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Synthesis, Characterization, and Crystal Structure of a New Potassium Borate, $KB_3O_5 \cdot 3H_2O$

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A solid 1:1 molar ratio mixture of $K_2B_4O_7 \cdot 4H_2O$ and $KB_5O_8 \cdot 4H_2O$ reacts upon exposure to high humidity or water at room temperature to produce a new potassium borate, $KB_3O_5 \cdot 3H_2O$, in quantitative yield. The complex is stable in air, but contact with water for prolonged periods results in decomposition. It is stable up to 100 °C, whereupon an amorphous compound is formed until reaching ~550 °C; two new crystalline phases of anhydrous KB_3O_5 can be isolated from the trihydrate at 550 °C, depending on heating conditions. The molecular structure, $KB_3O_3(OH)_4 \cdot H_2O$, was determined by single-crystal X-ray diffraction at −110 °C. The compound is monoclinic, space group $C2/c$, with a = 15.540 (5) Å, b = 6.821 (2) Å, c = 14.273 (4) Å, β = 104.44 (2)°, V = 1465.1 Å^3, and Z = 8. All atoms were located and refined; the final agreement factors were R_1 = 0.029 and R_2 = 0.041. The structure contains an isolated $B_3O_3(OH)_4^-$ anion formed from a B_3O_3 ring consisting of one tetrahedral and two trigonal boron atoms. The ring is nearly planar, with an average trigonal boron–oxygen distance of 1.366 Å and an average tetrahedral boron–oxygen distance of 1.470 Å. There are two independent potassium atoms, one eight-coordinate to two free water molecules and six O atoms from the anion and one approximately octahedrally coordinated to six O atoms from the anion. Six intermolecular hydrogen bonds further connect the three-dimensional crystalline network. This complex, characterized also by infrared and Raman spectroscopy, is the first synthetic example of the $B_3O_3(OH)_4^-$ ion in the solid state and thus the first readily accessible form of this anion.

The structural chemistry of the hydrated alkali-metal borates flowered for the most part during the 1950s and 1960s with systematic studies of both synthetic compounds and the naturally occurring minerals.[1-3] Due to the complex and somewhat unusual chemistry of these compounds, the literature of the synthetic borates contains many reports of new compounds characterized only by X-ray powder data. Although many metastable compounds have been detected in phase equilibrium and dehydration studies,[1] there are relatively few hydrated alkali-metal borates stable under ordinary conditions, and there have apparently been no new synthetic compounds reported in the last 10 years. In particular, the alkali-metal triborates are the least well characterized of the known borate phases. For Li, Rb, and Cs, no hydrated triborates have yet been reported. For Na, only the mineral ameghinite[4] from Argentina, $NaB_3O_5 \cdot 2H_2O$, has been well studied;[5] X-ray crystallography[6] showed it to be the first example of the $B_3O_3(OH)_4^-$ ion in the solid state. For K, no well-characterized, pure triborates have been identified, though "$KB_3O_3(OH)_4$" has been reported as an impure phase.[7,8] Reported here is the unusual synthesis, characterization, and crystal structure of a new potassium triborate, $KB_3O_5 \cdot 3H_2O$, or, more properly, $KB_3O_3(OH)_4 \cdot H_2O$. The X-ray data reveal this as the first confirmed synthesis of the $B_3O_3(OH)_4^-$ ion. This ion, very stable in aqueous solution and the most abundant polyborate species present over a wide pH range,[9] has been found previously in the solid state only in ameghinite.

Results and Discussion

Synthesis of $KB_3O_3(OH)_4 \cdot H_2O$ (I). It is well-known that potassium tetraborate, $K_2B_4O_7 \cdot 4H_2O$, and potassium pentaborate, $KB_5O_8 \cdot 4H_2O$, are independently stable to water or high humidity. However, when these two solids are finely ground and mixed in a 1:1 mole ratio, they react with water at room temperature to produce I according to

$$K_2B_4O_7 \cdot 4H_2O + KB_5O_8 \cdot 4H_2O + H_2O \rightarrow 3KB_3O_5 \cdot 3H_2O \quad (1)$$

The solid mixture converts quantitatively to I either in the presence of 100% humidity or by addition of a small amount of liquid water (insufficient for complete dissolution of the solids). Complete reaction occurs within two days if the particle size is small (≲0.05 mm). The tetraborate/pentaborate mixture does not react in air (~50–70% relative humidity) for at least 2 months at room temperature.

When the pentaborate and tetraborate salts are mixed in a different mole ratio than that given in eq 1 and treated with humidity, the deficient component is entirely consumed in the production of I, while some of the excess component remains unreacted.

