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Polyoxometalate−Diphosphate Complexes. 2.[1] Structure of 18-Molybdopyrophosphate, $[(P_2O_7)Mo_{18}O_{54}]^{4-}$, Which Encloses a Linear, Eclipsed Conformation of the Pyrophosphate Anion, and Preliminary Characterization of Its One- and Two-Electron Heteropoly Blues

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The structure of the heteropoly 18-molybdopyrophosphate anion $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ (**I**), originally synthesized by Himeno *et al.* (*Bull. Chem. Soc. Jpn.* **1990**, *63*, 1602), has been determined. The tetra-*n*-butylammonium salt of **I** crystallizes in the orthorhombic space group *Pnn*2 with a = 26.760(2) Å, b = 28.632(3) Å, c = 15.831(2) Å, V = 12130(2) Å^3, and Z = 4. Structural analysis based on 6525 independent reflections leads to a solution, R = 7.69% ($I > 2\sigma(I)$). The anion has virtual D_{3h} symmetry with a structure based on fusion of two B-type PMo_9O_{34} moieties. Consequently the enclosed pyrophosphate anion is constrained to have a linear P−O−P bond (177.7(13)°) and an eclipsed conformation. As for other molybdophosphates, the Mo−O(P) bonds are long, corresponding to bond orders of 0.1−0.25. The green one-electron-reduced species $[(P_2O_7)Mo_{18}O_{54}]^{5-}$ (**I′**) and the blue two-electron-reduced species $[(P_2O_7)Mo_{18}O_{54}]^{6-}$ (**I″**) show, in acetonitrile solution, a single ^{31}P NMR resonance at −22.8 ppm ($\Delta\nu_{1/2}$ 8.0 Hz) and −23.1 ppm ($\Delta\nu_{1/2}$ 2.1 Hz), respectively. The ESR spectrum of a frozen solution (77 K) of **I′** is a barely resolved axial pattern with $g_{\parallel}$ = 1.92 and $g_{\perp}$ = 1.94. Comparisons are made with reduced Keggin, $[(PO_4)Mo_{12}O_{36}]^{4-}$, and Dawson, $[(PO_4)_2Mo_{18}O_{54}]^{7-}$, anions.

Introduction

Although molybdate and tungstate complexes of pyrophosphate ($P_2O_7^{4-}$) were first reported over 100 years ago,[2,3] until recently[4] no pyrophosphate complex had been structurally characterized. A possible reason is the fact that hydrolysis of pyrophosphate in aqueous solution is catalyzed by acids and molybdate.[5] Recently, Himeno *et al.*[6] reported the synthesis of an 18-molybdopyrophosphate complex, $[P_2Mo_{18}O_{61}]^{4-}$ (**I**), in aqueous/organic solvents, but were unable to obtain crystals suitable for structural analysis. We are currently investigating heteropolyanion complexes with diphosphate species as hetero groups in order to understand the reactivity of polytungstates and -molybdates with biological oligophosphates and esters.[4,7] We have therefore reexamined the Himeno anion and report its structure, which contains the first *unambiguous* example of a pyrophosphate constrained to be linear.

Experimental Section

Synthesis. The tetra-n-butylammonium salt of **I** was prepared following the method of Himeno *et al.*[6] Anal. Calcd (found) for $(N(C_4H_9)_4)_4P_2Mo_{18}O_{61}$: Mo, 46.24 (45.90); P, 1.66 (1.68); C, 20.58 (20.59); H, 3.89 (3.89); N, 1.50 (1.51). Phosphorus-31 NMR (CD_3CN, 293 K): δ −21.7 ppm, $\Delta\nu_{1/2}$ 0.5 Hz. The IR and UV spectra agreed with those reported. A cyclic voltammogram was recorded with a Bioanalytical Systems (BAS) 100A electrochemical analyzer (0.144 mM **I** in 95% (v/v) CH_3CN/5% 0.1 M aqueous $HClO_4$, glassy carbon *vs* Ag/AgCl in CH_3CN (BAS, MF-2062) and Pt counter electrode) and shows reversible one-electron couples at 0.11, 0.03, −0.11, and −0.37 V. When corrected for the different reference electrode (ΔE = 350 mV), these are in agreement with Himeno's data. Solutions of the one- and two-electron-reduced anions, **I′** and **I″**, were generated by controlled potential electrolysis at 0.11 and 0.0 V, respectively, using a Brinkmann-Wenking 70 TS1 potentiostat, a Koslow Scientific Co. Model 541 coulometer, and carbon cloth as the working electrode.

