1874(7) Å.

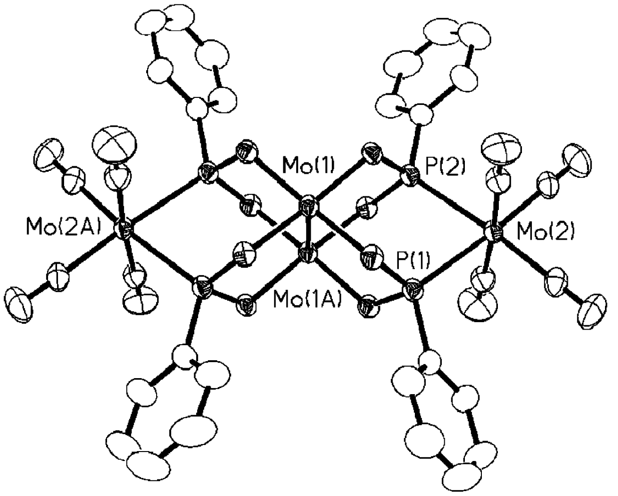

Figure 3. The dianion $\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}^{2-}$ in $\mathbf{1}\cdot 2CH_2Cl_2$, **1c**. The two halves of the anion are related by a crystallographic inversion center. Displacement ellipsoids are drawn at the 50% probability level. The Mo(1)−Mo(1A) distance is 2.1925(6) Å.

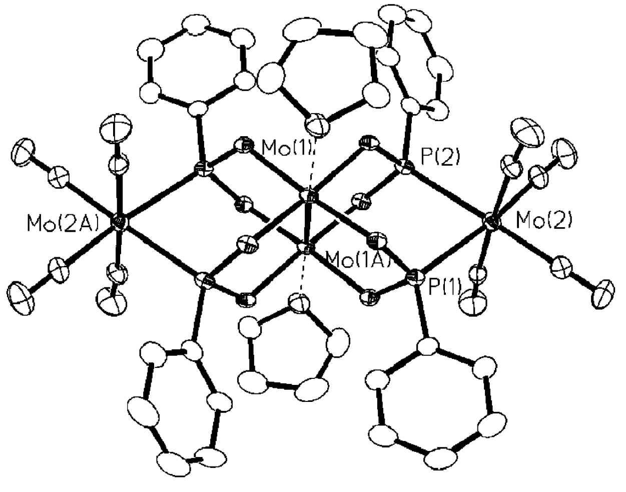

Figure 4. The dianion in $(Bu^n{}_4N)_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2\cdot 3.43THF$, **1d**. There are two weakly coordinated THF molecules occupying axial positions of the $Mo_2{}^{6+}$ unit (Mo···O(9) = 2.657 Å) which cause a small but significant elongation of the dimolybdenum triple bond (Mo(1)−Mo(1A) = 2.2225(7) Å). Displacement ellipsoids are given at the 40% probability level.

Fourier map for the neutron refinement is only ca. 20% of the height of a hydrogen atom. A plot of the Mo_2O_8 core and surroundings shown in Figure 6 clearly establishes the absence of additional peaks. Thus, there is no evidence for the two alleged hydrogen atoms. Without these two hydrogen atoms, the central Mo_2 unit must be classified as $Mo_2{}^{6+}$ and not $Mo_2{}^{4+}$.

Selected bond distances, given in Table 3, show that the Mo−Mo distances from X-ray data at 213 K for the three nonaxially ligated crystalline forms (**1a**, **1b**, and **1c**) vary within the narrow range of 2.1874(7)−2.19255(6) Å (compare to 2.186(2) Å reported earlier[1]). The distance determined from neutron data for **1a**, collected at the much lower temperature of 20 K, 2.178(8) Å, is ca. 1% shorter. For **1d** there are two axially coordinated THF molecules, and the Mo−O_{THF} distance is 2.657(3) Å. This induces a small but significant (1%) lengthening of the Mo−Mo distance to 2.2225(7) Å. Interestingly, for $[Mo_2(HPO_4)_4(H_2O)_2]^{2-}$ the Mo≡Mo distance was 2.223(2) Å and the Mo−O_{water} distances were 2.46(1) and 2.52(1) Å.[14] A comparison of the molecular dimensions of **1** with those of the quadruply bonded $K_4Mo_2(SO_4)_4\cdot 2H_2O$,[15] the monooxidized analogue $K_3Mo_2(SO_4)_4\cdot 3.5H_2O$,[15] and that of $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$ reveals an interesting pattern as shown in Table 4. Clearly, the Mo−Mo distance increases as the bond order decreases from 4 to 3.5 to 3 and the electronic configuration changes from $\sigma^2\pi^4\delta^2$ to $\sigma^2\pi^4\delta$ to $\sigma^2\pi^4$, respectively. An opposite trend is observed for the Mo−$O_{oxoanion}$ distances: these decrease as the oxidation state increases.