The synthesis of I is somewhat surprising in that no hydrated potassium triborates are predicted from phase studies[10] and that the starting materials are commonly available, stable compounds. This type of "fusion" reaction of two hydrated alkali-metal borates to give a new crystalline species with an intermediate M:B ratio is rare; however, a synthetic sodium triborate was also prepared in this fashion at 100 °C by reaction of $NaBO_2 \cdot 2H_2O$ with $Na_4B_{18}O_{29} \cdot 11H_2O$.[1] We found that mixtures of $Na_2B_4O_7 \cdot 5H_2O$ (or $Na_2B_4O_7 \cdot 10H_2O$) and $NaB_5O_8 \cdot 5H_2O$ do not react in the presence of water at room temperature to produce a triborate.

The new triborate I can also be quantitatively synthesized from a solid mixture of $KB_5O_8 \cdot 4H_2O$ and $K_2B_5O_8(OH) \cdot 2H_2O$ according to

$$KB_5O_8 \cdot 4H_2O + 2K_2B_5O_8(OH) \cdot 2H_2O + 6H_2O \rightarrow 5KB_3O_5 \cdot 3H_2O \quad (2)$$

In this case, the mechanism is not clear since the dipotassium pentaborate salt alone when exposed to humidity formed a mixture of $K_2B_4O_7 \cdot 4H_2O$ and I. It is probable that the dipotassium pentaborate salt, upon exposure to 100% humidity, initially forms a mixture of the stable tetraborate and pentaborate salts (this does

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(4) Aristarain, L. F.; Hurlbut, C. S., Jr. *Am. Mineral.* **1967**, *52*, 935.

(5) A synthetic compound of the same formula is known only from its different X-ray powder pattern; see: Kocher, J.; Lahlou, A. *Bull. Soc. Chim. Fr.* **1970**, *6*, 2083. See also ref 1.

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(8) Even though an X-ray powder pattern was reported for this complex, the infrared spectrum (ref 7d) is largely that of an amorphous compound and is nearly identical with the amorphous spectrum shown in Figure 1 (bottom).

(9) Ingri, N. *Sven. Kem. Tidskr.* **1963**, *75*, 199 and references therein.

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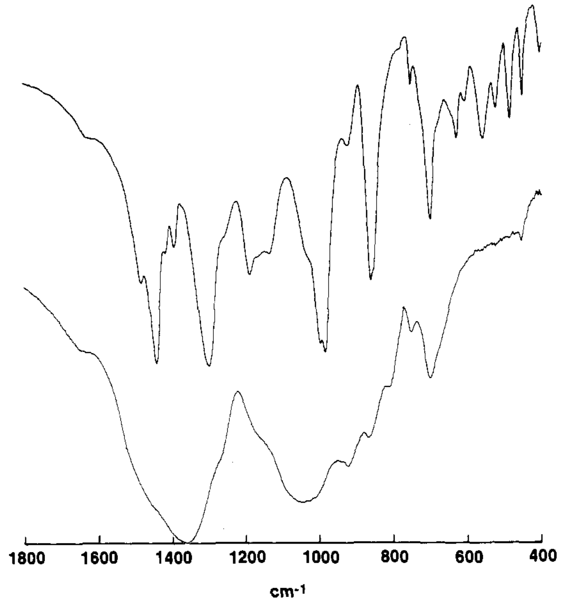

Figure 1. Infrared spectra of I (top) and I heated to 110 °C for 2 h (bottom).

occur in aqueous solution), which then react to form I, consuming all the $KB_5O_8 \cdot 4H_2O$:

$$6K_2B_5O_8(OH) \cdot 2H_2O + 13H_2O \rightarrow 5K_2B_4O_7 \cdot 4H_2O + 2KB_5O_8 \cdot 4H_2O \quad (3)$$

$$2KB_5O_8 \cdot 4H_2O + 2K_2B_4O_7 \cdot 4H_2O + 2H_2O \rightarrow 6KB_3O_5 \cdot 3H_2O \quad (4)$$

In attempts to isolate $KB_3O_3(OH)_4 \cdot H_2O$ from aqueous solution, it was found that "KB_3" solutions invariably deposited $KB_5O_8 \cdot 4H_2O$ initially upon evaporation at room temperature. As the B:K solution ratio approached 2.0, then $K_2B_4O_7 \cdot 4H_2O$ also crystallized. At evaporation temperatures higher than about 50 °C, crystalline species had insufficient time to form, and amorphous solids of formula $KB_3O_5 \cdot xH_2O$ ($x = \sim 0.8–1.5$ depending on temperature) were formed. These solids contained tightly bound residual water, driven off only in the range 200–500 °C, and displayed infrared spectra similar to that shown in Figure 1 (bottom). A thorough study to determine under what conditions, if any, I can be crystallized from solution has not yet been made. In one preliminary experiment a supersaturated "KB_3" solution (3.0% B) precipitated pure $KB_5O_8 \cdot 4H_2O$ soon after addition of seed crystals of I. This may be due in part to the lower relative solubility of the pentaborate salt (i.e., a saturated solution in contact with $KB_5O_8 \cdot 4H_2O$ at 20 °C contains 0.66% B vs. 0.78% B for the similar case of I; see below).

