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Crystalline Inclusion Compounds of Urea with Oxoboron Components. Stabilization of the Elusive Dihydrogen Borate Anion in a Hydrogen-Bonded Host Lattice

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Introduction

The chemistry of borates rivals those of the silicates and phosphates in terms of variation and complexity. Boric acid, $B(OH)_3$ (also known as orthoboric acid and commonly rewritten as H_3BO_3), is the archetype and primary source of oxo-boron compounds. It generally behaves not as a Brønsted acid with the formation of the conjugate-base anion $BO(OH)_2^-$, but rather as a Lewis acid with the formation of the tetrahedral anion $B(OH)_4^-$.[1] In dilute aqueous solution this weakly monobasic acid exists almost exclusively as an equilibrated mixture of the undissociated molecule $B(OH)_3$ and the tetrahydroxyborate anion $B(OH)_4^-$. At concentrations above 0.1 M, secondary equilibria involving condensation reactions of the two dominant monomeric species give rise to oligomers such as the triborate monoanion $[B_3O_3(OH)_4]^-$, the triborate dianion $[B_3O_3(OH)_5]^{2-}$, the tetraborate $[B_4O_5(OH)_4]^{2-}$, and the pentaborate $[B_5O_6(OH)_4]^-$.[2]

The Brønsted-acid behavior of $B(OH)_3$ has been observed in the gas phase by mass spectrometric studies.[3] Complete deprotonation of $B(OH)_3$ and $B(OH)_4^-$ leads to BO_3^{3-} and BO_4^{5-}, respectively, which occur in a wide range of solid anhydrous metal borates.[4] The natural borate vimsite, which has the stoichiometric formula $Ca[BO(OH)_2]_2$, does not contain the discrete $BO(OH)_2^-$ ion, and the crystal structure features an infinite anionic chain $[BO(OH)_2]_n^{n-}$ with ether-like oxygen atoms bridging sp^3 boron centers.[5] The simple dihydrogen borate anion $BO(OH)_2^-$ has thus far been reported to exist in $Cu_2[BO(OH)_2](OH)_3$[6] and $(Et_4N)_2[BO(OH)_2]_2 \cdot B(OH)_3 \cdot 5H_2O$.[7] Crystal structure analysis of the first compound, based on powder X-ray diffraction data, did not permit a determination of the hydrogen-atom positions, but the second study demonstrated that in a crystalline solid both $B(OH)_3$ and its conjugate base $BO(OH)_2^-$ could coexist.

The classical channel-type inclusion compounds of urea have been extensively studied and reported in a large body of chemical literature.[8] Urea also forms hydrogen-bonded host lattices with different inclusion topologies together with a variety of anionic species as the building blocks. For example, in two series of isomorphous urea−tetraalkylammonium salt hydrate complexes, $(C_2H_5)_4N^+X^- \cdot (NH_2)_2CO \cdot 2H_2O$ ($X = Cl, Br, CN$)[9] and $(n\text{-}C_3H_7)_4N^+X^- \cdot 3(NH_2)_2CO \cdot H_2O$ ($X = F, Cl, Br, I$),[10,11] the anionic host lattices are constructed from the cross-linkage of planar zigzag ribbons of hydrogen-bonded urea molecules by the water molecules and halide/pseudohalide anions, the guest component being the hydrophobic organic cations.

To develop new urea/thiourea-anion host lattices, we have used simple oxo-anions such as NO_3^-,[12] HCO_3^-,[13] HCO_2^-,[14] $CH_3CO_2^-$,[15] and spirocyclic $[B_5O_6(OH)_4]^-$ [16] that can act as proton donors or acceptors in hydrogen bonding. In a recent study, the elusive allophanate ion $NH_2CONHCO_2^-$ was generated in situ and employed to construct novel urea-anion host lattices of different architecture for the accommodation of $(CH_3)_4N^+$ and $(n\text{-}C_3H_7)_4N^+$ ions.[17] Our next attempt was to generate the transient species $BO(OH)_2^-$ from $B(OH)_3$ and incorporate it into a host lattice through hydrogen-bonding interactions with its nearest neighbors. In the course of this research, we have carried out the preparation and structural characterization of the following urea inclusion compounds:

$$(CH_3)_4N^+BO(OH)_2^- \cdot 2(NH_2)_2CO \cdot H_2O \ (\mathbf{1})$$

$$[(C_2H_5)_4N^+]_2CO_3^{2-} \cdot (NH_2)_2CO \cdot 2B(OH)_3 \cdot H_2O \ (\mathbf{2})$$

