Inorg. Chem. **2000,** *39,* 625−626

Polyoxometalate−Diphosphate Complexes. 6.[1] Possible Intermediates in the Molybdate-Catalyzed Hydrolysis of Pyrophosphate: Structure of Hexamolybdopyrophosphate $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$

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Received August 10, 1999

Introduction

Rosenheim and Shapiro[2] were the first to study the interaction of pyrophosphate ($P_2O_7^{4-}$) with molybdate (MoO_4^{2-}) many years ago, and they reported the formation of complexes. However, the lack of structural information is probably due to diphosphate hydrolysis in aqueous solution which is catalyzed by acid and molybdate. According to Weil-Malherbe and Green,[3] molybdate-catalyzed hydrolysis of pyrophosphate is most effective at pH 2 with a secondary maximum at pH 5.5. Until today only two molybdodiphosphates have been structurally characterized, the 18-molybdopyrophosphate $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ (P_2Mo_{18}) and the 30-molybdobispyrophosphate $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$ (P_4Mo_{30}).[4,5] However, both ions are synthesized in mixed aqueous/organic solvents, and therefore **1** is the first example of a complex of molybdate with diphosphate isolated from aqueous solution and structurally characterized. The structure of anion **1**, which has a pyrophosphate−molybdate stoichiometry of 1:6, was proposed by Kortz and Pope[6] on the basis of analogies of its ^{31}P NMR and IR spectra to those of the related hexamolybdomethylenediphosphonate $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ ($PCPMo_6$). Kortz et al.[7] also synthesized and structurally characterized the two macrocyclic dodecatungstates $[(O_3POPO_3)_4W_{12}O_{36}]^{16-}$ ($POPW_3$) and $[(O_3PCH_2PO_3)_4W_{12}O_{36}]^{16-}$ ($PCPW_3$) with a stoichiometry of 1:3. The 1:3 and the 1:6 structural types are related, and in both the heterogroups are external. In P_2Mo_{18} and P_4Mo_{30} the pyrophosphate heterogroups are internal and constrained to be linear.

Experimental Section

The synthesis of Kortz and Pope was followed, but phenyltrimethylammonim bromide was used for precipitation.[6] Recrystallization of the product in mixed 50% (volume) water/acetonitrile and slow evaporation led to colorless crystals suitable for structural analysis. A block-shaped crystal with dimensions 0.20 × 0.14 × 0.10 mm^3 was mounted on a glass fiber for indexing and intensity data collection at 173 K on a Siemens SMART-CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Direct methods were used to solve the structure and to locate all molybdenum atoms (SHELXS86). Then the remaining atoms (excluding H atoms) were found from successive difference maps (SHELXL93). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all molybdenum and phosphorus atoms), and isotropic thermal parameters (all oxygen, carbon, and nitrogen atoms), converged at $R = 0.070$ and $R_w = 0.184$ ($I > 2\sigma(I)$). In the final difference map the deepest hole was −2.183 eÅ^{-3} and the highest peak 3.381 eÅ^{-3}. An absorption correction was performed using the SADABS program.[8] Crystallographic data are summarized in Table 1.

Table 1. Crystallographic Data for $((C_6H_5)N(CH_3)_3)_4[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]$

empirical formula	$N_4C_{36}H_{64}P_2Mo_6O_{29}$	vol (Å^3)	2942.10(6)
fw	1654.6	Z	2
space group	$P\bar{1}$	temp (°C)	−100
unit cell dimensions	$a = 12.8718(2)$ Å	wavelength (Å)	0.710 73
	$b = 15.4366(1)$ Å	density(calcd) (Mg m^{-3})	1.867
	$c = 16.1842(2)$ Å		
	$\alpha = 72.021(0)°$	abs coeff (mm^{-1})	1.386
	$\beta = 74.193(0)°$	$R(F_o)^a$	0.070
	$\gamma = 83.831(1)°$	$R_w(F_o)^b$	0.184

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Anal. Calcd (Found) for $((C_6H_5)N(CH_3)_3)_4[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]$: Mo, 34.79 (34.28); P, 3.74 (3.71); N, 3.39 (3.26); C, 26.13 (25.33). IR: 1261 (w), 1233 (w), 1203 (w), 1177 (m), 1165 (m), 1123 (m), 1105 (sh), 1090 (m), 1033 (w), 1004 (w), 987 (w), 932 (sh), 917 (s), 902 (s), 880 (sh), 846 (w), 802 (w), 763 (m), 720 (sh), 691 (s), 677 (s), 612 (w), 590 (w), 554 (w), 532 (w), 522 (sh). Phosphorus-31 NMR (293 K) of crystalline $((C_6H_5)N(CH_3)_3)_4[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]$ redissolved in mixed 50% (volume) D_2O/CD_3CN: δ −2.5 (doublet, 1P), −6.4 (doublet, 1P), $^2J_{PP} = 10.3$ Hz. NMR experiments were made on a Bruker AM-300WB spectrometer. Elemental analysis was performed by the Service Central d'Analyse of CNRS at 69390 Vernaison, France.

