Ammine Borates

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High-Pressure Synthesis of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$: Pioneering the Way to the Substance Class of Ammine Borates**

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Dedicated to Professor Rüdiger Kniep on the occasion of his 70th birthday

Abstract: *To date, the access to the substance class of borates containing nitrogen, for example, nitridoborates, oxonitridoborates, or amine borates, was an extreme effort owing to the difficult starting materials and reaction conditions. Although a number of compounds containing boron and nitrogen are known, no adduct of ammonia to an inorganic borate has been observed so far. A new synthetic approach starting from the simple educts CdO, B_2O_3, and aqueous ammonia under conditions of 4.7 GPa and 800°C led to the synthesis of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ as the first ammine borate. We thoroughly characterized this compound on the basis of low-temperature single-crystal and powder X-ray diffraction data, IR and Raman spectroscopy, and by quantum theoretical calculations. This contribution shows that the adduct of NH_3 to the BO_3 group of a complex B–O network can be stabilized, opening up a fundamentally new synthetic route to nitrogen-containing borates.*

High pressure is a valuable tool in solid-state chemistry giving access to new polymorphs or new compositions not attainable under ambient pressure conditions. The structures of the technically important borates are dominated by triangular BO_3^{3-} and tetrahedral BO_4^{5-} groups in form of isolated or linked (corner-sharing) groups. The application of high-pressure using a multi-anvil set-up enabled us to synthesize new compositions, such as $Dy_4B_6O_{15}$ or HP-NiB_2O_4, in which the BO_4 tetrahedra were unusually linked by common edges.[1] The center of these groups is occupied by the element boron which generally has a deficiency of electrons. With its three valence electrons, a boron atom is able to form three bonds, leading to an electron sextet. To provide the desired octet, three major possibilities exist. First, p_π–p_π bonds can be formed using the lone pair of one of the ligands, for example from a fluorine atom in BF_3. The resulting bond is shorter than a single bond but still longer than a double bond. If the ligand does not have any lone pair, as in the case of BH_3, the second possibility is the formation of dimers taking advantage of two-electron three-center bonds, for example, in B_2H_6. The third possibility is the formation of adducts using electron pairs of other molecules, such as ammonia. In this case, the boron compound acts as a Lewis acid, while the donor of the electron pair is the corresponding Lewis base.[2] Textbook examples for these Lewis acid/Lewis base reactions are the adducts of BF_3 and NH_3 or BH_3 and NH_3,[3] leading to tetrahedrally coordinated boron centers with bond lengths corresponding to typical B−F or B−H single bonds, respectively. The adducts of many amines to borates are found in literature, as well as the adducts of ammonia to different boron compounds, for example, triptychboroxazolidine or tris(trifluoromethyl)borane-ammine tetrahydrate.[4] However, the compounds either show an intramolecular B−N bond within an organic amine containing a BO_3 group or between ammonia and a boron compound with a high Lewis acidity, such as BF_3.[4d] The Lewis acidity of a $B(OR)_3$ group is small compared to BF_3 or BH_3, so the question came up: is it possible to stabilize the adduct of ammonia to a BO_3 group, which is part of an inorganic boron–oxygen network?

A high-pressure/high-temperature experiment in a Walker-type multi-anvil apparatus starting from CdO, B_2O_3, and a 28% ammonia solution placed us in the lucky position to answer this question. At conditions of 4.7 GPa and 800°C, $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ was obtained in form of a colorless, air-stable solid together with HP-$(NH_4)B_3O_5$[5] (HP = high pressure) which is found as a side phase in the powder diffraction pattern (further details can be found in the Supporting Information).

The crystal structure of diammine cadmium(II) bis(ammine triborate) $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ was solved from low-temperature single-crystal X-ray diffraction data in the orthorhombic non-centrosymmetric space group *Fdd*2 (no. 43) using direct methods.[6] The structure was verified by the Rietveld method using the parameters derived from the single-crystal structure model as a starting point.