Experimental Section

Preparations. Tetramethylammonium hydroxide pentahydrate (99%) and tetraethylammonium hydroxide (25 wt % aqueous solution) were obtained from Aldrich and Eastman Kodak, respectively, whereas crystalline boric acid was purchased from Beijing Chemical Works. For the preparation of complexes **1** and **2**, hydroxide, boric acid, and urea were mixed in molar ratios of 1:1:2 and 1:1:3, respectively, and a minimum quantity of deionized water was added to dissolve the solid in each case. After stirring for about half a hour, the solution was subjected to slow evaporation at room temperature in a desiccator charged with drierite. Colorless transparent crystals of **1** appeared in the form of thin plates, and **2** in the form of small blocks, which were subjected to structural characterization by X-ray crystallography.

X-ray Crystallography. Information concerning crystallographic data and structure refinement of the two compounds is summarized in Table 1. Intensities (monochromatized Mo Kα radiation, $\lambda = 0.710\ 73$ Å) were collected at 291 K with the variable ω scan technique[18] on a Siemens P4 diffractometer for **1**, and using the same crystal in two

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Table 1. Data Collection and Processing Parameters

	1	**2**
empirical formula	$(CH_3)_4N^+BO(OH)_2^-\cdot 2(NH_2)_2CO\cdot H_2O$	$[(C_2H_5)_4N^+]_2CO_3^{2-}\cdot (NH_2)_2CO\cdot 2B(OH)_3\cdot H_2O$
fw	273.1	522.3
space group	*Pnma* (No. 62)	$P2_1/n$ (No. 14)
unit cell parameters		
a, Å	16.671(2)	14.165(1)
b, Å	6.940(1)	13.753(1)
c, Å	13.180(2)	15.612(1)
β, deg	90	108.87(1)
V, Å^3	1524.9(3)	2877.9(3)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.190	1.205
μ, cm^{-1}	0.101	0.096
cryst size, mm	0.30 × 0.34 × 0.44	0.20 × 0.26 × 0.30
transm coeff	0.807−0.861	0.944−0.972
R^a	0.046	0.068
$R_w{}^b$	0.047	0.205
S (GOF)^c	1.54	1.20

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/|F_o|^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$.

different mountings on a Ragaku RAXIS-IIC imaging-plate system for **2**. Empirical absorption correction based on ψ scan data[19] was applied for **1**, and absorption correction for **2** was computed using the ABSCOR program.[20]

All calculations were performed on a PC 486 computer with the SHELXTL PC program package.[21] All non-hydrogen atoms were located by direct methods and refined using anisotropic thermal parameters. The H atoms of the amido, methylene, and methyl groups were generated geometrically (C−H distance fixed at 0.96 Å), and those of the oxo-boron moieties and water molecules were located from difference Fourier maps. All hydrogen atoms were assigned appropriate isotropic temperature factors and included in the structure factor calculations. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[22] The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method, and the final *R* indices and other parameters are listed in Table 1. Precision of the structure analysis of compound **2** is affected by the presence of the disordered water molecule.

Results and Discussion

The final positional and equivalent isotropic thermal parameters of **1** and **2**, anisotropic temperature factors, hydrogen coordinates, and structure factors have been deposited as Supporting Information.

Channel Structure of $(CH_3)_4N^+BO(OH)_2^-\cdot 2(NH_2)_2CO\cdot H_2O$ (1). In compound **1**, both independent urea molecules and the $BO(OH)_2^-$ ion in the asymmetric unit occupy special positions of symmetry *m* such that only the C−O or B−O bond lies on the mirror plane. A perspective view of the crystal structure of **1** along the [010] direction is presented in Figure 1. The host lattice consists of a parallel arrangement of unidirectional channels whose cross-section has the shape of a peanut. The diameter of each spheroidal half is about 7.04 Å, and the separation between two opposite walls at the waist of the channel is about 5.85 Å. The well-ordered tetramethylammonium cations are accommodated in double columns within each channel.