Table 1. Crystal and Structure Refinement Data for $(N(C_4H_9)_4)_4[(P_2O_7)Mo_{18}O_{54}]$

empirical formula	$C_{59}H_{121}Mo_{18}N_4O_{61}P_2$
fw	3651.46
crystal system	orthorhombic
space group	*Pnn*2
unit cell dimens	a = 26.760(2) Å b = 28.632(3) Å c = 15.831(2) Å
volume	12130(2) Å^3
Z	4
density (calcd)	2.000 Mg/m^3
abs coeff	1.901 mm^{-1}
F(000)	7108
crystal size	0.3 × 0.1 × 0.01 mm^3
θ range for data collcn	1.52−25.00°
index ranges	$-1 \le h \le 31, -1 \le k \le 34, -1 \le l \le 18$
reflns collected	12 280
independent reflns	11 301 [R(int) = 0.0433]
refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	11 301/1/677
goodness-of-fit on F^2	1.023
final R indices [$I > 2\sigma(I)$]	R1 = 0.0769, wR2 = 0.1697
R indices (all data)	R1 = 0.1458, wR2 = 0.2093
largest diff peak and hole	1.004 and −0.868 e Å^{-3}

X-ray Crystallography. Crystal data and structure refinement for **I** are summarized in Table 1. Crystals suitable for X-ray analysis were obtained after recrystallization of **I** in CH_3CN. In contrast to the crystals of Himeno *et al.* our crystals were air stable. The X-ray structure determination was done at 293 K, using a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

The structure was solved by direct methods and refined by full-matrix least-squares with the SHELX-93 package (G. M. Sheldrick), the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 12.05P]$ where $P = (\mathrm{Max}\,(F_o^2, 0) + 2F_c^2)/3$. An empirical absorption correction (ψ scans)

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ (**I**)

