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Chains of Alkaline Metal Cations and Tetracyanidoborato Anions – Syntheses, Structures and Properties of the New $[A^{I}(18\text{-crown-6})][B(CN)_4]$ (A^{I} = Cs, Rb)

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Dedicated to Prof. Dr. R. Nesper on the occasion of his 60th birthday

Keywords: Alkali metals / Borates / Structure elucidation / Crown compounds

[Cs(18-crown-6)][$B(CN)_4$] and [Rb(18-crown-6)][$B(CN)_4$] can be obtained as colourless transparent crystals by slow evaporation of the solvent of aqueous solutions of these compounds. Both substances crystallise in the monoclinic crystal system; [Cs(18-crown-6)][$B(CN)_4$]: $C2/c$, a = 13.819(1), b = 15.841(1), c = 10.1717(7) Å, β = 92.117(4)°, V = 2225.0(3) Å^3, Z = 4; [Rb(18-crown-6)][$B(CN)_4$]: $P2_1/n$, a = 14.237(2), b = 9.455(1), c = 15.942(2) Å, β = 94.319(4)°, V = 2139.9(5) Å^3, Z = 4. These compounds are characterised by unprecedented linear coordination chains. Double rows of alkaline metal cations, encapsulated in 18-crown-6 ether molecules, which are oriented approximately face-to-face, are interconnected by tetracyanidoborato anions. Nevertheless, the connectivity differs significantly between the two compounds. In the Cs compound the $[B(CN)_4]^-$ anions are tetrafunctional with two CN groups coordinating in a chelate-type mode to one Cs cation, whereas the other two CN groups bridge two neighbouring Cs cations of the opposite row of $[Cs(18\text{-crown-6})]^+$ units. In the Rb compound only two of the four CN groups are bonded to the cations, the other two are uncoordinated. The bonded CN groups bridge between two Rb cations of opposite rows. These two compounds show that the $[B(CN)_4]^-$ anion has a tremendous variability of coordination modes. Not only can 3D network structures be formed by using $[B(CN)_4]^-$ anionic units but also low-dimensional structures, as shown by these two new compounds.
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Introduction

Whereas reports about the existence and preparation of tetracyanidoborates, salts with the tetrahedral $[B(CN)_4]^-$ ion, date back to 1951, it was not before the year 2000 that they were shown to be actually tetraisocyanidoborates.[1–5,11] In the same year the [nBu$_4$N], Ag, and K salts were synthesised, structurally characterised and clearly identified as tetracyanidoborates.[5,11] Since the development of an efficient synthetic procedure in 2003, this class of materials has been subject to intensive research.[6] Salts of the type $A^{I}[B(CN)_4]$ and $A^{II}[B(CN)_4]_2$ with singly charged cations A^{I} or doubly charged cations A^{II} exist in a large variety of mostly 3D-linked networks.[7–11] Furthermore, compounds are known, which contain solvent molecules within the coordination sphere of the cations, e.g. $Na[B(CN)_4]\cdot THF$, $NH_4[B(CN)_4]\cdot THF$[7] or $K[B(CN)_4]\cdot CH_3CN$.[12] Another group of tetracyanidoborato salts containing large organic counter cations can eventually be used as ionic liquids with high chemical stability and with large electrochemical windows.[5,13,14] Besides possible applications as ionic liquids, tetracyanidoborates offer other uses, e.g. as precursors for novel compounds and advanced materials[8,11,13–19] or as electrolytes.[20] In this paper we report about the syntheses, structures and some properties of two new tetracyanidoborates, [Cs(18-crown-6)][$B(CN)_4$] (**1**) and [Rb(18-crown-6)][$B(CN)_4$] (**2**), which contain both alkaline metal cations, coordinated by a macrocyclic polyether.

Results and Discussion

With all the possible technical applications in mind, which are offered by the weakly coordinating tetracyanidoborato anion, research activities have been launched aiming for new tetracyanidoborates with high solubilities in apolar organic solvents. Such tetracyanidoborates could be useful, for example, in catalytic organic reactions. A simple and well-known way to reach the goal of high solubility is to encapsulate the cation of the ionic salt within a large organic ligand. Quite often large cyclic polyethers (crown ethers) are used for this purpose.[21,22]

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Synthesis

The two new tetracyanidoborates containing alkaline metal cations (Cs and Rb) encapsulated by 18-crown-6 polyether molecules can be obtained through a two-step procedure. Starting from $K[B(CN)_4]$, which is available through a solid-state chemical procedure in molar amounts,[6] the potassium cation can be easily exchanged by Cs or Rb (or other) cations by using an ion exchanger or by means of an acid-base reaction with tetracyanidoboronic acid[23] and a corresponding alkaline metal carbonate or hydroxide. An aqueous solution of the crown ether is added to the solution of the tetracyanidoborates. Immediately the solid title compounds start to precipitate from theses solutions.