Figure 1 shows the structure of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$, which is built up from triborate rings ("dreier"[7] rings) each consisting of a BO_3 group, a BO_4 tetrahedron, and a

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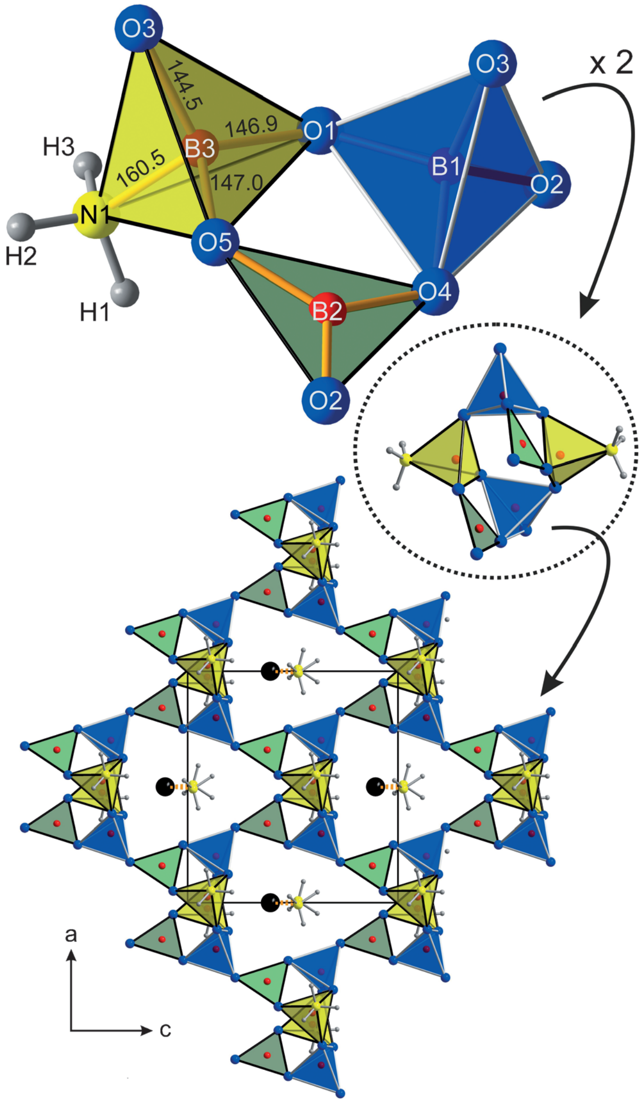

Figure 1. "Dreier" ring (top) forming the fundamental building block of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ (dotted circle in the middle). Sheets in the *ac* plane (bottom) are built up from these fundamental building blocks.