Discussion

The structure of anion **1** consists of a six-membered ring of MoO_6 octahedra, which alternate in sharing edges and corners. The $(O_3POPO_3)^{4-}$ anion is bound with P(1) in the center of the ring and P(2) off-center and bound above the ring to two adjacent MoO_6 octahedra (see Figure 1). The remaining four molybdenums have a terminal water ligand on the same side of the ring as P(2). Therefore, **1** is isostructural with the hexamolybdomethylenediphosphonate $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ ($PCPMo_6$), which was reported by Kortz and Pope.[6] In both ions relatively weak bonds from terminal phosph(on)ate oxygens and terminal water molecules to the molybdenums (2.262−2.458 Å) result in a distorted octahedral coordination environment for the latter. Therefore, **1** and $PCPMo_6$ may be described as a ring of six corner-shared MoO_4 tetrahedra, stabilized by the presence of a ditetrahedral heterogroup.[9] Four phenyltrimethylammonium cations were found crystallographically, balancing fully the negative charges of **1**. Selected bond distances and angles of **1** are shown in Table 2.

Anion **1** had been isolated earlier and its structure predicted, but a crystalline sample suitable for X-ray crystallography could not be obtained.[6] A possible explanation is that, according to Weil-Malherbe and Green, molybdate-catalyzed hydrolysis of pyrophosphate is most effective near pH 3, i.e., the optimum

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(1) Part 1: see ref 7. Part 2: see ref 4. Part 3: see ref 6. Part 4: Kortz, U.; Pope, M. T. *Inorg. Chem.* **1995**, *34*, 3848. Part 5: see ref 5.

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10.1021/ic990959r CCC: $19.00

Table 2. Selected Bond Length Ranges (Å) and Angles (deg) for$[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (**1**)

Mo−$O_{terminal}$ (trans to triply-bridging O)	1.708−1.732(5)	P2−$O(Mo)_{doubly-bridging}$	1.525−1.552(5)
Mo−$O_{terminal}$ (cis to triply-bridging O)	1.700−1.729(5)	P2−$O_{terminal}$	1.500(5)
Mo−$OH_{2\ terminal}$	2.373−2.458(5)	P1−$O(P2)_{doubly-bridging}$	1.605(5)
Mo−$O(Mo)_{doubly-bridging}$	1.894−1.943(5)	P2−$O(P1)_{doubly-bridging}$	1.647(5)
Mo−$O(P2)_{doubly-bridging}$	2.262−2.303(4)	P1−O−P2	122.6(3)
Mo−$O(Mo,P1)_{triply-bridging}$	2.308−2.439(4)	P1−O−Mo	125.4−134.3(3)
P1−$O(Mo)_{triply-bridging}$	1.525−1.532(5)	P2−O−Mo	125.9−129.1(3)

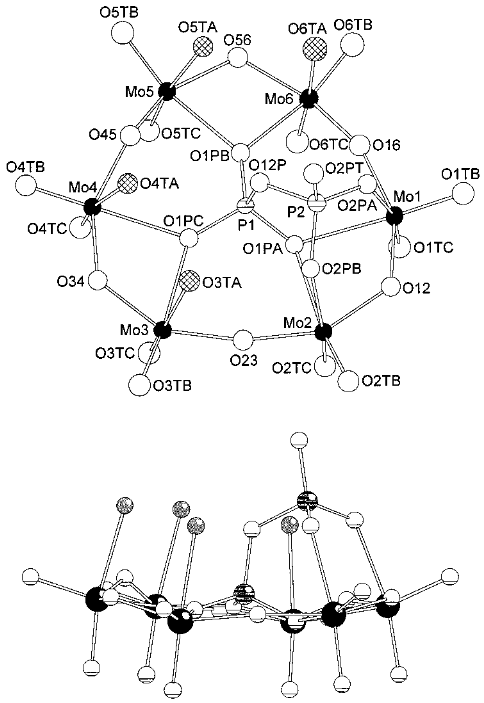

Figure 1. Ball and stick representations of $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (**1**): (top) top view showing 50% probability ellipsoids and the labeling scheme; (bottom) side view. The water molecules are represented by the small cross-hatched spheres.

condition for the synthesis of **1**. This problem could be circumvented by precipitation of **1** with phenyltrimethylammonium bromide, leading to a product which is soluble in a 50% (volume) water/acetonitrile mixture. It seems that hydrolysis of **1** in the mixed aqueous/organic solvent is slow enough to allow for crystallization.

Methylenediphosphonate (PCP) can be considered a hydrolytically stable analogue of pyrophosphate (POP). However, on the basis of the polyoxometalate structures of POP and PCP known to date and considering the structural constraints of both ditetrahedral heterogroups, it may be concluded that PCP and POP lead to isostructural products only if the heterogroups are in external positions (e.g., $PCPW_3$, $POPW_3$, and $PCPMo_6$, **1**). There are only two polyoxometalate structures with internal diphosphate heterogroups, P_2Mo_{18} and P_4Mo_{30}, and the respective analogues containing PCP are not known, most likely because the sp^3-hybridized carbon does not allow a linear conformation.

Since **1** is formed at pH 3 and molybdate-catalyzed hydrolysis of pyrophosphate is most efficient at pH 2, it can be concluded that **1** is the first structurally characterized intermediate in the molybdate-catalyzed hydrolysis of pyrophosphate.

Acknowledgment. This research has been supported by a URB grant from the American University of Beirut. The X-ray and NMR measurements were made during my visit to the laboratory of Professor M. T. Pope at Georgetown University. Figure 1 was generated by Diamond Version 2.1b (copyright Crystal Impact GbR).

Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990959R