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A Reduced Polyoxomolybdenum Borophosphate Anion Related to the Wells−Dawson Clusters

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The number of hydrothermally synthesized transition-metal borophosphates has grown exponentially during the few years after demonstrating that such compounds are hydrolytically stable and can form open-framework structures.[1] Some of these compounds are organically templated three-dimensional structures such as $M^{II}[B_2P_3O_{12}(OH)]\cdot enH_2$ (M = Co, Mn, Fe, Cu, Zn, Ni, Mg),[1,2a] $(VO)_5[B_2P_4O_{20}]\cdot 2.5H_2O\cdot 2enH_2$,[2b] and $M^{II}[B_2P_3O_{12}(OH)]\cdot pppznH_2$ (M = Co, Zn),[2c] and the first borophosphate templated by a transition-metal complex, $[Co^{III}(en)_3][B_2P_3O_{11}(OH)_2]$.[3] An interesting class of borophosphates are those containing cluster-like transition-metal borophosphate anions, known thus far only for vanadium.[4] All of them are wheel-like anions of different sizes that are often centered and stabilized by an alkali-metal or ammonium cation. The four known types are: triangles of $[(VO)_3(BP_3O_{16})]^{5-}$,[4a] squares of $[(VO)_8(BP_2O_{10})_4]^{n-}$,[4b] Na^+-centered pentagons of $[(VO)_{10}\{(BP_2O_{10}(OH)_2\}_5]^{n-}$,[4b,c] and NH_4^+-, K^+-, Rb^+-, or Cs^+-centered hexagons of $[(VO)_{12}(BP_2O_{10})_6]^{n-}$.[4b,d−f] Surprisingly, despite the numerous cluster anions known for molybdenum and tungsten phosphates no such borophosphate compound was reported before. Here we describe the synthesis and characterization of the first molybdenum borophosphate, $(C_3N_2H_5)_8[Mo^{V}_5Mo^{VI}_7O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3]\cdot nH_2O$ ($n \approx 4$) (**1**). It contains reduced heteropolyoxometalate borophosphate anions that resemble the α-Wells−Dawson cluster. The polyoxometalates have already proven effective in numerous applied sciences such as catalysis and medicine.[5] Compound **1** is the first molybdenum heteropolyoxometalate that incorporates both phosphate and borate and, therefore, offers the potential for new properties and applications.

The compound was synthesized hydrothermally from a mixture of MoO_3, Mo, H_3BO_3, $C_3N_2H_4$, H_3PO_4, HCl, and H_2O, in the molar ratio 1:0.13:1.67:3:3.33:1:74 (pH ≈ 1.5), heated for 5 days at 165 °C under autogenous pressure in a Teflon-lined autoclave. Dark blue polyhedral crystals of **1** were obtained as a pure phase in nearly 80% yield. Small changes of the pH or the ratio of the reactants led to impurities of recrystallized boric acid and red crystals of yet unidentified solid in the product. The compound is soluble in water, and the Mo^{V}: Mo^{VI} ratio of 5:7 was determined from cerimetric titration of such a solution. The number of imidazolium cations was corroborated by X-ray photoelectron spectroscopy (in addition to the structure refinement), while the overall formula of the compound was confirmed by elemental analysis.[6] The number of protonated phosphate oxygens was determined from requirements for electroneutrality. The IR spectrum of **1** (KBr pellet) displays a characteristic B−O stretching vibration at 1239 cm^{-1}, and the typical bands for a phosphate group (1077, 1049, and 1006 cm^{-1}), imidazolium (3270, 3147, 2981, 2853, and 1587 cm^{-1}), as well as some skeletal vibrations (839, 759, 644, 627, 572, an 492 cm^{-1}),[7] and the visible spectrum of the compound has $\lambda_{max} = 595$ nm. Thermogravimetric analysis, carried out in a flow of air, shows weight loss of 20.17% in a single broad step between 130 and 520 °C. This is attributed to simultaneous loss of the crystallization water, the imidazolium cations, and the hydroxyl groups (21.42%).