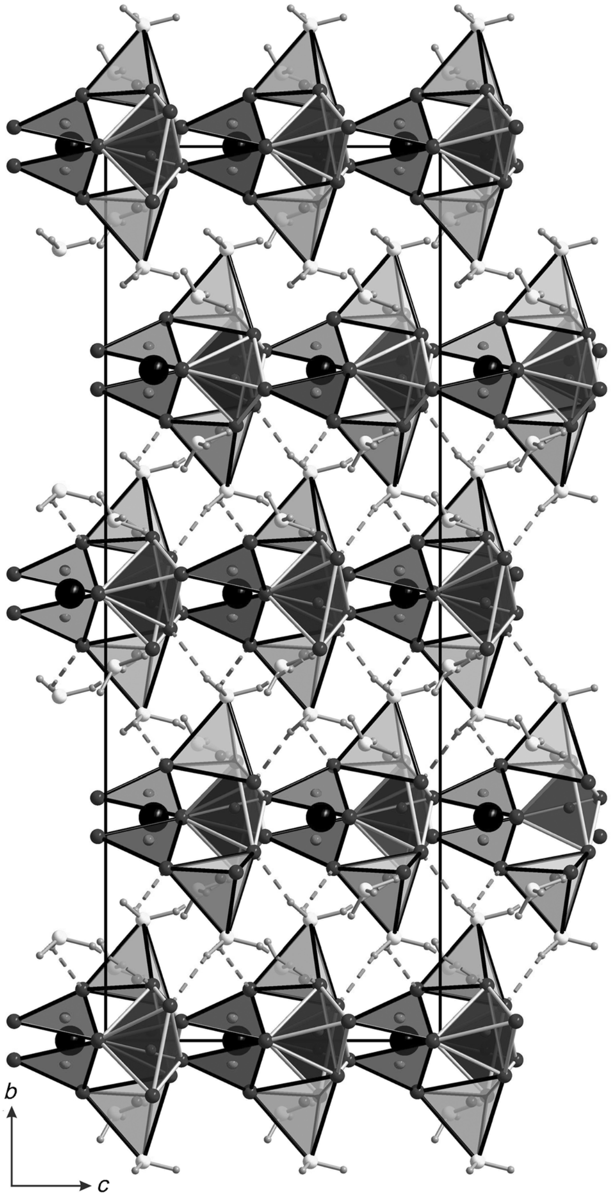

Figure 2. Projection of the unit cell down the *a* axis showing the stacking of the layers in $Cd(NH_3)_2[B_3O_5(NH_3)]_2$.

$BO_3(NH_3)$ tetrahedron (Figure 1, top). The $BO_3(NH_3)$ tetrahedron results from the formation of an adduct of ammonia to a BO_3 group of the B–O network positively answering the above question. To our knowledge, this is the first time that an adduct of a simple ammonia molecule to a common borate group has been observed. Independently, a second ammonia group is coordinated to the Cd^{2+} ion in $Cd(NH_3)_2[B_3O_5(NH_3)]_2$.

The "dreier" rings are connected to each other by the O3 atoms under formation of "vierer" rings to form the fundamental building block (FBB). According to Burns et al., this FBB can be specified with the descriptor $2\triangle4\square:<\triangle2\square>=<4\square>=<\triangle2\square>$ (see Figure 1, dotted circle).[8] These FBBs are linked to each other by the O2 atoms forming layers in the *ac* plane (see Figure 1). In these layers, the Cd^{2+} ions are stacked between the "vierer" rings of the FBB along the *c* axis. Along the *b* axis, the layers are interconnected by hydrogen bonds as displayed in Figure 2. The non-centrosymmetric character of the structure is clear from the orientation of the BO_3 groups which all point in one direction.

The BO_3 group has B–O bond lengths from 136.3(2) to 137.6(2) pm (av. 137.1 pm) and O-B-O bond angles from 118.0(2) to 121.7(2)° (av. 120.0°), while the BO_4 tetrahedron has B–O bond lengths between 146.4(3) and 148.7(3) pm (av. 147.7 pm) and bond angles between 106.5(2) and 112.0(2)° (av. 109.5°). All values fit to the values found in literature (BO_3 groups: 135.1–140.3 pm, av. 137.0 pm and 109–129°, av. 120.0°; BO_4 tetrahedra: 137.3–169.9 pm, av. 147.6(3.5) pm and 95.7–119.4°, av. 109.4(2.8)°).[9] The $BO_3(NH_3)$ tetrahedra show the typical geometry of B–N adducts.[4a] The three N-B–O bond angles are smaller (103.4(2)–107.5(2)°) than the ideal tetrahedral angle (109.47°), while the three O–B–O bond angles are larger (112.7(2)–114.8(2)°). The mean bond angle in the tetrahedron is 109.3°. The B–O bond lengths of 144.5(2)–147.0(2) pm are within the range of B–O bonds found in literature.[9b] A correlation between the covalence of the B–N bond, its bond length, and the N–B–Y bond angles has been confirmed.[4a] A short B–N bond as well as bond angle values near the ideal tetrahedral angle are caused by a high covalence of the B–N bond. In $Cd(NH_3)_2[B_3O_5(NH_3)]_2$, the B–N bond length of 160.5(3) pm, as well as the tetrahedral character[4a] THC_{DA} of 98.67 % (calculated from the N–B–O bond angles in the corresponding tetrahedron, see Supporting Information) indicate a strongly covalent character of the dative bond.

