

# Tetranuclear Complexes Containing Quadruply Bonded Dimolybdenum Units Joined by $\mu$ -Hydride Ions

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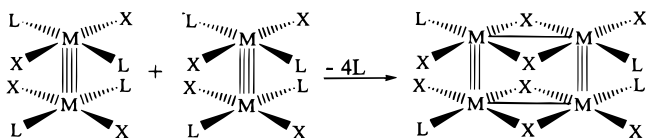
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**Abstract:** Two tetranuclear complexes of the type  $[\text{Mo}_2(\text{DArF})_3]_2(\mu\text{-H})_2$ ,  $\text{DArF} = N,N'$ -diarylformamidinate,  $\text{Ar} = p$ -tolyl (**1**) and  $p$ -anisyl (**2**), have been prepared by reaction of  $\text{Mo}_2(\text{DArF})_3\text{Cl}_2$  and  $\text{NaHBET}_3$ . The cores are similar and show two quadruply bonded dimolybdenum units joined by two hydrogen atoms. These are the first structurally characterized tetranuclear molecules with localized quadruple bonds and also the first molecules with two independent  $\text{M}-(\mu\text{-H})-\text{M}$  units, in which each metal atom is also bonded to another M atom. It is remarkable that in each case the compound resists hydrolysis by water but will react with HCl. The  $\delta \rightarrow \delta^*$  transitions, which are normally the lowest energy bands in the visible region of the electronic absorption spectra, appear as shoulders at 449 and 444 nm for **1** and **2**. However, each compound also shows two more transitions at lower energy (ca. 505 and 728 nm). These bands have been assigned to transitions involving the three center–two electron  $\text{Mo}-\text{H}-\text{Mo}$  bridges.

## Introduction

A few tetranuclear complexes with a rectangular  $\text{M}_4$  core are known, e.g.,  $\text{M}_4\text{X}_8\text{L}_4$  ( $\text{M} = \text{Mo}^{\text{II}}$  or a mixture of  $\text{Mo}^{\text{II}}$  and  $\text{W}^{\text{II}}$ ,  $\text{X} =$  halide ion, and  $\text{L} =$  neutral ligand, such as phosphine) and  $[\text{Re}^{\text{III}}_4\text{Cl}_8(\mu\text{-X})_2(\mu\text{-O})_2]^{2-3}$  ( $\text{X} = \text{Cl}$  or  $\text{OMe}$ ). Such metallocyclodiyne-type complexes are commonly obtained by displacement of ligands from multiply metal–metal bonded dinuclear compounds with concomitant coupling of such units as shown in Scheme 1:

Scheme 1



In this process, two quadruple bonds are rearranged to two triple and two single bonds, two groups bridge across the singly bonded units, and the oxidation number of the metal atoms remains unchanged.

Similarly, triply bonded  $\text{M}_2(\text{alkoxide})_6$  ( $\text{M} = \text{W}^{\text{III}}$ ) units can couple to give tetranuclear complexes containing pairs of alternating  $\text{W}=\text{W}$  and  $\text{W}-\text{W}$  bonds. There are also a few cases where the tetranuclear core retains two triple bonds between

two pairs of metal atoms and no metal–metal bonds between those units; an example is  $\text{Mo}_4(\mu\text{-OMe})_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_8$ .<sup>4</sup>

Recently we reported the synthesis and characterization of the dinuclear compound  $\text{Mo}_2(\text{DTolF})_3\text{Cl}_2$  ( $\text{DTolF} = N,N'$ -di- $p$ -tolylformamidinate) which contains three formamidinate ligands bridging an  $\text{Mo}_2^{5+}$  unit; each metal atom is also bound to a chloride ion. The dinuclear unit contains a formal bond order of 3.5.