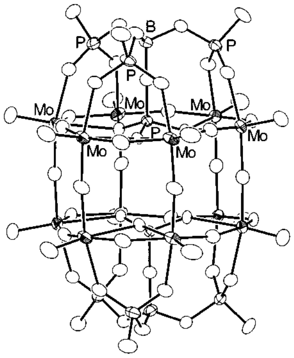

Figure 1. An ORTEP view (70% thermal ellipsoids) of the molecular polyanion $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$ (ellipsoids: Mo: full, B and P: crossed, O: open).

Compound **1** contains isolated polyanions of $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$, imidazolium cations, and water molecules.[8] The polyanion (Figure 1) is made of two crystallographically equivalent hemispheres of $[BP_4Mo_6O_{31}H_{1.5}]^{4-}$ that are linked together by six shared oxygen atoms. The 12 molybdenum atoms are octahedrally coordinated by oxygen, and the octahedra form two belts of six where in each belt the octahedra alternatingly share corners and edges. Two phosphate groups are inner for the cluster and are positioned near the centers of the molybdenum belts. They share three corners with molybdenum octahedra and one with a borate tetrahedron. The other six phosphate groups are outer (addenda) for the cluster sharing two vertexes with two edge-sharing molybdenum octahedra and one vertex with a borate tetrahedra. The forth vertex of these groups is terminal, either oxygen or hydroxyl group (valence sum calculations indicated the terminal phosphate oxygens as the most-likely protonated sites). The three oxygen and three hydroxyl groups are statistically disordered among these six terminal positions. They generate the observed hydrogen bonds between the polyanions (Figure in Supporting Information), some of them quite short (2.42−2.59 Å). The two borate groups of the anion (one in each hemisphere) share all corners with three outer and one inner phosphate groups. The imidazolium cations and water molecules of the structure are located between the anions and are involved in a vast net of hydrogen bonding.

The new molecular anion $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$ is structurally very closely related to the α-Wells−Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$.[9] As shown in Figure 2, they both contain the same $\{P_2Mo_{12}O_{50}\}$ core of two phosphate-centered hexamolybdenum belts. The Wells−

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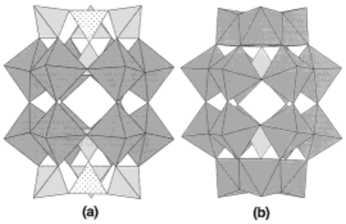

Figure 2. Polyhedral views of (a) $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$ and (b) the Wells−Dawson anion $[P_2Mo_{18}O_{62}]$.$^{6-}$ The PO_4-tetrahedra and MoO_6-octahedra are light- and dark-gray, respectively, while the BO_4 tetrahedra are dotted.

Dawson anion is formed by capping each side of this core with a trimetallic fragment made of three edge-sharing MoO_6 octahedra. In the case of the borophosphate anion $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$, the two sides of the core are capped by the corner-sharing borophosphate group $\{BP_3O_{13}\}$ instead. The main structural consequence of this is larger Mo−O−Mo angles between the two belts (averages of 163.0 and 174.0° in $[P_2Mo_{18}O_{62}]^{6-}$ and $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$, respectively) due to the larger size of the $\{BP_3O_{13}\}$ group compared to the trimer of MoO_6 octahedra.

Electronically, the cluster polyanion is remarkable in that it is partially reduced as synthesized, that is, without additional treatment after the synthesis. Thus, five of the 12 molybdenum atoms are Mo^V and therefore of d^1 configuration, while the other seven are fully oxidized Mo^{VI}. Furthermore, the five electrons from these atoms are delocalized over the cluster and four of them are paired. In support of this model are the results of the magnetic measurements which, despite the five Mo^V atoms (proved by redox titration, see above), indicate only one unpaired electron.[10] Reduced species of the parent Wells−Dawson family have been extensively studied before and have shown that the so-called "blue" electrons are "delocalized" over the 12 MoO_6 octahedra of the two belts.[11,12] Furthermore, it has been also shown that "blue" electrons in even numbers are always spin-paired and hop among different sites,[11,13] not necessarily always at adjacent metallic centers.[14] Valence sum calculations for **1** gave similar valences for all molybdenum atoms,[15] an indirect indication that the five "blue" electrons of this cluster are delocalized as well.