In the $BO_3(NH_3)$ tetrahedron, the hydrogen atoms of the ammonia group are in a staggered conformation relative to the oxygen atoms. The N–H distances are comparable to the values found in liquid solutions of NH_3, taking into account that bond lengths to hydrogen atoms are generally too short when determined by X-ray diffraction analysis. Each of the hydrogen atoms creates a hydrogen bond with an oxygen atom of the next sheet.

The second ammonia group coordinating to the Cd^{2+} ion also has N–H bond lengths in the expected range (further details on N–H and hydrogen bonds are listed in the Supporting Information). Two of these groups coordinate to the Cd^{2+} ions together with four oxygen atoms of the borate layer in a distorted trigonal prismatic fashion (see Figure 3). The coordination number six is very common in the system Cd-B-O(-H),[10] however, it is usually realized as an octahedron. The distances Cd–X (X = N, O) in the coordination sphere of the Cd^{2+} ions (Cd–N: 226.1(4) pm; Cd–O: 233.0(2) and 254.7(2) pm) are comparable to the distances found in other structures. (Cd–N: 205(2)–252(2) pm;[11] Cd–O: 214.3(2)[10e]–285.0(2) pm[12]).

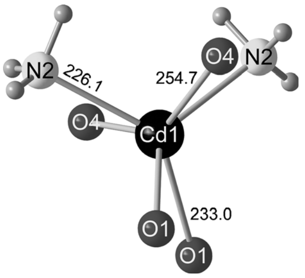

Figure 3. Distorted, trigonal prismatic coordination of the Cd^{2+} ions.

The title compound was further characterized using vibrational spectroscopy and quantum chemical density functional theory (DFT) calculations. Figure 4 shows the IR and the Raman spectra of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ with the corresponding calculated frequencies. The observed positions of the experimentally determined bands are presented in the Supporting Information together with the calculated frequencies and band assignments. According to the calculations, the stretching modes of the BO_4 groups are present at frequencies between 900–1140 cm^{-1}. The stretching modes of the tetrahedrally coordinate boron atoms forming a covalent bond with the ammonia group are in a narrow sub-region of the BO_4 frequencies between 930–1020 cm^{-1}. The planar BO_3 groups show stretching frequencies from 1300 to 1420 cm^{-1}. The stretching of the N–H bonds of ammonia occur at regions between 3000 and 3500 cm^{-1} while the bending of the ammonia is present at 1580–1650 and 1000–1050 cm^{-1} being similar to liquid ammonia. In contrast to liquid ammonia where the bands are degenerate, the symmetry of ammonia in the crystal is distorted which leads to numerous N–H bands. For example, a sharp peak occurs at 3400 cm^{-1} originating from an N–H stretching mode of the ammonia coordinated to the Cd^{2+} ion, while one of the N–H stretching modes of the ammonia group bound to the borate group leads to a band close to 3000 cm^{-1}. Bands for the other four N–H stretching modes cannot be assigned unambiguously as they all occur between 3100 and 3200 cm^{-1}. The bending of the B-N-H groups occurs at frequencies of 800–900 cm^{-1}, in the regions between 1100–1120 cm^{-1}, and between 1470–1490 cm^{-1}. The H-N-Cd bending mode can be found between 600–800 and 1130–1230 cm^{-1}. The bands around 1730 cm^{-1} and the remaining vibrations around 2900 cm^{-1} most likely originate from traces of acetone, in which the crystal was washed.[13]

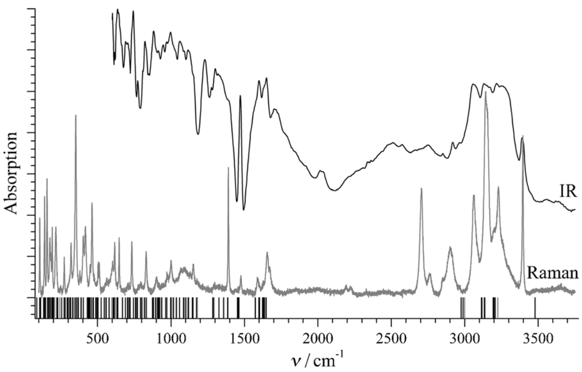

Figure 4. The single-crystal IR and Raman spectra of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ and the theoretical calculated vibrational frequencies at the Γ point.

