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$[Mo_5{}^{V}Mo_7{}^{VI}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$: A Phenyl-Substituted Molybdenum(V/VI) Boro-Phosphate Polyoxometalate

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The title polyanion is the first hybrid borophosphate–phenylphosphonate polyoxometalate. It was structurally characterized as its imidazolium salt, $(C_3N_2H_5)_5[Mo_{12}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]\cdot H_2O$ (monoclinic, $P2_1/c$, $a = 22.120(3)$ Å, $b = 13.042(2)$ Å, and $c = 32.632(4)$ Å, $\beta = 101.293(3)°$), which was synthesized hydrothermally from imidazole, molybdenum oxide and metal, and boric, phosphoric, and phenylphosphonic acids. The anion is the second example of a new class of polyoxometalates that resemble Dawson anions but where the two pole caps of three edge-sharing MoO_6 octahedra in the latter are replaced by other units, in this case tetrahedral borate sharing corners with three phenylphosphonic groups, $\{(OB)(O_3P\text{-}Ph)_3\}$. The 12 molybdenum atoms forming the two equatorial belts of the cluster are of mixed-valence, five are Mo^{V} and seven are Mo^{VI}, and the resulting five electrons are delocalized. Four of these electrons are paired according to the temperature dependence of the magnetic susceptibility. The new compound is soluble in a mixture of water and pyridine (in equal volumes) as well as in nitromethane, and the anions are intact in these solutions.

Introduction

Heteroatomic polyoxometalates (POMs), also known as “heteropoly blues” in their reduced forms, are relatively large polyanions based on oxides of predominantly molybdenum or tungsten.[1] The metal atoms are octahedrally coordinated, the octahedra share corners and edges, and are all bonded together by an internal heteroatom, typically a tetrahedrally coordinated nonmetal such as phosphorus. The two classical species are the Keggin and the Wells−Dawson anions, $[PMo_{12}O_{40}]^{3-}$ and $[P_2Mo_{18}O_{62}]^{6-}$, respectively.[2] Five of the six oxygen atoms around each molybdenum atom in these units are shared (M−O−M/P), and the sixth one is terminal and pointing outward. Thus, the surface of the polyanions is made of metal-bonded oxygen atoms that can be protonated to some extent, but not much more chemistry can be and has been done with them. The anions can be reduced by formally converting some of the Mo^{VI} atoms to Mo^{V}. Although the extra electrons are delocalized to a great extent over the anion, they are still somewhat localized at the metal sites, and this, in a way, means that formally the molybdenum atoms constantly switch their valence. The electronic transitions due to these intervalence transitions give the blue color of such reduced species.

The numerous uses of the polyoxometalates utilize their specific molecular composition, size, shape, charge density, redox potentials, acidity, and solubility, and span, perhaps, the widest possible range of applications as homo- and heterogeneous catalysts, electrocatalysts, coatings, antiviral agents in medicine, pigments, recording materials, toners, precursors for oxide films, sensors, etc.[3] However, this impressive list would be even more impressive if these anions were functionalized on the surface. For example, appropriate organic functionalities may allow for polymerization, attached metal complexes may bring needed spectroscopic and optical characteristics, etc. Steps have been made in this direction, and a number of functionalized species are known. Apparently, all of them are made from lacunary anions, i.e., defect anions missing one or more MO_6 octahedra, that are initially prepared and are then reacted with various reagents to add functionalities at the places of the missing octahedra. The most likely reason for the need of such defect anions is the inactivity of the surface of the pristine anions. The few

