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Compounds with Two Metal−Metal Multiple Bonds: New Ways of Making Doublets into Cyclic Quartets

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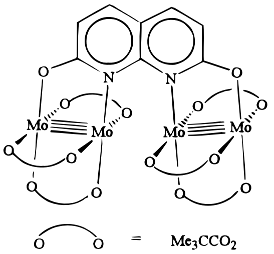
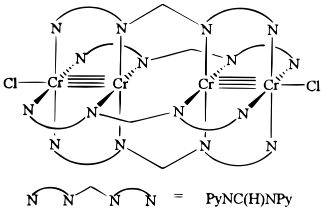
Abstract: New types of products obtained by combining two dinuclear multiply metal−metal bonded species (doublets) to obtain cyclic tetranuclear products (quartets) are reported. One new type consists of pairs of quadruply bonded Mo_2^{4+} units united by two μ-X links (X = H, OH, O) although in the last case oxidation has also occurred so that these are Mo_2^{5+} moieties. In these cases, the subunits are $Mo_2(DArF)_3$. The second new type consists of $Mo_2(DArF)_2$ subunits linked by four μ-X bridges, where X = Cl, Br, I. The previously known compound $Mo_4I_8(PBu^n_3)_4$ has been shown to differ from all previously known $Mo_4X_8(PR_3)_4$ molecules (X = Cl, Br) by retaining two quadruple bonds instead of being a metallacyclobutadiyne, as are the others.

Introduction

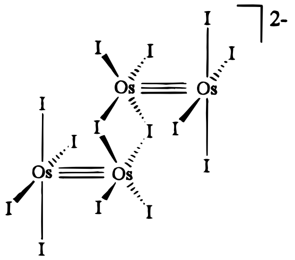
The chemistry of compounds containing pairs of transition metal atoms united by bonds ranging from single to quadruple is well developed.[1] An interesting but not as yet extensive part of this chemistry deals with the coupling of such units (doublets) in pairs to form quartets of metal atoms. Despite the relatively small number known, there is a variety of structural types. Some are not cyclic, good examples being **a**[2] and **b**.[3] In these, the quadruply bonded M_2^{4+} units show essentially no interaction with each other. Indeed, in **a** the two Mo_2 units are not even collinear. In **c** the two Os≡Os units do not interact.[4] There are other open-chain M_4 compounds of tungsten, rhodium, iridium, and platinum (the platinum blues) all described in ref 1, as well as heteronuclear chains.[5] These noncyclic quartets are not closely related to cyclic ones, to which we now turn our attention.



a

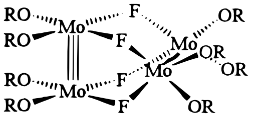


b

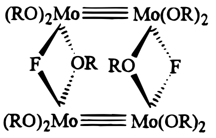


c

In some cyclic quartets, only the quartet is known; the doublet precursor is not known to exist independently. The majority of these are outside the scope of the present discussion, but perhaps not the following. While the molecules $Mo_2(OCMe_3)_4F_2$ and $Mo_2(OCHMe_2)_5F$ have never been isolated, their self-addition quartets **d** and **e** have been made.[6] A critical point to note here is that, in M_2X_6 molecules, the metal atoms are not coordinately saturated and thus when sterically possible they can achieve saturation by dimerizing, whereas this is not the case with M_2X_8 species to be discussed presently. A recently reported rhodium complex, $Rh_4(O_2CPr^n)_4Cl_4(CH_3CN)_4$, has a Rh_4X_4 core which is structurally similar to that of **d** but with Rh−Rh single bonds.[7]



d



e

The anion shown as **f** is an unusual case where the quartet was first made directly from mononuclear starting material[8] and

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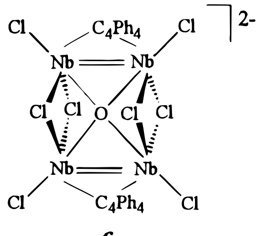
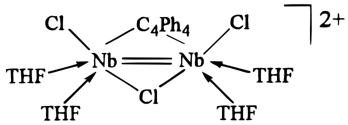
10.1021/ja982425f CCC: $15.00



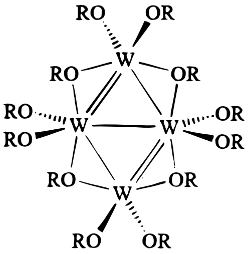
f

is still better made that way, but a doublet, **g**, was later found as well.[9] In this case, however, the doublet was never used to assemble the quartet.

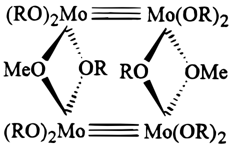


g

It is well-known through the work of Chisholm that $(RO)_3Mo\equiv Mo(OR)_3$ and $(RO)_3W\equiv W(OR)_3$ doublets can combine to form quartets in several ways. The case of $W_2(OCHMe_2)_6$ is unique;[10] here, a fluxional bicyclic W_4 unit is formed, ***h***. In a similar case involving $Mo_2(OCHMe_2)_5(OMe)$, the resulting quartet consists of two Mo≡Mo units bridged by alkoxides, **i**.

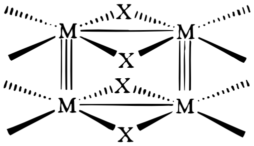


h



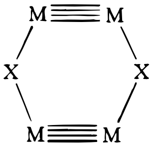
i

Most directly related to the new chemistry of quartets from doublets that we are reporting here are compounds that can be described as metallacyclobutadiynes. These have the type of core structure shown as **j**. The first one was made[11] by condensing two $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ molecules with elimination of the methanol ligands. The Mo–Mo single bonds,[12] each bridged by two Cl atoms, were 2.901 Å in length and the triple bonds were 2.211 Å. Obviously, isomers are possible for such a structure, depending on how the set of $Cl_4(PPh_3)_4$ terminal ligands are arranged. Several other Mo_4 compounds of this butadiyne type have subsequently been described,[13] as well as the compounds $Mo_2W_2Cl_8(PR_3)_4$ (R = Me, Bu^n).[14] More recently, compounds of this type were discovered for rhenium.[15] In one case, namely, $Mo_4I_8(PBu^n{}_3)_4$, it was proposed, based on spectroscopic data, that the quadruple bonds remained intact and no long Mo–Mo single bonds were found.[13a]



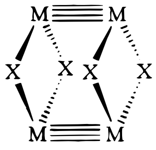
j

Finally we note that the only previous compounds with quartets of the type **k** are those we have very recently described in which the bridging groups, μ-X, are H[16] or OH.[17] We report here more information on these as well as a new example in which X = O and the doublets are now based on $Mo_2{}^{5+}$ units.