The synthesis of $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ with its new structural motif of a $BO_3(NH_3)$ tetrahedron is outstanding in several ways. To date, the introduction of nitrogen into boron oxygen groups or networks as, for example, in the first oxonitridoborate $Sr_3[B_3N_3O_3]$[14] or in the oxonitridoborate oxide $La_3(OBN_2)O_2$[15] required complex and expensive starting materials such as amines, imides, or azides. Besides the limitations set by the educts, for example, the explosiveness of some azides, further complications are added by the necessary reaction parameters, such as strict exclusion of water or operating at temperatures low enough to enable the use of liquid nitrogen. In contrast, the new synthetic strategy reported herein utilizes simple and cheap starting materials, such as ammonia solution and oxides, which can be handled under ambient air. So based on simple educts and high-pressure/high-temperature conditions, we could demonstrate that it is possible to establish an access to the new class of ammine borates by stabilizing the adduct of NH_3 to a BO_3 group inside of an inorganic borate network for the first time.

In principle, the formation of the adduct between the ammonia molecule and the BO_3 group leads to an increase of the coordination number of the boron atom from three to four ($BO_3(NH_3)$ tetrahedron). This fully corresponds to the pressure coordination rule saying that high coordination numbers are likely to occur in compounds synthesized under high-pressure.[16] According to the bond lengths and angles determined, the character of the N−B bond is highly covalent. Therewith we conclude that two factors positively influence the formation of the adduct between ammonia and the boron-oxygen network in $Cd(NH_3)_2[B_3O_5(NH_3)]_2$: 1) provision of the desired octet at the boron atom and 2) the trend to increase the coordination number under high-pressure conditions. Generally, this finding indicates a new access to nitrogen-containing borates, which has to be verified in the future.

As a last point it is noteworthy that $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ was synthesized at a temperature of 800 °C (at 4.7 GPa). Under ambient pressure conditions, adducts of ammonia are not stable at such high temperatures. This impressively shows the innovative potential of high-pressure/high-temperature syntheses using the multi-anvil technique to obtain macroscopic amounts of new materials, which are not accessible under ambient pressure conditions.

Keywords: ammonia · borate · cadmium · high-pressure chemistry · solid-state structures

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[6] Crystal data for $Cd(NH_3)_2[B_3O_5(NH_3)]_2$: crystal size: $0.02 \times 0.03 \times 0.03\ mm^3$, space group *Fdd*2 (no. 43), $a = 972.33(3)$, $b = 2357.95(6)$, $c = 883.19(2)$ pm, $V = 2.02489(9)\ nm^3$, $Z = 8$, ρ_{calcd}: $2.660\ g\,cm^{-3}$, Bruker D8 Quest Kappa, Mo-K_α-radiation (71.073 pm), multi-scan absorption correction, 14408 reflections, 2717 independent reflections, $R_{int} = 0.0369$, least-squares refinement on F^2, *R*-values (all data/$I \geq 2\sigma(I)$): $R1 = 0.0205/0.0172$, $wR2 = 0.0380/0.0369$, GooF = 1.122 for 2549 reflections ($I \geq 2\sigma(I)$) and 120 parameters, Flack-parameter: −0.00(2). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247–808–666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html), on quoting the depository number CSD-429059.

[7] a) The term "dreier" ring was initially coined by F. Liebau in his book *Structural Chemistry of Silicates* (Springer-Verlag, Berlin (Germany), **1985**). It is derived from the German word "drei", which means three. However, a "dreier" ring is not a three-membered ring, but a six-membered ring comprising three tetrahedral centers (B). Similar terms exist for rings made up of two, four, five, and six tetrahedral centers, namely "zweier", "vierer ", "fünfer ", and "sechser " rings, respectively; b) F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin, **1985**.

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