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derivatized lacunary Keggin anions are $[SiW_{11}O_{39}\{RhCH_2COOH\}]^{6-}$,[4] $[PW_{11}O_{39}\{RhOOCCH_3\}_2]^{5-}$,[5] $[PW_{11}O_{39}\{OPPh\}_2]^{3-}$,[6] $[SiW_{11}O_{40}\{SiC_6H_4CH{=}CH_2\}_2]^{4-}$,[7] $[SiW_9O_{37}\{SnPh\}_3]^{7-}$,[8] $[SiW_{10}O_{36}\{OSiC_3H_6OC(O)C(CH_3){=}CH_2\}_4]^{4-}$,[9] $[SiW_{10}O_{37}\{SiC_3H_6OC(O)C(CH_3){=}CH_2\}_2]^{4-}$,[10] $[PW_{10}O_{36}\{BuSiOSi(CH_3)_2OSiBu\}]^{3-}$,[11] and $[PW_{10}O_{36}\{BuSiOH\}_2]^{3-}$,[11] while $[P_2W_{15}O_{59}\{SnPh\}_3]^{9-}$ is a functionalized lacunary Dawson anion (the functionalities are shown in curly brackets).[12] Furthermore, the styrylsylil derivative has been polymerized,[4] while others have been copolymerized with polyacrylamide.[9,10] Another goal is to use such functionalized species as building blocks and create various extended structures of the open-framework type. Potentially, such new materials would combine large openings with all the useful properties of the monomers and may find unique application in areas such as redox and acid−base catalysis, separation, etc.

Recently, we reported the synthesis and structure of a radically different polyoxometalate, a polyoxomolybdenum anion with two different heteroatoms, boron and phosphorus.[13] This novel borophosphate polyoxometalate, $[Mo_5{}^{V}Mo_7{}^{VI}O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3]^{8-}$, is geometrically related to the oblonglike Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$ as both have two equatorial belts made of six MO_6 octahedra each.[2d,c] However, the polar caps of three edge-sharing octahedra $\{Mo_3O_{13}\}$ in the Dawson anion are replaced by $\{(BO)(PO_4)_3\}$, a tetrahedral borate that shares corners with three phosphate groups. The major effect of the replacement is that the resulting six outer phosphate groups of the new species provide better reactivity for the whole anion. Here, we report on the further functionalization of this anion by replacing the six terminal phosphate oxygen atoms with phenyl groups. This result shows that extended structures made of such polyxomolybdenum borophosphate anions interconnected by diphosphonic acids should be possible. The ultimate goal of the project is the synthesis of appropriately functionalized polyoxometalates that can be linked via their functionalities into such extended structures, and the compound reported here is just one step away from being such species.

Experimental Section

Synthesis. The imidazolium ($ImH_2{}^+$) salt of the title anion was synthesized hydrothermally from MoO_3 (Baker, 99.9%), elemental Mo (Acros, 99.99%), boric acid (Acros, 99.5%), imidazole (Alfa Aesar, 99%), phosphoric acid (Fisher, 85%), phenyl-phosphonic acid (Acros, 98%), and deionized water in a molar ratio of 1:0.2:5:3:1:8:220, respectively (pH ≈ 1). This mixture was heated for 5 days at 180 °C under autogenous pressure in a 23 mL Teflon-lined autoclave. Dark-blue crystals of the single-phase product of $(ImH_2)_5[Mo_{12}O_{30}(BPO_4)_2(PO_3\text{-}Ph)_6]\cdot H_2O$ (**1**) were collected by filtration, washed with water, and dried at room temperature (60% yield with respect to Mo). Smaller amounts of phenylphosphonic acid lead to formation of the already reported borophosphate $(ImH_2)_8[Mo_{12}O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3]\cdot nH_2O$ (**2**) in various amounts as a second phase.[13] When the same synthesis is carried out with pyridine instead of imidazole, the IR spectrum of the product (**3**) indicates that the same anion is formed. It is also blue but the X-ray diffraction pattern is different from that of **1**. However, none of the numerous syntheses at various conditions produced suitable single crystals, and the structure has not been determined. Both compounds **1** and **3** are soluble in nitromethane and in a mixture of water and pyridine in equal volumes, and the novel anion is stable in these solutions.

