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The Tetrakis(hydrogen phosphato)dimolybdenum Ion $[Mo_2(HPO_4)_4]^{2-}$. Compounds with a Metal–Metal Triple Bond Which Are Easily Prepared and Permanently Stable in Air

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Received June 28, 1979

The octachlorodimolybdate(II) ion, $[Mo_2Cl_8]^{4-}$, reacts with 2 M orthophosphoric acid in air to form the purple $[Mo_2(HPO_4)_4]^{2-}$ ion which can easily be isolated in combination with various cations, for example, as $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$, **1**, and $(C_5NH_6)_3[Mo_2(HPO_4)_4]Cl$, **2**, both of which have been fully characterized structurally. They are stable indefinitely in ordinary air at 25 °C. The $[Mo_2(HPO_4)_4]_2^{2-}$ ion has a paddlewheel structure very similar to that of the $[Mo_2(SO_4)_4]^{4-,3-}$ ions; the manner in which the rings are bent and the placement of the hydrogen atoms are such as to make the idealized symmetry C_{4h}. The Mo–Mo triple bond lengths are 2.223 (2) and 2.232 (1) Å in **1** and **2**, respectively. In each case there are axial ligands, but these are loosely bonded with Mo–OH$_2$ distances of 2.46 (1) and 2.53 (1) Å in **1** and Mo–Cl distances of 2.910 (1) Å in **2**. In **1** there is no crystallographically imposed symmetry, but the conformation is only 1.35° from being precisely eclipsed, while in **2** there is $2/m$ crystallographic symmetry and the conformation is perfectly eclipsed. Compound **1** crystallizes in space group $P2_1/c$ with a = 8.751 (3) Å, b = 11.217 (3) Å, c = 17.938 Å, β = 90.92 (2)°, V = 1761 (1) Å^3, and Z = 4. Compound **2** crystallizes in space group $Pbam$ with a = 18.329 (3) Å, b = 9.157 (2) Å, c = 8.053 (1) Å, V = 1351 (1) Å^3, and Z = 2.

Introduction

The results we report here are of unusual interest in the field of multiple metal-to-metal bonds in two respects. One concerns the redox behavior of metal–metal quadruple bonds and the other has to do with the stability and other properties of triple bonds between metal atoms.

Previous attempts to generate triple bonds from quadruple bonds by oxidation to remove both electrons from the δ-bonding orbital have been unsuccessful. The earliest such attempt was with the $[Re_2X_8]^{2-}$ ions using X_2 (X = Cl, Br) as the oxidizing agent.[1] The desired two-electron oxidation occurred, but this was followed (or accompanied) by a structural rearrangement to give the bioctahedral ions, $[Re_2X_9]^-$. The $[Mo_2(SO_4)_4]^{4-}$ ion can be oxidized without gross structural change but only by one electron, to give the $[Mo_2(SO_4)_4]^{3-}$ ion,[2] which is now well characterized as having a bond order of 3.5. McCarley and co-workers[3] have shown that iodine removes only one electron from $Mo_2(O_2CCMe_3)_4$ and $MoW(O_2CCMe_3)_4$ to give the +1 ions with bond orders of 3.5. Most recently, the action of Br_2 and I_2 on $Mo_2(S_2COEt)_4$ was shown to give products with the formula $Mo_2(S_2COEt)_4X_2$ in which, again, there has been extensive rearrangement and reduction of the Mo–Mo bond order all the way to unity.[4]

We can now report the first successful attempt to carry out the two-electron oxidation of a quadruple bond to yield a triple bond, the reaction in question being, formally

$$[Mo_2Cl_8]^{4-} + 4HPO_4^{2-} + 2H^+ + {}^1/{}_2O_2 \rightarrow [Mo_2(HPO_4)_4]^{2-} + 8Cl^- + H_2O$$

The product of this reaction, $[Mo_2(HPO_4)_4]^{2-}$, is intrinsically interesting in comparison with previously known molecules and ions containing M≡M bonds.[5] From the structural point of view it is unique in being a discrete species with a $\sigma^2\pi^4$ type triple bond[6] in an environment of regular fourfold symmetry with an eclipsed configuration. From the chemical point of view it is also unique in its stability toward water and air at 25 °C.