Once formed, I is stable to 100% humidity for moderate periods at room temperature (at least 30 days) and indefinitely stable in air. It is fundamentally unstable in solution, as discussed below.

Characterization of $KB_3O_3(OH)_4 \cdot H_2O$ and Two New Phases of KB_3O_5. Differential thermal analysis (DTA) of I produced a curve very similar to that reported for ameghinite.[4] A single endothermic peak was present at 150 °C due to dehydration. An exothermic peak at ~635 °C corresponded to crystallization of a new phase, while the endothermic peak at 760 °C indicated melting of the sample. Attempted isolation of the crystalline phase, presumably KB_3O_5, resulted in a rather curious discovery. Upon insertion into a hot furnace at 550 °C, I was converted to a new crystalline phase of KB_3O_5, designated β-KB_3O_5 (II) to distinguish it from the phase reported previously.[11] Major lines in the X-ray powder pattern of II occurred at d = 3.56 (100), 4.47 (80), 2.98 (70), 2.85 (35), and 2.67 (30) Å (relative intensity). If I was placed in a cold furnace and heated slowly to 550 °C, another phase was produced, γ-KB_3O_5 (III). This phase had the powder pattern d = 3.17 (100), 2.66 (80), 2.12 (55), 4.80 (50), and 4.69 (50) Å (relative intensity) and was stable up to 750 °C for 4 h. Although β-KB_3O_5 was stable up to 4 h at 550 °C, it transformed to γ-KB_3O_5 within 1 h at 650 °C. The DTA curve of II showed an exothermic crystallization peak at 620 °C (transformation to the γ-phase) and an endothermic melting at 765 °C. The DTA curve of III showed only melting at 760 °C. Both phases were air stable and did not rehydrate appreciably. Anhydrous sodium triborate, NaB_3O_5, has also been isolated in three phases.[12]

The possibility that II is a mixture, perhaps of disproportionation products or more than one phase, is unlikely since it reproducibly yields pure III after heating to 650 °C. The possibility that III is a mixture is also unlikely from the following data. It is reported[13] that $K_4B_{10}O_{17} \cdot 5H_2O$ becomes amorphous at ~500 °C as it loses its last mole of water. We found that the DTA curve showed two exothermic (crystallization) peaks at 510 and 640 °C and two close, endothermic (melting) peaks at ~750 and 770 °C, suggesting a high-temperature disproportionation. Heating of this salt to 660 °C for 24 h resulted in disproportionation to a mixture of III and $K_2B_4O_7 \cdot 4H_2O$ (after cooling to room temperature in air). It is known that "$Na_4B_{10}O_{17}$" disproportionates to a mixture of $Na_2B_4O_7$ and NaB_3O_5 at high temperature.[12] Therefore, it is likely that the X-ray powder patterns attributable to II and III represent single, pure phases of KB_3O_5.

As discussed earlier, various $KB_3O_5 \cdot xH_2O$ amorphous solids could be isolated from aqueous "KB_3" solutions. When exposed to 100% humidity for 24 h, these solids did not initially produce $KB_3O_3(OH)_4 \cdot H_2O$ but rather mixtures of the stable phases $K_2B_4O_7 \cdot 4H_2O$ and $KB_5O_8 \cdot 4H_2O$. These amorphous solids always showed an exothermic crystallization peak around 600 °C in the DTA curve and produced γ-KB_3O_5 as the only crystalline phase upon heating to 550–750 °C, irrespective of the method of heating. Therefore, γ-KB_3O_5 is obtainable from the starting materials $B(OH)_3$ and KOH, but β-KB_3O_5 seems to be a unique intermediate product of I. Further study of these new anhydrous phases is in progress.

The derivative of the TGA (thermogravimetric analysis) curve of I showed just one sharp peak in the range 100–170 °C corresponding to loss of 2 mol of water, with a gradual tail extending out to ~530 °C due to loss of the last mole of water. Although stable below 100 °C, when I is heated to ~110 °C, it becomes amorphous with the loss of 2 mol of water and forms a polymer of approximate formula $KB_3O_5 \cdot H_2O$ (see Figure 1). Oven experiments established that this polymer remains amorphous up to about 550 °C, whereupon γ-KB_3O_5 crystallizes. Exposure of the 110 °C amorphous product to 100% humidity for 6 h quantitatively regenerates I, in contrast to the reaction of the amorphous "$KB_3O_5 \cdot H_2O$" solids produced from aqueous "KB_3" solutions (above). This implies that the degree of disorder in the structures of amorphous borates[14] is highly variable, even when they are synthesized at the same temperature and with the same approximate formula. The apparent instability of a crystalline species corresponding to "$KB_3O_5 \cdot 2H_2O$" [$KB_3O_3(OH)_4$] may partly reflect the coordination requirements of the potassium atoms in the structure and could explain why Heller did not isolate pure $KB_3O_3(OH)_4$ free of a coordinating organic solvent.[7]

