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[BP_{2}O_{10}]+enH_{2} (M = Co, Mn, Fe, Cu, Zn, Ni, Mg),1,2a (VO)_{3}[BP_{2}O_{10}]â-2.5H_{2}Oâ-2enH_{2},2b and M[BP_{2}O_{10}]+ppznH_{2} (M = Co, Zn),2c and the first borophosphate templated by a transition-metal complex, [Co]^{2+}[en]_{3}[BP_{2}O_{10}](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)_{6}(BP_{2}O_{10})]^{4â-} and squares of [(VO)_{6}(BP_{2}O_{10})]^{3â-} â-4. Naâ-centered pentagons of [(VO)_{10}(BP_{2}O_{10})(OH)_{2}]^{5â-}, â- and NH_{4}â-â-, Kâ-â-, Rbâ-â-, or Csâ-â- centered hexagons of [(VO)_{12}(BP_{2}O_{10})]^{6â-} â- â- â- â- â- â-. 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_{3}N_{2}H_{5})_{8}[Mo_{V}Mo_{VI}O_{22}(BO_{4})_{2}-]â- â- and the visible spectrum of the compound has â-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%). Compound 1 contains isolated polyanions of [BP_{2}Mo_{3}O_{9+}(OH)]^{6â-}, imidazolium cations, and water molecules.7 The polyanion (Figure 1) is made of two crystallographically equivalent hemispheres of [BP_{2}Mo_{3}O_{9+}H_{1.5}]^{4â-} â- 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 alternately 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 tetrahedron. 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 (2.42â-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 [BP_{2}Mo_{3}O_{9+}(OH)]^{4â-} is structurally very closely related to the â-Wellsâ–Dawson anion [P_{2}Mo_{9}O_{33}]^{6â-}.9 As shown in Figure 2, they both contain the same [P_{2}Mo_{9}O_{33}] core of two phosphate-centered hexamolybdenum belts. The Wellsâ–
Figure 2. Polyhedral views of (a) [B₂P₈Mo₁₂O₅₉(OH)₃]° and (b) the Wells–Dawson anion [P₂Mo₉O₃₆]⁶⁻. The PO₄-tetrahedra and MoO₆-octahedra are light- and dark-gray, respectively, while the BO₄ tetrahedra are dotted.

Dawson anion is formed by capping each side of this core with a trimetalllic fragment made of three edge-sharing MoO₆ octahedra. In the case of the borophosphate anion [B₂P₈Mo₁₂O₅₉(OH)₃]°, the two sides of the core are capped by the corner-sharing borophosphate group [BP₂O₆]⁻ 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 [P₂Mo₉O₃₆]⁶⁻ and [B₂P₈Mo₁₂O₅₉(OH)₃]°, respectively) due to the larger size of the [BP₂O₆]⁻ group compared to the trimer of MoO₆ 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 MoV and therefore of d¹ configuration, while the other seven are fully oxidized MoVI. Furthermore, the five electrons from these atoms are delocalized over the cluster and four of them are paired.12,13 Furthermore, it has been also shown that “blue” electrons in even-numbered outer phosphate groups make it different from all other polyoxometalates including those of the Wells–Dawson family. This, the borate groups, and the five delocalized electrons contribute which, despite the five MoV atoms (proved by redox titration,11,13 calculations for the cluster,12 and have shown that the so-called “blue” electrons are partially reduced as synthesized, that is, without additional treatment after the synthesis. Thus, five of the 12 molybdenum atoms are MoV and therefore of d¹ configuration, while the other seven are fully oxidized MoVI. Furthermore, the five electrons from these atoms are delocalized over the cluster and four of them are paired.12,13 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 I 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 I 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 I (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 I (3.73 vs 3.83 Å), the Mo–O distances between the rings show less disparity in I (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 [HS₂Mo₉O₃₆]⁻ which 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 I and the Wells–Dawson cluster could be easily envisioned for other well-known heteropolyoxometalate clusters such as the Keggin ions, and novel borophosphate polyoxometalates 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 [B₂P₈Mo₁₂O₅₉(OH)₃]°, a plot of the measured and fitted molar magnetic susceptibility of I as a function of the temperature, the visible spectrum of I (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.

References

5. (a) X-ray photoelectron spectroscopy measurements were performed on a VG ESCALAB 200i-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 and N1s contributions. 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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