Table 1. Crystallographic Data for $(ImH_2)_5[Mo_{12}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]\cdot H_2O$

fw	3140.7
space group, Z	$P2_1/c$, 4
a (Å)	22.120(3)
b (Å)	13.043(1)
c (Å)	32.632(4)
β (deg)	101.293(3)
V (Å^3)	9232(1)
ρ_{calcd} (g/cm^3)	2.26
radiation, λ (Å)	Mo Kα, 0.71073
T (K)	293
μ (cm^{-1})	18.18
R1/wR2 for $I \geq 2\sigma_I$ (%)[a]	4.50/10.52
R1/wR2 for all data (%)[a]	17.98/17.65

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F^2{}_o)^2]\}^{1/2}$ for $F_o{}^2 > 2\sigma(F_o{}^2)$, $w = [\sigma^2(F_o)^2 + (0.0761P)^2]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Characterization. Single-crystal X-ray diffraction data were collected from a very small needlelike crystal of **1** (0.12 × 0.04 × 0.02 mm) at room temperature on a Bruker APEX diffractometer with a CCD area detector and graphite-monochromated Mo Kα radiation. An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods in $P2_1/c$ and was refined (on F^2) using the SHELXTL V5.1 package (the small size of the crystal resulted in somewhat large R_{int} and a GOF value lower than 1). The solution provided the position of the molybdenum and phosphorus atoms while all other non-hydrogen atoms (O, B, C, N) were located from subsequent Fourier difference maps. The hydrogen atoms were handled as riding on the corresponding N and C atoms. Details of the data collection and refinement are summarized in Table 1.

Thermogravimetric analysis was carried out on a Cahn TG-131 thermogravimetric analyzer in a flow of air (70 mL/min) up to 800 °C. The magnetization of 18 mg of **1** was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10−250 K. IR (pellets with KBr) and UV−Vis spectra were obtained on Perkin-Elmer Paragon 1000 FT and Lambda 6 spectrometers, respectively. EPR spectra of compound **1** and its solution in nitromethane were taken on a Bruker EMX spectrometer at 77 K.

Results and Discussion

The new polyoxomolybdate anion $[Mo^{V}{}_5Mo_7{}^{VI}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$ (Figures 1B and 2C) in compound **1** is very closely related to the recently reported borophosphate anion $[Mo^{V}{}_5Mo_7{}^{VI}O_{30}(BPO_4)_2(PO_4)_3(HPO_4)_3]^{8-}$ (Figures 1A and

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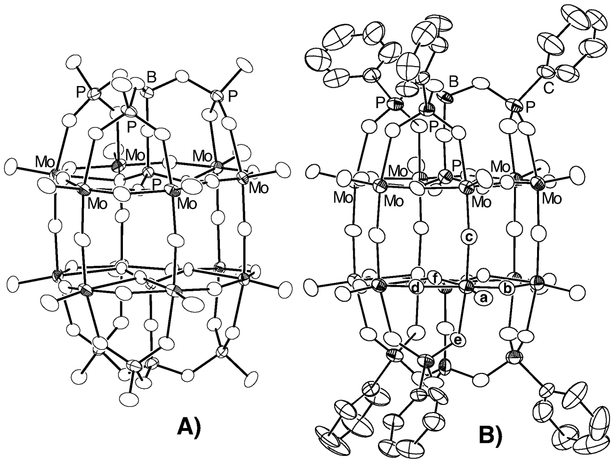