As the first synthetic example of the $B_3O_3(OH)_4^-$ ion, the infrared and Raman spectra of I are of interest, especially since these data were not reported for ameghinite. The infrared spectrum of I (Figure 1) shows the sharp peaks characteristic of a crystalline phase, whereas the dehydration product "$KB_3O_5 \cdot H_2O$" shows the typically broadened spectrum of an amorphous phase.[15] The strong bands at ~1450 and ~1310 cm^{-1} in the spectrum of I are characteristic of trigonally coordinated boron, while the bands

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at ~1000 and ~870 cm^{-1} are characteristic of tetrahedral boron.[15] This field is not sufficiently developed to allow a more detailed interpretation of the infrared spectrum. Krogh-Moe has pointed out that the idealized C_{2v} triborate anion has 21 infrared-active fundamental vibrations.[15c]

The Raman spectrum of I displayed bands at 1194 vw, 996 w, 753 s, 624 vs, 488 m, 453 m, 407 w, 212 vw, 176 m, 137 m, and 116 m cm^{-1}. This agrees very well with the Raman spectrum of the $B_3O_3(OH)_4^-$ ion in aqueous solution as deduced by Maeda et al.:[16] 995 w, 609 s, 490 w, 458 w, 430 w cm^{-1}. The 753-cm^{-1} band in the solid was not observed in solution probably due to overlap with the strong $B(OH)_4^-$ band at 745 cm^{-1}.

The solid phase in equilibrium with a saturated, aqueous solution of I is initially $KB_3O_3(OH)_4{\cdot}H_2O$ but slowly changes to $KB_5O_8{\cdot}4H_2O$ so that after 7–10 days crystals of $KB_5O_8{\cdot}4H_2O$ are the only solid phase present. In one experiment, the saturated solution was initially 0.78 wt % B at 21 °C with B:K = 3.0 and changed to 1.76 wt % B with B:K = 2.5 after 2 weeks. In this respect $KB_3O_3(OH)_4{\cdot}H_2O$ is a metastable potassium borate. This instability in contact with water can be viewed as a result of the aqueous chemistry of boron: equilibria exist in solution between $B(OH)_3$, $B(OH)_4^-$, and many different polyborate anions [e.g., $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$]. For example, in a recent ^{11}B NMR study,[17] a 0.15 M solution of $KB_5O_8{\cdot}4H_2O$ [$KB_5O_6(OH)_4{\cdot}2H_2O$] was shown to be only ~0.03 M in $B_5O_6(OH)_4^-$; the other species present were ~0.07 M $B_3O_3(OH)_4^-$, ~0.05 M $B(OH)_4^-$, and ~0.33 M $B(OH)_3$. These equilibria and the relatively low solubility[1] of $KB_5O_8{\cdot}4H_2O$ are factors in why the pentaborate will crystallize even from a solution with B:K = 3.0. As $KB_5O_8{\cdot}4H_2O$ crystallizes from such a solution, the pH increases as B:K approaches 2.0 and $K_2B_4O_7{\cdot}4H_2O$ crystallizes. Therefore, the aqueous equilibria, which are a function of pH and total boron concentration,[17] and the solubilities of the various salts both determine which salts are stable in contact with their solution.

The ease with which the $B_5O_6(OH)_4^-$ ion reacts with the $B_4O_5(OH)_4^{2-}$ ion and water to produce $B_3O_3(OH)_4^-$ as the only product is interesting, though not surprising, since the triborate ion is a more hydrated polyborate than $B_5O_6(OH)_4^-$ or $B_4O_5(OH)_4^{2-}$ and could be formed from either ion as they both contain the basic B_3O_3 ring structure. Apparently, 100% humidity provides a unique hydrating environment of limited water availability, in this case allowing a species that is unstable in excess liquid water to be synthesized and exist in the presence of saturated gaseous water (and the small amount of liquid water that is inevitably present).

Because of their relatively facile synthesis from I at approximately 200 °C below their melting points, it is likely that β-KB_3O_5 and γ-KB_3O_5 possess structures not significantly different from the parent hydrate $KB_3O_5{\cdot}3H_2O$. Therefore, since a major structural reorganization is unlikely, the structure of $KB_3O_5{\cdot}3H_2O$ (below) implies that the structures of β- and γ-KB_3O_5 are probably composed of polymeric three-dimensional networks of linked $B_3O_3^-$ rings, similar to CsB_3O_5.[18] In contrast, the structures of two phases of NaB_3O_5 have been solved and are quite different. The α-phase is a 1:1 combination of $B_5O_6^-$ and $B_4O_5^{2-}$ ring units,[19] while the β-phase is a combination of $B_5O_6^-$, $B_3O_3^-$, and BO_4^- units.[20] These two phases were synthesized from a glass melt prepared by fusion of $Na_2B_4O_7{\cdot}10H_2O$ and boric acid.