The reductive substitution reactions of  $\text{Mo}_2(\text{DTolF})_3\text{Cl}_2$ , or its anisyl ( $\text{DAniF}$ ) analogue, with  $\text{NaHBET}_3$  produces very stable tetranuclear complexes,  $[\text{Mo}_2(\text{DTolF})_3]_2(\mu\text{-H})_2$  and  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-H})_2$ , which have an unusual structure wherein two quadruply bonded  $\text{Mo}_2(\text{DArF})_3$  units are connected to each other by two hydride ions forming a  $\text{Mo}^4-\text{Mo}-\text{H}-\text{Mo}^4-\text{Mo}-\text{H}$  ring never before observed for metal–metal bonded complexes<sup>6</sup> nor for any of the multitude of transition metal hydride compounds which have been characterized.<sup>7</sup>

## Experimental Section

**General Considerations.** All syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under nitrogen according to conventional methods. Triethylorthoformate,  $p$ -anisidine,  $p$ -toluidine,  $\text{SiMe}_3\text{Cl}$  (1.0 M in THF), and  $\text{NaHBET}_3$  (1.0 M in THF) were purchased from Aldrich; molybdenum hexacarbonyl was from Strem. Ferrocenium chloride was prepared by bubbling  $\text{Cl}_2$  through a hexanes solution of ferrocene;

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(7) See, for example: Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, *259*, 27–50 and references therein.

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Mo<sub>2</sub>(DAniF)<sub>4</sub><sup>8</sup> and Mo<sub>2</sub>(DTolF)<sub>3</sub>Cl<sub>2</sub><sup>5</sup> were prepared according to the literature. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia; the results were satisfactory. <sup>1</sup>H NMR spectra were recorded on a XL-200E NMR spectrometer, with chemical shifts (δ) referenced to CH<sub>2</sub>Cl<sub>2</sub>. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr disks. UV-vis spectral data were obtained in degassed CH<sub>2</sub>Cl<sub>2</sub>, using a Cary 17 UV-vis spectrophotometer.

**Preparation of Mo<sub>2</sub>(DAniF)<sub>3</sub>Cl<sub>2</sub>.** The following method was modified from ref 5. To a suspension of Mo<sub>2</sub>(DAniF)<sub>4</sub> (1.21 g, 1.0 mmol) in 160 mL of THF was added a solution of Cp<sub>2</sub>FeCl (225 mg, 1.0 mmol) in 20 mL of THF with stirring, whereupon the color immediately changed from yellow to brown. After the reaction mixture was stirred for 24 h, SiMe<sub>3</sub>Cl (1.1 mmol) was added and the mixture was refluxed for 4 h. The solvent was removed, and the residue was extracted with acetone. The crude product was precipitated by addition of ether to the extracts and recrystallized from acetone to yield 815 mg (79.2%) of a dark brown crystalline material. IR (KBr, cm<sup>-1</sup>): 1608 (w), 1503 (s), 1466 (w), 1293 (m), 1249 (s), 1212 (s), 1175 (m), 1032 (m), 941 (w), 830 (m), 590 (w), 531 (w). UV-vis, λ<sub>max</sub> (nm, ε (M<sup>-1</sup> cm<sup>-1</sup>)): 276 (34 400), 455 (5880), 570 (sh).

**Preparation of [Mo<sub>2</sub>(DTolF)<sub>3</sub>]<sub>2</sub>(μ-H)<sub>2</sub> (1).** To a brown suspension of Mo<sub>2</sub>(DTolF)<sub>3</sub>Cl<sub>2</sub> (189 mg, 0.203 mmol) in 30 mL of THF was added NaHBEt<sub>3</sub> (3.0 mmol). After 12 h of stirring, the reaction mixture was warmed to 50–55 °C for 4 h. After the removal of solvent, the residue was washed with copious amounts of Et<sub>2</sub>O and redissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and then filtered. Evaporation of the solvent from the golden orange filtrate yielded 120 mg of polycrystalline material (68.5%). Small golden orange crystals of 1·C<sub>6</sub>H<sub>14</sub> were grown by diffusion of a CH<sub>2</sub>-Cl<sub>2</sub> solution layered with hexanes. <sup>1</sup>H NMR δ (ppm): 8.97 (s, 4H, -NCHN-), 8.01 (s, 2H, -NCHN-), 6.57 (d, 8H, aromatic, <sup>3</sup>J = 7.8 Hz), 6.39 (d, 16H, aromatic, <sup>3</sup>J = 8.1 Hz), 5.95 (m, 24H, aromatic), 2.09 (s, 12H, -CH<sub>3</sub>), 2.08 (s, 24H, -CH<sub>3</sub>), 1.22 (s, 2H, MoHMo). IR (KBr, cm<sup>-1</sup>): 3018 (w), 2917 (w), 2857 (w), 1685 (m), 1609 (m), 1540 (vs), 1506 (vs), 1329 (s), 1310 (s), 1207 (s), 934 (w), 920 (w), 816 (s), 803 (s), 534 (w), 506 (w), 451 (m). UV-vis, λ<sub>max</sub> (nm, ε (M<sup>-1</sup> cm<sup>-1</sup>)): 728 (300), 505 (sh), 449 (sh).