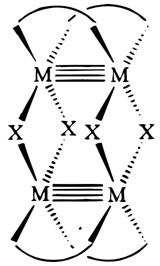


k

In this paper, we also provide the first conclusive evidence for quartets of type **l** that retain their quadruple bonds, with bridging ligands as shown in **m**.



l



m

Experimental Section

General Considerations. All the syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under nitrogen by following conventional methods. Chlorotrimethylsilane (1.0 M in THF), $BrSiMe_3$, $ISiMe_3$, and $NaHBEt_3$ (1.0 M in THF) were purchased from Aldrich. Potassium graphite (KC_8) was prepared by reaction of potassium with graphite at 160 °C for 24 h.[18] The dinuclear complexes $Mo_2(O_2CCH_3)_4$, $Mo_2(DAniF)_4$, $Mo_2(DTolF)_4$, $Mo_2(DAniF)_3Cl_2$, $Mo_2(DTolF)_3Cl_2$, and $Mo_2(DPh^fF)_3Cl_2$ were prepared by following published procedures.[19,20] (Throughout this paper the formamidinate anions, $ArNC(H)NAr^-$, will be abbreviated as $DArF^-$, with specific Ar groups represented by Ani for *p*-anisyl, Tol for *p*-tolyl, and Ph^f for *p*-fluorophenyl.) Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia; the results were satisfactory. ^1H NMR spectra were recorded on a Varian XL-200E NMR spectrometer, with chemical shifts (δ) referenced to CH_2Cl_2, except for **3**, which was referenced to acetone, and **4c**, which was referenced to THF; ^{31}P NMR spectra were recorded

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on an Unity Plus 300 NMR spectrometer, with chemical shifts (δ) externally referenced to 75% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr disks. Electronic spectra were obtained in degassed CH_2Cl_2, using a Cary 17 spectrophotometer. Magnetic susceptibilities were measured at 293 K by the Evans method[21] in CH_2Cl_2 solution on a Varian XL-200E NMR spectrometer.

$[Mo_2(DAniF)_3]_2(\mu\text{-}H)_2$ (1x and 1n). The tetranuclear compound $[Mo_2(DAniF)_3]_2(\mu\text{-}H)_2$ (**1**) was synthesized as previously reported.[16] Before recrystallization, the crude solid was washed with copious amounts of ether, water, and ethanol. Crystalline samples were prepared by layering CH_2Cl_2 solutions of **1** with hexanes; two types of crystals, which differed in the amount of interstitial solvent, were obtained: small dark orange crystals of **1**·C_6H_{14}, the structure of which has been reported,[16] and large block-shaped crystals of **1**·$0.5C_6H_{14}$ which were suitable for single-crystal neutron diffraction (**1n**) and X-ray diffraction (**1x**) studies.

$[Mo_2(DTolF)_3]_2(\mu\text{-}OH)_2$ (2). To a suspension of $Mo_2(DTolF)_3Cl_2$ (100 mg, 0.107 mmol) in 25 mL of THF was added 0.25 mL of slightly hydrolyzed 0.3% K(Hg) amalgam (0.26 mmol) under a stream of N_2. The reaction mixture was stirred at room temperature for 12 h, during which time the color of the solution gradually changed from brownish-yellow to green. The resulting mixture was then filtered through Celite, and the solvent was removed from the filtrate under vacuum. The yellowish green residue was washed with several small portions of toluene and then extracted with CH_2Cl_2. Layering of the CH_2Cl_2 solution with hexanes provided large dark brownish crystals of **2**·n-C_6H_{14} after several days. Yield, 40 mg (41%). ^1H NMR δ (ppm): 8.94 (s, 4H, NCHN), 8.24 (s, 2H, NCHN), 6.58 (d, 8H, aromatic, $^3J = 8.0$ Hz), 6.45 (d, 16H, aromatic, $^3J = 7.7$ Hz), 6.06 (m, 24H, aromatic), 2.44 (s, 2H, OH), 2.10 (b, 36H, CH_3), 1.27 (m, 8H, C_2H_4 of n-hexane), 0.88 (t, 6H, CH_3 of n-hexane). IR (KBr, cm^{-1}): 3552 (w), 3021 (m), 2919 (m), 2858 (m), 1610 (m), 1541 (s), 1507 (s), 1318 (s), 1219 (s), 1180 (w), 1113(w), 1016 (w), 937 (w), 816 (m), 583 (w), 536 (w), 437 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1} cm^{-1})): 726 (13200), 577 (350), 432 (sh).

$[Mo_2(DTolF)_3]_2(\mu\text{-}O)_2$ (3). Dark crystals of **2** (34 mg, 0.019 mmol) were dissolved in 100 mL of benzene and stirred in the air for 24 h, during which time the color of the solution gradually changed from greenish-yellow to dark red. The volume of the resulting solution was reduced to ~5 mL. The product was precipitated with hexanes in quantitative yield. Single crystals of **3**·THF were obtained from a THF solution layered with hexanes. ^1H NMR δ (ppm): 8.75 (sb, NCHN), 7.91 (sb, NCHN), 7.22 (mb, aromatic), 2.34 (b, CH_3). IR (KBr, cm^{-1}): 1691 (s), 1649 (m), 1508 (s), 1336 (m), 1214 (s), 1111 (w), 1023 (w), 939 (m), 907 (m), 817 (s), 717 (s), 509 (w), 443 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1} cm^{-1})): 485 (7770), 800 (sh). Magnetic data (293 K): χ_{mol}, 2.959×10^{-3} emu, μ_{eff}, 2.63 μ_B.

$[Mo_2(DAniF)_2]_2(\mu\text{-}Cl)_4$ (4a). To a mixture of $Mo_2(DAniF)_3Cl_2$ (206 mg, 0.200 mmol) and $ClSiMe_3$ (1.0 mmol) in 75 mL of THF was gradually added KC_8 (34 mg, 0.25 mmol) through a solid additions tube. After the reaction mixture was stirred for 24 h at 60−65 °C, the volatile materials were removed under vacuum, and the resulting residue was first washed with copious amounts of Et_2O and then extracted with acetone (4 × 20 mL). The combined extracts were concentrated to 15 mL and cooled to −10 °C. A brick-red microcrystalline product was isolated. Yield, 60 mg (39%). Single crystals of **4a**·2acetone, suitable for X-ray analysis, were grown by diffusion of ether into an acetone solution. ^1H NMR δ (ppm): 8.75 (s, 4H, NCHN), 6.67 (m, 32H, aromatic), 3.69 (s, 24H, OCH_3). IR (KBr, cm^{-1}): 1695 (m), 1609 (m), 1533 (s), 1504 (s), 1464 (m), 1442 (m), 1289 (s), 1248 (s), 1215 (s), 1180 (m), 1112 (w), 1032 (s), 940 (w), 828 (s), 766 (w), 657 (w), 591 (w), 527 (w), 448 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1} cm^{-1})): 825 (700), 765 (600), 540 (sh), 500 (3830), 380 (sh).