In separate experiments we have also isolated two metastable dehydration reaction products of I, $K_2B_6O_7(OH)_6{\cdot}2H_2O$[21] with a probable structure of two $B_3O_3(OH)_4^-$ rings linked by a B–O–B bridge[22] and $K_2B_8O_{10}(OH)_6{\cdot}3H_2O$[23] (by reaction of $KB_5O_8{\cdot}4H_2O$ with I) with a probable structure of a $B_3O_3(OH)_4^-$ ring linked to a $B_5O_6(OH)_4^-$ ion.[24] These complexes will be described more fully at a later date.

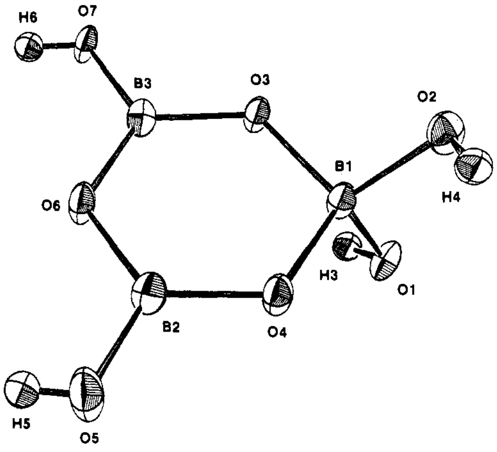

Figure 2. $B_3O_3(OH)_4^-$ anion showing the atom-numbering scheme and 50% probability ellipsoids.

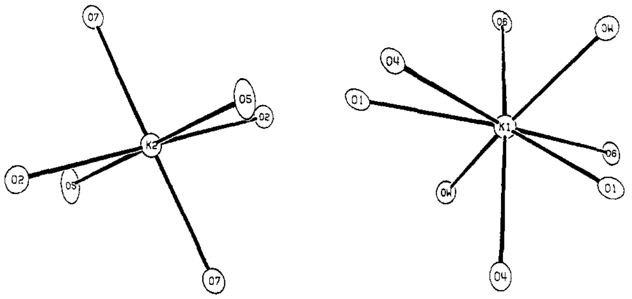

Figure 3. ORTEP diagrams of the coordination spheres of the two independent potassium atoms in $KB_3O_3(OH)_4{\cdot}H_2O$.

Crystal Structure of I. The structure consists of the isolated $B_3O_3(OH)_4^-$ anion (Figure 2) with an associated potassium cation and water of hydration. All the B–O bond distances in the anion are equivalent within 3σ to those found for the $B_3O_3(OH)_4^-$ anion in ameghinite.[6] The B–O distances in I average 1.470 Å for the tetrahedrally coordinated boron atoms and 1.366 Å for the trigonal borons, in accordance with previous observations.[3] The bond angles about the trigonal and tetrahedral boron atoms do not deviate significantly from the ideal values. In this regard, the overall anion structure in I is less distorted than found in ameghinite.

The major difference between the anion in I and in ameghinite is the degree of planarity of the B_3O_3 ring. In ameghinite, the tetrahedral boron is 0.315 Å from the plane of the three ring oxygen atoms, while the ring is much more planar in I. The largest deviation from the weighted least-squares plane containing all six atoms of the B_3O_3 ring is with B1, at only 0.036 Å from the plane.

There are two crystallographically unique potassium atoms, each on a special position (Figure 3). Atom K1 is on a twofold axis and is coordinated to eight oxygen atoms comprised of two crystallographically identical free water molecules and six oxygen atoms from four anions (four cyclic O atoms and two exocyclic OH groups). The K1–O distances range from 2.764 (1) to 3.050

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(21) X-ray powder pattern: *d* = 11.8 (100), 3.01 (100), 3.52 (70), 3.59 (70), 8.35 (60) Å (relative intensity).

(22) Heller claimed synthesis of impure "$K_2B_6O_7(OH)_6$" with the same proposed structure; see: Heller, G. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3511.

(23) X-ray powder pattern: *d* = 7.78 (100), 10.9 (80), 6.67 (40), 4.82 (30), 2.93 (30) Å (relative intensity).

(24) A compound of this formula was mentioned by Toledano and Benhassaine as a metastable high-temperature phase, though no characterization data were reported.[10d] Additionally, $(NH_4)_2B_8O_{13}{\cdot}6H_2O$ is a known compound with the same proposed structure. See: Bowden, G. H. In *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Mellor, J. W., Ed.; Longman: London, 1980; Vol. 5, Part A, Supplement 1, p 687.