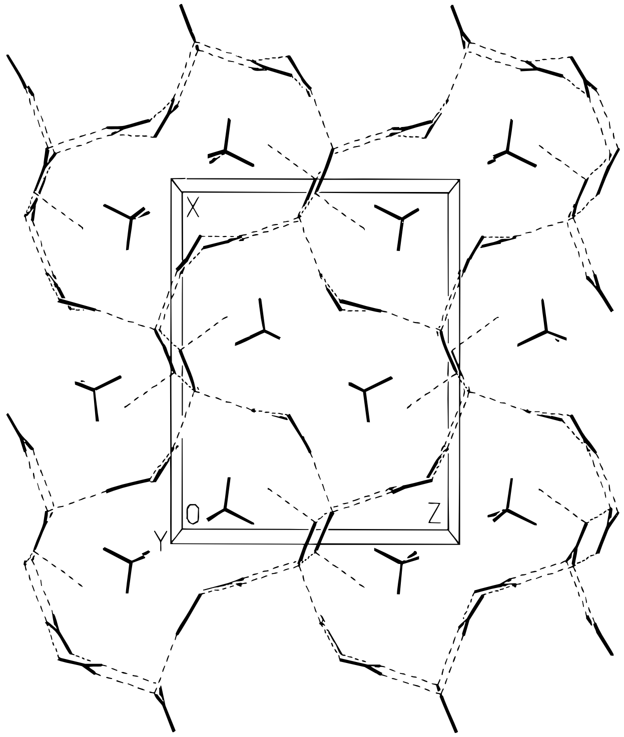

Figure 1. Crystal structure of $(CH_3)_4N^+BO(OH)_2^-\cdot 2(NH_2)_2CO\cdot H_2O$ (**1**) showing the channels extending parallel to the *b* axis and the enclosed cations. Broken lines represent hydrogen bonds, and the atoms are shown as points for clarity.

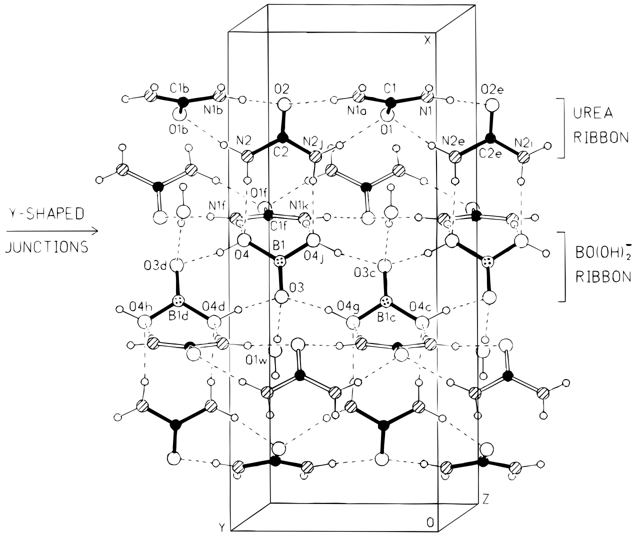

Figure 2. Hydrogen-bonding scheme in the urea−$BO(OH)_2^-$ host layer of complex **1**. Broken lines represent hydrogen bonds.

As shown in Figure 2, the two independent urea molecules are alternately connected by hydrogen bonds to form a zigzag ribbon running parallel to *b*, which has a highly twisted configuration as shown by the torsion angles C(1)−N(1a)$\cdots$O(2)−C(2) = 55.0 and C(2)−N(2)$\cdots$O(1b)−C(1b) = 48.3°. The $BO(OH)_2^-$ ions generated from successive inversion centers aligned parallel to the *c* direction are linked into a zigzag ribbon by O−H$\cdots$O hydrogen bonds, but the torsion angle between neighboring ions, B(1)−O(4)$\cdots$O(3d)−B(1d) = −9.1°, shows that this ribbon is almost planar. Each $BO(OH)_2^-$ anion is further connected to two urea molecules belonging to different

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Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in the Host Lattices[a]