atom	*x*	*y*	*z*	*U*(eq)
Mo(1)	207(1)	5792(1)	3224(2)	49(1)
Mo(2)	788(1)	5257(1)	5111(2)	47(1)
Mo(3)	1482(1)	5290(1)	3110(2)	55(1)
Mo(4)	2016(1)	6300(1)	2377(2)	50(1)
Mo(5)	715(1)	6803(1)	2396(2)	46(1)
Mo(6)	12(1)	6841(1)	4221(2)	44(1)
Mo(7)	544(1)	6292(1)	6179(2)	49(1)
Mo(8)	1721(1)	5817(1)	6221(2)	47(1)
Mo(9)	2460(1)	5804(1)	4204(2)	54(1)
Mo(10)	2444(1)	7469(1)	2854(2)	61(1)
Mo(11)	1146(1)	7964(1)	2998(2)	64(1)
Mo(12)	541(1)	7940(1)	4911(2)	58(1)
Mo(13)	1130(1)	7393(1)	6814(2)	54(1)
Mo(14)	2317(1)	6938(1)	6648(2)	49(1)
Mo(15)	3008(1)	6955(1)	4579(2)	57(1)
Mo(16)	1570(1)	8654(1)	4628(2)	56(1)
Mo(17)	2133(1)	8126(1)	6547(2)	53(1)
Mo(18)	2839(1)	8144(1)	4524(2)	56(1)
P(1)	1277(2)	6390(2)	4293(4)	31(2)
P(2)	1738(2)	7367(2)	4772(4)	33(2)
O(1P)	1514(6)	6870(5)	4540(12)	40(4)
O(2P)	1663(5)	6127(5)	3780(10)	31(4)
O(3P)	814(6)	6472(5)	3799(10)	37(4)
O(4P)	1174(6)	6134(5)	5116(11)	39(4)
O(5P)	2232(6)	7416(5)	4366(11)	43(4)
O(6P)	1387(6)	7751(5)	4447(11)	40(4)
O(7P)	1774(6)	7397(5)	5725(10)	33(4)
O(1A)	−225(7)	5451(7)	2823(14)	69(6)
O(1B)	363(5)	5484(5)	4264(11)	39(4)
O(1C)	847(7)	5519(6)	2902(13)	58(5)
O(1D)	331(6)	6243(5)	2364(11)	38(4)
O(2A)	461(6)	5648(6)	5916(12)	48(5)
O(2B)	1260(7)	5156(6)	4200(13)	55(5)
O(2C)	575(7)	4723(6)	5311(13)	56(5)
O(2D)	1344(6)	5278(6)	5862(12)	47(5)
O(3A)	1755(6)	5695(6)	2249(12)	51(5)
O(3B)	1476(7)	4776(7)	2646(13)	62(6)
O(4A)	2284(7)	6364(7)	1393(14)	67(6)
O(4B)	2069(7)	6926(6)	2826(14)	59(5)
O(4C)	1301(6)	6511(6)	2135(11)	44(5)
O(5A)	132(6)	7035(6)	3135(11)	43(4)
O(5B)	2531(6)	6075(6)	3007(12)	46(5)
O(5C)	−561(7)	7072(6)	4439(13)	56(5)
O(5D)	150(6)	6498(5)	5319(10)	35(4)
O(5E)	543(6)	7039(6)	1451(12)	52(5)
O(5F)	1059(6)	7311(6)	2883(12)	46(5)
O(6A)	435(6)	7302(5)	4686(11)	41(4)
O(6B)	−184(6)	6234(5)	3801(11)	38(4)
O(7A)	165(7)	6338(7)	7041(13)	61(6)
O(8A)	1178(6)	6053(5)	6769(11)	37(4)
O(8B)	2153(6)	5693(6)	5217(12)	45(4)
O(8C)	2071(6)	5580(6)	7024(12)	48(5)
O(8D)	2013(5)	6433(5)	6120(11)	36(4)
O(9A)	2139(6)	5307(6)	3634(12)	51(5)
O(9B)	3038(7)	5567(6)	4337(14)	62(5)
O(10A)	2969(7)	7090(7)	3417(13)	60(5)
O(10B)	2699(8)	7488(7)	1870(16)	82(7)
O(11A)	951(8)	8161(7)	2068(15)	74(6)
O(11B)	566(7)	8005(7)	3649(14)	62(6)
O(11C)	1855(7)	7823(6)	2785(13)	55(5)
O(12A)	−43(7)	8137(6)	5072(14)	60(5)
O(12B)	777(6)	7760(6)	5980(12)	50(5)
O(12C)	892(7)	8514(6)	4908(13)	57(5)
O(13A)	746(7)	7405(6)	7650(13)	58(5)
O(13B)	1524(6)	7922(6)	7028(12)	46(4)
O(13C)	1669(6)	7031(6)	7243(12)	46(5)
O(13D)	881(5)	6881(5)	6203(11)	33(4)
O(14A)	2648(7)	6678(7)	7433(14)	64(6)
O(15A)	2786(6)	6991(5)	5788(11)	37(4)
O(15B)	3580(7)	6690(6)	4675(14)	61(5)
O(15C)	2575(6)	6443(6)	4492(12)	49(5)
O(16A)	2226(6)	8486(6)	4328(13)	55(5)
O(16B)	1741(6)	8469(6)	5740(12)	49(5)
O(16C)	1565(7)	9244(6)	4652(14)	66(6)
O(16D)	1379(7)	8525(6)	3452(13)	55(5)
O(17A)	2337(8)	8544(7)	7219(16)	76(6)
O(17B)	2625(7)	8113(6)	5664(13)	55(5)
O(17C)	2434(6)	7588(6)	6963(13)	54(5)
O(18A)	2816(7)	7958(6)	3342(13)	54(5)
O(18B)	3210(6)	7612(6)	4703(12)	47(5)
O(18C)	3271(7)	8560(6)	4530(14)	60(5)

Table 3. Average Bond Lengths (Å) and Angles (deg) for $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ (**I**)

$Mo-O_{terminal}$(cap)	1.665(20)
$Mo-O_{terminal}$(belt)	1.700(20)
$Mo-O_{doubly\ bridging}$	
corner-sharing MoO_6 octahedra	1.906(18)
edge-sharing MoO_6 octahedra	1.940(18)
$Mo-O_{quadruply\ bridging}$(belt)	2.451(16)
$Mo-O_{quadruply\ bridging}$(cap)	2.669(16)
$P-O_{bridge}$	1.575(17)
$P-O_{outer}$	1.507(17)
P−O−P	177.7(13)

was applied. Thermal vibrations were treated anisotropically for all Mo and P atoms. Some of the TBA cations were disordered, so that 5 out of 64 carbon atoms could not be found. Hydrogen atoms of the cations were added in calculated positions and constrained to ride on their attached carbon atom with isotropic thermal parameters constrained to 1.2 times that of the carbon atom. The atomic coordinates of atoms of the anion are reported in Table 2, and average bond lengths and angles in Table 3. A complete tabulation of bond lengths and angles is available as supplementary material.