Solid-State Structures

Single crystals of both title substances were grown by slow evaporation of the solvent from clear solutions obtained after filtering the precipitated solid materials. For both compounds, single-crystal X-ray structures were determined. Both salts crystallise in the monoclinic system, **1** in the space group $C2/c$ and **2** in $P2_1/n$. The complex anion $[B(CN)_4]^-$, which consists of a boron atom, tetrahedrally surrounded by cyanido groups, shows only small deviations from the ideal tetrahedral angle around the B atom. The C–B–C angles in **1** are within the range from 109.01(7) to 110.4(1)°, and in **2** they are between 107.7(2) and 113.1(2)°. The Rb and Cs counter cations of the title phases are encapsulated in 18-crown-6 cyclic ether molecules. This gives rise to very interesting low-dimensional chains of interconnected ions as described below. The molecular structure of each compound is shown as a thermal ellipsoid plot with 50% probability in Figures 1 and 2.

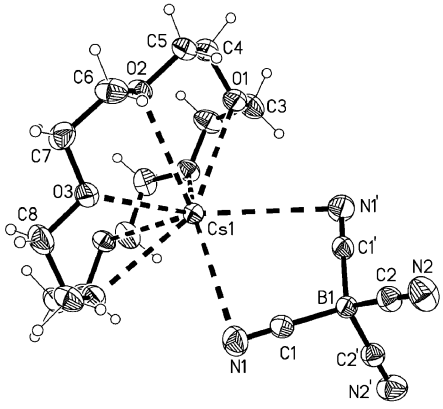

Figure 1. Molecular structure and atom-numbering scheme of [Cs(18-crown-6)][B(CN)$_4$] (**1**) (ionic contacts to the Cs cation are drawn dashed; atomic displacement ellipsoids at the 50% probability level; symmetry operations used to generate primed atoms: $-x$, y, $1/2 - z$).

Both, the $[B(CN)_4]^-$ and the $[Cs(18\text{-crown-6})]^+$ ion in **1** have twofold rotational symmetry, with Cs1 and B1 being located on the twofold axis. In contrast, all the atoms of **2** are located in general positions. Selected bond lengths and angles of both compounds are compiled in Table 1.

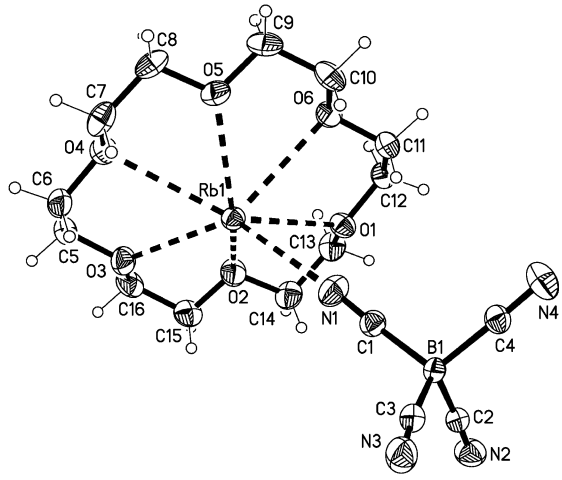

Figure 2. Structure and atom-numbering scheme of [Rb(18-crown-6)][B(CN)$_4$] (**2**) (ionic contacts to the Cs cation are drawn dashed; atomic displacement ellipsoids at the 50% probability level).