Table I. Crystallographic Data

	$Cs_2[Mo_2(HPO_4)_4\cdot 2H_2O]$, 1	$(pyH)_3Mo_2(HPO_4)Cl$, 2
space group	$P2_1/c$	$Pbam$
a, Å	8.751 (3)	18.329 (3)
b, Å	11.217 (3)	9.157 (2)
c, Å	17.938 (4)	8.053 (1)
β, deg	90.92 (2)	
V, Å^3	1761 (1)	1351 (1)
d, g/cm^3	3.31	2.09
Z	4	2
μ, cm^{-1}	59.88	13.29
range of 2θ, deg	3 → 50	3 → 45
no. of unique data	2171	1081
data with $F_o^2 > 3\sigma(F_o^2)$	1900	1046
R_1	0.050	0.042
R_2	0.078	0.072
goodness of fit	1.65	1.84

Experimental Section

Preparations. $Cs_2[Mo_2(HPO_4)_4\cdot 2H_2O]$, 1. $K_4Mo_2Cl_8\cdot 2H_2O$ (0.05 g), prepared by a literature method,[7] was dissolved in 20 mL of an aqueous solution (2 M) of H_3PO_4. CsCl (0.02 g) was added and the solution was left to stand in an open beaker. After 2 days, purple crystals were obtained.

$(C_5NH_6)_3[Mo_2(HPO_4)_4\cdot Cl]$, 2. This compound was prepared in a way analogous to the Cs salt by using pyridinium chloride (0.03 g). The purple crystals were obtained after 24 h.

X-ray Crystallography. Collection of Data. Data were collected for both compounds on a Syntex P$\bar{1}$ automated four-circle diffractometer using Mo (λ 0.71073 Å) radiation with a graphite-crystal monochromator in the incident beam. Rotation photographs and ω scans of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range 25° < 2θ < 35°. Data were collected at 22 ± 3 °C by use of the θ–2θ scan technique with a variable scan rate from 4.0 to 24°/min. General procedures for data collection have been reported elsewhere.[8a]