Figure 1. ORTEP views (thermal ellipsoids at the 50% probability level) of (A) $[Mo_{12}O_{30}(BPO_4)_2(PO_4)_3HPO_4)_3]^{8-}$ in **2** and (B) $[Mo_{12}O_{30}(BPO_4)_2(PO_3C_6H_5)_6]^{5-}$ in **1**. The different types of oxygen atoms around one molybdenum in B are indicated with letters: (a) terminal, (b) and (c) Mo−O−Mo corner-shared, (d) Mo−O−Mo edge-shared, (e) Mo−O−P corner-shared, (f) M−O−M edge-shared and M−O−P corner-shared (three-bonded). Ranges of distances (Å) in B: $Mo-O_a$ 1.648−1.693, $Mo-O_b/O_c$ 1.839−1.897, $Mo-O_d$ 1.888−1.924, $Mo-O_e$ 2.068−2.138, $Mo-O_f$ 2.335−2.387; P−O 1.522−1.551 and 1.502−1.577 for the inner and outer P-atoms, respectively; P−C 1.75−1.78; B−O 1.43−1.52.

2B) of compound **2**, also an imidazolium salt (dark-blue). The geometry of the latter, in turn, is best understood as derived from the well-known oblonglike Dawson anion $[P_2M_{18}O_{62}]^{6-}$ (Figure 2A) which has a double-belt equatorial section of $\{P_2Mo_{18}O_{36}\}$ and two polar caps made of $\{Mo_3O_{13}\}$ each.[2d,c] The replacement of these $\{Mo_3O_{13}\}$ polar caps with $\{(BO)(PO_4)_3\}$ units, a tetrahedral borate sharing corners with three outer phosphate groups, converts the Dawson anion into the anion of compound **2** (Figure 2A,B). The latter is already a highly functionalized anion with six terminal phosphate oxygens. Furthermore, it was shown that this anion has five delocalized electrons, and therefore, 5 of the 12 molybdenum atoms are formally Mo^{V}. This can be considered as reduction by five electrons from a hypothetical fully oxidized state with 12 Mo^{VI} atoms. Three of the six outer phosphate groups in this anion are protonated to give the overall charge of 8−. The new anion in **1** can be viewed as formally derived by substitution of the six terminal oxygen and hydroxyl groups of the outer phosphates with phenyl groups (Figures 1 and 2). This leads to a decrease of the charge of the anion by 3 units to 5−, $[Mo^{V}{}_5Mo_7{}^{VI}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$. One of the effects of the change of the character of the polar caps from hydrophilic in **2** to hydrophobic in **1** is that while the anions in the former are held together by hydrogen bonds, these forces in the latter are predominantly van der Waals (see figure in Supporting Information). This, perhaps, is one of the reasons for the observed poor crystallinity of both **1** and **3** as well as the low thermal stability of **1**. The latter is stable only up to about 200 °C above which temperature it loses its imidazole, water molecules, and phenyl groups (weight loss: measured 24.6%, theoretical 24.5%).

The bond distances and angles of the anions in **1** and **2** are very similar, as might be expected, while some of them differ from those of the Dawson anion. It should be mentioned that, as in all polyoxometalates of this type, the six distances around the metal atoms are quite different depending upon the bonding of the oxygen atom (Figure 1B). The most noticeable difference between the Dawson anion and the anions in **1** and **2** are the Mo−O−Mo angles between the two belts with an average of 163.0° in the Dawson anion but 174.5° and 174.0° in **1** and **2**, respectively (Figure 2). This is clearly due to the different sizes of the polar caps. The smaller trimers of edge-sharing octahedra in the Dawson anion pull the polar sides of the two belts inward. The resulting tilt of the octahedra, pivoted at the central molybdenum atoms, moves outward the equatorial oxygen atoms, i.e., the atoms shared between the two belts, and the corresponding angles at these atoms decrease. The effect is quite evident from the drawings in Figure 2.