$(CH_3)_4N^+BO(OH)_2^-\cdot 2(NH_2)_2CO\cdot H_2O$ (**1**)			
(i) Urea and Borate Ion			
O(1)−C(1)	1.247(5)	C(1)−N(1)	1.328(3)
O(2)−C(2)	1.248(5)	C(2)−N(2)	1.334(3)
B(1)−O(3)	1.323(5)	B(1)−O(4)	1.395(3)
O(1)−C(1)−N(1)	120.7(2)	N(1)−C(1)−N(1A)	118.5(4)
O(2)−C(2)−N(2)	121.7(2)	N(2)−C(2)−N(2A)	116.5(4)
O(3)−B(1)−O(4)	124.3(2)	O(4)−B(1)−O(4A)	111.3(3)
(ii) Hydrogen Bonding (Donor Atom Listed First)			
N(2a)···O(1)	2.849	N(1a)···O(2)	2.936
O(4d)···O(3)	2.619	O(1W)···O(3)	2.811
N(1f)···O(4)	2.904	N(2)···O(4)	2.926
N(2j)···O(1)−C(1)	115.7	N(2j)···O(1)···N(2e)	110.1
N(1a)···O(2)−C(2)	111.0	N(1a)···O(1)···N(1b)	104.9
O(4g)···O(3)−B(1)	116.1	O(4g)···O(3)···O(4h)	124.6
O(1W)···O(3)−B(1)	103.4	O(1W)···O(3)···O(4g)	92.7
N(1f)···O(4)···O(3d)	113.9	N(2)···O(4)···O(3d)	102.8
N(1f)···O(4)···N(2)	92.6		
C(1)−N(1a)···O(2)−C(2)	55.0	C(1)−N(2)···O(1b)−C(1b)	48.3
C(1f)−N(1f)···O(4)−B(1)	−25.0	C(2)−N(2)···O(4)−B(1)	18.4
B(1c)−O(4g)···O(3)−B(1)	−9.1		
$[(C_2H_5)_4N^+]_2CO_3^{2-}\cdot(NH_2)_2CO\cdot 2B(OH)_3\cdot H_2O$ (**2**)			
(i) Urea, Boric Acid, and Carbonate			
B(1)−O(2)	1.349(3)	B(1)−O(3)	1.359(3)
B(1)−O(1)	1.377(3)	B(2)−O(5)	1.347(3)
B(2)−O(4)	1.358(3)	B(2)−O(6)	1.379(3)
C(1)−O(7)	1.257(3)	C(1)−N(1)	1.339(3)
C(1)−N(2)	1.341(3)	C(2)−O(10)	1.281(3)
C(2)−O(8)	1.284(3)	C(2)−O(9)	1.283(3)
O(2)−B(1)−O(3)	123.4(2)	O(2)−B(1)−O(1)	120.2(2)
O(3)−B(1)−O(1)	116.4(2)	O(5)−B(2)−O(4)	123.1(2)
O(5)−B(2)−O(6)	120.6(2)	O(4)−B(2)−O(6)	116.3(2)
O(7)−C(1)−N(1)	122.5(2)	O(7)−C(1)−N(2)	121.1(2)
N(1)−C(1)−N(2)	116.4(2)	O(10)−C(2)−O(8)	119.2(2)
O(10)−C(2)−O(9)	120.7(2)	O(8)−C(2)−O(9)	120.1(2)
(ii) Hydrogen Bonding (Donor Atom Listed First)			
O(1Wb)···O(1)	2.830	N(1)···O(2)	2.917
O(1W)···O(4)	2.748	N(2d)···O(5)	2.922
O(1)···O(7)	2.819	O(6c)···O(7)	2.840
O(2)···O(8)	2.543	N(1a)···O(8)	2.828
O(3)···O(9)	2.665	O(4)···O(9)	2.651
O(5)···O(10)	2.558	N(2a)···O(10)	2.835
N(1)···O(2)−B(1)	116.8	N(1)···O(2)···O(8)	125.3
N(1a)···O(8)···O(2)	110.9	N(2a)···O(10)···O(5)	119.8
N(2d)···O(5)···O(10)	126.0	O(4)···O(9)···O(3)	122.5
O(1)···O(7)···O(6c)	118.9	O(1Wb)···O(1)···O(7)	108.9
O(1W)···O(4)···O(9)	131.2		
B(1)−O(1)···O(7)−C(1)	−9.8	B(2c)−O(6c)···O(7)−C(1)	14.9
C(1)−N(1)···O(2)−B(1)	−4.6	B(1)−O(2)···O(8)−C(2)	21.2
B(1)−O(3)···O(9)−C(2)	14.5	C(1a)−N(1a)···O(8)−C(2)	10.6
C(1a)−N(2a)···O(10)−C(2)	3.0	C(1)−N(2)···O(5c)−B(2c)	−25.9
B(2)−O(4)···O(9)−C(2)	−3.6		