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 1

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cs(1)	0.2721 (2)	0.4879 (1)	0.86661 (8)	3.96 (6)	1.89 (5)	4.07 (6)	0.03 (5)	1.43 (5)	−0.15 (5)
Cs(2)	0.1993 (2)	−0.0063 (1)	0.90001 (8)	3.32 (5)	1.85 (5)	3.22 (5)	−0.16 (4)	−0.33 (5)	−0.12 (5)
Mo(1)	0.2337 (2)	0.3415 (1)	0.61948 (7)	1.16 (5)	1.12 (5)	1.17 (5)	0.07 (5)	−0.02 (4)	−0.02 (5)
Mo(2)	0.2767 (2)	0.1462 (1)	0.61922 (7)	1.53 (5)	1.10 (5)	1.03 (5)	0.12 (5)	−0.10 (4)	0.02 (5)
P(1)	0.4948 (5)	0.2725 (4)	0.7300 (2)	0.9 (1)	2.4 (2)	0.8 (1)	0.1 (1)	−0.1 (1)	0.0 (1)
P(2)	0.0357 (5)	0.2147 (4)	0.7363 (2)	1.3 (2)	1.9 (2)	0.8 (1)	0.1 (1)	0.1 (1)	0.2 (1)
P(3)	0.0154 (5)	0.2099 (4)	0.5069 (2)	1.0 (1)	1.6 (2)	1.0 (2)	−0.2 (1)	0.2 (1)	0.0 (1)
P(4)	0.4764 (5)	0.2791 (4)	0.5025 (2)	1.0 (2)	1.9 (2)	1.1 (1)	0.1 (1)	0.0 (1)	−0.2 (1)
Ow(1)	0.196 (1)	0.565 (1)	0.6202 (8)	2.7 (5)	1.8 (5)	3.3 (6)	0.1 (5)	−0.7 (5)	0.5 (5)
Ow(2)	0.287 (2)	−0.072 (1)	0.6137 (8)	4.5 (7)	1.1 (5)	3.3 (6)	0.7 (5)	−0.7 (6)	−0.5 (5)
O(11)	0.383 (1)	0.371 (1)	0.7032 (6)	2.4 (5)	2.0 (5)	1.1 (4)	0.3 (4)	−0.5 (4)	0.5 (4)
O(12)	0.062 (1)	0.334 (1)	0.6918 (6)	0.8 (4)	2.1 (5)	1.5 (4)	0.8 (4)	0.3 (4)	−0.6 (4)
O(13)	0.078 (1)	0.333 (1)	0.5331 (6)	1.9 (5)	1.8 (5)	1.3 (4)	0.5 (4)	−0.7 (4)	−0.2 (4)
O(21)	0.436 (1)	0.152 (1)	0.7014 (6)	1.1 (4)	3.3 (5)	1.4 (5)	0.4 (4)	0.1 (4)	−0.5 (5)
O(22)	0.112 (1)	0.112 (1)	0.6958 (6)	2.1 (5)	1.6 (4)	1.7 (5)	0.5 (4)	1.1 (4)	−0.5 (4)
O(23)	0.128 (1)	0.114 (1)	0.5364 (6)	2.1 (5)	1.5 (4)	1.0 (4)	0.0 (4)	−0.7 (4)	0.0 (4)
O(24)	0.443 (1)	0.159 (1)	0.5442 (6)	1.6 (4)	1.7 (4)	2.0 (5)	1.3 (4)	0.6 (4)	−0.4 (4)
O(15)	0.530 (1)	0.274 (1)	0.8112 (6)	1.2 (5)	4.2 (6)	1.3 (4)	−0.8 (5)	0.3 (4)	0.3 (5)
O(16)	0.647 (1)	0.297 (1)	0.6889 (7)	1.2 (5)	3.3 (6)	2.7 (6)	0.8 (4)	−0.1 (4)	0.1 (5)
O(25)	0.124 (1)	0.229 (1)	0.8123 (7)	1.8 (5)	3.2 (6)	1.6 (5)	0.6 (5)	−0.3 (4)	0.8 (5)
O(26)	−0.131 (1)	0.190 (1)	0.7488 (6)	1.6 (4)	3.0 (5)	1.5 (4)	0.8 (4)	1.3 (4)	0.5 (4)
O(35)	−0.137 (1)	0.191 (1)	0.5464 (7)	1.7 (5)	2.2 (5)	2.2 (5)	−0.3 (4)	0.2 (4)	−0.1 (4)
O(36)	−0.009 (1)	0.200 (1)	0.4256 (6)	2.3 (5)	2.9 (5)	1.3 (5)	−0.8 (5)	−1.1 (4)	0.2 (4)
O(45)	0.387 (1)	0.273 (1)	0.4261 (6)	2.1 (5)	3.6 (6)	0.6 (4)	0.7 (5)	0.1 (4)	−0.6 (4)
O(46)	0.639 (1)	0.304 (1)	0.4920 (6)	1.0 (4)	2.6 (5)	1.7 (5)	0.5 (4)	0.7 (4)	0.4 (4)
O(14)	0.397 (1)	0.3786 (9)	0.5467 (6)	1.0 (2)	1.5 (2)	1.0 (2)	−0.2 (1)	0.1 (1)	0.0 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*\cdot c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound **2**