**Preparation of [Mo<sub>2</sub>(DAniF)<sub>3</sub>]<sub>2</sub>(μ-H)<sub>2</sub> (2).** It was prepared in a method similar to that of 1 using 300 mg (0.292 mmol) of Mo<sub>2</sub>(DAniF)<sub>3</sub>-Cl<sub>2</sub> in 50 mL of THF and 3.0 mmol of NaHBEt<sub>3</sub> (yield 175 mg (62.4%)). Large single crystals of 2·C<sub>6</sub>H<sub>14</sub> were grown by diffusion of hexanes into a CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR δ (ppm): 8.93 (s, 4H, -NCHN-), 7.97 (s, 2H, -NCHN-), 6.34 (d, 8H, aromatic, <sup>3</sup>J = 8.9 Hz), 6.18 (d, 16H, aromatic, <sup>3</sup>J = 9.0 Hz), 6.02 (m, 24H, aromatic), 3.60 (s, 24H, -OCH<sub>3</sub>), 3.59 (s, 12H, -OCH<sub>3</sub>), 1.17 (s, 2H, MoHMo). IR (KBr, cm<sup>-1</sup>): 1612 (w), 1546 (s), 1502 (s), 1465 (m), 1440 (m), 1323 (m), 1289 (m), 1246 (s), 1219 (s), 1173 (m), 1109 (w), 1037 (s), 935 (w), 821 (s), 789 (w), 763 (w), 645 (w), 621 (w), 589 (w), 533 (w). UV-vis, λ<sub>max</sub> (nm, ε (M<sup>-1</sup> cm<sup>-1</sup>)): 729 (390), 505 (sh), 444 (sh).

**Crystallographic Procedures.** Single-crystal X-ray work on 1·C<sub>6</sub>H<sub>14</sub> and 2·C<sub>6</sub>H<sub>14</sub> was performed on a Nonius FAST diffractometer at -60 °C utilizing the program MADNES.<sup>9</sup> In each case, a suitable crystal was mounted on the tip of a quartz fiber with a small amount of silicone grease and transferred to a goniometer head. Cell parameters were obtained from an auto-indexing routine and were refined with 178 (compound 1) or 250 (compound 2) strong reflections within a 2θ range of 18.1–41.6°. Cell dimensions and Laue symmetry for all crystals were confirmed with axial photographs. All data were corrected for Lorentz and polarization effects. Data were processed using an ellipsoid-mask algorithm (program PROCOR<sup>10</sup>), and the program SORTAV<sup>11</sup> was used to correct for absorption.

In structures 1 and 2, the positions of all non-hydrogen atoms of the metal complex were found via direct methods by way of the program

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**Table 1.** Crystal and Structure Refinement Data for Compounds 1 and 2

	1·C <sub>6</sub> H <sub>14</sub>	2·C <sub>6</sub> H <sub>14</sub>
formula	Mo <sub>4</sub> (N <sub>2</sub> C <sub>15</sub> H <sub>15</sub> ) <sub>6</sub> (H) <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub>	Mo <sub>4</sub> (N <sub>2</sub> C <sub>15</sub> H <sub>15</sub> O <sub>2</sub> ) <sub>6</sub> (H) <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub>
formula weight	1811.67	2003.69
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	16.051(3)	13.487(2)
<i>b</i> , Å	17.430(4)	13.665(2)
<i>c</i> , Å	17.284(2)	14.354(2)
α, deg	90	110.28(1)
β, deg	115.97(1)	94.90(1)
γ, deg	90	108.55(1)
<i>V</i> , Å <sup>3</sup>	4347(1)	2294.9(6)
<i>Z</i>	2	1
R1, <sup>a</sup> wR2 <sup>b</sup>	0.058, 0.131	0.045, 0.106
R1, wR2	0.086, 0.158	0.052, 0.114
goodness-of-fit <sup>c</sup>	1.079	1.118

