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Tetracyanoborate Salts $M[B(CN)_4]$ with M = Singly Charged Cations: Properties and Structures

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A series of tetracyanoborate salts $M[B(CN)_4]$ with the singly charged cations of Li^+, Na^+, Rb^+, Cs^+, $[NH_4]^+$, Tl^+, and Cu^+ as well as the THF solvate tetracyanoborates $Na[B(CN)_4]\cdot THF$ and $[NH_4][B(CN)_4]\cdot THF$ were synthesized and their X-ray structures, vibrational spectra, solubilities in water, and thermal stabilities determined and compared with already known $M[B(CN)_4]$ salts. Crystallographic data for these compounds are as follows: $Na[B(CN)_4]$, cubic, $Fd\bar{3}m$, $a = 11.680(1)$ Å, $Z = 8$; $Li[B(CN)_4]$, cubic, $P\bar{4}3m$, $a = 5.4815(1)$ Å, $Z = 1$; $Cu[B(CN)_4]$, cubic, $P\bar{4}3m$, $a = 5.4314(7)$ Å, $Z = 1$; $Rb[B(CN)_4]$, tetragonal, $I4_1/a$, $a = 7.1354(2)$ Å, $c = 14.8197(6)$ Å, $Z = 4$; $Cs[B(CN)_4]$, tetragonal, $I4_1/a$, $a = 7.300(2)$ Å, $c = 15.340(5)$ Å, $Z = 4$; $[NH_4][B(CN)_4]$, tetragonal, $I4_1/a$, $a = 7.132(1)$ Å, $c = 14.745(4)$ Å, $Z = 4$; $Tl[B(CN)_4]$, tetragonal, $I4_1/a$, $a = 7.0655(2)$ Å, $c = 14.6791(4)$ Å, $Z = 4$; $Na[B(CN)_4]\cdot THF$, orthorhombic, $Pnma$, $a = 13.908(3)$ Å, $b = 9.288(1)$ Å, $c = 8.738(1)$ Å, $Z = 4$; $[NH_4][B(CN)_4]\cdot THF$, orthorhombic, $Pnma$, $a = 8.831(1)$ Å, $b = 9.366(2)$ Å, $c = 15.061(3)$ Å, $Z = 4$. The cubic Li^+, Na^+, and Cu^+ salts crystallize in a structure consisting of two interpenetrating independent tetrahedral networks of M cations and $[B(CN)_4]^-$ ions. The compounds with the larger countercations (Rb^+, Cs^+, Tl^+, and $[NH_4]^+$) crystallize as tetragonal, also with a network arrangement. The sodium and ammonium salts with the cocrystallized THF molecules are both orthorhombic but are not isostructural. In the vibrational spectra the two CN stretching modes A_1 and T_2 coincide in general and the band positions are a measure for the strength of the interionic interaction. An interesting feature in the Raman spectrum of the copper salt is the first appearance of two CN stretching modes.

Introduction

In the search for new materials with improved properties, salts containing chemically robust anions are of general interest. Such anions can be used in ionic liquids,[1] in electrolytes,[2] for the stabilization of unusual cations,[3,4] and to develop new chemistry.

A few years ago we reported the synthesis of the first salts containing the tetracyanoborate, $[B(CN)_4]^-$, anion.[5] The vibrational and NMR spectra of this anion have been measured and thoroughly analyzed and the structures of the $[Bu_4N]^+$, Ag^+, and K^+ salts determined by single-crystal X-ray diffraction. A few months later the formation of $Li[B(CN)_4]$ by treating $Li[BF_4]$ with Me_3SiCN was reported independently.[6] Another route to $[B(CN)_4]^-$ salts was found by reacting $BF_3\cdot OEt_2$ with Me_3SiCN,[7] and in addition, the spectroscopic and structural properties of the mixed species $[BF_x(CN)_{4-x}]^-$ ($x = 0-4$) have been investigated.

There is now an increasing interest in the $[B(CN)_4]^-$ ion because it is (i) the precursor for the promising weakly coordinating $[B(CF_3)_4]^-$ ion[8] and the highly reactive boron

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carbonyl $(CF_3)_3BCO$,[9,10] (ii) part of fascinating three-dimensional networks e.g. in the mercury salts[11] and others,[12,13] (iii) the counterion in ionic liquids with high thermal and chemical stability,[14] and (iv) potentially useful for the synthesis of light element ceramics.[6] Therefore we have developed an efficient synthetic method by reacting a mixture of $K[BF_4]$, LiCl, and KCN at 300 °C. After the products are worked up, high-purity $K[B(CN)_4]$ is obtained in 65% yield on a molar scale.[15]

In this contribution a systematic comparison of physical, spectroscopic, and structural properties of known and new $[B(CN)_4]^-$ salts with singly charged cations is presented.

Experimental Section

Safety Notes. *Thallium(I) compounds and most cyanides are highly toxic, especially if dissolved in organic solvents. They should be handled always with high precaution.*

(A) Syntheses. (i) Chemicals. The starting materials $M[B(CN)_4]$ ($M = Na^+$, K^+, $[NH_4]^+$, and Cs^+) were synthesized as described in the literature.[15] All other chemicals and solvents were obtained from commercial sources and used as received.