$[Mo_2(DTolF)_2]_2(\mu\text{-}Cl)_4$ (4b). This was prepared similarly to **4a** using 186 mg (0.199 mmol) of $Mo_2(DTolF)_3Cl_2$, 0.70 mmol of $ClSiMe_3$, and 34 mg (0.25 mmol) of KC_8 in 70 mL of THF. Yield, 15 mg (11%). Dark-red single crystals suitable for X-ray analysis were grown by diffusion of hexanes into a CH_2Cl_2 solution. ^1H NMR δ (ppm): 8.82 (s, 4H, NCHN), 6.90 (d, 16H, aromatic, $^3J = 8.3$ Hz), 6.60 (d, 16H, aromatic, $^3J = 8.3$ Hz), 2.21 (s, 24H, CH_3). IR (KBr, cm^{-1}): 1691 (w), 1610 (w), 1531 (s), 1506 (s), 1451 (m), 1368 (w), 1308 (s), 1217 (s), 1111 (w), 1037 (w), 1016 (w), 940 (w), 918 (w), 817 (s), 767 (w), 711 (w), 653 (w), 626 (w), 583 (w), 517 (w), 482 (w), 446 (w), 424 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1} cm^{-1})): 820 (140), 765 (130), 544 (sh), 500 (2660), 381 (sh).

$[Mo_2(DPh^fF)_2]_2(\mu\text{-}Cl)_4$ (4c). This was prepared similarly to **4a** using 150 mg (0.160 mmol) of $Mo_2(DPh^fF)_3Cl_2$, 1.0 mmol of $ClSiMe_3$, and 27 mg (0.20 mmol) of KC_8 in 50 mL of THF. After washing with Et_2O, the solid residue was extracted with THF (5 × 15 mL). The solvent from the combined extracts was removed under vacuum, and the solids were redissolved in CH_2Cl_2 (10 mL). Cooling to −10 °C followed by filtration afforded a brick-red product. Yield, 20 mg (17%). Single crystals suitable for X-ray analysis of **4c**·2THF were grown by diffusion of hexanes into a THF solution. ^1H NMR δ (ppm): 8.89 (s, 4H, NCHN), 6.84 (m, 32H, aromatic). IR (KBr, cm^{-1}): 1701 (w), 1535 (s), 1500 (s), 1307 (m), 1232 (m), 1209 (s), 1156(m), 1098 (m), 940 (w), 831 (m), 780 (m), 622 (w), 583 (w), 515 (w), 486 (w), 464 (w), 450 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1} cm^{-1})): 822 (375), 765 (340), 541 (sh), 497 (2010), 377 (sh).

$[Mo_2(DAniF)_2]_2(\mu\text{-}Br)_4$ (5). This was prepared by the following two methods.

Method A. This method was similar to that used for **4a**: 206 mg (0.200 mmol) of $Mo_2(DAniF)_3Cl_2$, 1.1 mL (8.3 mmol) of $BrSiMe_3$, and 34 mg (0.25 mmol) of KC_8 in 70 mL of THF were used. Yield, 20 mg (11%).

Method B. To a solution of $Mo_2(DAniF)_4$ (242 mg, 0.200 mmol) in 50 mL of CH_2Cl_2 was added 2.0 mL of $BrSiMe_3$ (15 mmol) at room temperature. The resulting solution was stirred for 2 days, and the volatile materials were then removed. The solid was thoroughly washed with Et_2O and then extracted with acetone (3 × 15 mL). The combined extracts were concentrated to 10 mL and cooled to −10 °C. A microcrystalline product was isolated and washed with ice-cold acetone. Yield, 148 mg (86%). ^1H NMR δ (ppm): 8.70 (s, 4H, NCHN), 6.66 (m, 32H, aromatic), 3.69 (s, 24H, OCH_3). IR (KBr, cm^{-1}): 1692 (m), 1609 (m), 1534 (s), 1504 (s), 1461 (m), 1441 (m), 1288 (m), 1248 (s), 1214 (s), 1179 (m), 1109 (m), 1034 (s), 940 (w), 827 (m), 766 (w), 591 (w), 527 (w), 446 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1}cm^{-1})): 820 (455), 765 (430), 543 (sh), 498 (2000), 385 (sh).

$[Mo_2(DAniF)_2]_2(\mu\text{-}I)_4$ (6). To a solution of $Mo_2(DAniF)_4$ (121 mg, 0.100 mmol) in 60 mL of CH_2Cl_2 was added 1.0 mL of $ISiMe_3$ (7.0 mmol) at 0 °C. The resulting dark-brown solution was stirred at 0 °C for 2 days; then the volatile materials were pumped off. The solid was dissolved in 50 mL of acetone, and the mixture was filtered. After removal of the solvent from the filtrate, the residue was extracted with CH_2Cl_2 (2 × 10 mL). The extracts were combined and concentrated to 8 mL and layered with hexanes to afford a crystalline product. Yield, 90 mg (94%). ^1H NMR δ (ppm): 8.61 (s, 4H, −NCHN-), 6.65 (m, 32H, aromatic), 3.69 (s, 24H, −OCH_3). IR (KBr, cm^{-1}): 1686 (s), 1608 (m), 1556 (w), 1511 (s), 1454 (m), 1439 (m), 1378 (w), 1332 (s), 1307 (m), 1293 (s), 1251 (s), 1212 (s), 1178 (s), 1111 (w), 1028 (s), 827 (s), 730 (w), 646 (w), 578 (w), 522 (w), 412 (w). UV−vis, λ_{max} (nm, ϵ (M^{-1}cm^{-1})): 810 (220), 765 (210), 507 (3000), 402 (7300).

