

### Polyoxometalate–Diphosphate Complexes. 3. Possible Intermediates in the Molybdate-Catalyzed Hydrolysis of Pyrophosphate. The Structure of Hexamolybdomethylenediphosphonate, $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ †

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Two new polyoxomolybdate-diphosphate complexes with the formula  $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$  (I, X = CH<sub>2</sub>; II, X = O) have been synthesized and characterized by <sup>31</sup>P-, <sup>13</sup>C-, <sup>1</sup>H-NMR, IR, and elemental analysis. Anions I and II are formed under weakly acidic conditions (pH 3–3.5). An X-ray structure determination was carried out on Cs<sub>4</sub>[(O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>)Mo<sub>6</sub>O<sub>18</sub>(H<sub>2</sub>O)<sub>4</sub>]·7H<sub>2</sub>O, which crystallizes in the triclinic system, space group *P* $\bar{1}$ , with *a* = 11.301(2) Å, *b* = 11.499(3) Å, *c* = 16.024(4) Å, α = 98.43°, β = 107.92°, γ = 106.61°, *V* = 1834.7(7) Å<sup>3</sup>, *Z* = 2, and ρ<sub>calcd</sub> = 3.152 g/cm<sup>3</sup>. Structural analysis based on 9312 independent reflections leads to a solution, *R* = 6.51% (*I* > 2σ(*I*)). Anion I consists of a six-membered ring of MoO<sub>6</sub> octahedra, which alternate in sharing edges and corners. The [O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>]<sup>4-</sup> anion is bound with P(2) in the center of the ring and P(1) off-center and bound above the ring to two adjacent MoO<sub>6</sub> octahedra. Each of the remaining four molybdenums has a terminal water ligand on the same side of the ring as P(1). Anion II almost certainly has an analogous structure based on spectroscopic evidence. A second polyoxomolybdate-pyrophosphate complex with a [O<sub>3</sub>POPO<sub>3</sub>]<sup>4-</sup>:MoO<sub>3</sub> ratio of 1:3 has been synthesized at pH 6. This complex and anion II are possible intermediates in the molybdate-catalyzed hydrolysis of pyrophosphate which is known to be most effective at pH 2 with a secondary maximum at pH 5.5.

#### Introduction

The catalytic effect of molybdate on the hydrolysis of diphosphate (P<sub>2</sub>O<sub>7</sub><sup>4-</sup>) and oligophosphate esters (e.g. ADP, ATP) has been known for many years. Weil-Malherbe and Green<sup>1</sup> studied the effect of the pH on the hydrolysis of phosphate bonds for a variety of substrates in the presence and absence of molybdate. Jenkins and Patrick<sup>2</sup> investigated ATP hydrolysis in some detail and showed that ATP forms an ATP–molybdate complex with a stoichiometry of 1:3 at pH 5.5. Geraldes and Castro<sup>3</sup> performed <sup>1</sup>H- and <sup>31</sup>P-NMR studies of the interaction of molybdate with ADP and ATP. They concluded that molybdate forms strong complexes in different stoichiometries with ADP and ATP in acidic media. Katsoulis, Lambrianidou, and Pope<sup>4</sup> synthesized some heteropoly molybdate complexes of mononucleotides and proposed a structure with a 2:5 stoichiometry. On the basis of <sup>31</sup>P NMR they proposed the same structure for a diphosphate molybdate complex at pH 3.5.

To date no complex of molybdate with diphosphate or oligophosphate esters has been isolated from aqueous solution and structurally characterized.<sup>5</sup> We are currently investigating the interaction of polytungstates and polymolybdates with biological oligophosphates and esters. In order to understand the hydrolysis of diphosphate, we have also studied its hydrolytically stable analog, methylenediphosphonate, [O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>]<sup>4-</sup>.

We have reported elsewhere the synthesis and X-ray characterization of two new polyoxotungstates incorporating as heterogroups four diphosphates and methylenediphosphonates, respectively.<sup>6</sup> Here we describe the synthesis and characterization of three new diphosph(on)ate complexes of polyoxomolybdates.