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.5000 (0)	0.5000 (0)	0.13861 (7)	1.41 (2)	1.17 (2)	1.06 (2)	0.00 (1)	0	0
Cl	0.5000 (0)	0.5000 (0)	0.5000 (0)	4.5 (1)	3.5 (1)	1.5 (1)	0.40 (9)	0	0
P(1)	0.38028 (9)	0.2912 (2)	0.0000 (0)	1.50 (6)	1.08 (6)	2.51 (7)	−0.24 (5)	0	0
P(2)	0.39210 (9)	0.7352 (2)	0.0000 (0)	1.53 (6)	1.43 (6)	2.72 (7)	0.37 (5)	0	0
O(1)	0.4234 (2)	0.3441 (3)	0.1553 (4)	2.1 (1)	1.8 (1)	2.1 (1)	−0.4 (1)	0.2 (1)	0.1 (1)
O(2)	0.4228 (2)	0.6538 (3)	0.1545 (4)	2.1 (1)	1.7 (1)	2.2 (1)	0.4 (1)	0.4 (1)	−0.0 (1)
O(3)	0.3653 (3)	0.1310 (5)	0.0000 (0)	2.4 (2)	1.2 (2)	3.7 (2)	−0.3 (1)	0	0
O(4)	0.4291 (3)	0.8875 (5)	0.0000 (0)	2.6 (2)	1.9 (2)	4.1 (3)	0.1 (2)	0	0
O(5)	0.3115 (2)	0.7427 (6)	0.0000 (0)	1.3 (2)	3.1 (2)	7.4 (4)	1.0 (2)	0	0
O(6)	0.3087 (3)	0.3778 (5)	0.0000 (0)	1.9 (2)	1.3 (2)	7.1 (3)	0.3 (1)	0	0
N	0.0000 (0)	0.500 (0)	0.3380 (14)	6.0 (6)	21 (2)	2.7 (4)	4.4 (5)	0	0
N(1)	0.2504 (5)	0.577 (1)	0.3334 (8)	10.1 (5)	9.3 (5)	3.0 (2)	−0.1 (4)	1.1 (3)	0.5 (3)
C(1)	0.0168 (5)	0.380 (1)	0.417 (1)	9.7 (5)	5.1 (4)	8.3 (6)	1.9 (3)	−2.2 (4)	−3.1 (4)
C(2)	0.3060 (5)	0.533 (1)	0.417 (1)	4.1 (3)	9.9 (5)	7.3 (5)	1.2 (3)	1.9 (3)	0.8 (4)
C(3)	0.1883 (5)	0.632 (1)	0.416 (1)	7.0 (5)	11.3 (7)	5.3 (4)	2.2 (4)	−0.9 (4)	0.9 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*\cdot c^*)]$.

Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. No absorption correction was applied for compound **2**. Intensity data for **1** were corrected for absorption by the empirical ψ-scan method.

Solution and Refinement of the Structure.[8b] The heavy-atom positions in **1** were obtained by direct methods using the MULTAN program. This structure was refined in space group $P2_1/c$ to convergence by using anisotropic thermal parameters for all atoms. The heavy-atom positions in **2** were obtained through a three-dimensional Patterson function. The structure was refined in space group *Pbam* to convergence by using anisotropic thermal parameters for all atoms. The final discrepancy indices defined as

$$R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

are listed in Table I. The final difference maps showed no peaks of structural significance. Lists of observed and final calculated structure factors for both compounds are available as supplementary material.

Results

The atomic positional and thermal parameters for **1** and **2** are listed in Tables II and III, respectively. Figures 1 and 2 show the $[Mo_2(HPO_4)_4(H_2O)_2]^{2-}$ and $[Mo_2(HPO_2)_4Cl_{2/2}]^{3-}$ units, respectively, and define the atom numbering schemes. The dimensions are listed in Tables IV and V. The Mo₂(H-