Spectroscopy. Phosphorus-31 NMR spectra of **I**, **I′** and **I″** were recorded in CD_3CN at 121.496 MHz on a Bruker AM-300WB spectrometer using 10 mm tubes (pulse width 11.0 μs, acquisition time 0.41 s, relaxation delay 0.5 s, sweep width 5000 Hz). Chemical shifts are reported with reference to 85% H_3PO_4 (external replacement method), upfield shifts being recorded as negative. X-band ESR spectra of **I′** in acetonitrile solution were recorded on a Varian E-4 spectrometer at 297 and 77 K, and DPPH ($g = 2.0036$) was used to determine g values.

Results and Discussion

The structure of **I** is shown in Figure 1, with the related Dawson structure of α-$[(PO_4)_2Mo_{18}O_{54}]^{6-}$ (**II**)[8] for comparison. Both anions have nominal D_{3h} symmetry, although there is a slight chiral distortion of **II** (D_3 symmetry), which has been discussed elsewhere.[9] While **II** is formed by condensation of two A-type $[(PO_4)Mo_9O_{27}(H_2O)_3]^{3-}$ moieties,[10] anion **I** can be viewed hypothetically as a fused dimer of B-type PMo_9 units.[11]

There are three noteworthy features of the structure of **I**.

(1) The molybdenum atoms in the two "caps" have extremely long bonds to the pyrophosphate oxygens (2.640−2.715 Å), with corresponding "bond strengths" of *ca.* 0.1.[12] Analogous bonds in α-$[(PO_4)_2Mo_{18}O_{54}]^{6-}$ and α-$[(PO_4)Mo_{12}O_{36}]^{3-}$ are also long (*ca.* 2.4 Å) and this has provoked descriptions of these structures as clathrates of phosphate anions in neutral shells of linked MoO_5 square pyramids. All other bond lengths and angles of **I** are within normal ranges.

(2) The corner-linking of polyhedra in the caps places those molybdenum atoms further apart (3.673−3.719 Å) than the

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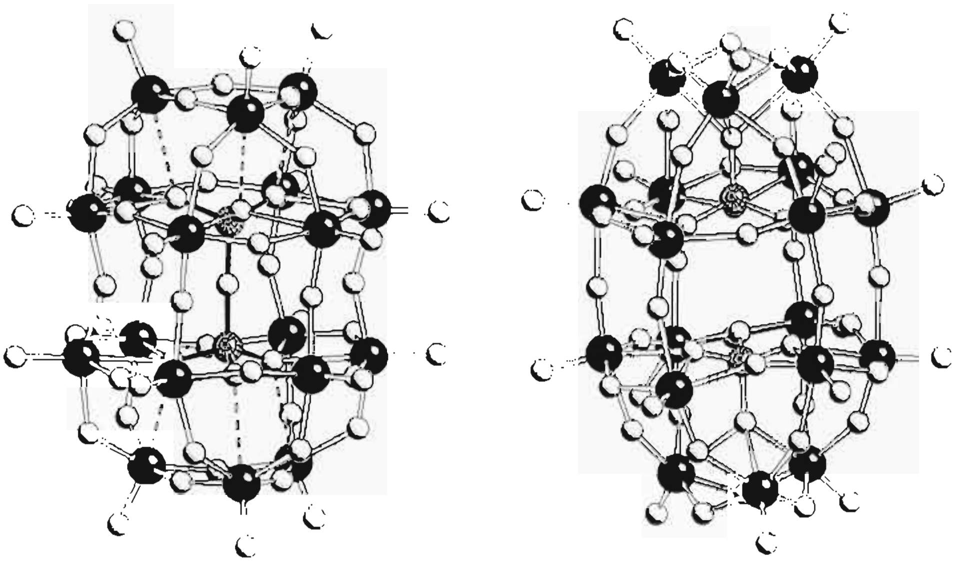

Figure 1. Ball and stick representations of the structures of $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ (**I**, left) and the related Dawson anion, $[(PO_4)_2Mo_{18}O_{62}]^{6-}$ (**II**, right). The bonds of the pyrophosphate anion in **I** are emphasized, and the very long Mo−O bonds are indicated by broken lines.