The charge of 5− of the anion can be achieved only if it is reduced by five electrons, i.e., $[(Mo^{V})_5(Mo^{VI})_7O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$. This was confirmed by the magnetic measurements which showed Curie−Weiss behavior for the molar magnetic susceptibility as a function of the temperature. It was fitted with $\chi_m = C/(T - \theta) + \chi_{TIP}$, where χ_{TIP} is a temperature-independent contribution resulting from mixing

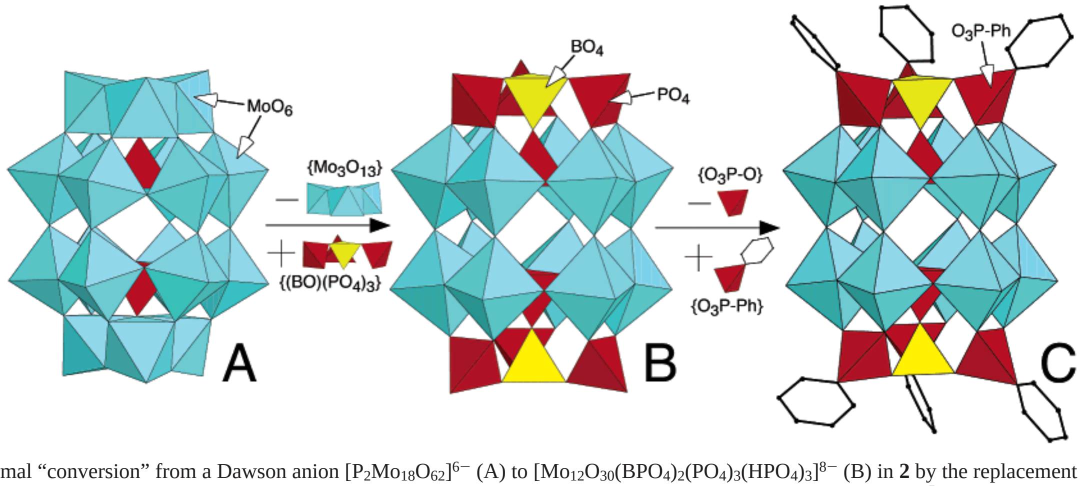

Figure 2. Formal "conversion" from a Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$ (A) to $[Mo_{12}O_{30}(BPO_4)_2(PO_4)_3(HPO_4)_3]^{8-}$ (B) in **2** by the replacement of the two pole caps of $\{Mo_3O_{13}\}$ in the former with $\{(BO)(PO_4)_3\}$ in the latter. The "conversion" from B to $[Mo_{12}O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$ (C) in **1** involves replacement of phosphate with phenylphosphonate groups.

of the ground state with empty and low lying paramagnetic states. Derived from the fit were the following parameters: $C = 0.325$ emu·K/mol, $\theta = -1.08$ K, and $\chi_{TIP} = 2.2 \times 10^{-3}$ emu/mol. This Curie constant corresponds to an effective magnetic moment of 1.61 μ_B and indicates the presence of one unpaired electron per polyanion. This means that four of the five extra electrons are paired, exactly as it was observed for compound **2**. As a matter of fact, the magnetic parameters for the latter are virtually the same: $\mu_{eff} = 1.82$ μ_B, $\theta = -1.09$ K, and $\chi_{TIP} = 1.5 \times 10^{-4}$ emu/mol. This and all other similarities between the two anions such as geometry, distances, angles, and IR and UV−Vis spectra lead to the conclusion that they are identical electronically; i.e., each has five Mo^V and seven Mo^{VI} atoms. However, while for compound **2** this was not clear without redox titration due to the number of possibilities for the protonation of the six outer phosphate groups, it is absolutely unambiguous for compound **1**. Thus, it confirms, in a way, the correct assignment of the degree of protonation and reduction for the anions in **2** as $[(Mo^V)_5(Mo^{VI})_7O_{30}(BPO_4)_2(PO_4)_3(HPO_4)_3]^{8-}$. The paramagnetic behavior of the anion was also confirmed in solution of nitromethane by electron paramagnetic resonance spectroscopy at 77 K.