Table 1. Selected bond lengths [Å] in **1** and **2**.[a]

[Cs(18-crown-6)][B(CN)$_4$] (**1**)		[Rb(18-crown-6)][B(CN)$_4$] (**2**)	
Cs–O (min)	3.078(1)	Rb–O (min)	2.899(2)
Cs–O(max)	3.2219(9)	Rb–O(max)	3.075(2)
avg.	3.150	avg.	2.988
Cs1–N1	3.565(1) (×2)	Rb1–N1	3.188(3) (×1)
Cs1–N2$^{\#1}$	3.350(1) (×2)	Rb1–N3$^{\#2}$	3.103(3) (×1)
C1–N1	1.137(2) (×2)	C1–N1	1.139(4) (×1)
C2–N2	1.140(2) (×2)	C2–N2	1.138(4) (×1)
avg.	1.139	C3–N3	1.134(4) (×1)
		C4–N4	1.140(4) (×1)
		avg.	1.138
B1–C1	1.604(2) (×2)	B1–C1	1.602(4) (×1)
B1–C2	1.588(2) (×2)	B1–C2	1.591(4) (×1)
avg.	1.596	B1–C3	1.605(4) (×1)
		B1–C4	1.589(4) (×1)
		avg.	1.597
avg. C–C	1.497	avg. C–C	1.495
avg. C–O	1.423	avg. C–O	1.425

[a] Symmetry operations used to generate equivalent atoms: $^{\#1}$: $-x$, $-y$, $1/2 - z$; $^{\#2}$: $-3/2 - x$, $y - 1/2$, $-z + 1/2$.

The range of B–C distances in both structures varies from 1.588(2) Å in **1** to 1.605(4) Å in **2**. This range compares well with that found in other tetracyanidoborates such as $Rb[B(CN)_4]$ [1.590(1) Å] or $Cs[B(CN)_4]$ [1.582(5) Å].[7]

As shown in Table 1 two groups of B–C distances exist in each structure, two short and two long ones; **1**: 1.588 and 1.604 Å, **2**: 1.590 and 1.604 Å (both lengths for **2** are given as the average of two values). In the crown-ether-free parent

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compounds, $Rb[B(CN)_4]$ and $Cs[B(CN)_4]$, which both crystallise isotypically, the tetracyanidoborato anion is located on a site with $\bar{4}$symmetry. Thereby the four B–C single bonds are equivalent and of the same length. The reason for two different groups of B–C bond lengths in the title compounds is the different coordination behaviour of the nitrogen atoms of the attached CN groups. In **1**, two of the four CN groups of each $[B(CN)_4]^-$ anion coordinate through the N atom to one Cs cation in a chelate-type manner with a Cs1–N1–C1 angle of 84.64(9)°. The other two CN groups are bonded to two other Cs cations in a terminal fashion with an almost linear Cs–N2–C2 angle [173.5(1)°]. This different coordination behaviour evidently reflects the two different groups of B–C distances. A similar trend is visible for the B–C distances in **2**. The N atoms of two CN groups (N1 and N3) are coordinated to two different Rb cations with Rb–N–C angles of 172.9(2) and 146.6(2)°. The corresponding B–C bond lengths average 1.604 Å. This value is significantly longer than that of the other two CN groups (1.590 Å), which do not coordinate to any cation. The situation whereby the B–C bond lengths vary according to the strength of the coordinative bonding of each of the CN groups is much less pronounced for the C–N distances. They are found in a small range from 1.134(4) Å (**2**) to 1.140(2) Å (**1**). Within the 18-crown-6 moieties, the average C–C distances of 1.497 Å (**1**) and 1.495 Å (**2**), as well as the average C–O distances of 1.423 Å (**1**) and 1.425 Å (**2**) are similar to the values found in the free 18-crown-6 molecule (average C–C distance: 1.510 Å, average C–O distance: 1.420 Å).[24] As is typical for the crown ether molecule in many metal ion complexes, the C–O bonds are arranged in an all-gauche conformation.[21,24] In both compounds the alkaline metal cation is located outside of the mean plane of the six oxygen atoms of each ring by 1.503 Å in **1** and with the smaller Rb cation in **2** by 1.001 Å. This is also found in almost all other (crown ether) Cs or -Rb complexes if the cyclic ring carries 6 or less donor atoms.[21,24,25] The fact that the Cs or Rb cation is located outside of the ring of the six oxygen atoms is usually discussed in terms of ionic volumes of the cation and ring diameter.[21] The ability of the $[B(CN)_4]^-$ ion to coordinate in various multi-functional ways and the fact that one hemisphere of the coordination environment of the Cs and the Rb cation is blocked by a crown ether molecule are the underlying prerequisites for the formation of low-dimensional chain structures.