(1) Å. Atom K2, on an inversion center, shows a somewhat distorted octahedral coordination to hydroxyl groups from six different $B_3O_3(OH)_4^-$ ions. The K2–O distances range from 2.684 (2) to 2.785 (1) Å.

The three-dimensional framework is further interconnected by six intermolecular hydrogen bonds between H2–O2 [1.85 (3) Å], O1–H6 [1.91 (3) Å], OW–H5 [2.00 (3) Å], H1–O3 [2.00 (3) Å], O7–H3 [2.15 (3) Å], and O4–H4 [2.16 (3) Å].

Summary. The relatively simple isolation of a new compound in a well-established field is always intriguing, and raises the question as to how $KB_3O_5 \cdot 3H_2O$ remained undiscovered for so long, when its two precursors have been known for over a hundred years. One implication is that the type of synthetic method described here has not been exploited and warrants further investigation.

Experimental Section

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Nicolet MX-1 FTIR instrument. Raman spectra were measured by using the 514.5-nm excitation from an Ar ion laser on a modified Jarrell-Ash instrument at the Oregon Graduate Center. Thermogravimetric analyses (TGA) were performed on a Du Pont Model 951 TGA controlled by a Northstar computer at a heating rate of 10 °C/min and a flow rate of 100 cm^3 of N_2/min. Differential thermal analysis (DTA) to 1200 °C was conducted on a Du Pont high-temperature DTA equipped with a Model 900 controller at a heating rate of 10 °C/min and a flow rate of 100 cm^3 of N_2/min with an aluminum oxide reference and a Pt/Pt + 13% Rh thermocouple. X-ray powder diffraction spectra were measured on a Norelco Type 12045 unit using Co Kα radiation (λ = 1.7889 Å) with an Fe filter; the camera diameter was 57.3 mm.

Materials. Potassium pentaborate, $KB_5O_8 \cdot 4H_2O$, and potassium tetraborate, $K_2B_4O_7 \cdot 4H_2O$, were obtained from U.S. Borax and Chemical Corp. as fine powders and were used as received. Boric acid and potassium hydroxide were purchased from Mallinckrodt. $K_2B_5O_8(OH) \cdot 2H_2O$ was prepared as described previously.[17]

Synthesis of $KB_3O_3(OH)_4 \cdot H_2O$ (I). Potassium pentaborate and potassium tetraborate were combined in a 1:1 mole ratio (29.3 mg of $KB_5O_8 \cdot 4H_2O$ and 30.6 mg of $K_2B_4O_7 \cdot 4H_2O$), and the solid mixture was placed in a vial in a 100% humidity chamber (formed from a covered beaker containing water) at room temperature. Infrared analysis indicated that after 24 h the mixture contained approximately 60% I, 20% $KB_5O_8 \cdot 4H_2O$, and 20% $K_2B_4O_7 \cdot 4H_2O$. After 48–72 h, the solid was I, pure by IR and X-ray powder diffraction. The yield is quantitative. Anal. Calcd for $B_3H_6O_8K$: B, 15.78; H, 2.94; K, 19.02. Found: B, 15.4; H, 2.92; K, 19.1. Infrared spectrum (KBr disk): 3502 ms, 3462 ms, 3374 m, 3144 m, br, 2390 w, br, 1492 s, 1454 vs, 1401 ms, 1313 vs, 1199 s, 1174 ms, 1144 ms, 1010 vs, 997 vs, 929 mw, 870 s, 754 w, 707 m, 632 mw, 610 w, 561 mw, 526 mw, 488 mw, 453 mw, 405 w cm^{-1}.

Alternately, the above pentaborate/tetraborate mixture was treated with a small amount of water insufficient for complete dissolution of the solids, and the water was left to evaporate slowly over 48 h at room temperature. Typically, ~0.1 g of water was added to 20 mg of the mixture. This method gave a product of variable purity (~80–100% with ~0–20% unreacted starting material). Too much water inhibited the reaction, and only starting materials were recovered.

Single crystals over 0.1 mm could sometimes be obtained by mixing about 10 g of total solids with a stoichiometric quantity of water according to eq 1; the wet mixture was then covered with mineral oil and left for 1–4 weeks at room temperature.