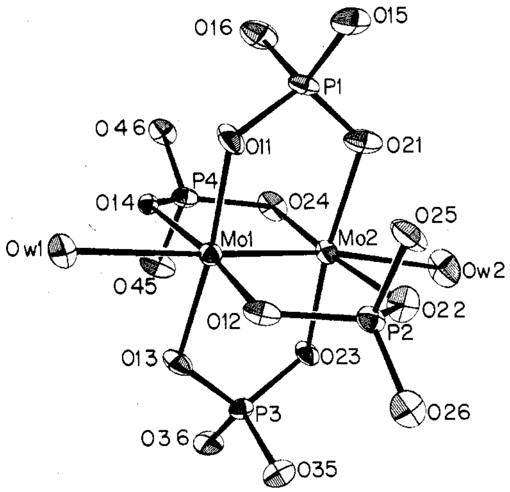

Figure 1. $[Mo_2(HPO_4)_4(H_2O)_2]$ moiety in **1**.

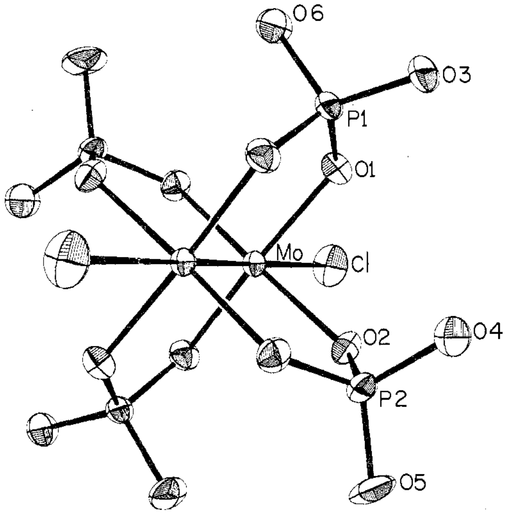

Figure 2. $[Mo_2(HPO_4)_4Cl_{2/2}]$ moiety in **2**.

Table IV. Bond Distances and Bond Angles for $Cs_2Mo_2(HPO_4)_4 \cdot 2H_2O$ (**1**)

Distances (Å)			
Mo(1)-Mo(2)	2.223 (2)		
O(11)	2.002 (9)	Mo(2)-O(21)	2.014 (9)
O(12)	2.004 (9)	O(22)	2.040 (9)
O(13)	2.047 (9)	O(23)	1.995 (9)
O(14)	1.996 (9)	O(24)	2.005 (9)
Ow(1)	2.52 (1)	Ow(2)	2.46 (1)
P(1)-O(11)	1.54 (1)	P(2)-O(12)	1.58 (1)
O(21)	1.53 (1)	O(22)	1.520 (9)
O(15)	1.48 (1)	O(25)	1.57 (1)
O(16)	1.55 (1)	O(26)	1.51 (1)
P(3)-O(13)	1.56 (1)	P(4)-O(14)	1.541 (9)
O(23)	1.543 (9)	O(24)	1.57 (1)
O(35)	1.53 (1)	O(45)	1.57 (1)
O(36)	1.474 (9)	O(46)	1.469 (9)
Angles (deg)			
Mo(2)-Mo(1)-O(11)	93.1 (3)	Mo(1)-Mo(2)-O(21)	94.7 (3)
O(12)	95.0 (3)	O(22)	93.5 (3)
O(13)	93.6 (3)	O(23)	94.1 (3)
O(14)	94.7 (2)	O(24)	93.1 (3)
Ow(1)	178.1 (4)	Ow(2)	172.8 (8)
O(11)-Mo(1)-O(12)	90.5 (4)	O(21)-Mo(2)-O(22)	90.0 (4)
O(13)	173.2 (4)	O(23)	171.1 (4)
O(14)	89.5 (4)	O(24)	89.2 (4)
O(12)-Mo(1)-O(13)	89.5 (4)	O(22)-Mo(2)-O(23)	90.5 (4)
O(14)	170.3 (4)	O(24)	173.4 (4)
O(13)-Mo(1)-O(14)	89.3 (4)	O(23)-Mo(2)-O(24)	89.3 (4)
Mo(1)-O(11)-P(1)	121.3 (6)	Mo(1)-O(12)-P(2)	118.7 (5)
Mo(2)-O(21)-P(1)	119.8 (6)	Mo(2)-O(22)-P(2)	120.2 (6)
O(11)-P(1)-O(21)	108.6 (5)	O(12)-P(2)-O(22)	109.3 (5)
O(15)	114.6 (6)	O(25)	106.3 (5)
O(16)	105.5 (5)	O(26)	112.3 (5)
O(21)-P(1)-O(15)	113.7 (6)	O(22)-P(2)-O(25)	106.0 (6)
O(16)	106.4 (6)	O(26)	111.7 (6)
O(15)-P(1)-O(16)	107.4 (6)	O(25)-P(2)-O(26)	110.9 (5)
Mo(1)-O(13)-P(3)	119.8 (5)	Mo(1)-O(14)-P(4)	121.2 (5)
Mo(2)-O(23)-P(3)	122.3 (5)	Mo(2)-O(24)-P(4)	121.6 (5)
O(13)-P(3)-O(23)	107.1 (5)	O(14)-P(4)-O(24)	106.7 (5)
O(35)	106.7 (5)	O(45)	104.9 (5)
O(36)	114.2 (5)	O(46)	112.0 (5)
O(23)-P(3)-O(35)	107.5 (5)	O(24)-P(4)-O(45)	106.7 (6)
O(36)	111.6 (6)	O(46)	114.3 (5)
O(35)-P(3)-O(36)	109.5 (6)	O(45)-P(4)-O(46)	111.6 (5)