Both title compounds contain linear strands of 18-crown-6 molecules encapsulating Cs or Rb cations, which are interconnected by multifunctional $[B(CN)_4]^-$ units. Figures 3 and 4 show excerpts of a strand of **1** and **2**.

In both structures, the neutral coordination-chain polymers consist of two rows of cationic $[A^I(18\text{-crown-}6)]$ units (A^I = Cs or Rb) running in the same direction but shifted in the chain direction with respect to each other. The $[A^I(18\text{-crown-}6)]$ units are oriented such that the alkaline metal cations are located inside the double-chain row. Both rows of each structure are interconnected by the $[B(CN)_4]^-$ anions.

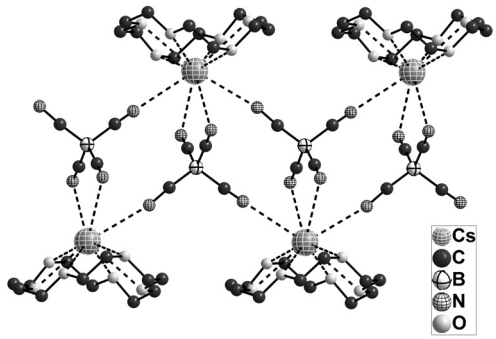

Figure 3. View of a part of the chain structure of [Cs(18-crown-6)][$B(CN)_4$] (Cs–N and Cs–O coordinative bonds are drawn as dashed lines).

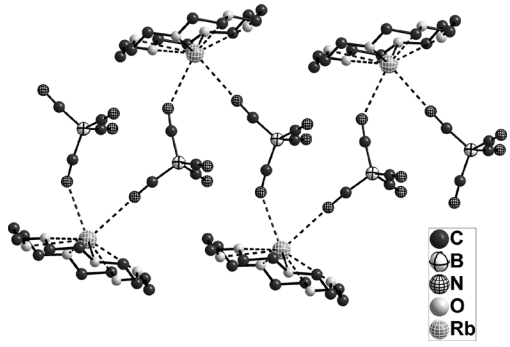

Figure 4. View of a part of the chain structure of [Rb(18-crown-6)][$B(CN)_4$] (Rb–N and Rb–O coordinative bonds are drawn as dashed lines).

Comparing the two chain structures, it is clear that they differ significantly in the way the tetracyanidoborato anions connect the encapsulated ("crowned") alkaline metal cations. In **1**, which carries the larger alkaline metal cation (Cs compared to Rb), a higher coordination number of the metal cation is achieved through a chelate-type coordination of two of the CN groups of each complex anion. Thereby a chelate ring composed of six atoms exist with an N–Cs–N angle of 78.65(4)° (see Figure 3 and also Figure 1). The other two CN groups of each tetracyanidoborato anion bridge two neighbouring Cs cations of the opposite cationic row with almost linear B–C–N–Cs units (see above). Thereby each Cs cation is coordinated by two terminal CN groups, two chelate-type bridging CN groups and the six O atoms of the 18-crown-6 ring. In the Rb compound **2**, the coordination behaviour of the tetracyanidoborato anion between the two rows of lined-up "crowned" cations is completely different. Two CN groups of each $[B(CN)_4]^-$ ion are noncoordinating, whereas the other two bridge in a terminal fashion between two Rb cations of opposite rows (see Figure 4). Each Rb cation is attached to two $[B(CN)_4]^-$ units resulting in a coordination number of 2 + 6 (O atoms of the crown ether molecule). This lower coordination number compared with that in the Cs compound (4 + 6) can be rationalised with the smaller ionic radius of Rb^+ (1.75 Å, coordination number 8; Shannon values)[26] com-

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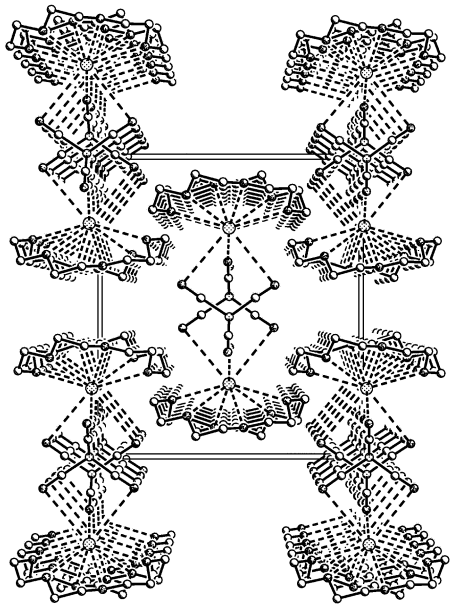

Figure 5. View of the structure of $[Cs(18\text{-crown-6})][B(CN)_4]$ along the crystallographic *c* direction, showing the stacking of double-row chains.