$[Mo_2I_2(PBu^n_3)_2]_2(\mu\text{-}I)_4$ (7). This was prepared according to the literature[13a] with slight modifications. To a mixture of $Mo_2(O_2CCH_3)_4$ (2.00 g, 4.68 mmol) and PBu^n_3 (2.3 mL, 9.4 mmol) in 50 mL of CH_2Cl_2 was added 6.0 mL of $ISiMe_3$ (42 mmol) at 0 °C. The resulting mixture was stirred for 2 days at 0 °C. The volatile materials were removed under vacuum while the temperature was kept at 0 °C; then the solid residue was further pumped under vacuum at room temperature for 2 days. The solids were washed with ether (5 × 40 mL), and the extracts were combined and concentrated to 10 mL. Cooling to −10 °C followed by filtration gave a polycrystalline product. Yield, 1.50 g (40%). This compound was found to be stable in only a few solvents, e.g., CH_2Cl_2, hexanes, and diethyl ether. Single crystals suitable for X-ray analysis were obtained by cooling a saturated hexanes solution to −10 °C. ^1H NMR δ (ppm): 2.37 (b, 8H, PCH_2), 1.37 (m, 16H, CH_2CH_2), 0.90 (t, 12H, CH_3, $^3J = 8.5$ Hz). ^{31}P NMR δ (ppm): 0.35 (s). IR (KBr, cm^{-1}): 1462 (m), 1411 (m), 1378 (m), 1342 (w), 1303 (w), 1262 (s), 1234 (w), 1189 (w), 1094 (s,b), 1021 (s, b), 972 (w),

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Table 1. Crystal and Structure Refinement Data

	compound				
	1x·0.5hexanes	**1n**·0.5hexanes[a]	**2**·*n*-hexane	**3**·THF	**4a**·2acetone
formula	$C_{93}H_{99}Mo_4N_{12}O_{12}$		$C_{96}H_{106}Mo_4N_{12}O_2$	$C_{94}H_{98}Mo_4N_{12}O_3$	$C_{66}H_{72}Cl_4Mo_4N_8O_{10}$
formual weight	1960.6		1843.69	1827.6	1662.88
crystal system	triclinic		monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$		$P2_1/n$	$Fdd2$	$P2_1/n$
a, Å	14.555(2)		16.036(4)	28.574(5)	11.867(2)
b, Å	17.001(4)		17.347(2)	35.214(6)	12.354(2)
c, Å	17.179(4)		17.649(4)	19.572(7)	23.776(8)
α, deg	87.49(2)		90	90	90
β, deg	84.48(2)		115.02(1)	90	95.99(2)
γ, deg	89.16(2)		90	90	90
volume, Å^3	4227(2)		4449(2)	19693(9)	3467(2)
Z	2		2	8	2
$R1$,[b] $wR2$[c]	0.059, 0.140	0.107,0.220	0.047, 0.121	0.066, 0.175	0.046, 0.105
$R1$, $wR2$	0.098, 0.161	0.154, 0.236	0.056, 0.130	0.080, 0.191	0.056, 0.117
goodness of fit[d]	1.026	14.2	1.056	1.192	1.166

	compound			
	4b	**4c**·2THF	**6**	**7**
formula	$C_{60}H_{60}Cl_4Mo_4N_8$	$C_{60}H_{52}Cl_4F_8Mo_4N_8O_2$	$C_{60}H_{60}I_4Mo_4N_8O_8$	$C_{48}H_{108}I_8Mo_4P_4$
formula weight	1418.72	1594.66	1912.52	2208.18
crystal system	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$I222$
a, Å	13.105(4)	10.003(1)	13.393(2)	12.190(3)
b, Å	10.392(2)	13.027(3)	10.852(1)	15.673(4)
c, Å	21.290(7)	14.099(3)	22.278(3)	19.605(4)
α, deg	90	67.93(1)	90	90
b, deg	95.73(2)	70.12(2)	94.60(1)	90
γ, deg	90	76.15(2)	90	90
volume, Å^3	2885(2)	1588.0(5)	3227.5(7)	3746(2)
Z	2	1	2	2
$R1$,[b] $wR2$[c]	0.033, 0.080	0.048, 0.124	0.048, 0.118	0.053, 0.133
$R1$, $wR2$	0.056, 0.088	0.053, 0.132	0.058, 0.136	0.058, 0.138
goodness of fit[d]	1.042	1.117	1.142	1.117

[a] Lattice parameters used for neutron diffraction were those from X-ray data. [b] $R1 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. [d] Quality of fit, $[\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

865 (m), 800 (s), 708 (m), 455 (w). UV−vis, λ_{max} (nm, ϵ ($M^{-1}cm^{-1}$)): 712 (sh), 638 (2450), 519 (sh), 460 (sh), 400 (6210), 325 (sh).

Crystallographic Procedures. (a) X-ray. Single-crystal X-ray work on **2**·C_6H_{14}, **3**·THF, **4a**·2acetone, **4c**·2THF, **6**, and **7** was performed on a Nonius FAST diffractometer at −60 °C utilizing the program MADNES.[22] 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 autoindexing routine and were refined with 250 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[23]), and the program SORTAV[24] was used to correct for absorption.

Single-crystal X-ray data of **1x**·0.5C_6H_{14} and **4b** were collected on a Nonius CAD4 diffractometer at −150 °C. Unit cell refinement for **1x**·0.5C_6H_{14} and **4b** utilized 25 strong reflections in the range of $28.0 \le 2\theta \le 35.9°$ for **1x** and $28.3 \le 2\theta \le 35.4°$ for **4b**. An empirical absorption correction based on ψ-scans was applied. Data were processed into SHELXL format using the program XCAD. All other data collection procedures were similar to those used on the FAST diffractometer (vide supra).

In all structures, the positions of some or all of the non-hydrogen atoms of the metal complex were found via direct methods by way of the program package SHELXTL.[25] For all structures, subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. The approximate position of the unique hydride ion in structure **1x** was determined from a Fourier map but was not refined. All other hydrogen atoms for this and all other compounds were used in calculated positions. Other details of data collection and refinement for all complexes are given in Table 1. Selected atomic distances and angles are provided in Table 2. Other crystallographic data are available as Supporting Information.

(b) Neutron. Single-crystal time-of-flight neutron data of **1n** were collected on the SCD diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. A position-sensitive area detector was used to obtain time-of-flight Laue data with a wavelength range of 0.7−4.2 Å for 45 χ and ϕ angular settings of the goniometer to cover a full hemisphere of reciprocal space.[26] The details of the data collection and analysis procedures have been described previously.[27] A single crystal (2 × 3 × 3 mm^3) wrapped in aluminum foil and mounted on the tip of an aluminum pin with epoxy was maintained at a temperature of −150 °C with a Displex closed-cycle helium refrigerator.

An autoindexing routine was used to obtain an orientation matrix.[28] Integrated intensities were corrected for the Lorentz factor, the incident spectrum, and the detector efficiency. A wavelength-dependent spherical absorption correction was applied.[29] Since extinction is also strongly wavelength dependent, symmetry-related reflections were not averaged.