<sup>a</sup> R1 = [Σw(F<sub>o</sub> - F<sub>c</sub>)<sup>2</sup>/ΣwF<sub>o</sub><sup>2</sup>]<sup>1/2</sup>. <sup>b</sup> wR2 = [Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)]/Σw(F<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>, w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (aP)<sup>2</sup> + bP], where P = [max(F<sub>o</sub><sup>2</sup> or 0) + 2(F<sub>c</sub><sup>2</sup>)]/3, for 1, a = 0.05, b = 29.0, for 2, a = 0.036, b = 6.60. <sup>c</sup> Quality-of-fit = [Σw(|F<sub>o</sub><sup>2</sup> - |F<sub>c</sub><sup>2</sup>||<sup>2</sup>)/(N<sub>obs</sub> - N<sub>parameters</sub>)]<sup>1/2</sup>.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for 1·C<sub>6</sub>H<sub>14</sub><sup>a</sup>

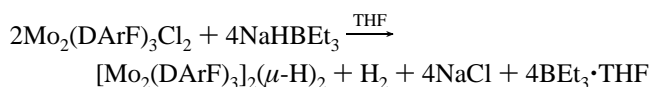
Mo(1)–Mo(2)	2.0930(9)	Mo(1)–N(4)	2.162(5)
Mo(1)–Mo(2)′	3.5317(9)	Mo(1)–N(6)	2.138(5)
Mo(2)–H(1)	1.83(7)	Mo(2)–N(1)	2.155(5)
Mo(1)–H(1)′	1.85(7)	Mo(2)–N(3)	2.166(5)
Mo(1)–N(2)	2.165(5)	Mo(2)–N(5)	2.143(5)
Mo(2)–Mo(1)–N(6)	92.8(2)	Mo(1)–Mo(2)–N(1)	92.7(2)
Mo(2)–Mo(1)–N(4)	93.0(2)	N(5)–Mo(2)–N(1)	174.4(2)
N(6)–Mo(1)–N(4)	90.4(2)	Mo(1)–Mo(2)–N(3)	92.5(2)
Mo(2)–Mo(1)–N(2)	93.2(2)	N(5)–Mo(2)–N(3)	91.6(2)
N(6)–Mo(1)–N(2)	174.0(2)	N(1)–Mo(2)–N(3)	89.8(2)
N(4)–Mo(1)–N(2)	89.6(2)	Mo(2)–H(1)–Mo(1)′	147(4)
Mo(1)–Mo(2)–N(5)	92.61(14)		

<sup>a</sup> Symmetry transformations used to generate primed atoms: -x+1, -y, -z+1.

package SHELXTL.<sup>12</sup> Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed a molecule of *n*-hexane in each structure. The position of the unique hydride atom in each structure was refined with a fixed displacement parameter. All other hydrogen atoms were used in calculated positions. In 2, two of the *p*-MeOPh groups exhibit a slight disorder. The disordered groups were each refined as a pair, comprising a major and a minor orientation, but the members of each pair were constrained to have the same bond distances and angles. The major orientation of the group containing atom O(2) had an occupancy of 0.53(2) and that of the group containing atom O(5) was 0.64(1). Other details of data collection and refinement are given in Table 1. Selected atomic distances and angles for 1·C<sub>6</sub>H<sub>14</sub> and 2·C<sub>6</sub>H<sub>14</sub> are provided in Tables 2 and 3, respectively. Other crystallographic data are given as Supporting Information.