#### Experimental Section

**Synthesis.** As indicated by <sup>31</sup>P NMR both heteropolyanions are formed rapidly at room temperature in aqueous solution. Anion I is formed by addition of 10 mL of 0.5 M methylenediphosphonic acid to 60 mL of 0.5 M sodium molybdate, followed by adjustment of pH to 3.5 with 12 M HCl. Crystals suitable for X-ray analysis were obtained 1 day after layering this solution with a saturated solution of CsCl. Anal. Calcd (found) for Cs<sub>4</sub>[(O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>)Mo<sub>6</sub>O<sub>18</sub>]·11H<sub>2</sub>O: Cs, 30.12 (30.39); Mo, 32.61 (32.72); P, 3.51 (3.63). <sup>31</sup>P NMR: δ 18.5 (d of t, 1P), 25.4 (d of t, 1P), <sup>2</sup>J<sub>PH</sub> = 19.1 Hz, <sup>2</sup>J<sub>PP</sub> = 10.4 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 26.9 (t, 1C), <sup>1</sup>J<sub>CP</sub> = 118.7 Hz. <sup>1</sup>H NMR: δ 2.4 (t, 2H), <sup>2</sup>J<sub>HP</sub> = 19.2 Hz. IR: 1360 (w), 1170 (m), 1110 (m), 1050 (m), 1025 (m), 925 (s), 900 (s), 800 (m), 750 (m), 690 (s, b), 520 (m, b) cm<sup>-1</sup>. Anion II is formed when 25 mL of a solution which contains 0.3 M potassium molybdate and 0.05 M potassium pyrophosphate is adjusted to pH 3 with 12 M HCl. Immediate addition of ethanol gives a white precipitate. Anal. Calcd (Found) for K<sub>4</sub>[(O<sub>3</sub>POPO<sub>3</sub>)Mo<sub>6</sub>O<sub>18</sub>]·5H<sub>2</sub>O: K, 12.18 (12.39); Mo, 44.83 (44.19); P, 4.83 (4.81); H<sub>2</sub>O, 7.0 (6.9). <sup>31</sup>P NMR: δ -3.6 (d, 1P), -6.8 (d, 1P), <sup>2</sup>J<sub>PP</sub> = 10.4 Hz. IR: 1153 (m), 1107 (m), 1044 (m), 932 (s), 903 (s), 804 (sh), 752 (sh), 691 (s, b), 595 (m), 559 (sh), 528 (m) cm<sup>-1</sup> [w, weak; m, medium; s, strong; b, broad; sh, shoulder]. Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, NY.

**X-ray Crystallography.** Diffraction data from a platelike colorless crystal of I suitable for X-ray analysis were collected on a Siemens P4/RA diffractometer with Mo Kα radiation (λ = 0.710 73 Å) at 295 K. Crystal and structure refinement data for Cs<sub>4</sub>[(O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>)Mo<sub>6</sub>O<sub>18</sub>·(H<sub>2</sub>O)<sub>4</sub>]·7H<sub>2</sub>O are summarized in Table 1. Three check reflections

† Part 1: See ref 6. Part 2: Kortz, U.; Pope, M. T. *Inorg. Chem.* **1994**, *33*, 5643.

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- (3) Geraldes, C. F. G. C.; Castro, M. M. C. A. *J. Inorg. Biochem.* **1986**, *28*, 319.
- (4) Katsoulis, D. E.; Lambrianidou, A. N.; Pope, M. T. *Inorg. Chim. Acta* **1980**, *46*, L55.
- (5) The [(P<sub>2</sub>O<sub>7</sub>)Mo<sub>18</sub>O<sub>54</sub>]<sup>4-</sup> anion was synthesized in a mixed aqueous/organic solvent. (Himeno *et al.* *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1602; Kortz *et al.* *Inorg. Chem.* **1994**, *33*, 5643).