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(22) Pflugrath, J.; Messerschmitt, A. *MADNES, Munich Area Detector (New EEC) System*, Version EEC 11/1/89, with enhancements by Nonius Corp., Delft, The Netherlands. A description of MADNES appears in: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306−315.

(23) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67−71. (b) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916−924.

(24) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

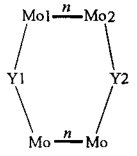
(25) SHELXTL, Version 5.03. Siemens Industrial Automation Inc., Madison, WI.

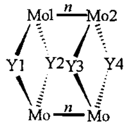
(26) Schultz, A. J. *Trans. Am. Crystallogr. Assoc.* **1987**, *23*, 61−69.

(27) Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999−1003.

(28) Jacobson, R. A. *J. Appl. Crystallogr.* **1986**, *19*, 283−286.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	Compound		$\mathrm{Mo}\overset{n}{-}\mathrm{Mo}$ [a]	$\mathrm{Mo}\cdots\mathrm{Mo}$	Mo(1) – Y(1)	Mo(2) – Y(2)	Mo – N	Mo – Y – Mo
 Type *k*	**1** (Y = H)	X-ray (**1x**)	2.086[4] [b]	3.48[1]	-	-	2.145[4]	-
		Neutron (**1n**)	2.075[3]	3.512[3]	1.84[2]	1.84[2]	2.143[6]	145[1]
	2 (Y = OH)		2.107(1)	4.073(1)	2.123(3)	2.118(3)	2.149[4]	147.7(2)
	3 (Y = O)		2.140(2)	3.739[3]	1.925(4)	1.929(4)	2.17[1]	151.8[9]

	Compound	$\mathrm{Mo}\overset{n}{-}\mathrm{Mo}$	$\mathrm{Mo}\cdots\mathrm{Mo}$	Mo(1) – Y(1)	Mo(1) – Y(2)	Mo(2) – Y(3)	Mo(2) – Y(4)	Mo – N	Mo – Y – Mo
 Type *l*	**4a** (Y = Cl)	2.119(1)	3.602(1)	2.532(2)	2.500(2)	2.510(2)	2.523(2)	2.095[5]	91.42[5]
	4b (Y = Cl)	2.118(1)	3.592(1)	2.512(1)	2.514(1)	2.514(1)	2.512(1)	2.096[4]	91.25[5]
	4c (Y = Cl)	2.123(1)	3.563(1)	2.502(2)	2.516(2)	2.516(2)	2.506(2)	2.102[5]	90.44[5]
	6 (Y = I)	2.117(1)	3.915(1)	2.834(1)	2.852(1)	2.852(1)	2.845(1)	2.100[6]	87.02[2]
	7 (Y = I)	2.129[3]	3.998[3]	2.794[2]	2.794[2]	2.794[2]	2.794[2]	-	90.57[5]

[a] The bond order, *n*, is four for all compounds except **3** for which $n = 3.5$. [b] Brackets in standard errors indicate that the value given has been averaged.

The complexity of the structure required a combined X-ray/neutron refinement using the GSAS program.[30] The starting model was obtained from the X-ray structural refinement. The initial positions of the aromatic hydrogen atoms of the anisyl groups were calculated geometrically, whereas all methyl hydrogen atoms and the bridging hydride groups were located by successive difference Fourier maps derived from the neutron data. Thus, all hydrogen atoms except for those on the solvent molecule were located. The unit cell contains two independent formula units located on centers of inversion, one of which is ordered and one of which appears to exhibit disorder based on the X-ray analysis. The large number of variables combined with the complexity of the structure permitted only the positional and isotropic thermal parameters to be refined for a completely ordered structure. However, the $\mathrm{Mo_4H_2}$ units are unambiguously characterized. Additional information is available in the Supporting Information.

Results and Discussion

Syntheses, Reactivity, and Spectroscopic Studies. [$\mathbf{Mo_2(DAniF)_3]_2(\mu\text{-}H)_2{\cdot}0.5C_6H_{14}}$, ($\mathbf{1{\cdot}0.5C_6H_{14}}$). As previously reported, the reaction of $\mathrm{Mo_2(DAniF)_2Cl_2}$ and $\mathrm{NaHBEt_3}$ in warm THF gives, upon solvent removal, a crude residue containing **1** contaminated with NaCl:

$$2\mathrm{Mo_2(DAniF)_3Cl_2} + 4\mathrm{NaHBEt_3} \xrightarrow{\mathrm{THF}} [\mathrm{Mo_2(DAniF)_3}]_2(\mu\text{-H})_2 + \mathrm{H_2} + 4\mathrm{NaCl} + 4\mathrm{BEt_3{\cdot}THF}$$

A purification process is crucial to obtain analytically pure samples; it involves washing the crude residue with copious amounts of $\mathrm{Et_2O}$, then water, and finally ethanol. Crystallization is accomplished by dissolving the solid residue in $\mathrm{CH_2Cl_2}$ and then allowing hexanes to diffuse slowly into the solution.

The process just described yields dark orange crystals some of which are relatively small, but of a size suitable for X-ray diffraction, and others much larger. In our earlier report, we presented the X-ray structure of the small crystals, which have the composition $\mathbf{1}{\cdot}\mathrm{C_6H_{14}}$. When a fragment of a large crystal was examined by X-ray diffraction, it was found to have a different unit cell with the composition $\mathbf{1}{\cdot}0.5\mathrm{C_6H_{14}}$. The molecule of **1** is essentially the same in both cases, but crystallographically, the two substances are distinct. We use the numbers **1x** and **1n** to designate structural results obtained on $\mathbf{1}{\cdot}0.5\mathrm{C_6H_{14}}$ by the X-ray and neutron data.

Although compound **1**, in either crystal form, is sensitive to air, it is stable toward water, which is actually used to wash away NaCl from the crude precipitate. Such stability toward water is unusual among metal hydrides.

[$\mathbf{Mo_2(DTolF)_3]_2(\mu\text{-}OH)_2{\cdot}}$*n*-hexane, (2·*n*-hexane). An initial attempt to reduce $\mathrm{Mo_2(DTolF)_3Cl_2}$ with potassium amalgam with the intention of producing a chloro analogue of **1** yielded a few crystals of **2**. This result can be attributed to a small amount of adventitious moisture; the yield is greatly increased (∼40%) when the hydrolysis is intentional but controlled, thus producing KOH in situ.

$$2\mathrm{Mo_2(DTolF)_3Cl_2} + 2\mathrm{K} + 2\mathrm{KOH} \xrightarrow{\mathrm{THF}} [\mathrm{Mo_2(DTolF)_3}]_2(\mu\text{-OH})_2 + 4\mathrm{KCl}$$

The sharp signals in the ^{1}H NMR spectrum of this compound clearly indicate it is diamagnetic; a singlet at 2.44 ppm integrates as two protons and corresponds to the hydrogen atoms of the OH groups. The $\upsilon_{\mathrm{O-H}}$ stretching vibration appears in the infrared spectrum as a weak but sharp signal at 3552 cm^{-1}.