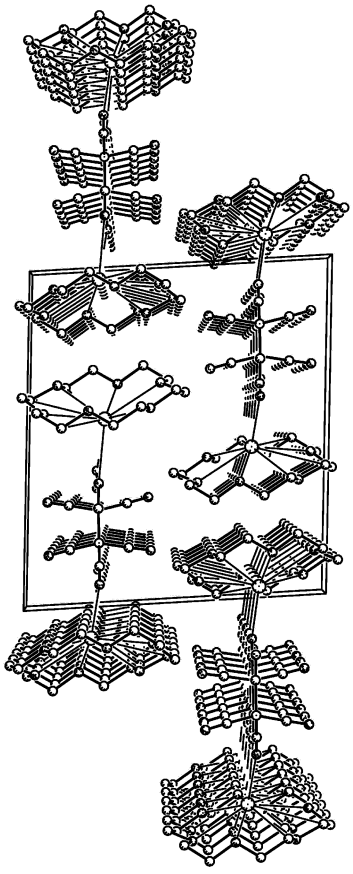

Figure 6. View of the structure of $[Rb(18\text{-crown-6})][B(CN)_4]$ along the crystallographic *c* direction, showing the stacking of double-row chains.

pared with Cs^+ (1.88 Å). The neutral double-row chains of interlinked ions are stacked in the crystals along the crystallographic *c* direction. Figures 5 and 6 give a view of the chain stacking along the chain direction of compound **1** and **2**, respectively.

From these figures it is clear that the double-row chains are isolated, and no strong bonding exists between them.

Thermal Properties

The differential scanning calorimetry (DSC) and thermogravimetry (TG) curves of $[Cs(18\text{-crown-6})][B(CN)_4]$ (**1**) and $[Rb(18\text{-crown-6})][B(CN)_4]$ (**2**) are shown in Figures 7 and 8.

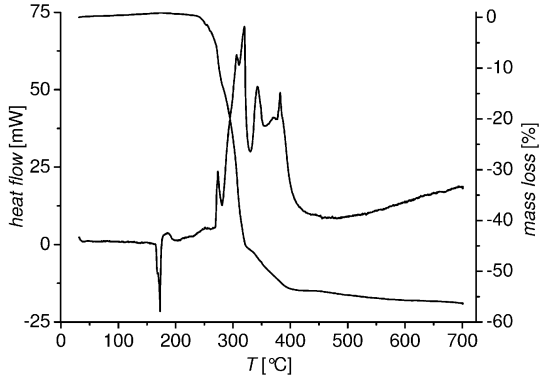

Figure 7. DSC and TG curve of $[Cs(18\text{-crown-6})][B(CN)_4]$.

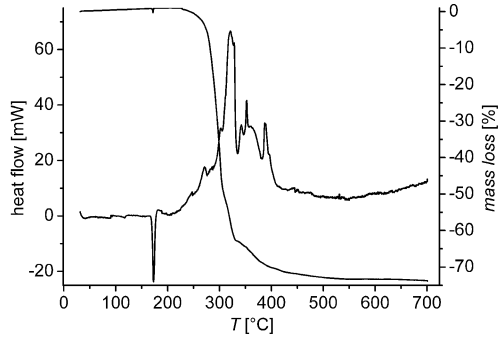

Figure 8. DSC and TG curve of $[Rb(18\text{-crown-6})][B(CN)_4]$.

Both compounds have identical melting points of 173 °C. The crown-ether-free parent compounds $Cs[B(CN)_4]$ and $Rb[B(CN)_4]$ have much higher melting points of 420 °C and 430 °C, respectively.[6,7] The reason therefore can be found in the reduced amount of strong ionic bonding.

