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Polyoxometalate-Diphosphate Complexes. 5.[1] Cigar-Shaped 30-Molybdobispyrophosphate: Structure of $(N(C_4H_9)_4)_2H_9[\{(P_2O_7)Mo_{15}O_{45}\}_2][PMo_{12}O_{40}]$

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Introduction

The interaction of pyrophosphate ($P_2O_7^{4-}$) with molybdate was first investigated many years ago, and the formation of complexes has been reported by Rosenheim and Shapiro,[2] but the lack of structural information is probably due to diphosphate hydrolysis in aqueous solution, which is catalyzed by acid and molybdate.[3] Until today only the 18-molybdopyrophosphate $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ has been structurally characterized by Kortz and Pope.[4] The synthesis of this polyanion in a mixed aqueous/organic solvent had been developed by Himeno et al.[5] Since then Himeno et al. have reported the spectroscopic and electrochemical properties of the tetra-*n*-propylammonium salts of a 15-molybdopyrophosphate and a 12-molybdopyrophosphate.[6,7] As a possible structure for the pentadecamolybdopyrophosphate they proposed a lacunary ion with the formula $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$, which is derived from the 18-molybdopyrophosphate (P_2Mo_{18}) missing one cap of Mo_3O_6.

Experimental Section

The synthesis of Himeno et al.[6] was followed, but tetra-*n*-butylammonium bromide was used for precipitation. Recrystallization of the product in acetonitrile led to orange crystals suitable for structural analysis. A block-shaped crystal with dimensions 0.25 × 0.20 × 0.15 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 ($\lambda = 0.710\,73$ Å). Direct methods were used to solve the structure and to locate all molybdenum atoms (SHELXS86). Then the remaining atoms (excluding H and some disordered C 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 $R = 0.085$ and $R_w = 0.242$ ($I > 2\sigma(I)$). In the final difference map the deepest hole was -1.591 eÅ^{-3} and the highest peak 1.740 eÅ^{-3}. An absorption correction was performed using the SADABS program.[8] Crystallographic data are summarized in Table 1.

Table 1. Crystallographic Data for $(N(C_4H_9)_4)_2H_9[\{(P_2O_7)Mo_{15}O_{45}\}_2][PMo_{12}O_{40}]$

empirical formula	$N_2C_{32}H_{81}P_5Mo_{42}O_{144}$	wavelength (Å)	0.710 73
fw	6982.5	density(calcd) (Mg m^{-3})	1.524
space group (no.)	I23 (197)		
unit cell dimension	$a = 41.6910(4)$ Å	abs coeff (mm^{-1})	1.684
vol (Å^3)	72 464.8(12)	$R(F_o)^a$	0.085
Z	12	$R_w(F_o)^b$	0.242
temp (°C)	−100		

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

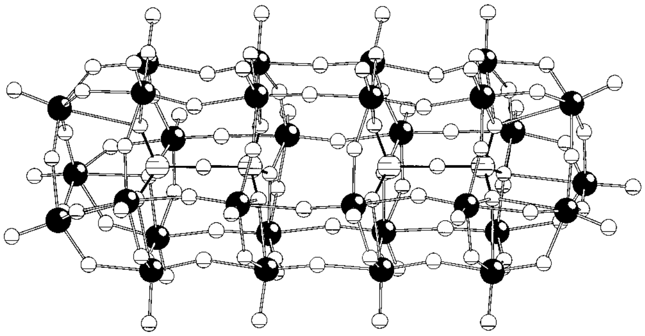

Figure 1. Ball and stick representation of $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$ (**1**). All bonds of the two pyrophosphate ions are emphasized.

Himeno's original synthesis[6] involves precipitation by tetra-*n*-propylammonium bromide (TPABr), and indeed on the basis of our ^{31}P NMR studies, TPA seemed to be the only alkylammonium cation allowing us to selectively precipitate the 30-molybdobispyrophosphate. However, when trying to recrystallize this crude product, we were unable to obtain single crystals of sufficient size for X-ray diffraction. On the other hand, use of tetra-*n*-butylammonium bromide (TBABr) easily led to large crystals of the 30-molybdobispyrophosphate, but always cocrystallized with the Keggin ion $[PMo_{12}O_{40}]^{3-}$. Phosphorus-31 NMR clearly showed that the crude TBA precipitate already contained the Keggin ion, whereas the TPA precipitate did not, indicating that the Keggin ion was formed during the course of the reaction as a result of partial hydrolysis of pyrophosphate.

Phosphorus-31 NMR (CD$_3$CN, 293 K) of $(N(C_4H_9)_4)_2H_9[\{(P_2O_7)Mo_{15}O_{45}\}_2][PMo_{12}O_{40}]$: $[PMo_{12}O_{40}]^{3-}$, δ −0.37 (singlet, 1P); $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$, δ −21.7 (doublet, 2P), −23.6 (doublet, 2P), $^2J_{PP} = 36.0$ Hz. Phosphorus-31 NMR (CD$_3$CN, 293 K) of $(N(C_3H_7)_4)_8[\{(P_2O_7)Mo_{15}O_{45}\}_2]$: $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$, δ −21.7 (doublet, 2P), −23.6 (doublet, 2P), $^2J_{PP} = 36.0$ Hz. NMR experiments were made on a Bruker AM-300WB spectrometer.