[a] Symmetry transformations for **1**: a (*x*, 0.5 − *y*, *z*); b (*x*, 1 + *y*, *z*); c (1 − *x*, 1 − *y*, −*z*); d (1 − *x*, 2 − *y*, −*z*); e (*x*; −1+ *y*, *z*); f (1.5 − *x*, 1 − *y*, −0.5 + *z*); g (1 − *x*, −0.5 + *y*, −*z*); h (1 − *x*; 0.5 + *y*, −*z*); i (*x*, 0.5 − *y*, *z*); j (*x*, 1.5 − *y*, *z*); k (1.5 − *x*; 0.5 + *y*, −0.5 + *z*). Symmetry transformations for **2**: a (1 − *x*, 1 − *y*, 1 − *z*); b (1 − *x*, 1 − *y*, −*z*); c (−1 + *x*, *y*, *z*); d (1 + *x*, *y*, *z*). Standard deviations in hydrogen bond lengths and bond angles: 1, $\sigma(l) \approx 0.004$ Å, $\sigma(\theta) \approx 0.3°$; **2**, $\sigma(l) \approx 0.004$ Å, $\sigma(\theta) \approx 0.2°$.

neighboring urea ribbons (mutually related by a 2_1 axis) by four N−H···O hydrogen bonds that extend outward on the same side of the ribbon (Figure 2). The dihedral angles between the planar moieties involved in the cross-linkage are 106.7° for urea with urea and 126.7° for urea with $BO(OH)_2^-$, so that a cross-section of each junction is shaped like the capital letter Y. With these Y-shaped junctions oriented normal to (010) and concentrated at the layers $y = {}^1/_4$ and ${}^3/_4$, a unidirectional channel-like host lattice is formed (Figure 1). Notably, the water molecule makes no contribution to the construction of the host network, and its role is limited to that of a spectator guest that forms a donor O−H···O hydrogen bond to a $BO(OH)_2^-$ oxygen host atom.

Sandwich-Like Structure of $[(C_2H_5)_4N^+]_2CO_3^{2-}\cdot(NH_2)_2CO\cdot 2B(OH)_3\cdot H_2O$ (2). In the crystal structure of **2**, the tetraethylammonium cations are located in the space between anionic layers, which correspond to the (020) family of planes. The layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 3. The pairs of independent tetraethylammonium ions and boric acid molecules, as well as the urea molecule and carbonate ion, are each

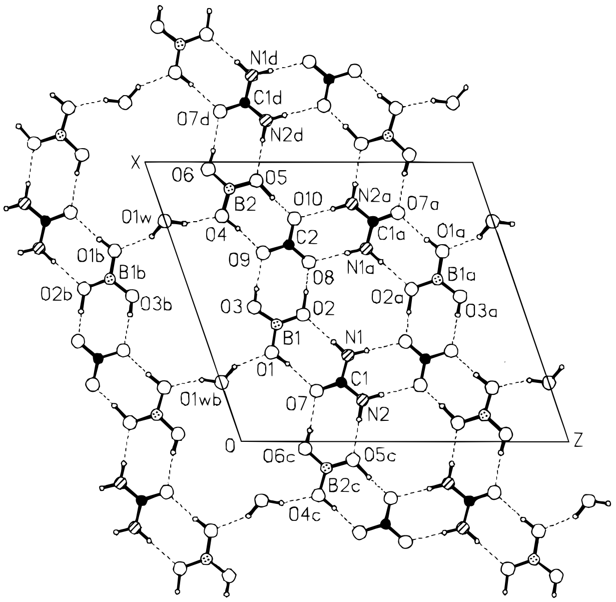
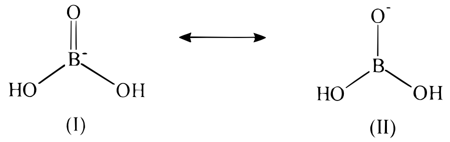