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**Table 1.** Crystal Data and Structure Refinement for  $Cs_4[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4] \cdot 7H_2O$ 

empirical formula	$Cs_4Mo_6P_2O_{35}CH_{24}$
fw	1765.2
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 11.301(2) \text{ \AA}$ , $\alpha = 98.43^\circ$ $b = 11.499(3) \text{ \AA}$ , $\beta = 107.92^\circ$ $c = 16.024(4) \text{ \AA}$ , $\gamma = 106.61^\circ$
volume	$1834.7(7) \text{ \AA}^3$
Z	2
density (calcd)	$3.152 \text{ Mg/m}^3$
abs coeff	$6.092 \text{ mm}^{-1}$
$F(000)$	1576
cryst size	$0.2 \times 0.1 \times 0.01 \text{ mm}^3$
$\theta$ range for data collcn	$1.91\text{--}28.80^\circ$
index ranges	$-1 \leq h \leq 14$ , $-15 \leq k \leq 14$ , $-21 \leq l \leq 21$
no. of reflcns colld	10706
no. of indep reflcns	9312 ( $R(\text{int}) = 0.0353$ )
refinement method	full-matrix least-squares on $F^2$
data/restraints/params	9312/0/253
goodness-of-fit on $F^2$	1.033
final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0651$ , $\omega R2 = 0.1660$
R indices (all data)	$R1 = 0.0953$ , $\omega R2 = 0.1859$
largest diff peak and hole	$4.584$ and $-4.327 \text{ e \AA}^{-3}$

measured every 100 scans indicated that the chosen crystal did not decompose during data collection. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELX-93 package (G. M. Sheldrick). With all Cs, Mo, and P atoms refined anisotropically and no H-atoms included,  $R = 6.51\%$ , the minimized function being  $\sum_w(|F_o| - |F_c|)^2$ . The weighting scheme employed was  $w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 16.52P]$  where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$ . A list of atomic coordinates and equivalent isotropic displacement parameters for **I** is given in Table 2. Selected bond distances and angles are listed in Table 3.

**Spectroscopy.** All NMR experiments were made on a Bruker AM-300WB spectrometer. Phosphorus-31 NMR spectra were recorded in  $D_2O$  at 121.496 MHz using 10 mm tubes (pulse width 11.0  $\mu\text{s}$ , acquisition time 0.41 s, relaxation delay 0.64 s, sweep width 5000 Hz). Chemical shifts are reported with reference to 85%  $H_3PO_4$  (external replacement method), upfield shifts being reported as negative. Carbon-13 and proton NMR spectra were recorded in  $D_2O$  at 75.469 and 300.134 MHz respectively, using 5 mm tubes.  $^{13}\text{C}$  ( $^1\text{H}$ ): pulse width 2.1  $\mu\text{s}$  (9.0), acquisition time 0.819 s (1.171), relaxation delay 0.5 s (2.0), and sweep width 5000 Hz (3497). The IR spectra were recorded on a Mattson FTIR instrument (KBr pellets).

## Results and Discussion

The structure of the new anion **I** consists of a six-membered ring of  $MoO_6$  octahedra, which alternate in sharing edges and corners. The  $[O_3PCH_2PO_3]^{4-}$  anion is bound with P(2) in the center of the ring and P(1) off-center and bound above the ring to two adjacent  $MoO_6$  octahedra (see Figure 1). Each of the remaining four molybdenums has a terminal water ligand on the same side of the ring as P(1). The characteristic  $^{31}\text{P}$  NMR spectrum of **I** is observed immediately upon mixing the constituents or dissolution of the solid and remains unchanged if the solution is stored for one year at room temperature or heated to 150  $^\circ\text{C}$  in a bomb for 24 h. The spectrum does not exclude the possibility of intramolecular exchange and pseudorotation processes in which the P(1) phosphate visits all adjacent pairs of molybdenums.<sup>7</sup> On the basis of stoichiometry, NMR, and IR similarities (see Figure 2) anion **II** almost certainly has the same structure as **I**.