$PO_4)_4(H_2O)_2$ unit has no imposed crystallographic symmetry, but, as shown by the torsional angles in Table VI, which have a mean value of only 1.35°, the conformation is essentially eclipsed. The $[Mo_2(HPO_4)_4Cl_{2/2}]$ unit (where $Cl_{2/2}$ denotes two doubly shared Cl atoms) resides on a position of $2/m$ crystallographic symmetry and thus has a rigorously eclipsed structure.

Table V. Bond Distances and Bond Angles for $(pyH)_3[Mo_2(HPO_4)_4Cl]$ (**2**)

Distances (Å)			
Mo-Mo′	2.232 (1)	Mo-O(1)	2.006 (3)
Cl	2.910 (1)	O(2)	2.001 (3)
P(1)-O(1)	1.557 (3)	P(2)-O(2)	1.556 (3)
O(3)	1.492 (4)	O(4)	1.550 (4)
O(6)	1.533 (4)	O(5)	1.479 (4)
N-C(1)	1.30 (1)	N(1)-C(2)	1.28 (1)
		C(3)	1.412 (9)
C(1)-C(1)′	1.34 (2)	C(2)-C(2)′	1.34 (2)
		C(3)-C(3)′	1.35 (1)
Angles (deg)			
Mo′-Mo-O(1)	93.85 (8)	O(1)-Mo-O(2)	90.1 (1)
O(2)	93.66 (8)	O(2)′	89.4 (1)
O(1)-Mo-O(1)′	172.3 (1)	O(2)-Mo-O(2)′	172.7 (1)
Mo-O(1)-P(1)	121.5 (1)	Mo-O(2)-P(2)	122.8 (1)
O(1)-P(1)-O(1)′	106.9 (2)	O(2)-P(2)-O(2)′	106.2 (2)
O(3)	113.5 (1)	O(4)	105.8 (1)
O(6)	105.9 (1)	O(5)	112.5 (1)
O(3)-P(1)-O(6)	110.5 (2)	O(4)-P(2)-O(5)	113.3 (2)
C(1)-N-C(1)′	121 (1)	C(2)-N(1)-C(3)	120.2 (6)
N-C(1)-C(1)′	119.2 (5)	N(1)-C(2)-C(2)′	121.5 (4)
		N(1)-C(3)-C(3)′	118.1 (4)