In contrast to the alkaline metal tetracyanidoborates $Cs[B(CN)_4]$ and $Rb[B(CN)_4]$, which decompose above 510 °C,[7] the title substances decompose starting at about 230 °C. Above this temperature the organic part of the compound, i.e. the crown ether molecule, apparently starts to decompose. Similar observations have been made for tetracyanidoborates with organic, sterically demanding cations, for example $[Et_3S][B(CN)_4]$ (m.p. 44 °C; decomposition temperature 195 °C).[14]

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NMR Spectroscopy

The ^{13}C NMR spectrum shows, besides a single peak at δ = 69.8 (**1**) and 70.0 (**2**) ppm, a quartet and a septet at δ = 122.6 ppm. Whereas the single peak is caused by the methylene groups of the cyclic (crown) ether, the other signals result from the coupling of the spins of the carbon atom with the two isotopes of boron ^{11}B (80.42% I = 3/2) and ^{10}B (19.58% I = 3) as described in ref.[5] In addition, the crown ether can be identified for both title substances by a single signal at δ = 3.6 ppm in the ^{1}H NMR spectra.

Solubilities

The solubilities of both title substances in water, dichloromethane and acetonitrile are listed in Table 2. As expected, the complexation of the cations by the crown ether molecules leads to a serious change of the solubility compared with the crown-ether-free parent compounds. Whereas the tetracyanidoborates $Cs[B(CN)_4]$ and $Rb[B(CN)_4]$ show quite good solubility in water (0.071 mol L^{-1} and 0.100 mol L^{-1}, respectively),[7] the values for **1** are lower by a factor of approximately 14 and for **2** by approximately 20. A similar effect has been observed for the tetracyanidoborates with the organic cations [1-Bu-3-Me-imidazolium] and $[Bu_4N]$, which are insoluble in water.[7,13a] Furthermore, due to the complexation of the Rb and Cs cations by 18-crown-6, the tetracyanidoborates become soluble in dichloromethane and acetonitrile.

Table 2. Solubility data of **1** and **2** [mol L^{-1}].

Solvent	H_2O	CH_2Cl_2	CH_3CN
[Rb(18-crown-6)][$B(CN)_4$]	<0.005	0.36	1.85
[Cs(18-crown-6)][$B(CN)_4$]	<0.005	0.55	0.85

Vibration Spectra

The vibration spectra of compounds with the tetracyanidoborato anion as well as of 18-crown-6 have been described before.[5,7,27] The published peak positions compare well with those of the title compounds. In the Raman spectra of the title compounds, very strong signals for the CN stretching modes can be observed. Whereas for **1** only a single signal at 2222 cm^{-1} is observed, the band for **2** is split (2232 and 2224 cm^{-1}). The difference of 8 cm^{-1} is quite small compared with those observed for $Hg[B(CN)_4]_2$ (2265 – 2234 = 31 cm^{-1}) and for $Hg[B(CN)_4]_2$ (split into four signal 2263, 2253, 2245 and 2225 cm^{-1}).[8] The splitting of the CN stretching mode is caused by different coordination modes of the N atoms of the cyanide ligands. In **1**, each N atom of the four CN groups is bonded to a single Cs cation with almost identical C–N bond lengths (see the discussion above and also Figure 3 and Table 1). In **2**, only two of the CN ligands are bonded, the other two are noncoordinating. Therefore, the signal at 2232 cm^{-1} for **2** can be related to the stretching mode of C1–N1 and C3–N3 (coordinating N atoms) and that at 2224 cm^{-1} to the C2–N2 and C4–N4 vibration (noncoordinating N atoms). A comparable effect can be seen in the mercury tetracyanidoborates.[8]

Conclusions

The structures of the new tetracyanidoborato coordination compounds [Cs(18-crown-6)][$B(CN)_4$] and [Rb(18-crown-6)][$B(CN)_4$] are interesting new examples of linear-chain compounds. Double rows of alkaline metal cations encapsulated by 18-crown-6 polyether molecules ("crowned") are interconnected by $[B(CN)_4]^-$ anions. The coordination behaviour is different in both compounds. Both coordination types have not been observed in previously known tetracyanidoborates. These two compounds show that the $[B(CN)_4]^-$ anion has a much larger variability of coordination modes than so far expected, and more interesting structures are to be expected in the future.