(7) Although the upfield (18.5-ppm)  $^{31}\text{P}$ -NMR resonance of **I** is slightly broader than the other, no change in line width was observed between 20 and 80  $^\circ\text{C}$ . The crystal structure reveals a cesium cation coordinated to the underside of the  $Mo_6$  ring, and it is therefore possible that one phosphorus is subject to quadrupolar relaxation via ion-pairing.

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $Cs_4[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4] \cdot 7H_2O$ 

atom	x	y	z	U(eq)
Mo(1)	1803(1)	7120(1)	3734(1)	18(1)
Mo(2)	3616(1)	5347(1)	3434(1)	18(1)
Mo(3)	1977(1)	2058(1)	2188(1)	19(1)
Mo(4)	-1334(1)	953(1)	1094(1)	19(1)
Mo(5)	-3277(1)	2829(1)	1408(1)	18(1)
Mo(6)	-1812(1)	5755(1)	2786(1)	18(1)
Cs(1)	-4345(1)	416(1)	-1321(1)	56(1)
Cs(2)	111(1)	3347(1)	4124(1)	45(1)
Cs(3)	-190(1)	-474(1)	3567(1)	40(1)
Cs(4)	4166(1)	6739(1)	6152(1)	37(1)
P(1)	2073(3)	6413(3)	1696(2)	17(1)
P(2)	224(3)	4255(2)	2067(2)	14(1)
C(1)	572(11)	5035(10)	1225(7)	21(2)
O(1A)	2228(8)	6960(7)	918(5)	24(2)
O(1B)	-49(8)	6751(7)	3035(5)	21(2)
O(1C)	1522(9)	6526(8)	4610(6)	30(2)
O(1D)	1891(8)	7342(7)	2401(5)	21(2)
O(1E)	1340(7)	5041(6)	2985(4)	14(1)
O(1F)	2284(9)	8715(8)	4152(6)	27(2)
O(2A)	3448(9)	4699(8)	4306(6)	29(2)
O(2B)	5278(9)	5826(8)	3649(6)	31(2)
O(2C)	3233(8)	5978(7)	2165(5)	19(2)
O(2D)	3485(8)	6939(7)	3907(5)	22(2)
O(3B)	235(7)	2919(7)	1863(5)	18(1)
O(3C)	3121(10)	1348(9)	2170(7)	36(2)
O(3D)	3019(8)	3755(7)	2550(5)	21(2)
O(3E)	1686(10)	1847(9)	3149(6)	36(2)
O(4A)	-1510(9)	717(8)	2088(6)	31(2)
O(4B)	-2303(9)	-461(8)	317(6)	32(2)
O(4C)	381(8)	809(7)	1303(5)	21(2)
O(4D)	-2471(8)	1909(7)	812(5)	20(2)
O(5B)	-4895(10)	2052(9)	733(6)	33(2)
O(5C)	-1131(8)	4240(7)	2091(5)	19(1)
O(5D)	-3131(9)	2216(8)	2335(6)	29(2)
O(6B)	-1599(9)	5159(8)	3719(6)	30(2)
O(6C)	-2470(9)	6876(8)	3008(6)	29(2)
O(6D)	-3358(8)	4420(7)	1934(5)	21(2)
O(1W)	-2002(9)	6341(8)	1387(6)	28(2)
O(2W)	-3099(9)	3867(8)	308(6)	27(2)
O(3W)	-825(9)	1712(8)	-56(6)	27(2)
O(4W)	2046(9)	2466(8)	752(6)	29(2)
O(5W)	5781(23)	8720(20)	5305(15)	154(7)
O(6W)	2154(20)	9217(18)	5979(13)	103(6)
O(7W)	-4264(22)	8394(19)	2812(14)	106(6)
O(8W)	89(10)	8468(9)	1751(6)	35(2)
O(9W)	4119(10)	4642(9)	1056(6)	33(2)
O(10W)	-4025(13)	7249(12)	944(9)	57(3)
O(11W)	-2006(16)	8043(14)	4868(10)	76(4)

