Pentapotassium dodecatungstoborate(III) hexadecahydrate

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The title compound, $K_5[BW_{12}O_{40}] \cdot 16H_2O$, contains a $[BW_{12}O_{40}]^{5-}$ polyanion of 222 crystallographic symmetry, with a central tetrahedrally coordinated B^{III} atom surrounded by four groups of three edge-sharing octahedra (W_3O_{13} subunits), which are linked in turn to each other and to the central BO_4 tetrahedron by shared O atoms at the vertices. There is a crystallographically unique B—O bond of 1.554 (10) Å, while the average W—O distances are 2.344 (17) Å for four coordinate O atoms, 1.917 (12) and 1.89 (2) Å for two coordinate O atoms within and connecting the W_3O_{13} subunits, respectively, and 1.709 (8) Å for terminal O atoms. Not all of the K^+ ions and H_2O groups were located.

Comment

The condensation of $[WO_4]^{2-}$ and borate has been known for a long time to produce heteropoly species. Klein (1883) reported two tungstoboric acid isomers which crystallized with tetragonal and hexagonal lattices. These were examined by Copaux (1909) and suggested to have W/B ratios of 12 and 14, respectively. Somewhat later, Souchay (1951) reported the $[BW_{11}O_{39}]^{9-}$ ion. Recently, the new tungstoborate species $[BW_{13}O_{46}H_3]^{8-}$ has been identified in solution, and the hexagonal acid shown to have the composition $H_{21}[B_3W_{39}O_{132}] \cdot 69H_2O$ by an X-ray single-crystal study (Tézé et al., 1997). The quadratic acid is known to have the α-Keggin structure. As part of our studies of the structures and range of heteroatoms found for heteropolyoxomolybdates and -tungstates, we have examined the structure of the α-$[BW_{12}O_{40}]^{5-}$ ion as the K^+ salt to allow comparisons with our recent examination of the structures of α-$[Co^{II}W_{12}O_{40}]^{6-}$ and α-$[Co^{III}W_{12}O_{40}]^{5-}$ (Nolan et al., 2000). Kraus (1936) reported unit-cell dimensions for $K_5[BW_{12}O_{40}] \cdot 18H_2O$ which appear to be similar to the present compound (a = 19.0 and c = 12.50 Å). The structure of the title compound consists of potassium cations, a $[BW_{12}O_{40}]^{5-}$ anion and water molecules of crystallization. The geometry of the anion is based on the α-Keggin structure (Pope, 1983) and confirms the previous structural

determination of the anion in the related compound $K_5[BW_{12}O_{40}] \cdot 9H_2O$ (Yamase & Ishikawa, 1996). The anion exhibits a central tetrahedrally coordinated B^{III} atom surrounded by four groups of three edge-sharing octahedra (W_3O_{13} subunits) which are linked in turn to each other and to the central BO_4 tetrahedron by shared O atoms at the vertices. A view of the anion is shown in Fig. 1. The central B^{III} atom sits at a site of 222 symmetry and is coordinated to four O atoms with a B—O distance of 1.554 (10) Å. This bond distance may be compared with that of the B—O distance of 1.51 (3) or 1.52 (2) Å (this depends on the anion point symmetry) in $[BW_{11}O_{39}Co^{II}(H_2O)]^{7-}$ (Weakley, 1984), the three unique B—O distances in $H_{21}[B_3W_{39}O_{132}] \cdot 69H_2O$ of 1.46 (5), 1.47 (3) and 1.58 (7) Å [average 1.50 (5) Å], although in the latter compound the boron sits in an environment intermediate between trigonal BO_3 and tetrahedral BO_4, and the B—O distances found for the two crystallographically unique $[BW_{12}O_{40}]^{5-}$ ions (with 222 and 2 symmetry) of 1.46 (3), and 1.25 (6) and 1.79 (9) Å, respectively [average 1.49 (6) Å]. For tetrahedral coordination, B—O bond lengths vary from 1.43 to 1.55 Å, with an average of 1.475 Å (Wells, 1984). The B—O bond length in the present compound is therefore at the upper limit of this range, and results from the relatively rigid polyoxotungstate framework of the $[W_{12}O_{40}]^{8-}$ unit, which contains a central cavity in which the small B^{III} atom resides (Nolan et al., 2000). The O—B—O bond angles of the title compound vary from 108.8 (7) to 110.5 (7)°, and may be compared with values of 110 (2) and 111 (2)° in the anion of 222 symmetry of $K_5[BW_{12}O_{40}] \cdot 9H_2O$, and values of 84 (6), 106 (4), 108 (4) and 134 (11)° for the lower symmetry 2 site. This latter site is obviously considerably distorted. The W—O bond lengths increase with increasing coordination, as found previously, with ranges of 2.320 (9)–2.358 (10) Å for four-coordinate O atoms {$K_5[BW_{12}O_{40}] \cdot 9H_2O$, range for both sites 2.33 (3)–2.47 (3) Å}, 1.853 (10)–1.938 (10) Å for two-coordinate O atoms {$K_5[BW_{12}O_{40}] \cdot 9H_2O$ 1.82 (3)–1.96 (4) Å},
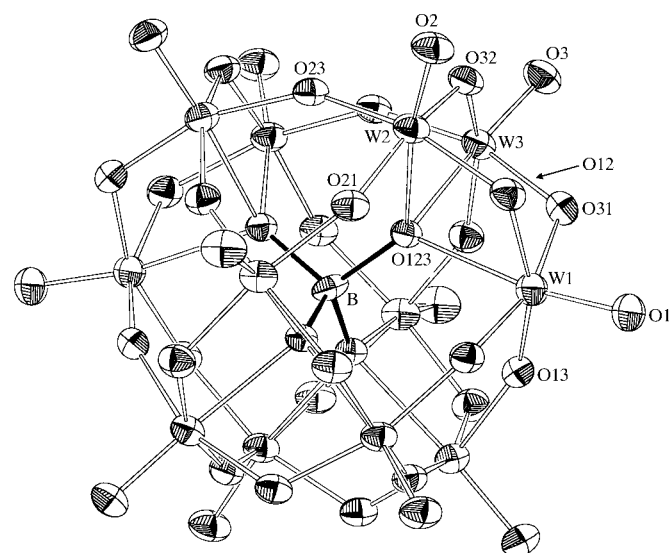