Experimental Section

Syntheses and Chemicals: All chemicals were obtained from commercial sources and used without further purification. The potassium tetracyanidoborate, which is routinely used in our laboratories as a starting material, was synthesised as described by E. Bernhardt et al.[6] $Cs[B(CN)_4]$ and $Rb[B(CN)_4]$ were synthesised by ion exchange. An aqueous solution of the potassium tetracyanidoborate salt was rinsed through a cation exchange column loaded with CsCl or RbCl, respectively. After the evaporation of the solvent, each tetracyanidoborate (50 mg) was dissolved in water (5 mL). An aqueous solution of 18-crown-6 in a molar excess (with respect to the cation) was added to both solutions. In both cases a fine white precipitate appeared immediately, which became a sediment after a short time. During the following slow evaporation of the solvent, a large number of colourless crystals could be obtained. The solid was filtered, washed with a small amount of water and used for the following characterisation procedures without any further purification. The weighed amounts of solid material are 101 mg (98% with respect to the tetracyanidoborate used as starting material) of **1** and 112 mg (97%) of **2**.

[Cs(18-crown-6)][$B(CN_4)$] (1): $C_{16}H_{24}BCsN_4O_6$ (512.11): calcd. C 37.53, H 4.72, N 10.94; found C 37.73, H 4.74, N 10.96. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 69.8 (CH_2), 122.6 [sept, $^{1}J(^{10}B,C)$ = 21.1 Hz, CN], 122.6 [q, $^{1}J(^{11}B,C)$ = 71.4 Hz, CN] ppm. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.62 (CH_2) ppm. IR: CH: λ = 2963 (w), 2903 (w), 2866 (w), 2817 (w), 1480 (w), 1470 (w), 1460 (w), 1352 (m), 1292 (m), 1254 (m), 1243 (w), 1233 (w), 990 (w) cm^{-1}; CO: λ = 1127 (w), 1096 (s), 1048 (w), 1042 (w) cm^{-1}; BC: λ = 934 (s), 925 (s), 948 (m), 863 (w), 837 (m), 820 (w), 814 (w), 553 (w) cm^{-1}. Raman: 2963 (w), 2907 (w), 2888 (m), 2222 (vs), 1476 (w), 1447 (w), 1297 (w), 1281 (w), 1245 (w), 1144 (w), 865 (w), 834 (w), 816 (w), 521 (w), 485 (w), 273 (w), 155 (w), 118 (w), 99 (w), 68 (w) cm^{-1}.

[Rb(18-crown-6)][$B(CN_4)$] (2):. $C_{16}H_{24}BN_4O_6Rb$ (464.67): calcd. C 41.36, H 5.21, N 12.06; found C 41.54, H 5.20, N 12.22. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 70.0 (CH_2), 122.6 [sept, $^{1}J(^{11}BC)$ = 71.4 Hz, CN], 122.6 [q, $^{1}J(^{10}BC)$ = 24.1 Hz, CN] ppm. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (CH_2) ppm. IR: CH: λ = 2894 (m), 2868 (w), 2830 (w), 1480 (w), 1454 (w), 1435 (w), 1350 (m), 1286 (w), 1254 (m), 1298 (w), 998 (w) cm^{-1}; CO: λ = 1132 (w), 1099 (s) cm^{-1}; BC: λ = 938 (m), 920 (m) 868 (w), 956 (m), 834 (m) cm^{-1}. Raman: λ = 2967 (w), 2911 (m), 2897 (s), 2883 (m), 2851 (m), 2814 (m), 2789

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(w), 2757 (w), 2733 (w), 2703 (w), 2685 (w), 2232 (s), 2224 (s), 1482 (w), 1277 (w), 1248 (w), 1138 (w), 1081 (w), 868 (w), 828 (w), 550 (w), 525 (w), 489 (w), 282 (w), 149 (w), 134 (m), 97 (w), 68 (w) cm^{-1}.

Infrared/Raman Spectra: Infrared spectra were recorded at room temperature with a Nicolet 380 FTIR spectrometer with a Smart Orbit diamond ATR accessory. Raman spectra were recorded at room temperature with a combined IR/Raman Vertex 70 spectrometer (Bruker) by using the 1064 nm excitation line of an Nd/YAG laser.

TG/DSC Measurements: Thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out with a Setaram Labsys thermal analyser.

NMR Spectra: NMR spectra were measured with a Bruker AC 250 F instrument by using $CDCl_3$ as a solvent. TMS was used as internal standard for the ^1H and ^{13}C measurements.