## Results and Discussion

**Properties and Structures.** Reductive substitution of the Mo<sub>2</sub>(DArF)<sub>3</sub>Cl<sub>2</sub> molecules with NaHBEt<sub>3</sub> gives the tetranuclear complexes [Mo<sub>2</sub>(DArF)<sub>3</sub>]<sub>2</sub>(μ-H)<sub>2</sub> according to the equation:



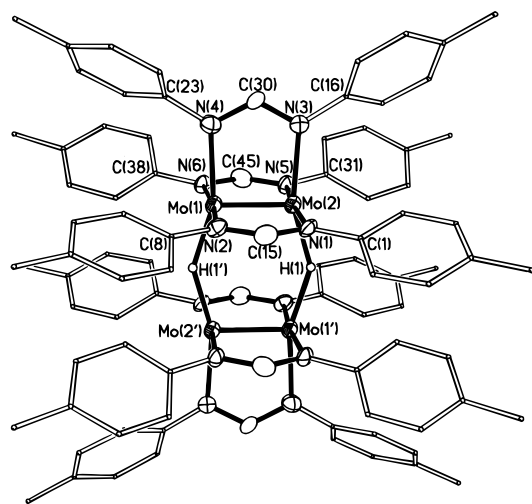
where DArF = *N,N*-diarylformamidinate and Ar = *p*-tolyl or *p*-anisyl (*p*-methoxyphenyl). The purification of these hydride complexes was difficult mainly because of the low solubility

(12) SHELXTL, Version 5.03. Bruker AXP, Inc., Madison, Wisconsin.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for  $2 \cdot C_6H_{14}^a$ 

Mo(1)–Mo(2)	2.0980(5)	Mo(1)–N(4)	2.150(3)
Mo(1)–Mo(2)'	3.5397(7)	Mo(1)–N(6)	2.151(3)
Mo(1)–H(1)'	1.87(4)	Mo(2)–N(1)	2.143(3)
Mo(2)–H(1)	1.86(4)	Mo(2)–N(3)	2.163(3)
Mo(1)–N(2)	2.143(3)	Mo(2)–N(5)	2.164(3)
Mo(2)–Mo(1)–N(2)	92.96(9)	Mo(1)–Mo(2)–N(1)	92.37(9)
Mo(2)–Mo(1)–N(4)	91.65(9)	Mo(1)–Mo(2)–N(3)	93.42(9)
N(2)–Mo(1)–N(4)	91.41(13)	N(1)–Mo(2)–N(3)	90.59(13)
Mo(2)–Mo(1)–N(6)	93.21(9)	Mo(1)–Mo(2)–N(5)	92.36(9)
N(2)–Mo(1)–N(6)	173.81(12)	N(1)–Mo(2)–N(5)	175.27(12)
N(4)–Mo(1)–N(6)	88.95(12)	N(3)–Mo(2)–N(5)	89.35(12)
Mo(2)–H(1)–Mo(1)'	144(3)		

<sup>a</sup> Symmetry transformations used to generate primed atoms:  $-x, -y+1, -z$ .

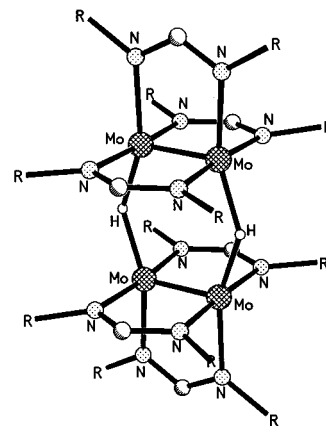


**Figure 1.** A drawing of the molecular structure of  $Mo_4(\mu-H)_2(DTolF)_6$  in  $1 \cdot C_6H_{14}$ . 50% probability ellipsoids are shown for non-hydrogen atoms except those of the *p*-tolyl rings, which are drawn as arbitrarily small spheres for clarity.

(especially for **1**) in most common organic solvents. Thus, to obtain analytically pure samples in satisfactory yields, it is imperative to use very pure starting materials followed by extensive washing of the products and by recrystallization.

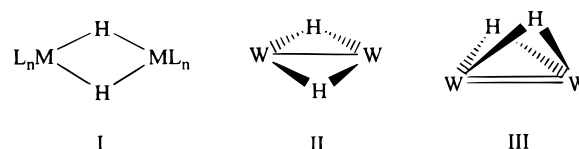
The structures of the two compounds are very similar; that of the *p*-tolyl derivative (**1**) is shown in Figure 1. It consists of a centrosymmetric arrangement of two quadruply bonded  $Mo_2(DArF)_3$  units connected by two hydride ions. The Mo–Mo distances of 2.0930(9) Å for **1** and 2.0980(5) Å for **2** are consistent with the description of a quadruple bond.<sup>6</sup> This is also supported by the  $\delta \rightarrow \delta^*$  transitions observed in the electronic absorption spectra (vide infra).