[$\mathbf{Mo_2(DTolF)_3]_2(\mu\text{-}O)_2{\cdot}THF}$, (3·THF). When the reaction conditions for the preparation of **2** are modified and oxygen is also allowed in the system, a series of oxidation processes take place. So far we have isolated, in low yield, and structurally characterized two complexes. One of them has the anion $\{[\mathrm{Mo_2(DTolF)_3}]_3(\mathrm{MoO_4})_2\}^-$; it consists of three quadruply bonded dimolybdenum units connected by two molybdate ions, each one of which uses three oxygen atoms to bind to the molybdenum atoms as shown schematically in **n**.[31] The other compound obtained, **3**, has been crystallographically characterized. Since these oxidation reactions appear to be very complex we are studying them as a separate project. However, **3** can be prepared cleanly in essentially quantitative yields by the air oxidation of solutions containing pure samples of **2**.

$$2[\mathrm{Mo_2(DTolF)_3}]_2(\mu\text{-OH})_2 + \mathrm{O_2} \rightarrow 2[\mathrm{Mo_2(DTolF)_3}]_2(\mu\text{-O})_2 + 2\mathrm{H_2O}$$

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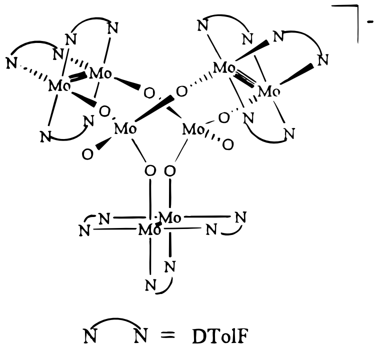
(29) Howard, J. A. K.; Johnson, O.; Schultz, A. J.; Stringer, A. M. *J. Appl. Crystallogr.* **1987**, *20*, 120−122.

(30) Larson, A. C.; Von Dreele, R. B. *GSAS−General Structure Analysis System*; Los Alamos National Laboratory, 1994.

(31) This structure will be reported elsewhere along a detailed study of the oxidation process.



n

The disappearance of the υ_{O-H} stretching vibration is accompanied by a change in color of the solution from greenish-yellow to red and a change in the magnetic properties. Compound **2** is diamagnetic because of the presence of the quadruply bonded Mo_2^{4+} units, but the one-electron oxidation of such units generates the Mo_2^{5+} species with an electronic configuration $\sigma^2\pi^4\delta$. The observed magnetic susceptibility of 2.63 μ_B is consistent with the presence of two unpaired electrons in the tetranuclear compound. The ^{1}H NMR spectrum shows, as expected, broad signals, but it is consistent with the solid-state structure.

[Mo_2(DArF)$_2$]$_2$(μ-Cl)$_4$ (4). Three compounds of this type were prepared by reduction of the corresponding $Mo_2(DArF)_3Cl_2$ complexes with KC_8 in the presence of $ClSiMe_3$:

$$2Mo_2(DArF)_3Cl_2 + 2KC_8 + 2ClSiMe_3 \xrightarrow{THF} [Mo_2(DArF)_2]_2(\mu\text{-}Cl)_4 + 2(DArF)SiMe_3 + 2KCl + 16C$$

The addition of $ClSiMe_3$ is very important for the formation of these complexes. It removes one formamidinate ligand per dinuclear unit by forming a strong Si−N bond in $(DArF)SiMe_3$. In the absence of $ClSiMe_3$, we can isolate only $Mo_2(DArF)_4$ from the reaction mixture.

The first compound of type **4** that was made was **4b**, where Ar = *p*-tolyl; it was obtained from $Mo_2(DTolF)_3Cl_2$. We suspected that the low yield (11%) might be due to the fact that the starting material is not very soluble in THF and therefore turned to the appropriate starting compounds to obtain **4a** (where Ar = *p*-anisyl) and **4c** (where Ar = *p*-fluorophenyl). There were obtained in 39% and 17% yields, respectively. Probably the yields of all these compounds could still be improved but we have not made any further effort to do so.

It is probably simplistic to associate yields only with the solubility of starting materials. While the better yield of **4a** compared to **4b** correlates with increased solubility, the use of the *p*-FC_6H_4 ligand made only a small difference even though $Mo_2(DPh^fF)_3Cl_2$ is still more soluble. There also seems to be no correlation of yield with the electronic properties of the ligand substituents.

The well-resolved ^{1}H NMR spectra of these compounds show one set of aromatic chemical shifts, which indicate a diamagnetic ground state and the magnetic equivalence of all four formamidinate ligands.

[Mo_2(DAniF)$_2$]$_2$(μ-X)$_4$ (X = Br, 5; X = I, 6). Compound **5** was first prepared similarly to the corresponding chloro analogue. However, the yield of the crystalline sample was much lower (∼11% compared to 39%). A better source employs $Mo_2(DArF)_4$ instead of $Mo_2(DArF)_3Cl_2$ as the starting material:

$$2Mo_2(DArF)_4 + 4XSiMe_3 \xrightarrow{CH_2Cl_2} [Mo_2(DArF)_2]_2(\mu\text{-}X)_4 + 4(DArF)SiMe_3 \quad (X = Br, I)$$

Unfortunately, this reaction is totally ineffective for the synthesis of the chloroanalogue. Evidently, it is the increased reactivity of $BrSiMe_3$ and $ISiMe_3$ that makes this a good method of preparation of bromo and iodo complexes of the type $[Mo_2(DArF)_2]_2(\mu\text{-}X)_4$, X = Br, I. All of the $[Mo_2(DAniF)_2]_2(\mu\text{-}X)_4$ complexes are air-sensitive, but susceptibility to aerobic oxidation increases with the size of the halogen atom. Thus, a solution of the iodo complex reacts immediately with air while a solution of the chloro complex remains unchanged for some hours when exposed to air. A solution of the bromo analogue changes color within an hour.