Table 4. Reported Bond Lengths and Angles for the Pyrophosphate Anion in Selected Compounds

compound	$P-O_{outer}$/Å	$P-O_{bridge}$/Å	P−O−P/deg	ref
$Cs_{13}Na_3[(P_2O_7)W_{12}O_{36}]\cdot 24H_2O$	1.52	1.63	123	4
$Ca_2P_2O_7\cdot 2H_2O$	1.52	1.62	123	20
$Na_4P_2O_7\cdot 10H_2O$	1.51	1.61	134	21
SiP_2O_7	1.51	1.59	139	22
α-$Mg_2P_2O_7$	1.52	1.59	144	23
$Fe_2P_2O_7$	1.52	1.60	153	18
$((C_4H_9)_4N)_4[(P_2O_7)Mo_{18}O_{54}]$ (I)	1.51	1.58	178	this work
ZrP_2O_7[a]	1.52	1.56	180	24
$Fe_2P_2O_7$[a]	1.52	1.55	180	17

[a] See discussion of these structural types in the text.

corresponding cap molybdenums of the Dawson anion (3.386−3.388 Å). Since the "belts" of both anions are comparable, anion **I** has an overall hour-glass shape in contrast to the ellipsoidal Dawson anion. This difference may affect electron delocalization in the heteropoly blue, **I′**; see below.

(3) The enclosed pyrophosphate anion is constrained to be in an unprecedented linear, eclipsed conformation. The thermal parameter of the bridging oxygen is unexceptional and the equatorial plane of the heteropolyanion can be viewed as a layer of seven close-packed oxygens with the pyrophosphate oxygen at the center. Reported literature values for P−O−P bond angles in crystalline pyrophosphates range from 123 to 180°. Selected examples are listed in Table 4. For the nonlinear cases the bridging P−O bond length appears to decrease with increasing bond angle, presumably a result of P−O−P π-bond variation.

As shown for the last two entries in Table 4, there are two classes of pyrophosphate structure, $M^{IV}P_2O_7$ (M^{IV} = Ti, Zr, Hf, Sn, Pb) and the thortveitite type, $M_2P_2O_7$ (M^{II} = Mg(β-form), Mn, Fe, etc.), in which the P−O−P angle appears to be strictly linear. However in these structures the bridging oxygen lies on a special position and the two phosphorus atoms are related by inversion symmetry. Since the original powder diffraction investigation[13] of ZrP_2O_7 which proposed a linear P−O−P bond, the configuration has been the subject of controversy.[14] Chaunac *et al.*[15] reported a careful X-ray and IR study of ZrP_2O_7. They distinguished three forms depending on the temperature (polymorphism). In none of these forms is the P−O−P group truly linear. This observation is supported by work of Tillmanns *et al.*[16] Huang *et al.*[14] made X-ray, IR and Raman studies on MP_2O_7 (M = Zr, Ti, Hf, Sn, Pb) and conclude that "no support has been found for the view that the P−O−P groupings of the pyrophosphate anion in these compounds are linear". For $Fe_2P_2O_7$ the "large thermal parameters for the bridging oxygen atom in the P_2O_7 group make the exact geometry uncertain".[17] Another X-ray structure of the same compound by different authors[18] shows 153° for the P−O−P angle. For β-$Mg_2P_2O_7$ "the central oxygen atom of the $P_2O_7^{4-}$ ion exhibits large thermal motion, which suggests that P−O−P only appears to be linear, as a result of thermal averaging".[19]

Electrolytic reduction of **I** at 0.11 V proceeds smoothly yielding a dark green solution with a single ^{31}P NMR line at −22.8 ppm ($\Delta\nu_{1/2}$ 8.0 Hz) consistent with rapid intramolecular

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Table 5. Magnetic Resonance Data for Selected Reduced Polyoxomolybdates[a]

	ESR		^{31}P-NMR		
anion	form	$g_\perp - g_\parallel$	$\Delta\nu_{1/2}$/Hz[b]	$\Delta\delta$/ppm[c]	ref
$[Mo_6O_{19}]^{3-}$ [d]	axial (77 K)	+0.011			26
α-$[(P_2O_7)Mo_{18}O_{54}]^{5-}$ (**I′**)	axial (77 K)	+0.02	8.0	−1.1	this work
α-$[(PO_4)_2Mo_{18}O_{54}]^{7-}$ (**II′**)	axial (77 K)	−0.020	220	+13.3	29
α-$[(PO_4)Mo_{12}O_{36}]^{4-}$ (**III′**)	isotropic (77 K)		2.6	+3.9	27, 28
	axial (10 K)	−0.011			
α-$[(SO_4)_2Mo_{18}O_{54}]^{5-}$	isotropic (253 K)				31

[a] As tetra-*n*-butylammonium salts in acetonitrile except where noted. [b] NMR line width at *ca.* 295 K. [c] Chemical shift relative to that of the oxidized anion. [d] In *N,N′*-dimethylformamide.