**Table 3.** Selected Bond Length Ranges ( $\text{\AA}$ ) and Angle (deg) for  $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$  (**I**)

Mo–O <sub>terminal</sub> (trans to doubly bridging O)	1.696–1.719(9)
Mo–O <sub>terminal</sub> (cis to doubly bridging O)	1.707–1.723(9)
Mo–OH <sub>2</sub>	2.295–2.434(9)
Mo–O <sub>doubly bridging</sub>	1.862–1.940(8)
Mo–O <sub>triply bridging</sub>	2.304–2.400(7)
Mo–O(P)	2.217–2.218(8)
P–O <sub>triply bridging</sub>	1.527–1.546(7)
P–O <sub>doubly bridging</sub>	1.541–1.553(8)
P–O <sub>terminal</sub>	1.510(8)
P–C	1.804–1.812(11)
P–C–P	113.1(6)

It is of interest to compare the unsymmetric structure of **I** with the hexamolybdomethylarsonate,  $[CH_3AsO_3Mo_6O_{18}(H_2O)_6]^{2-}$ , reported by Matsumoto.<sup>8</sup> Both anions contain rings of edge- and corner-shared  $MoO_6$  octahedra but the water molecules alternate above and below the ring in the Matsumoto anion ( $C_3$  symmetry). As is clearly shown in Figure 1, the P(1) phosphate group of **I** generates a polar side to the hexamolybdate ring and all the water molecules occupy that side.

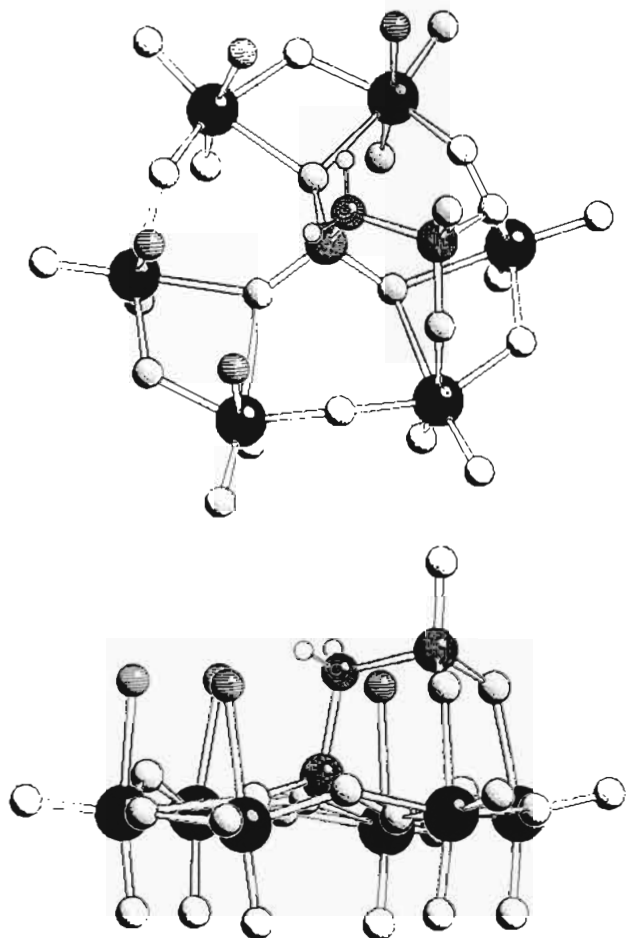


Figure 1. Ball and stick representations of the structure of  $[(O_3PCH_2PO_3)_4Mo_6O_{18}(H_2O)_4]^{4-}$  (I): upper, top view; lower, side view. The positions of the hydrogen atoms were calculated, and the water molecules are represented by the small shaded spheres.