Structural Results. All of the compounds, except **5**, have been structurally characterized. There are two types of core: Type **k** (see Table 2) is found in $[Mo_2(DArF)_3]_2(\mu\text{-}Y)_2$ complexes which have two multiply bonded $Mo_2(DArF)_3$ units joined by two bridging ions; type **l**, observed in $[Mo_2(DArF)_2]_2(\mu\text{-}Y)_4$ compounds, consists of two quadruply bonded $Mo_2(DArF)_2$ units joined by four bridging ions.

A previous X-ray crystal structure and ^{1}H NMR spectroscopic study of $\mathbf{1}\cdot C_6H_{14}$,[16] a type **k** complex, had provided evidence to support the presence of two bridging hydrogen atoms for each molecular unit. However, since X-ray data cannot always locate bridging hydrogen atoms with precision, a neutron diffraction experiment was undertaken. During this experiment, it was found that the larger crystals (**1n**) that made a neutron study feasible were different from the small ones used in the earlier X-ray study. A new X-ray diffraction study (**1x**), done on a fragment of the same crystal used in the neutron study, revealed that the basic features of the molecular structure were very similar to those reported earlier. In this second crystal type, there are two independent tetranuclear units, each residing on an inversion center. The molecule at one site is ordered, but the other is severely disordered, due to variations in the orientations of the *p*-anisyl groups.

In the neutron study, the bridging hydride species unambiguously appear as negative troughs in the neutron Fourier maps in both of the crystallographically independent tetranuclear units found in the crystal. The mean Mo−H distances are ∼1.84 Å and the mean Mo−H−Mo bond angles are ∼142°. The bent M−H−M units are similar to those found in other species containing singly bridged 3c−2e M−H−M bonds.[32] The structure is shown in Figure 1. Due to the relatively low number of observed data extending only to $d_{min} = 0.8$ Å, where only ∼10% of the possible data was observed, the atoms in the neutron structure were refined isotropically and the disorder observed in the X-ray structure was not resolved.

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with two tetranuclear molecules per unit cell. The general structural features of the core are shown in Figure 2; these are similar to those of **1**, but with OH as the bridging ligands instead of H. The Mo−Mo distance of 2.1070(7) Å is consistent with the presence of a quadruply bonded Mo_2^{4+} unit. The relatively long Mo−O distances of 2.123(3) and 2.118(3) Å support the formulation of the bridging groups as OH. This is confirmed by the crystal structure of the oxo-bridging analogue (**3**). Compound **3** crystallizes in the space group *Fdd*2, with eight molecules per unit cell. The Mo−O distances of 1.925(4) and 1.912(4) Å are ∼0.2 Å shorter than those in **2**. The Mo−Mo

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(32) See, for example: Peterson, J. L.; Brown, R. K.; Williams, J. M. *Inorg. Chem.* **1981**, *20*, 158−165.

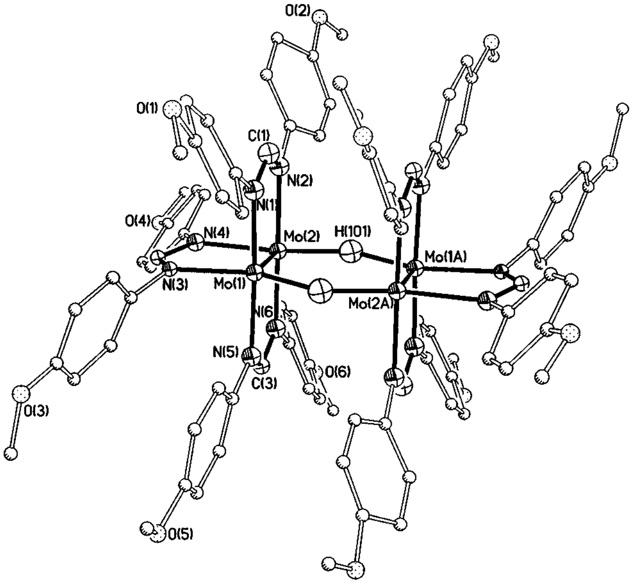

Figure 1. Representation of the neutron structure of **1**. Carbon and O atoms are shown as small spheres; Mo, H, and N atoms are 40% probability ellipsoids. The bridging hydride ions are shown, but all other hydrogen atoms have been omitted for clarity. The crystal structure of **1** contains two independent molecules; only one is shown here. Both reside on inversion centers.

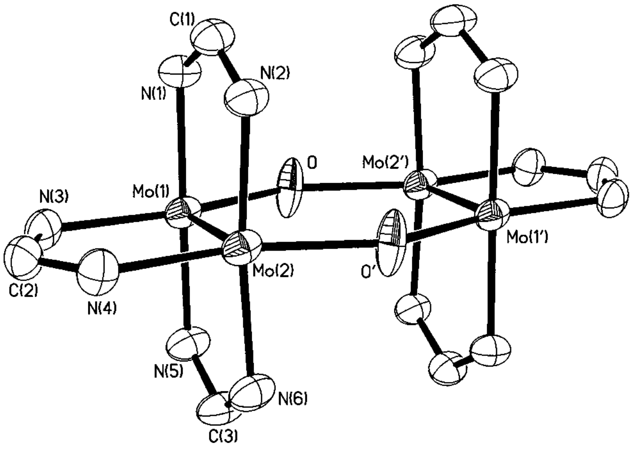

Figure 2. Thermal ellipsoid plot of the core in **2**, shown with 50% probability ellipsoids. The molecule resides on a crystallographic inversion center.

bond distance of 2.140(2) Å is longer than that in **2** but similar to that for $Mo_2(DAniF)_3Cl_2$ (2.146(1) Å)[33] and $Mo_2(DTolF)_3Cl_2$ (2.151(1) Å).[20] The increase in the Mo–Mo distance is the result of the oxidation of the quadruply bonded Mo_2^{4+} units to Mo_2^{5+} units, which decreases the bond order to 3.5. As illustrated in Figure 3, the torsion angle Mo(1)–O(1)–O(2)–Mo(2) in **3** is ~14°, while for **1** and **2**, all four Mo atoms and both bridging atoms are essentially coplanar. Comparison of Figures 2 and 3 makes the difference between **2** and **3** very clear.

In compounds **4a**, **4b**, and **4c** the short Mo–Mo distances are 2.119(1), 2.118(1), and 2.123(1) Å, respectively. These are well within the well-established range[1] for Mo–Mo quadruple bonds. The long Mo···Mo distances are ~3.56 Å, which is well outside of bonding range. Clearly, these compunds are of type **l** and are the first of that class to be structurally characterized.