As expected Himeno's original elemental analysis[6] of his TPA salt (Found: Mo, 46.28; P, 2.02; C, 18.44; H, 3.51; N, 1.80) agrees well with the calculated values for the TPA salt of the dimeric 30-molybdobispyrophosphate $(N(C_3H_7)_4)_8[\{(P_2O_7)Mo_{15}O_{45}\}_2]$ (Calcd: Mo, 46.74; P, 2.01; C, 18.72; H, 3.67; N, 1.82).

Discussion

In the present work it is shown that Himeno's 15-molybdodiphosphate in reality is a 30-molybdobispyrophosphate, a dimeric species with the formula $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$ (see Figures 1 and 2). In the title compound the tetra-*n*-butylammonium salt of the novel dimeric ion is cocrystallized with the well-known 12-molybdomonophosphate Keggin ion $[\alpha\text{-}PMo_{12}O_{40}]^{3-}$.[9] All bond distances and angles of the Keggin ion are within the expected ranges.

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Table 2. Minimum and Maximum Bond Lengths (Å) and Angles (deg) for $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$ (**1**)

Mo−O$_{terminal}$ (cap)	1.64−1.65(3)
Mo−O$_{terminal}$ (outer belt)	1.67−1.76(2)
Mo−O$_{terminal}$ (inner belt)	1.709−1.717(16)
Mo−O$_{doubly-bridging}$	
(corner-sharing MoO_6 octahedra)	1.740−2.205(14)
(edge-sharing MoO_6 octahedra)	1.755−2.166(16)
Mo−O$_{triply-bridging}$	2.339−2.374(15)
Mo−O$_{quadruply-bridging}$ (cap)	2.701−2.731(18)
Mo−O$_{quadruply-bridging}$ (outer belt)	2.398−2.454(17)
P−O$_{doubly-bridging}$	1.53−1.66(3)
P−O$_{triply-bridging}$	1.509−1.514(14)
P−O$_{quadruply-bridging}$	1.502−1.555(17)
P−O−P	180.0(10)

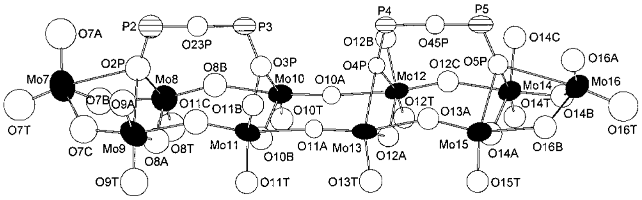

Figure 2. Ball and stick representation of the asymmetric unit of $[\{(P_2O_7)Mo_{15}O_{45}\}_2]^{8-}$ (**1**) showing 50% probability ellipsoids and the labeling scheme.

The mechanism for the formation of the 30-molybdobispyrophosphate (P_4Mo_{30}) is most likely fusion of two lacunary $[(P_2O_7)Mo_{15}O_{48}H_6]^{4-}$ moieties. With its four belts and two caps leading to a cigar-shaped structure, P_4Mo_{30} can be viewed as an extended P_2Mo_{18}. The most interesting structural features of P_4Mo_{30} are the two linear, eclipsed pyrophosphate heterogroups (180.0(10)°) as well as the long bonds between pyrophosphate oxygens and molybdenum atoms (2.339−2.731 Å) (see Table 2). Both features have already been observed in the parent P_2Mo_{18}. For the cocrystallized $[\alpha\text{-}(PO_4)Mo_{12}O_{36}]^{3-}$ the bonds between molybdenum atoms and monophosphate oxygens are also long (2.407−2.483 Å) and support the view of such polyoxometalates as clathrates of the anionic heterogroup(s) in neutral shells of linked MoO_5 square pyramids.

The dimeric P_4Mo_{30} has D_3 symmetry, unlike P_2Mo_{18} (D_{3h}), because of a chiral distortion which is similar to that of the Dawson ion $[(PO_4)_2Mo_{18}O_{54}]^{6-}$.[10] As a result the arrangement of the six molybdenum atoms in each belt of P_4Mo_{30} resembles a chair conformation.

Two tetra-*n*-butylammonium cations were found crystallographically, but as a result of disorder only 23 of the expected 32 carbon atoms could be located. Charge-balance considerations therefore require the presence of nine protons, which are expected to be bound to surface oxygens of the polyanions. However, the binding sites of the protons could not be identified by bond-valence sum calculations;[11] most likely they are disordered over various positions.

The structure of the 12-molybdopyrophosphate is still unknown, but ^{31}P NMR studies suggest that the ion is an *oligomeric* analogue of the *dimeric* P_4Mo_{30}. This is further supported by attempts to crystallize the 12-molybdopyrophosphate in acetonitrile, which always resulted in crystals of the title compound. This suggests that in acetonitrile the 12-molybdopyrophosphate easily breaks down into smaller units of P_4Mo_{30}.

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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.

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