The core, shown in Figure 2, is remarkable in that the two  $Mo^4-Mo$  units are joined only by two hydrogen bridges. The hydrogen atoms were clearly defined in the electron density maps, and the positions were refined without constraints, but the Mo–H distances of 1.83(7) and 1.85(7) Å for **1** and 1.87(4) and 1.86(4) Å for **2** carry large standard deviations as expected for X-ray diffraction studies. The bent Mo–H–Mo angles of ca. 147(4)° for **1** and 144(3)° for **2** are similar to those found in other species containing singly bridged three-center–two electron ( $3c-2e$ ) M–H–M bonds. For example, it is 145.2(3)° in the classic example of  $[K(cryp-222)]^+[Cr_2(CO)_{10}(\mu-H)]^-$ .<sup>13</sup> All four molybdenum atoms and both hydrogen atoms are essentially coplanar; the planarity is not significantly altered if the methine carbon and nitrogen atoms, C(30), N(3),



**Figure 2.** Schematic drawing of the centrosymmetric environments of **1** and **2** showing the two quadruply bonded  $Mo_2(DArF)_3$  units connected by a pair of bridging hydrogen atoms.

### Scheme 2



and N(4) and their symmetry related atoms, are included in the calculation of the least-squares plane.

The presence of bridging atoms is also consistent with the relatively short  $Mo \cdots Mo$  separation of 3.5317(9) Å for **1** and 3.5397(7) Å for **2** and by the requirement to compensate for the charge of the  $Mo^{II}$  atoms which is necessary to sustain the quadruple bonds between Mo atoms in these diamagnetic species. Furthermore, the signals in the  $^1H$  NMR spectra at 1.22 and 1.17 ppm for **1** and **2**, respectively, integrate as two hydrogen atoms; they can be assigned to the bridging hydrogen atoms.

These are the first compounds to contain this type of core. All previously known double hydrogen-bridged systems are of the cis-bridged type I.<sup>7</sup> Similarly, complexes containing singly or multiply bonded metal atoms and two hydrogen atoms are known but those hydrogen atoms normally bridge within dimetal units. Examples are  $W_2(\mu-H)_2(\mu-O_2CC_6H_5)Cl_2(P(C_6H_5)_3)_2$ <sup>14</sup> or various siloxide complexes, e.g.,  $[W(OSiBu'_3)_2Cl]_2(\mu-H)_2$ ,<sup>15</sup> which have cores of the type II and III, respectively (Scheme 2).

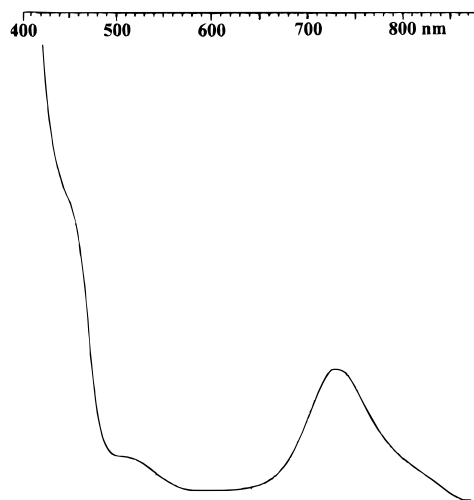
As indicated in the Introduction, the retention of the quadruple bonds in **1** and **2** is a new feature for tetranuclear complexes. There is only one report<sup>1a</sup> in which the electronic absorption spectrum of  $Mo_4I_8(PBu^t_3)_4$  seems to indicate that there are  $Mo^4-Mo$  bonded units, but a crystallographic study has not been done.