Alternately, potassium pentaborate and dipotassium pentaborate were combined in a 1:2 mole ratio [9.8 mg of $KB_5O_8 \cdot 4H_2O$ plus 20.9 mg of $K_2B_5O_8(OH) \cdot 2H_2O$], and the solid mixture was treated with 100% humidity as above. After 48 h, the product was $KB_3O_5 \cdot 3H_2O$, pure by IR and X-ray powder diffraction.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*
K1	0.0000	0.1479 (1)	0.2500
K2	0.2500	0.2500	0.0000
OW	−0.15393 (10)	0.2652 (2)	0.1158 (1)
O1	−0.14801 (9)	0.0206 (2)	0.3071 (1)
O2	−0.12477 (9)	−0.0265 (2)	0.4775 (1)
O3	−0.17146 (9)	−0.2940 (2)	0.3710 (1)
O4	−0.02179 (9)	−0.1637 (2)	0.3937 (1)
O5	0.09421 (10)	−0.3740 (2)	0.3880 (1)
O6	−0.05168 (9)	−0.5039 (2)	0.3585 (1)
O7	−0.19963 (9)	−0.6241 (2)	0.3372 (1)
B1	−0.1164 (1)	−0.1151 (3)	0.3876 (2)
B2	0.0069 (2)	−0.3463 (4)	0.3803 (2)
B3	−0.1409 (2)	−0.4734 (3)	0.3552 (2)
H1	−0.202 (2)	0.242 (4)	0.124 (2)
H2	−0.151 (2)	0.202 (4)	0.065 (2)
H3	−0.180 (1)	−0.036 (4)	0.264 (2)
H4	−0.083 (1)	0.011 (4)	0.505 (2)
H5	0.105 (2)	−0.463 (4)	0.382 (2)
H6	−0.183 (2)	−0.718 (4)	0.329 (2)

Table II. Bond Distances (Å) and Their Estimated Standard Deviations

K1–OW	2.783 (2)	B3–O6	1.392 (3)
K1–O1	2.764 (1)	B3–O7	1.356 (3)
K1–O4	3.031 (1)	H1–OW	0.80 (3)
K1–O6	3.050 (1)	H2–OW	0.85 (3)
K2–O2	2.785 (1)	H3–O1	0.79 (3)
K2–O5	2.684 (2)	H4–O2	0.72 (2)
K2–O7	2.767 (1)	H5–O5	0.64 (3)
B1–O1	1.462 (3)	H6–O7	0.71 (3)
B1–O2	1.453 (3)	H1···O3	2.00 (3)
B1–O3	1.475 (2)	H2···O2	1.85 (3)
B1–O4	1.489 (2)	H3···O7	2.15 (3)
B2–O4	1.353 (3)	H4···O4	2.16 (3)
B2–O5	1.347 (3)	H5···OW	2.00 (3)
B2–O6	1.393 (3)	H6···O1	1.91 (3)
B3–O3	1.352 (3)		

Crystal Structure Determination. The structural study was conducted at Molecular Structure Corp. A colorless prismatic crystal of $B_3H_6O_8K$, ~0.30 × 0.35 × 0.40 mm, was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, by using the setting angles of 24 reflections in the range $5 < \theta < 9°$, measured by the computer-controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are a = 15.540 (5) Å, b = 6.821 (2) Å, c = 14.273 (4) Å, β = 104.44 (2)°, and V = 1465.1 Å^3. For Z = 8 and fw = 205.58, the calculated density is 1.86 g/cm^3. The measured density was 1.78 (5) g/cm^3 at 25 °C. As a check on crystal quality, ω-scans of several intense reflections were measured; the width at half-height was 0.20° with a takeoff angle of 2.8°, indicating good crystal quality. From the systematic absences of

$$hkl \quad h + k = 2n + 1$$

$$h0l \quad h, l = 2n + 1$$

and from subsequent least-squares refinement, the space group was determined to be $C2/c$ (No. 15).

The data were collected at a temperature of −110 ± 1 °C using the ω–θ scan technique. The scan rate varied from 2–20°/min (in ω). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 52.0°. The scan range (in deg) was determined as a function of θ to correct for the separation of the Kα doublet; the scan width was calculated as follows:

$$\theta \text{ scan width} = 0.7 + 0.350 \tan \theta$$

Moving-crystal, moving-counter background counts were made by scanning an additional 25% above and below this range. Thus, the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.5 mm; the vertical aperture was set at 2.0 mm. The diameter of the incident beam collimator was 0.7 mm, and the crystal-to-detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 20.7.

A total of 1668 reflections were collected, of which 1445 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 43 min. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.2 cm^{-1} for Mo Kα radiation. No absorption correction was made. A secondary extinction correction was applied.[25]

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[25] Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