In summary, the values of molecular dimensions of compound **1** in all its forms appear to be consistent with the presence of a triple bond, but not a quadruple bond.

2. Other Characterization Data. We may begin with the analytical data reported not for **1b** but for the so-called

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[14] Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 3562.

[15] Cotton, F. A.; Frenz, B. A.; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391.

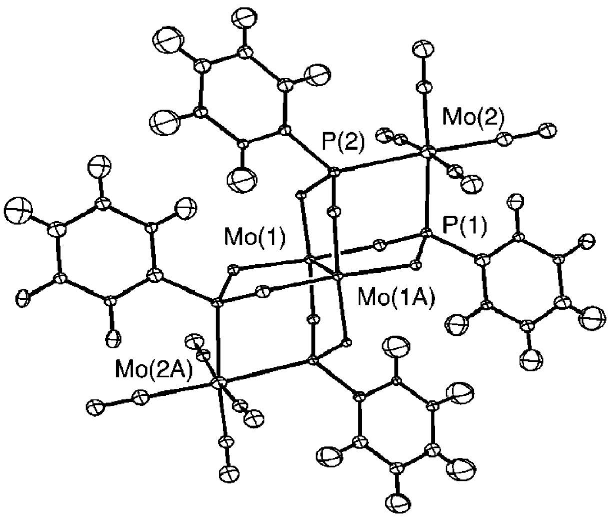

Figure 5. Perspective view of the anion in $(Bu^n{}_4N)_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$, **1a**, as determined from neutron diffraction data. Atoms are drawn at their 80% thermal probability level. The Mo(1)−Mo(1A) distance is 2.178(8) Å.

sodium analogue $(Bu^n{}_4N)_2Na_2\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}$.[1] To the level of the accuracy of the experimental data, it is impossible to distinguish from the C, H, N elemental analyses between this formula, the same formula with H_2 in place of Na_2, or the same formula with neither H_2 nor Na_2.

(a) ^{1}H NMR Spectrum. The presence of H_2 in the formula was reported to be confirmed by a peak at δ 2.79 ppm in acetone-d_6 corresponding to two protons. We have been unable to reproduce the result, but we have noticed that there is a signal at 2.85 ppm when water is present in the deuterated acetone. The rest of our ^{1}H NMR spectrum in acetone is completely consistent with that reported for the supposedly $(Bu^n{}_4N)_2H_2\{Mo_2[Mo(CO)_4(PhPO_2)_2]_2\}$ formula. The spectrum is equally consistent when run in CD_2Cl_2, in which case a signal due to any water present appears at ca. 1.54 ppm. When the two deuterated solvents are not properly dried, the amount of water present varies from run to run, depending on the batch used. In the original report, water may well have been, by chance, close to the concentration required to suggest that two additional hydrogen atoms were present in the compound.

(b) ^{31}P NMR Spectrum. We have confirmed the original report that the compound displays only a single ^{31}P resonance. If two additional hydrogen atoms were present, the only reasonable place for them to be would be on two of the $PhPO_2$ oxygen atoms. However, this would mean that not all phosphorus atoms could be equivalent. To rule out the possibility that these protons might have been removed and solvated by acetone molecules, we also recorded the ^{31}P spectrum in CH_2Cl_2, but here again, only one ^{31}P signal was seen.