We have investigated the speciation of the  $P_2O_7^{4-}/MoO_4^{2-}$  system by means of  $^{31}P$  NMR in the pH range 1–7. The only pyrophosphate/molybdate species that could be detected were anion II at pH 3.5 and another complex (III) with a 1:3 stoichiometry<sup>9</sup> at pH 6. By  $^{31}P$  NMR we have observed that hydrolysis of pyrophosphate is more effective at pH 3 than at pH 6, which is in agreement with Weil-Malherbe and Green,<sup>1</sup> who reported that the catalytic effect of molybdate on the hydrolysis of diphosphate reaches its maximum at pH 2 with a secondary maximum at pH 5.5. In a solution of II (0.07 M  $P_2O_7^{4-}$ , 0.42 M  $MoO_4$ , pH 3) 54% of the pyrophosphate is hydrolyzed at room temperature after 18 h (6% after 2 h). The only products of hydrolysis are the pentamolybdodiphosphate anion,  $[(OPO_3)_2Mo_5O_{15}]^{6-}$  and, presumably, heptamolybdate,  $[H_7Mo_7O_{24}]^{6-}$ . In a solution of III (0.13 M  $P_2O_7^{4-}$ , 0.39 M  $MoO_4$ , pH 6) hydrolysis at room temperature is much slower. After 18 h about 4% of the pyrophosphate is hydrolyzed. The products are free monophosphate, pentamolybdodiphosphate as well as, presumably, unprotonated heptamolybdate.<sup>10–13</sup>

Both anions I and II, and the structural types  $[(O_3PXPO_3)_4W_{12}O_{36}]^{16-}$  ( $X = O, CH_2$ ) and  $[(RPO_3)_2M_5O_{15}]^{n-}$  ( $M = W, Mo$ ;  $R = O, C_6H_5$ ) contain external heterogroups. Differences in  $^{31}P$  NMR chemical shifts of each polyoxomolybdate diphosph(on)ate complex and its corresponding tungstate are surprisingly small (see Table 4). This observation applies for structures with external dinuclear (e.g.  $O_3POPO_3^{4-}$ ) as well

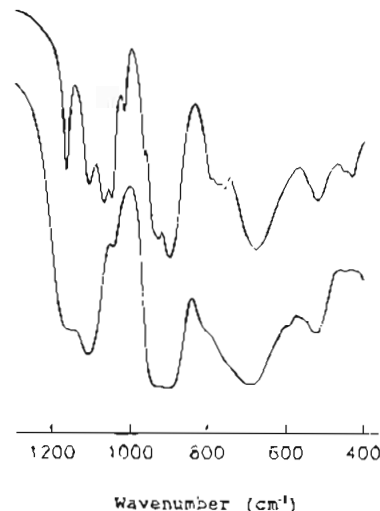


Figure 2. Infrared spectra of  $K_4[(O_3POPO_3)_4Mo_6O_{18}] \cdot 5H_2O$  (upper) and  $Cs_4[(O_3PCH_2PO_3)_4Mo_6O_{18}] \cdot 11H_2O$  (lower) recorded in KBr pellets.

Table 4.  $^{31}P$ -NMR Chemical Shifts for Selected Polyoxomolybdates and -tungstates<sup>a</sup>

compound	chem shift/ppm	$\Delta$ /ppm <sup>b</sup>	ref
III <sup>c</sup>	-5.8, -8.3		this work
$[(O_3POPO_3)_4W_{12}O_{36}]^{16-}$	-3.8, -8.1	2.0, 0.2	6
$[(OPO_3)_2Mo_5O_{15}]^{6-}$	2.35	4.75	10
$[(OPO_3)_2W_5O_{15}]^{6-}$	-2.4		11
$[(C_6H_5PO_3)_2Mo_5O_{15}]^{4-}$	21.3	4.9	12
$[(C_6H_5PO_3)_2W_5O_{15}]^{4-}$	16.4		7
$\alpha$ - $[(PO_4)Mo_{12}O_{36}]^{3-}$ <sup>d</sup>	-3.9	11.0	13
$\alpha$ - $[(PO_4)W_{12}O_{36}]^{3-}$ <sup>d</sup>	-14.9		13
$\alpha$ - $[(PO_4)_3Mo_{18}O_{54}]^{6-}$ <sup>d</sup>	-3.4	9.3	13
$\alpha$ - $[(PO_4)_3W_{18}O_{54}]^{6-}$ <sup>d</sup>	-12.7		13

<sup>a</sup> In aqueous solution, vs 85%  $H_3PO_4$  (upfield shifts negative).