Table VI. Torsional Angles in Compound **1**

atoms	angle, deg
O(14)-Mo(1)-Mo(2)/Mo(2)-Mo(1)-O(24)	1.1
O(13)-Mo(1)-Mo(2)/Mo(2)-Mo(1)-O(23)	1.0
O(12)-Mo(1)-Mo(2)/Mo(2)-Mo(1)-O(22)	1.9
O(11)-Mo(1)-Mo(2)/Mo(2)-Mo(1)-O(21)	1.4
average	1.35

The entire structure of **2** is closely constrained by crystal symmetry elements. The molybdenum atoms and Cl atoms form infinite chains lying along crystallographic twofold axes parallel to the c axis at 0, 0, z and $^1/_2$, $^1/_2$, z. The Cl atoms are at 0, 0, $^1/_2$ and $^1/_2$, $^1/_2$, $^1/_2$. The P atom, the two uncoordinated oxygen atoms, and the H atom of each HPO_4 unit lie in the x, y, 0 plane. The pyridinium ions are of two kinds. One set of four are disordered on positions of $2/m$ symmetry and the other set of two are disordered on positions of m symmetry.

The hydrogen atoms in the HPO_4 groups have not been directly determined, but from the large, systematic variation in the outer P–O distances it is not difficult to sort out the P—OH and P=O groups. In **1** the distances to O(15), O(26), O(36), and O(46) average 1.48 ± 0.01 Å while those to O(16), O(25), O(35), and O(45) average 1.56 ± 0.01 Å, identifying the former as P=O and the latter as P—OH. The arrangement is consistent with the presence of a fourfold symmetry axis. Similarly, in **2** P(1)–O(3) and P(2)–O(5) average 1.485 ± 0.006 Å while P(1)–O(6) and P(2)–O(4) average 1.542 ± 0.009 Å.

Discussion

There are a number of ways in which triple bonds between metal atoms may be formed.[5] The type that is at present most thoroughly studied has a $\sigma^2\pi^4$ electron configuration in an $X_3M{\equiv}MX_3$ molecule of D_{3d} symmetry, where M is Mo or W and X is a univalent group such as an alkyl group, NR_2, or OR. There are essentially similar compounds with mixed sets of ligands, e.g., $W_2(NEt_2)_4Cl_2$ or $Mo_2(NMe_2)_4Me_2$. The total electron count per metal atom in these cases is only 12 and they exhibit distinctly unsaturated characteristics.[5] They can add additional ligands, L, to form $LX_3M{\equiv}MX_3L$ species[9] and the OR and NR_2 molecules react with CO_2 to form more complex[10] molecules in which triple bonds are retained. All of these species are sensitive to air and protonic media. The electronic structures of the $X_3M{\equiv}MX_3$ molecules are well

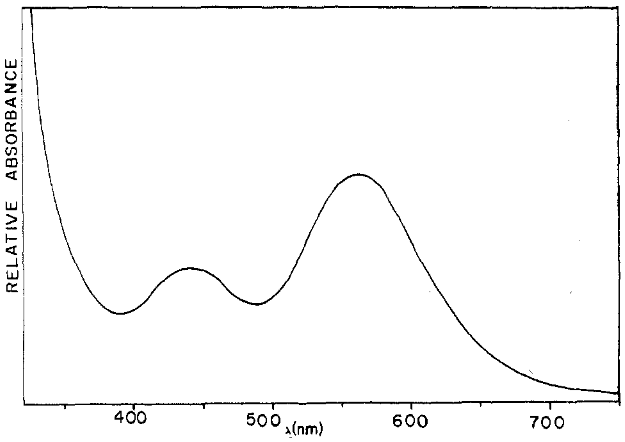

Figure 3. Visible absorption spectrum of $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$.

understood on the basis of photoelectron spectra and SCF–Xα–SW calculations.[11]

Other types of compounds containing triple bonds include V_2(2,6-dimethoxyphenyl)$_4$,[12] $CpM(CO)_2{\equiv}M(CO)_2Cp$ (M = Cr, Mo, W),[13] and several additional compounds that do not seem to represent general classes.