Figure 3. Hydrogen-bonded layer in **2** formed by urea−boric acid−carbonate double ribbons cross-linked by water molecules. Broken lines represent hydrogen bonds.

related by pseudo-translation x_1 which is very nearly equal to $x_2 + {}^1/_2$. The urea molecule (u), the two independent boric acid molecules (ba_1, ba_2), and the carbonate ion (c) are alternately arranged, in the order of ...(u...ba_1...c...ba_2)..., and connected by hydrogen bonds to form a nearly planar zigzag ribbon running parallel to the *a* axis; the slight deviation of its structural units from coplanarity is shown by the torsion angles C(1)−N(1)···O(2)−B(1) = −4.6, B(1)−O(1)···O(7)−C(1) = −9.8, B(1)−O(2)···O(8)−C(2) = 21.2 and B(1)−O(3)···O(9)−C(2) = 14.5°. A pair of ribbons, related by the inversion center, are linked by lateral N−H···O hydrogen bonds between urea molecules and carbonate ions to form a puckered double ribbon extending in the [001] direction. The water molecules are located between parallel double ribbons and link them by hydrogen bonds of the type O(1W)−H···O(4) and O(1W)−H···O(1b) to generate a layer orientated normal to the *b* axis (Figure 3).

The two independent tetraethylammonium cations are arranged alternately to form a straight column running parallel to the [001] direction. Furthermore, these columns are arranged side by side to generate a two-dimensional cationic array. Such planar arrays are located at $y = {}^1/_4$ and ${}^3/_4$ in the unit cell, each being sandwiched between two hydrogen-bonded urea−boric acid−carbonate−water layers.

The Dihydrogen Borate Anion. Different types of oxoboron species exist in the present inclusion compounds, which were prepared by the same procedure using different tetraalkylammonium ions as quest templates. The elusive species $BO(OH)_2^-$ was generated from $B(OH)_3$ and stabilized in **1**, but $B(OH)_3$ remained intact in **2**, and the anionic species CO_3^{2-} was derived from absorption of CO_2 in air.



(I) (II)

B-O	1.323(5)Å	O-B-OH	124.3(2)°
B-OH	1.395(3)Å	HO-B-OH	111.3(3)°

Figure 4. Valence-bond structural formulas for the dihydrogen borate ion, $BO(OH)_2^-$, and its measured dimensions in inclusion compound **1**.

In complex **1**, the measured dimensions of the $BO(OH)_2^-$ anion, which has crystallographically imposed symmetry *m*, show that structural formula **I** with a formal B−O double bond (Figure 4) makes a significant contribution to its electronic structure. The measured bond distances B−O = 1.323(5) Å and B−OH = 1.395(3) Å are in good agreement with those in $(Et_4N)_2[BO(OH)_2]_2 \cdot B(OH)_3 \cdot 5H_2O$: B−O between 1.316 and 1.326 Å and B−OH between 1.346 and 1.396 Å.[7] These values may be compared with the B−O single bond distance of 1.367 Å (average value) in crystalline orthoboric acid,[23,24] 1.360 Å in $(n\mathrm{Pr})_4N[B_5O_6(OH)_4] \cdot 2B(OH)_3$ and $(n\mathrm{Bu})_4N[B_5O_6(OH)_4] \cdot 2B(OH)_3$,[25] and 1.355 Å in the bis(triphenylphosphoranediyl)−ammonium chloride−boric acid adduct.[26] In this context it is noted that B−O distances in the range 1.28−1.43 Å (average 1.365 Å) are found for the trigonal planar BO_3 moiety in metal borates.[27] An abnormally short B−O distance of 1.2062(2) Å was reported for the boroxane Cl−B═O in the gas phase,[28] but comparison of the latter value with the interatomic distance of 1.2045 Å in diatomic BO[29] indicates that the molecular structure of the boroxane is more faithfully represented by $Cl-B\overset{\leftarrow}{\equiv}O$.

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Supporting Information Available: Structure determination summaries (Tables S1 and S5), bond lengths and bond angles (Tables S2 and S6), anisotropic displacement coefficients (Tables S3 and S7), and H atom coordinates and isotropic displacement coefficients (Tables S4 and S8) for complexes **1** and **2**, respectively (9 pages). Ordering information is given on any current masthead page.

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