Table III. Bond Angles (deg) and Their Estimated Standard Deviations

OW–K1–OW	146.57 (7)	K1–O1–H3	109 (2)
OW–K1–O1	69.97 (4)	B1–O1–H3	109 (2)
OW–K1–O1	121.54 (5)	K2–O2–B1	127.1 (1)
OW–K1–O4	116.45 (4)	K2–O2–H4	105 (2)
OW–K1–O4	87.59 (4)	B1–O2–H4	111 (2)
OW–K1–O6	80.52 (4)	B1–O3–B3	124.2 (2)
OW–K1–O6	73.55 (4)	K1–O4–B1	94.6 (1)
O1–K1–O1	143.39 (6)	K1–O4–B2	117.0 (1)
O1–K1–O4	48.60 (4)	B1–O4–B2	123.5 (2)
O1–K1–O4	102.76 (4)	K2–O5–B2	138.1 (1)
O1–K1–O6	75.60 (4)	K2–O5–H5	98 (3)
O1–K1–O6	137.55 (4)	B2–O5–H5	115 (3)
O1–K1–O4	102.76 (4)	K1–O6–B2	118.3 (1)
O4–K1–O4	90.95 (5)	K1–O6–B3	119.1 (1)
O4–K1–O6	96.58 (4)	B2–O6–B3	118.8 (2)
O4–K1–O6	167.85 (4)	K2–O7–B3	113.2 (1)
O6–K1–O6	77.71 (5)	K2–O7–H6	93 (2)
O2–K2–O2	180.00	B3–O7–H6	117 (3)
O2–K2–O5	74.33 (5)	O1–B1–O2	110.1 (2)
O2–K2–O5	105.67 (5)	O1–B1–O3	109.3 (2)
O2–K2–O7	76.17 (4)	O1–B1–O4	108.7 (2)
O2–K2–O7	103.83 (4)	O2–B1–O3	108.1 (2)
O5–K2–O5	180.00	O2–B1–O4	110.2 (2)
O5–K2–O7	90.03 (5)	O3–B1–O4	110.5 (2)
O5–K2–O7	89.97 (5)	O4–B2–O5	118.6 (2)
O7–K2–O7	180.00	O4–B2–O6	121.5 (2)
K1–OW–H1	121 (2)	O5–B2–O6	119.9 (2)
K1–OW–H2	103 (2)	O3–B3–O6	121.2 (2)
H1–OW–H2	105 (3)	O3–B3–O7	118.1 (2)
K1–O1–B1	106.8 (1)	O6–B3–O7	120.7 (2)

The final coefficient, refined by least squares, was 0.000 000 7 (in absolute units).

The structure was solved by using direct methods. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined by full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows:

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, L is the Lorentz-polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.050. Scattering factors were those tabulated by Cromer and Waber.[26] Anomalous dispersion effects were included in F_c;[27] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[28] Only the 1165 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 136 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.029$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.041$$

The standard deviation of an observation of unit weight was 1.22. The highest peak in the final difference Fourier had a height of 0.28 e/Å^3 with an estimated error based on ΔF[29] of 0.07. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The computer was a PDP-11/60-based system. Positional parameters are listed in Table I. Bond distances and angles are collected in Tables II and III. Tables of observed and calculated structure factor amplitudes, thermal parameters, least-squares planes, and intermolecular contacts are available as supplementary material. The calculated X-ray powder pattern for Cu radiation is also available.

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Supplementary Material Available: Tables of anisotropic thermal parameters, weighted least-squares planes, and intermolecular contacts to 3.50 Å for I, the 40 most intense lines in the calculated X-ray powder pattern of I for Cu radiation, and complete X-ray powder patterns for β-KB_3O_5 and γ-KB_3O_5 and a stereoview of the unit cell of I (9 pages); a table of observed and calculated structure factors for I (4 pages). Ordering information is given on any current masthead page.

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Metal–Nitroxyl Interactions. 49. Molecular Structure and EPR Spectra of Dichloro(bis((1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II) and EPR Studies of Copper–Nitroxyl Exchange in Related Compounds

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The structure of the title compound, Cu(bp-NO)Cl_2, has been investigated by single-crystal X-ray diffraction. Discrete molecules of Cu(bp-NO)Cl_2 crystallize in the monoclinic space group $P2_1/c$ ($Z = 4$), with $a = 11.737$ (4) Å, $b = 11.744$ (4) Å, $c = 15.326$ (4) Å, and $\beta = 94.03$ (2)°. In Cu(bp-NO)Cl_2, the three nitrogen atoms of the bp-NO ligand and two chloride ions surround the copper(II) ion in a distorted square pyramidal array. One of the chloride ions occupies the more weakly bound apical position (Cu–Cl1 = 2.495 (1) Å), while the second occupies a basal position (Cu–Cl2 = 2.231 (1) Å). The Cu–N(amine) bond distance (2.195 (3) Å) is much longer than the Cu–N(pyrazole) bond distances (1.965 (3), 1.957 (4) Å). The magnitude of the copper–nitroxyl exchange coupling constant, J, in a series of copper(II) complexes of spin-labeled bis(pyrazolyl)amines ranged from >3500 to <100 G. It is proposed that the magnitude of J reflects the strength of the bond between the copper(II) and the amine nitrogen that is attached to the spin label.

Introduction

Recently, it has been shown that reaction of 1-(hydroxymethyl)-3,5-dimethylpyrazole with primary amines (RNH_2) produces the bis(pyrazolyl)amine bdmp-R.[2] The structures of four transition-metal complexes of these ligands have been determined. In Ni(bdmp-ae)$(NO_3)_2$, the metal was in a distorted octahedral environment and the distance between the Ni(II) atom

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