Solubility: The solubilities of the two new tetracyanidoborates in various solvents were determined by using weight measurements. In each case, a defined volume of a saturated solution was placed in a vial of known weight. After evaporation of the solvent, the mass of the vial plus material was recorded and the solubility was calculated from the mass difference.

Elemental Analysis: The analyses (C, H and N) were carried out with a Thermoquest Flash EA 1112 CHNS-analyser.

Crystal Structure Studies: Suitable crystals of the two phases were obtained by slow evaporation of the solvent from aqueous solutions and glued on the tip of a thin glass rod. X-ray intensity data were collected at room temperature with the aid of a Bruker-Nonius Apex-X8 diffractometer, equipped with a CCD detector. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used in both cases. Crystal data, data collection and refinement parameters for both compounds are given in Table 3. CCDC-676972 (**1**) and -676971 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Cs(18-crown-6)][B(CN$_4$)] (1): Preliminary unit-cell dimensions of **1** were determined from the reflections of 60 frames measured in 3 different directions. The final unit-cell parameters were refined to values of a = 13.8188(2), b = 15.8406(2) and c = 10.1717(1) Å, β = 92.117(1)° for the *C*-centred monoclinic cell. Data collection up to 78° for 2θ was carried out by using the Bruker-Nonius APEX-2, vers. 1.6–8 software.[28] The data reduction included corrections for background, Lorentz and polarisation effects by using the SAINT program, vers. 7.06A.[28] A multiscan absorption correction was applied with the aid of SADABS[28] giving a data set with R_{int} = 0.0373. The structure of **1** was solved by using direct methods in the monoclinic space group *C*2/*c* (no. 15). The structural model was completed by using difference Fourier maps and refined by full-matrix least-squares methods on F^2 using the SHELX-97 program package.[29] All atoms except hydrogen were refined by using anisotropic thermal parameters. Hydrogen atoms on the crown ether molecules were fixed on idealised positions and refined with isotropic thermal parameters based on the bonded atom. The final refinements converged at $R_1(F)$ = 0.0275, and $wR_2(F^2)$ = 0.0611.

[Rb(18-crown-6)][B(CN$_4$)] (2): The data collection and reduction procedure as well as the structure solution and refinement were done according to the same procedure as for **1**. The unit-cell dimensions of the monoclinic cell of **2** are: a = 14.237(2), b = 9.455(1) and c = 15.942(2), β = 94.319(4)°. After the multiscan absorption correction, a data set with R_{int} = 0.0364 resulted. The structure solution of **2** was performed in the monoclinic, centrosymmetric space group $P2_1/n$ (no. 14). The final refinements converged at $R_1(F)$ = 0.0455, and $wR_2(F^2)$ = 0.1163.

Table 3. Crystal, structure solution and refinement data for compounds **1** and **2**.

	1	**2**
Empirial formula	$C_{16}H_{24}BCsN_4O_6$	$C_{16}H_{24}BN_4O_6Rb$
Formula mass [g mol^{-1}]	512.11	464.67
Space group	*C*2/*c*	$P2_1/n$
Unit cell dimensions		
a [Å]	13.819(1)	14.237(2)
b [Å]	15.841(1)	9.455(1)
c [Å]	10.1717(7)	15.942(2)
β [°[	92.117(4)	94.319(4)
V [Å^3]	2225.0(3)	2139.9(5)
Z	4	4
Crystal size [mm]	0.32 × 0.29 × 0.11	0.47 × 0.24 × 0.17
$2\theta_{max}$ [°]	78.2	64
T [K]	193(2)	173(2)
λ [Å]	0.71073	0.71073
Reflections collected	37074	25029
Independent reflections	6102 (R_{int} = 0.0373)	7358 (R_{int} = 0.0364)
Density (calcd.) [g cm^{-3}]	1.529	1.442
μ [mm^{-1}]	1.700	2.351
Largest residual peak [e Å^{-3}]	1.74	1.699
Number of parameters	128	254
Goodness-of-fit on F^2	0.982	1.075
R indices [$I > 2\sigma(I)$]	R_1 = 0.0275, wR_2 = 0.0583	R_1 = 0.0455, wR_2 = 0.1094
R indices (all data)	R_1 = 0.0443, wR_2 = 0.0611	R_1 = 0.0650, wR_2 = 0.1163
Weighting scheme x/y[a]	0.0335/0.0	0.0344/3.88

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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