Figure 1
The anion in $K_5[BW_{12}O_{40}] \cdot 16H_2O$ indicating the labelling of the atoms. Displacement ellipsoids are shown at the 50% probability level.

and 1.699 (11)–1.719 (10) Å for the terminal O atoms {$K_5[BW_{12}O_{40}] \cdot 9H_2O$ 1.66 (3)–1.79 (5) Å}. For the title compound, the W—W distances within the W_3O_{13} subunits average 3.317 (5) Å, while those connecting the W_3O_{13} sub-units average 3.641 (7) Å; these may be compared with values of 3.313 (3) and 3.645 (3) Å, respectively, in $K_5[BW_{12}O_{40}] \cdot 9H_2O$. In terms of (average) bond-distance comparisons, the $[W_{12}O_{40}]^{8-}$ framework appears to be most similar to the polyoxotungstate framework of the $[SiW_{12}O_{40}]^{4-}$ ion in the sequence of frameworks of the $[XW_{12}O_{40}]^{n-}$ anions, where $X = P^V$, Si^{IV}, Co^{III} and Co^{II}, which exhibit progressively increasing size of the central heteroatom (Nolan *et al.*, 2000). There are, however, some differences in that the W_3O_{12} group (the W_3O_{13} subunit minus the centrally bound O atom) is slightly closer to the central boron, which is a consequence of the small size of the (formal) B^{III} atom, and necessitates that the angle at the O atoms bridging the W_3O_{13} subunits is the smallest in the series of $[XW_{12}O_{40}]^{n-}$ anions [149.3 (8)° for the B^{III}-containing anion *versus* a range of 154.9 (20) to 151.8 (8)° in the above sequence]. All K^+–anion oxygen and K^+–water oxygen distances are greater than 2.65 (1) Å, with those surrounding the fully occupied K1 atom ranging from 2.65 (1) to 3.10 (1) Å and those surrounding the partially occupied potassium sites ranging from 2.65 (1) to 3.39 (1) Å. These are similar to the distances found in $K_6[Co^{II}W_{12}O_{40}] \cdot 16H_2O$ and $K_5[Co^{III}W_{12}O_{40}] \cdot 16H_2O$ (Nolan *et al.*, 2000).

Experimental

A solution of H_3BO_3 (1.25 g) was added to one (25 ml) of $Na_2WO_4 \cdot 2H_2O$ (25.0 g) with constant stirring, followed by the addition of 6 *M* HCl (15 ml). The pH of the resulting solution was adjusted to 6 and the solution was then refluxed for 24 h. The resulting precipitate of $Na_{10}[H_2W_{12}O_{42}] \cdot nH_2O$ was filtered off. The pH of the filtrate was adjusted to 2 using 6 *M* HCl and was again refluxed for 30 min. Precipitation was effected by addition of KCl (5 g). The resulting product was then isolated by filtration and redissolved in water at pH 6 using 6 *M* HCl. Colourless needle-like crystals were obtained by slow evaporation of the solvent. IR (KBr disc, cm^{-1}): 1001 (*m*), 958 (*s*, W—O asymmetric stretch), 920 (*s*, B—O stretch), 906 (*sh*, W—O—W stretch), 807 (*vs*, W—O—W stretch), 507 (*m*, W—O—W bending). Thermogravimetric analysis was used to establish the actual water content of the bulk compound. Based on a loss of mass of 8.75% up to 573 K, there were 16.3 water molecules per formula unit, and so the composition was therefore close to

Table 1
Selected bond lengths (Å).