Compared to the fully oxidized Wells−Dawson clusters,[9] the polyanion in **1** shows a few subtle structural differences that are most likely caused by the five delocalized "blue" electrons. For example, the two hexanuclear belts are less puckered in **1** (maximum deviation from the least-squares plane of 0.03 Å compared to 0.24 Å for the fully oxidized species), the average Mo···Mo distances between the rings are shorter in **1** (3.73 vs 3.83 Å), the Mo−O distances between the rings show less disparity in **1** (range 1.856(5)−1.878(5) Å) than in the fully oxidized Wells−Dawson cluster (range 1.76−2.12 Å). The same effects have been observed for a four-electron reduced Wells−Dawson species $[H_3S_2Mo_{18}O_{62}]^{5-}$ with the electrons delocalized on the two hexanuclear belts compared with the fully oxidized parent anion $[S_2Mo_{18}O_{62}]^{4-}$.[16] This corroborates further the electron-delocalization model for the borophosphate polyanion.

$[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$ is the first heteropolyoxomolybdate that contains simultaneously boron and phosphorus as heteroelements. The presence of six outer phosphate groups makes it different from all other polyoxometalates including those of the Wells−Dawson family. This, the borate groups, and the five delocalized electrons could provide access to different chemical reactivity as well as different catalytic and antiviral properties. Structural relationships such as those between the cluster in **1** and the Wells−Dawson cluster could be easily envisioned for other well-known heteropolyoxometalate clusters such as the Keggin ions, and novel borophosphate polyoxomtelates could be thus foreseen. The described here anion might very well be just one of a class of many such similar species.

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Supporting Information Available: A figure showing the hydrogen bonding between the anions of $[B_2P_8Mo_{12}O_{59}(OH)_3]^{8-}$, a plot of the measured and fitted molar magnetic susceptibility of **1** as a function of the temperature, the visible spectrum of **1** (both in PDF format), and an 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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(6) X-ray photoelectron spectroscopy measurements were performed on a VG ESCALAB 220i-XL spectrometer. The X-ray source was monochromatic Al Kα radiation. The ratio of molecular anions to imidazolium cations was obtained as 1:8.4. This value was determined by fitting the Mo $3p_{3/2}$ and N 1s contributions in the spectrum. The quantification was then carried out using the atomic sensitivity factors for Mo $3p_{3/2}$ and N 1s reported by Scofield, 5.94 and 1.8, respectively. Elemental analysis of the compound was performed by Galbraith Laboratories: C, 8.68; H, 1.89; N, 6.62; B, 0.64; Mo, 37.83 (calculated: C, 9.48; H, 1.69; N, 7.37; B, 0.71; Mo, 37.87.).

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(8) X-ray diffraction data were collected at room temperature from a dark blue crystal (0.24 mm × 0.12 mm × 0.12 mm) of **1** on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation ($2\theta_{max} = 50°$). Crystal data: $(C_3N_2H_5)_8[B_2P_8Mo_{12}O_{62}H_3]\cdot 4H_2O$, monoclinic, $C2/c$, $Z = 4$, $a = 25.060(5)$ Å, $b = 15.001(2)$ Å, $c = 21.979(2)$ Å, $\beta = 105.06(2)°$, $V = 7978(2)$ Å^3, R1/wR2 = 0.0490/0.1339 for the observed 7021 reflections ($I \geq 2\sigma(I)$), R1/wR2 = 0.0612/0.1441 for all 7192 reflections.

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(10) The magnetization of 22 mg of **1** was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range of 10−250 K with a step of 10 K. It revealed Curie−Weiss behavior and the molar susceptibility data as function of the temperature were fitted with $\chi_m = C/(T - \theta) + \chi_{TIP}$ where χ_{TIP} is temperature-independent paramagnetism (due to mixing of the ground state with empty, low-lying paramagnetic states). This provided $\mu_{eff} = 1.82$ B. M., $\theta = -1.09$ K and $\chi_{TIP} = 1.5 \times 10^{-4}$ emu/mol. The effective magnetic moment corresponds to one unpaired electron per molecular anion.

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