The formation of triple bonds by oxidation or reduction of quadruple bonds is now a well-recognized logical possibility. The reductive route was the first to be realized in practice. The reactions of phosphines with $[Re_2Cl_8]^{2-}$ to give species such as $Re_2Cl_4(PR_3)_4$ were first reported in 1974.[14] The triple bonds in these compounds are of the $\sigma^2\pi^4\delta^2\delta^{*2}$ type, where there is a cancellation of the δ bond by the pair of δ* electrons and the electron count per metal atom is 18.[15] The Re_2(allyl)$_4$ molecule[16] has a similar electronic structure.[17] The more obvious possibility of reducing the bond order of 4 to 3 by removal of the δ electrons from a $\sigma^2\pi^4\delta^2$ configuration has proved difficult to realize.

As noted in the Introduction, attempts to oxidize species such as $[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$ have led to structural reorganizations, giving $[Re_2Cl_9]^-$ and $[Mo_2Cl_8H]^{3-}$ ions,[1,18] and with $[Mo_2(SO_4)_4]^{4-}$, one-electron oxidation to give the $[Mo_2(SO_4)_4]^{3-}$ ion is not difficult,[2,19] but removal of the second δ electron has not been accomplished.

It is, therefore, somewhat surprising how easily the objective of oxidatively converting a $\sigma^2\pi^4\delta^2$ configuration to a stable $\sigma^2\pi^4$ configuration while preserving a typical X_4MMX_4 type of structure has been accomplished for the first time in the present work. Moreover, the product, $[Mo_2(HPO_4)_4]^{2-}$, forms salts that are completely stable toward air and protic media.

The Mo–Mo bond in the $[Mo_2(HPO_4)_4]^{2-}$ ion has a length of 2.223 (2) Å in **1** and 2.232 (1) Å in **2**. This sort of distance is virtually identical with that which would be extrapolated by considering the $[Mo_2(SO_4)_4]^{4-}$ to $[Mo_2(SO_4)_4]^{3-}$ pair, where the change is from 2.111 to 2.165 Å, thus suggesting a value of ~2.22 Å for the species with a $\sigma^2\pi^4$ configuration. The character of the HPO_4^{2-} ion is so similar to that of SO_4^{2-} that such an extrapolation seems justified. Even the packing patterns of infinite chains of alternating $Cl\cdots Mo_2\cdots Cl\cdots$ units in **2** are extremely similar to that in $K_4[Mo_2(SO_4)_4]Cl\cdot 4H_2O$;[20] the Cl···Mo distances here are 2.91 Å and in the latter they are 2.88 Å.

The only other closely related compound previously reported is, perhaps, $Mo_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$, which is obtained by carbonylation of $Mo_2(O\text{-}t\text{-}Bu)_6$ and has a Mo–Mo distance of 2.241 (1) Å.[10a] This molecule deviates considerably from fourfold symmetry, however.

The spectrum of **1** was measured on a sample ground with KBr and pressed into a pellet.[20] No absorption was found in the near-infrared region and the absorption bands shown in Figure 3 are extremely weak. While their intensities are not known quantitatively, they appear to be far weaker than the $\delta \rightarrow \delta^*$ transition in the $[Mo_2(SO_4)_4]^{4-}$ ion.[21]

The results presented here appear to us to be quite seminal since they demonstrate that there are conditions under which simple $\sigma^2\pi^4$ triple bonds can be obtained in compounds that have a conventional existence in aqueous media and in presence of air.

Acknowledgment. We thank the Robert A. Welch Foundation for financial support.

Registry No. **1**, 70281-26-4; **2**, 71597-13-2; $K_4Mo_2Cl_8\cdot 2H_2O$, 22239-46-9.

Supplementary Material Available: Tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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