B—O123	1.554 (10)	W2—O32	1.917 (10)
W1—O123	2.354 (10)	W2—O21	1.905 (10)
W1—O1	1.699 (11)	W2—O23	1.876 (11)
W1—O12	1.938 (10)	W3—O123	2.358 (10)
W1—O13	1.853 (10)	W3—O3	1.708 (10)
W1—O31	1.923 (10)	W3—O32	1.902 (10)
W1—O21^i	1.876 (10)	W3—O31	1.914 (11)
W2—O123	2.320 (9)	W3—O13^{ii}	1.923 (10)
W2—O2	1.719 (10)	W3—O23^{iii}	1.891 (10)
W2—O12	1.908 (10)		

Symmetry codes: (i) $1 - x, -y, z$; (ii) $x - y, -y, 1 - z$; (iii) $1 + y - x, y, 1 - z$.

$K_5[BW_{12}O_{40}] \cdot 16H_2O$, although only eight water molecules could be established by X-ray crystallography.

Crystal data

$K_5[BW_{12}O_{40}] \cdot 16H_2O$	Mo *Kα* radiation
$M_r = 3340.72$	Cell parameters from 10
Trigonal, $P6_222$	reflections
$a = 18.970 (4)$ Å	$\theta = 9–11°$
$c = 12.414 (5)$ Å	$\mu = 27.740$ mm^{-1}
$V = 3869 (2)$ Å^3	$T = 294$ K
$Z = 3$	Prism, colourless
$D_x = 4.30$ Mg m^{-3}	$0.34 \times 0.13 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffract-ometer	$R_{int} = 0.047$
ω–2θ scans	$\theta_{max} = 25°$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = 0 \rightarrow 22$
	$k = -22 \rightarrow 0$
$T_{min} = 0.04$, $T_{max} = 0.11$	$l = 0 \rightarrow 14$
5003 measured reflections	1 standard reflection
2288 independent reflections	frequency: 30 min
2122 reflections with $I > 3\sigma(I)$	intensity decay: 21%

Refinement

Refinement on F	H-atom parameters not defined
$R = 0.036$	$w = 1/[\sigma^2(F) + 0.0016F^2]$
$wR = 0.048$	$(\Delta/\sigma)_{max} = 0.006$
$S = 1.54$	$\Delta\rho_{max} = 1.79$ e Å^{-3}
2122 reflections	$\Delta\rho_{min} = -2.70$ e Å^{-3}
78 parameters	

The standard reflection showed a 21% loss in intensity over the data collection, and a correction for this was applied. This may perhaps be associated with water loss from the crystal, leading to disorder of much of the H_2O molecules (see below). The systematic absences for the compound are unique for the space group $P6_222$. Moreover, the compound is isomorphous and isostructural with $K_5[Co^{III}W_{12}O_{40}] \cdot 16H_2O$ (Nolan *et al.*, 2000) and the atomic coordinates for the heavy atoms for this structure were therefore used for the present structure. The cations and water molecules were subsequently found using difference Fourier methods. Four crystallographically unique sites containing potassium were located. One of these was fully occupied by potassium and located along a twofold axis, while the other three only exhibited partial occupancy by potassium together with the oxygen of a water molecule. A similar situation has been found previously in $K_5[Co^{III}W_{12}O_{40}] \cdot 16H_2O$. Two of these latter sites were located along twofold axes, while the third was in a general position. Based on the electron densities at these sites, new scattering factors were constructed from those of potassium and oxygen. These sites, OKW1, OKW2 and OKW3, had 83, 30 and 48% K, with the remainder oxygen%. Upon completion of the refinement, 4.92 K atoms (*i.e.* about the expected 5 per formula unit) and 8.08 water molecules had been located, the latter less than the 16 water molecules per formula unit suggested by thermogravimetric analysis. The remaining water molecules were highly disordered and correspond, assuming a volume per water molecule of about 40 Å^3 (Peterson & Levy, 1957), to some 960 Å^3 per unit cell which are located in the interanionic voids. This assumes that the composition of the crystal was typical of the bulk sample, with 16 water molecules per formula unit. This remaining water is zeolitic in nature, as was observed in the case of $K_5[Co^{III}W_{12}O_{40}] \cdot 16H_2O$ (Nolan *et al.*, 2000). This latter study, performed on a crystal exposed to the atmosphere, allowed the location of only three water molecules per formula unit. For the related compound $K_6[Co^{II}W_{12}O_{40}] \cdot nH_2O$, a crystal was sealed in a glass capillary to minimize efflorescence, and a subsequent X-ray study allowed the location of 11 water molecules per formula unit,

while chemical analysis of an air-dried sample indicated only a trihydrated species (Casañ-Pastor *et al.*, 1991). Attempted refinement in the enantiomeric space group $P6_422$ gave a final R factor of 0.042 with 846 Friedel pairs not averaged, significantly higher than the value of 0.036 observed for $P6_222$. The maximum peak and minimum trough were located in the region of the W atoms, but not in chemically significant positions.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: local software; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 1989); molecular graphics: *ORTEP*II (Johnson, 1976).

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