A very remarkable property of these complexes is that they are very stable toward hydrolysis. Although they decompose in the presence of oxygen, addition of water at room temperature or even above to either the solids or their solutions does not alter their composition, as indicated by the invariability of the bands in the  $^1H$  NMR spectrum. However, a rapid reaction does occur when the hydride-containing complexes are brought into contact with HCl, generated by reacting  $Me_3SiCl$  and

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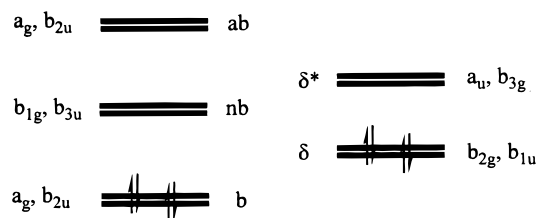
**Figure 3.** Electronic absorption spectrum of **2**; the corresponding spectrum for **1** is very similar. The shoulder at 444 nm corresponds to the  $\delta \rightarrow \delta^*$  transition; the others involve the 3c–2e Mo–H–Mo bridges (see text).

methanol. The color of the  $\text{CD}_2\text{Cl}_2$  solution changes from orange to red and the  $^1\text{H}$  NMR bands at ca. 1.2 ppm disappear while those corresponding to the formamidinate ligands are moved but still present. We have been unable to isolate the reaction products, but the sharp signals of the NMR spectrum indicate that they are diamagnetic.

**Electronic Absorption Spectra.** Apart from steeply rising absorption into the blue (see Figure 3), the electronic spectra of **1** and **2** present three features: (1) a shoulder at 449 and 444 nm, (2) a second shoulder at 505 and 505 nm, and (3) a nice Gaussian band at 728 and 729 nm, respectively. Band 3 is 15 times more intense than band 2, which, in turn, is about 6 times stronger than band 1. Since band 1 is about where the  $\delta \rightarrow \delta^*$  transition might be expected on the basis of results for a series of  $\text{Mo}_2(\text{formamidinate})_4$  compounds,<sup>8</sup> and may be so assigned, we are left with the problem of assigning bands 2 and 3. Ordinarily, in compounds with quadruple bonds, it is assumed that the lowest-energy transition must be the  $\delta \rightarrow \delta^*$  transition, but here, that would not be reasonable.

The assignment of bands 2 and 3 can be deduced by considering the nature of the  $\mu\text{-H}$  bridge bonding. To a good approximation, the Mo–H–Mo bridges are 3c–2e bonds, and associated with each one, there is a bonding orbital that is occupied, a nonbonding orbital (to which the H atom does not contribute) that is unoccupied, and an unoccupied antibonding orbital. To make an appropriate symmetry-based analysis of the possibilities, it is necessary to treat these three-center bonds as well as the  $\delta$  bonds all together in conformity with the  $D_{2h}$  symmetry of the entire molecule.

### Mo–H–Mo



**Figure 4.** Molecular orbitals involved in the Mo–H–Mo bridge bonding.

The six molecular orbitals involved in the bridge bonding are shown on the left in Figure 4 and the four  $\delta$  and  $\delta^*$  orbitals are shown on the right. The symmetry properties, i.e., the irreducible representations to which they correspond, are given for each one. Since it seems likely that the lowest-energy electronic transition would be of the  $\delta \rightarrow \text{nb}$  type and the next highest of the  $\delta \rightarrow \text{ab}$  type, the selection rules have been examined to see if such transitions are allowed. In fact, it is found that there is just one allowed transition of each type. Of the four possible  $\delta \rightarrow \text{nb}$  transitions, one,  $b_{2g} \rightarrow b_{3u}$ , is allowed in  $z$  polarization. Of the four possible  $\delta \rightarrow \text{ab}$  transitions, one,  $b_{1u} \rightarrow a_g$  is allowed, again in  $z$  polarization.

It is not possible to rule out the assignment of band 2 or 3 to a  $b \rightarrow \delta^*$  transition since there is one,  $b_{2u} \rightarrow b_{3g}$ , that is allowed. We doubt, however, that such a transition, from a  $\sigma$  bonding orbital to a  $\delta^*$  orbital would occur at as low an energy as band 2 or 3.

Whatever the correct assignments for bands 2 and 3 may be, the most important point is that there are reasonable assignments available and thus the occurrence of bands at lower energies than the  $\delta \rightarrow \delta^*$  (normally not possible) need not be considered a problem.

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**Supporting Information Available:** Tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, anisotropic displacement parameters, least-squares planes, and thermal ellipsoid plots of the molecules (23 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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