The increased hydrophobicity of the new anion compared to that of **2** is manifested by its solubility in a mixture of pyridine and water (in equal volumes) as well as nitromethane but, unlike compound **2**, insolubility in water. The solutions are blue, and the UV−Vis spectra show the two bands characteristic for similar heteropolyoxomolybdates. These two bands in the pyridine/water solution, a stronger one at 606 nm and another at 805 nm (figure in Supporting Information), match the pairs of bands observed in the same region for the 2-, 4-, and 6-electron reduced Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$ at 758/1110, 676/892, and 599/690 nm, respectively.[14] They also compare well with the spectrum of compound **2** dissolved in water at low pH, a stronger band at 600 cm^{-1}, and a weaker one at 794 cm^{-1}. The IR spectrum of the solid after evaporation of the solvent of pyridine/water is virtually identical with that of the compound before dissolution (Figure 3) with characteristic bands for the following: imidazolium at 1585 cm^{-1}, aromatic C−C at 1437 and 1384 cm^{-1}, B−O at 1255 cm^{-1}, P−Ph at 1140 cm^{-1}, P−O at 1050 and 1010 cm^{-1}, and various skeletal vibrations below 1000 cm^{-1}. Unfortunately, the solid was not crystalline enough and could not be characterized by X-ray diffraction. Compound **3** shows the same overall IR spectrum as that of **1** except for the additional bands at 1543 and 1485 cm^{-1} due to the pyridine (Figure 3).

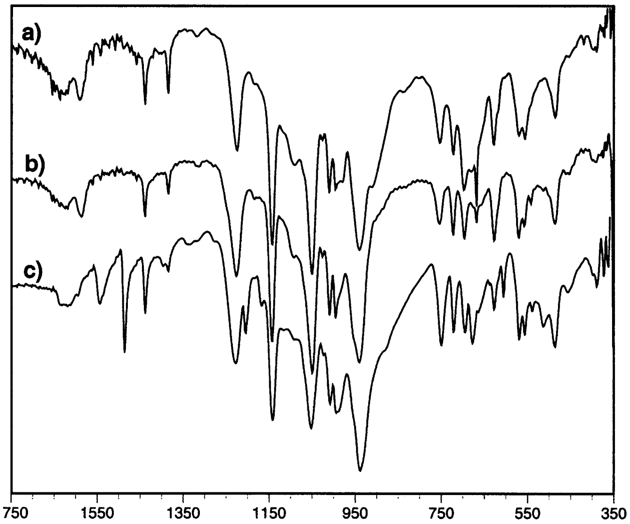

Figure 3. IR spectra (in KBr) of (a) compound **1** as made, (b) the solid product after evaporation of a pyridine/water (in equal volumes) solution of **1**, (c) compound **3** (pyridine as countercation).

The anion of $[(Mo^V)_5(Mo^{VI})_7O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6]^{5-}$ described here is, in a way, the second step toward building extended structures of covalently interconnected polyoxometalates. The first step was the synthesis, for the first time, of an anion with more than one outer phosphate group, $[(Mo^V)_5(Mo^{VI})_7O_{30}(BPO_4)_2(PO_4)_3(HPO_4)_3]^{8-}$, which made possible its further surface derivatization with phenyl groups. The next step toward connecting the anions is finding appropriate di- or multiphosphonic linkers such as $\{O_3P-R-PO_3\}$ that may have their phosphonate groups as intrinsic parts of two or more different anions. Also, the anion described here is a step closer to polymerization of such large polyoxometalate species. It is conceivable that similar anions can be synthesized using phenylphosphonic acid with phenyl groups that are appropriately functionalized for subsequent polymerization or copolymerization with other monomers. In summary, we think that the fact that such extensively functionalized polyoxometalates exist can generate ideas about many other possible species and their eventual use.

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Supporting Information Available: A figure showing packing of the anions in **1**, a plot showing the UV−Vis spectra of **1** in the solid state and in solution and of **2** in solution, a plot of the molar magnetic susceptibility of **1** and its fit, 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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