(c) Electronic Absorption Spectrum. The spectrum is shown in Figure 7. A characteristic $\delta \rightarrow \delta^*$ transition that is diagnostic for the $Mo_2{}^{4+}$ core might be expected to occur approximately where it does in $[Mo_2(SO_4)_4]^{4-}$, which is to say around 520 nm.[16] Clearly, there is no absorption at or near this energy. There is, however, a well-defined band at 380 nm (ca. 26 000 cm^{-1}, which is much too high to be a $\delta \rightarrow \delta^*$ transition) that can be assigned to a $\pi \rightarrow \delta$ transition according to the analysis of the spectrum of $[Mo_2(HPO_4)_4]^{2-}$ given by Hopkins et al.[17] Thus, the electronic spectrum furnishes evidence that the δ orbital is empty.

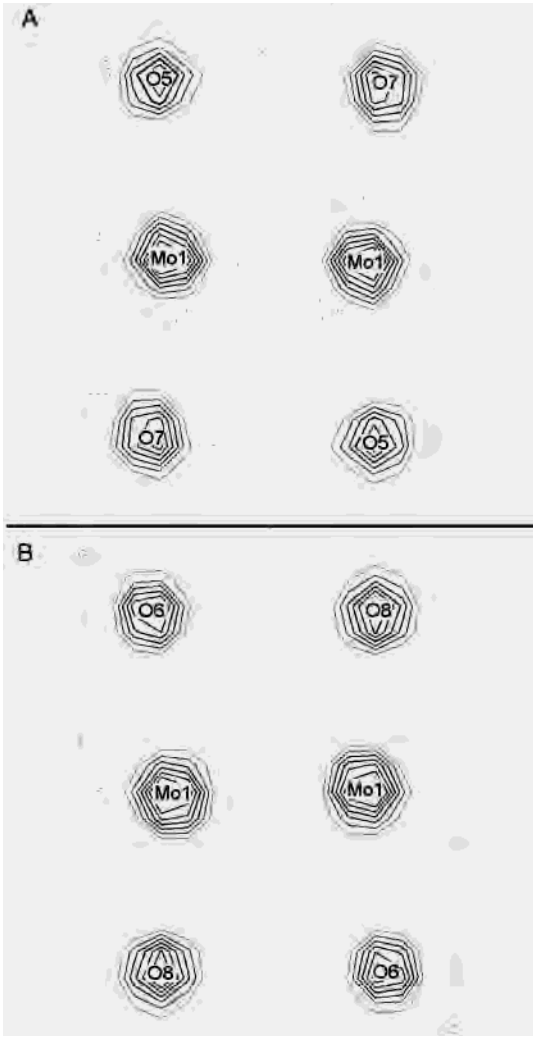

Figure 6. Plots of neutron Fourier maps of the two mutually perpendicular planes defined by the two metal atoms and the oxygen atoms of trans phosphonate groups showing the absence of H atoms in the dianion of **1**. For contrast, see the plot of one of the PC_6H_5 groups, given in Supporting Information, which clearly shows each of the 5 hydrogen atoms of the phenyl group.

Table 3. Selected Bond Lengths (Å) for **1**[a]

	neutron[b]	X-ray[c]			
	1a	**1a**	**1b**	**1c**	**1d**
Mo≡Mo	2.178(8)	2.1902(3)	2.1874(7)	2.1925(6)	2.2225(7)
$Mo-O_{phosphonate}$	2.002[1]	2.002[8]	2.004[3]	2.006[3]	2.011[3]
$Mo-O_{THF}$					2.657(3)
Mo^0-C^d	2.017[2]	2.016[6]	2.015[5]	2.016[5]	2.013[6]
Mo^0-P	2.515[6]	2.508[8]	2.515[1]	2.488[1]	2.524[2]

[a] Numbers in square brackets are the standard deviations for average distances. [b] 20 K. [c] 213 K. [d] Mo^0 represents the molybdenum atom in the phosphonate ligand.