<sup>b</sup> Difference (in ppm) of the corresponding NMR signals for molybdate and tungstate species. <sup>c</sup> See ref 9. <sup>d</sup> Structures with internal heterogroups.

as mononuclear (e.g.  $PO_4^{3-}$ ) heterogroups. In structures where the heteroatom is completely surrounded by  $MO_6$  ( $M = Mo, W$ ) octahedra, e.g.  $\alpha$ - $[(PO_4)M_{12}O_{36}]^{3-}$  (Keggin) or  $\alpha$ - $[(PO_4)_3M_{18}O_{54}]^{6-}$  (Dawson) the chemical shift differences are much larger. It seems that for heteropolyanions with external het-

(9) We believe that this anion is the molybdenum analog of the dodecatungstate anion, which we have reported elsewhere (see ref 6) and therefore has the formula  $[(O_3POPO_3)_4Mo_{12}O_{36}]^{16-}$  (III). It is formed when 25 mL of a solution which contains 0.1 M sodium pyrophosphate and 0.3 M sodium molybdate is adjusted to pH 6 with 12 M HCl. A white precipitate is obtained by addition of 5 mL of a saturated solution of CsCl and 25 mL ethanol. Anal. Calcd (found) for  $Cs_{16}Na_4[(O_3POPO_3)_4Mo_{12}O_{36}] \cdot 15H_2O$ : Cs, 31.95 (33.05); Na, 3.32 (3.23); Mo, 27.67 (28.20); P, 5.96 (6.10);  $H_2O$ , 6.49 (6.49).  $^{31}P$  NMR:  $\delta$  -5.8 (d, 1P), -8.3 (d, 1P),  $^2J_{PP} = 15.4$  Hz. IR: 1177 (m), 1099 (m), 1080 (m), 1039 (m), 990 (m), 889 (s), 841 (sh), 785 (m), 634 (m, b), 546 (m)  $cm^{-1}$ . The methylenediphosphonate analog of anion III,  $[(O_3PCH_2PO_3)_4Mo_{12}O_{36}]^{16-}$  (IV), seems to be formed when 25 mL of a solution which contains 0.1 M methylenediphosphonic acid and 0.3 M sodium molybdate is adjusted to pH 7.0 with 0.1 M NaOH.  $^{31}P$  NMR:  $\delta$  16.5 (d of t, 1P), 20.8 (d of t, 1P),  $^2J_{PP} = 19.3$  Hz,  $^2J_{PP} = 10.8$  Hz.  $^{13}C\{^1H\}$  NMR:  $\delta$  29.8 (t, 1C),  $^1J_{CP} = 124.4$  Hz.  $^1H$  NMR:  $\delta$  2.1 (t, 2H),  $^2J_{HP} = 19.5$  Hz. We have so far not been able to obtain a pure solid sample of this compound.

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erogroups containing phosphorus the chemical shift of phosphorus depends much less on the type of addenda atoms than in structures with internal heterogroups.

### Conclusions

Although the catalytic effect of molybdate in pyrophosphate hydrolysis was established many years ago, no structural information about the interaction of pyrophosphate with molybdate in aqueous solution has been presented. Anion **II** is the first example of a diphosphate complex of polyoxomolybdate synthesized in aqueous solution and structurally characterized. The formation of **II** and **III** at pH close to where the molybdate-catalyzed pyrophosphate hydrolysis is most effective

suggests that these anions are intermediates in this pH dependent reaction.

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**Supplementary Material Available:** Tables of bond lengths and angles and anisotropic displacement parameters (5 pages). Ordering information is given on any current masthead page.

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