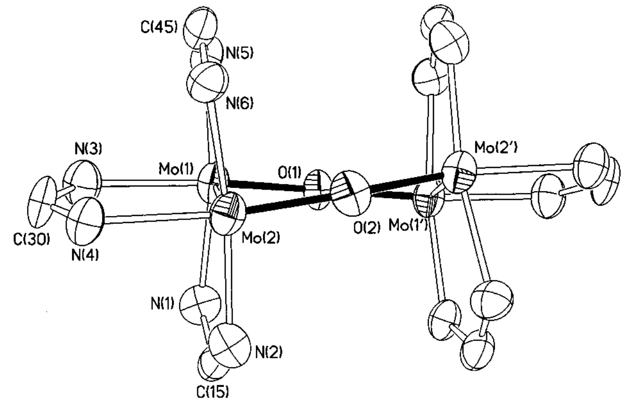

Figure 3. Core of **3**, shown with 50% probability ellipsoids. This view emphasizes the twist in the Mo–O–Mo–Mo–O–Mo ring. Atoms O(1) and O(2) reside on a crystallographic 2-fold axis.

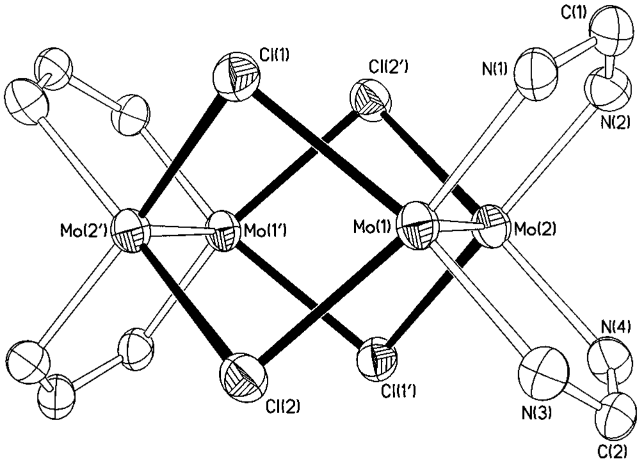

Figure 4. A view of the core in **4a**, which is similar to that of **4b** and **4c**.

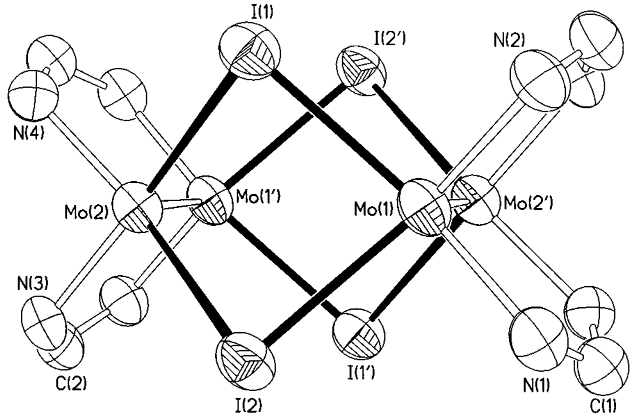

Figure 5. A drawing of the core in **6**, shown with 50% probability ellipsoids.

The Mo–Cl–Mo angles in these compounds are ~90° whereas those for the type **k** compounds (metallabutadiynes) are in the 72–74° range, exactly as expected in view of the difference in Mo–Mo bonding in the two types. A drawing of the core appears in Figure 4.

Compound **6**, in which there is a crystallographic center of inversion, as shown in Figure 5, is another example of a type **l** structure. Like **4a**, **4b**, and **4c**, it has two short Mo–Mo bonds, 2.117(1) Å, that bespeak the presence of quadruple bonding and very long, 3.915 Å, nonbonded Mo–Mo distances.

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(33) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A., unpublished results.

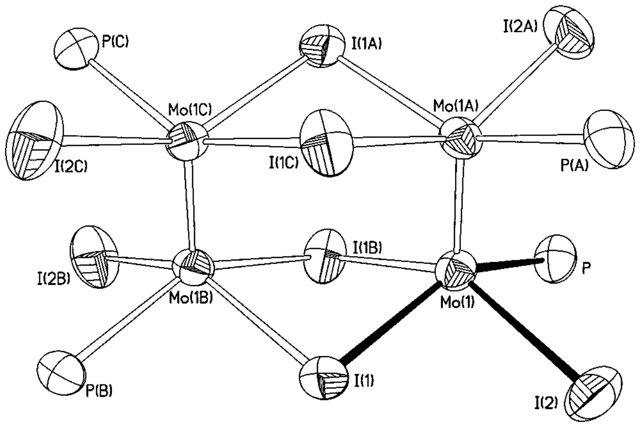

Figure 6. A drawing of one of the orientations of the disordered structure of **7**. The unique part of the molecule is shown by the solid bonds; all other atoms are generated by the 222 site symmetry. The I and P atoms form a double cube in which the Mo−Mo unit can fit two different ways; the second orientation of the Mo−Mo unit (not shown) is rotated 90° from the first.

Compound **7**, previously suspected[13a] to be of type **l** is now shown conclusively to be so. Without a structure determination, it could not have been said with certainty that it was not of type **d**, but with Mo−Mo quadruple bonds. The molecule occupies a special position of 222 symmetry. The bonded and nonbonded Mo−Mo distances are 2.129(3) and 3.998(3) Å, respectively, which are very similar to the corresponding ones in compound **6**. For **7** there is a very significant crystallographic disorder, such that 51% of the molecules are oriented in one sense and 49% in a direction perpendicular to that, as previously shown to occur in $Mo_4Cl_8(PEt_3)_4$.[12] A drawing of the core is provided in Figure 6.

Concluding Remarks

The new work reported in this paper, when contrasted with previous observations concerning the ways of combining dinuclear, multiply bonded units (doublets) to form tetranuclear products (quartets), shows that there are two important but previously unknown (or at least unproved) ways to do so: (1) by linking two quadruply bonded doublets into a cyclic quartet by means of two μ-X links (where X = H, OH, O) where the quadruple bonds may be fully preserved (X = H, OH) or partially oxidized (X = O) and (2) by linking two quadruply bonded doublets into a cyclic quartet by means of four μ-X links (where X = Cl, Br, I) with full retention of the two quadruple bonds and no additional M−M bond formation. In addition, it has been shown that the molecule $Mo_4X_8(PR_3)_4$ (X = I, R = Bu^n) retains two Mo−Mo quadruple bonds, in contrast to all molecules of the same stoichiometry with X = Cl or Br, wherein a 4 + 4 cycloaddition occurs to give metallacyclobutadiyne products.

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Supporting Information Available: Tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters and thermal ellipsoid plots of the molecules (36 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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