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Table 4. A Comparison of the Molecular Dimensions of Ionic Mo_2^{n+} Species Bound to Oxoanions[a,b]

compd	Mo−Mo	$Mo-O_{oxoanion}$	$Mo\cdots L_{ax}$	Mo−Mo bond order	ref
$K_4Mo_2(SO_4)_4\cdot 2H_2O$	2.111(1)	2.139[4]	2.591(4)	4	15
$K_3Mo_2(SO_4)_4\cdot 3.5H_2O$[c]	2.167(1)	2.067[3]	2.550(4)	3.5	15
	2.162(1)	2.062[3]	2.545(3)	3.5	15
$Cs_2Mo_2(HPO_4)_4\cdot 2H_2O$	2.223(2)	2.013[10]	2.52(1), 2.46(1)	3.0	14
$(pyH)_3[Mo_2(HPO_4)_4Cl]$	2.232(1)	2.003[4]	2.910(1)	3.0	14
1a	2.1902(3)	2.002[8]			this work
1b	2.1874(7)	2.004[3]			this work
1c	2.1925(6)	2.006[3]			this work
1d	2.2225(7)	2.011[3]	2.657(3)		this work

[a] Distances in Å. [b] Numbers in square brackets are the standard deviations for average distances. [c] Two independent molecules.

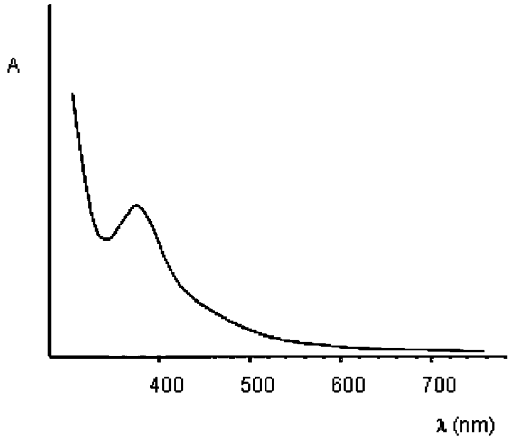

Figure 7. Electronic spectrum of **1** in acetonitrile showing the absence of the $\delta \rightarrow \delta^*$ transition, expected for a quadruply bonded Mo_2^{4+} unit but not expected for a triply bonded Mo_2^{4+} species, in the region around 520 nm. The band at 380 nm corresponds to a $\pi \rightarrow \delta$ transition (see text).

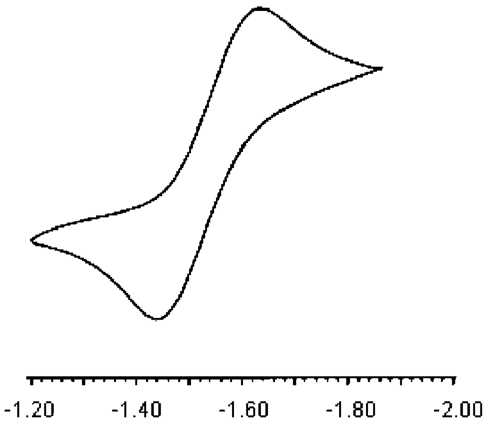

Figure 8. The cyclovoltammogram of **1** in THF, with the potential in volts, referenced to Ag/AgCl, and showing the only chemically reversible wave at $E_{1/2} = -1.54$ V corresponding to the Mo_2^{6+}/Mo_2^{5+} couple. Under these conditions, the $E_{1/2}$ for the ferrocene/ferrocenium couple appeared at 0.620 V.

3. How Is the Triple Bond Formed? If it is now accepted that there is overwhelming experimental evidence in favor of **1** containing an Mo−Mo triple bond not a quadruple bond, then the conversion of the $\text{Mo}\overset{4}{-}\text{Mo}$ in the starting material, e.g., $Mo_2(O_2CH_3)_4$, to an $\text{Mo}\equiv\text{Mo}$ bond in the anion of **1** must be accounted for to close the story. At no point in the preparation of the various crystalline forms of **1** was any reagent present that would be ordinarily identified as an oxidant. Also, all possible precautions were taken to exclude oxygen.