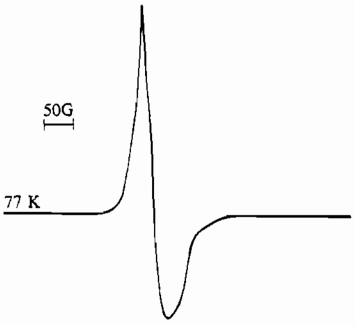

Figure 2. X-band ESR spectrum (frozen acetonitrile solution) of 0.5 mM **I′**, recorded at 77 K.

electron hopping delocalization. The same solution yields a broad (105 G peak to peak) ESR signal at 297 K and a partially resolved axial signal at 77 K (see Figure 2). When this solution is further reduced at 0.0 V, a dark blue solution is obtained with a single ^{31}P NMR line at −23.1 ppm ($\Delta\nu_{1/2}$ 2.1 Hz). Incompletely reduced solutions give NMR spectra with two lines (**I** + **I′** or **I′** + **I″**) indicating that *inter*ionic electron transfer is slow on the NMR time scale.

A summary of magnetic resonance data for several reduced polymolybdates is given in Table 5. These species are viewed as class II[25] mixed valence complexes with a thermally delocalized (hopping) electron which becomes trapped at a molybdenum site as the temperature is lowered. The trapping is revealed by the conversion of an isotropic ESR signal to an axial or rhombic pattern. According to this criterion, the unpaired electron in $[Mo_6O_{19}]^{3-}$ and α-$[(PO_4)_2Mo_{18}O_{54}]^{7-}$ (**II′**) is firmly trapped at 77 K but is still mobile in α-$[(PO_4)Mo_{12}O_{36}]^{4-}$ (**III′**) at this temperature. In the case of **I′**, the extent of trapping at 77 K appears to be intermediate between that of the Dawson (**II′**) and Keggin (**III′**) anions. Phosphorus-31 NMR line widths of **I′**, **II′** and **III′** (Table 5) imply more rapid *intra*molecular electron hopping (pseudotumbling of the anion) at room temperature for **I′** and **III′**, consistent with a less tightly bound electron in these structures. On the basis of "anomalous" axial ESR spectra ($g_\perp < g_\parallel$) of **II′** and of belt-substituted α$_1$-$[(PO_4)_2MoW_{17}O_{54}]^{7-}$, it was argued that the unpaired electron became trapped on one (or two) of the molybdenum atoms in the belt of the Dawson structure.[29] The very different ESR (and NMR[30]) behavior of **I′**, coupled with the similar environments of the belt molybdenum atoms in both heteropolyanion structures, indicates that the unpaired electron in **I′** (and both extra electrons in **I″**) become preferentially trapped on the cap molybdenums, or are fairly evenly trapped in both cap and belt sites. The reduced forms of **I** could imaginatively be viewed as molecular analogs of an atomic p orbital.

Conclusions

The pyrophosphate anion is only metastable in aqueous molybdate solutions because of hydrolysis, but it is possible to synthesize heteropolymolybdate complexes of this anion. Although it is not essential,[4,7] it can be beneficial to use a mixed aqueous/organic solvent. In the title compound the pyrophosphate moiety is completely encapsulated in a cage of Mo and O, so that direct attack by the solvent is impossible. This may explain why **I**, once formed, is very stable in solution or in the solid state. Anion **I** (and presumably its reduced forms) provides the first unambiguous example of a linear pyrophosphate ion.

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Supplementary Material Available: Tables of anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, complete atomic coordinates and isotropic displacement parameters, and complete bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

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(30) Note that the chemical shift for (paramagnetic) **I′** relative to **I** is much smaller (and in the opposite direction, −1.1 ppm vs +13.3 ppm) than the corresponding shift for **II′** relative to **II**.

(31) Cooper, J. B.; Way, D. M.; Bond, A. M.; Wedd, A. G. *Inorg. Chem.* **1993**, *32*, 2416.