The answer to the question is that the necessary oxidants are the solvents, CH_2Cl_2 or C_2H_5OH. The ability of all chloroaliphatic compounds to act as oxidizing agents is well-known.[3,18] Ethanol can react acidicly to generate hydrogen, as it will do with any sufficiently electropositive coreactant, e.g., Na. An electrochemical study of the anion of **1** in tetrahydrofuran (Figure 8) showed that there is only one chemically reversible one-electron wave at the very negative potential of −1.54 V vs Ag/AgCl that corresponds to a reduction process that has been assigned as $Mo_2^{6+} \rightarrow Mo_2^{5+}$. Clearly the oxidation to Mo_2^{6+} is highly favorable. Furthermore, at such a potential CH_2Cl_2 and C_2H_5OH are not stable against reduction. Consequently, the oxidation of the Mo_2^{4+} units in the starting materials takes place. Thus, from these solvents it must be impossible to isolate the reported 4− anion (containing Mo_2^{4+}), but only the 2− anion (containing Mo_2^{6+}). It appears that the key feature for the stabilization of the highly oxidized Mo_2^{6+} unit by *cis*-$[Mo_2(CO)_4(PhPO_2)_2]^{4-}$ anions is the large amount of negative charge, 8−, distributed over the 8 oxygen atoms of the 2 anions.

Final Observations

This work has made it evident that the quadridentate anion *cis*-$[Mo(CO)_4(PhPO_2)_2]^{4-}$ has a great capacity to stabilize the Mo_2^{6+} core relative to Mo_2^{4+}. This remarkable property (shared, no doubt, by the $[Cr(CO)_4(PhPO_2)_2]^{4-}$ and $[W(CO)_4(PhPO_2)_2]^{4-}$ ions) was not anticipated. It is very interesting that the only other ligand to share this property, as recently reported,[3,19] is the hpp^- ligand. The two are shown side by side for comparison as **I** and **II**, which raises the question: what do they have in common? We propose that they have nothing in common and achieve their effect by different means.

The guanidinate anion in hpp^- is a very strong base, both in the σ sense and in the π sense.[20] It therefore stabilizes the more highly charged Mo_2^{6+} core by transferring negative charge to it. The tetranegative anion **I** stabilizes the more highly charged Mo_2^{6+} by offsetting positive charge electrostatically with its own large negative charge.

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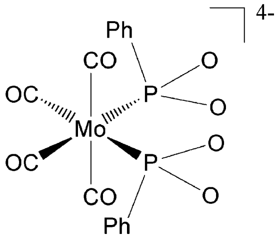
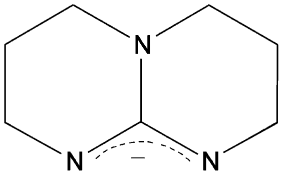


I

cis-$[Mo(CO)_4(PhPO_2)_2]^{4-}$



II

The anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate (hpp−)

This is not the first example of these alternative ways of stabilizing a highly charged central ion. For the Mo_2^{6+} ion itself there are other examples. The hpp^- anion, **II**, stabilizes the Mo_2^{6+} core in the paddlewheel complexes $Mo_2(hpp)_4XY$ (X = Y = Cl; X = Cl, Y = BF_4; X = Y = BF_4) by the π/σ basicity effect[3,19] while the HPO_4^{2-} ion allows the formation of the stable $[Mo_2(HPO_4)_4(H_2O)_2]^{4-,3-,2-}$ ions.[21] However, it should be mentioned that there is an important difference between the present phosphonate ligand and the phosphate anions, for which reversible waves were reported at −0.67 and 0.25 V vs SCE.[21] The potentials for the latter were measured in phosphoric acid where protonation must occur, thereby lessening the capacity of the phosphate ligand to stabilize the higher oxidation state. The $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ ion is another example[22] of the ability of a highly charged set of bridging ligands to stabilize the core Ru_2^{6+}, which is usually unstable relative to the Ru_2^{5+} and Ru_2^{4+} cores. This same dichotomy can sometimes be found in mononuclear chemistry, where, for example, formally hexavalent tungsten can be stabilized by six electron-donating methyl groups in $W(CH_3)_6$ or six electron-withdrawing fluorine atoms in WF_6. Further discussion will be provided in an upcoming publication.[3]

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Supporting Information Available: X-ray crystallographic files in CIF format for four crystalline forms **1a**, **1b**, **1c**, and **1d** and a CIF file with neutron diffraction data for **1a** and a PDF file of the plot of the neutron Fourier map of one of the PC_6H_5 groups showing each of the 5 hydrogen atoms of the phenyl group. This material is available free of charge via the Internet at http://pubs.acs.org.

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