(ii) Apparatus. Volatile materials were manipulated in a glass vacuum line (internal volume ~ 100 mL) equipped with a capacity pressure gauge (Setra 205-2, $p = 0-3.45$ bar, Boxborough, MA) and a Pirani pressure gauge. The glass line was fitted with PTFE stem valves (Young POR10, London, U.K.) and NS14.5 standard ground joints. As reaction vessels, different round-bottom flasks equipped with a valve (Young POR10, London, U.K.) and a PTFE-coated magnetic stirring bar were used.

(iii) Synthetic Reactions. (a) Li[B(CN)$_4$]. In a separating funnel 12.32 g (80.0 mmol) of $K[B(CN)_4]$ was dissolved in 100 mL of water. The solution was treated with 18.2 mL (80 mmol) of tri-*n*-propylamine and 4.0 mL (130 mmol) of concentrated hydrochloric acid and shaken. The resulting white precipitate was extracted three times with CH_2Cl_2 (100, 50, and 50 mL, respectively). The collected organic phases containing $[(C_3H_7)_3NH][B(CN)_4]$ were combined, dried over $MgSO_4$, and filtered through a glass frit (D4).

The colorless solution was transferred into a 500 mL round-bottom flask together with 5.75 g (130 mmol) of $LiOH{\cdot}H_2O$ in 20 mL of water. The mixture was stirred vigorously for 60 min and finally dried under reduced pressure. The solid residue ($Li[B(CN)_4$ and $LiOH{\cdot}H_2O$) was extracted with 50 mL of CH_3CN in a Soxhlet extractor. The resulting solution was taken to dryness in a vacuum and washed with dichloromethane to yield 5.94 g (48.7 mmol, 61%) of $Li[B(CN)_4]$.

Anal. Calcd for C_4BLiN_4 ($M_r = 121.823$): C, 39.44; N, 45.99. Found: C, 38.94; N, 44.84.

(b) Rb[B(CN)$_4$]. In a 100 mL glass beaker 1.38 g (10.0 mmol) of $Na[B(CN)_4]$ was dissolved in 50 mL of water. To the vigorously stirred solution 2.0 mL (≈24 mmol) of concentrated hydrochloric acid and 2.8 mL (20 mmol) of triethylamine were added. After a few minutes the emulsion was transferred into a separating funnel and extracted three times with dichloromethane (50, 25, and 25 mL, respectively). The organic phases were collected, dried over $MgSO_4$, and filtered through a glass frit (D4). The obtained clear solution was treated under stirring with 2.5 mL (21 mmol) of RbOH solution (50 wt %). A colorless suspension ($Rb[B(CN)_4]$ and $RbOH{\cdot}xH_2O$) appeared, and after 1 h the dichloromethane phase containing $N(C_3H_7)_3$ was separated. The solid residue was washed with 50 mL of CH_2Cl_2, and 50 mL of CH_3CN was added. The suspension was stirred for 30 min, and the organic phase containing $Rb[B(CN)_4]$ was separated. The extraction was repeated twice with 50 mL of acetonitrile. The combined organic phases were dried over Rb_2CO_3 and filtered through a glass frit (D4), and the solvent was removed under reduced pressure. The obtained solid residue was washed with dichloromethane and dried in a vacuum to yield 1.90 g (9.5 mmol, 95%) of $Rb[B(CN)_4]$.

Anal. Calcd for C_4BN_4Rb ($M_r = 200.352$): C, 23.98; N, 27.96. Found: C, 24.14; N, 27.77.

(c) Tl[B(CN)$_4$]. A 1.38 g (10.0 mmol) amount of $Na[B(CN)_4]$ was dissolved in 50 mL of water and treated with 2.80 mL (20 mmol) of triethylamine as well as 2.0 mL (≈24 mmol) of concentrated HCl. The clear solution was transferred into a separating funnel and extracted four times with dichloromethane (75, 50, 50, and 25 mL, respectively). Afterward the combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure.

The obtained $[NEt_3H][B(CN)_4]$ salt was suspended in a solution of 4.67 g (10.00 mmol) of Tl_2CO_3 in 100 mL of water. Subsequently, all volatiles (H_2O, some NEt_3, and CO_2) were removed at 50 °C under reduced pressure. A 100 mL volume of water was added, and the suspension was evaporated again. This procedure was repeated three times, and by washing of the colorless solid residue with CH_2Cl_2, the last traces of NEt_3 were removed. The solid was suspended in 250 mL of acetonitrile and filtered through a glass frit (D4) to separate excess Tl_2CO_3, and the solvent was removed under reduced pressure. A 2.13 g (6.7 mmol, 67%) amount of colorless $Tl[B(CN)_4]$ was obtained.

Anal. Calcd for C_4BN_4Tl ($M_r = 319.265$): C, 15.05; N, 17.55. Found: C, 15.26; N, 17.47.

(d) Cu[B(CN)$_4$]. A 2.60 g (10.0 mmol) amount of $CuSO_4{\cdot}5H_2O$, 1.94 g (30.5 mmol) of copper powder, and 2.72 g (19.7 mmol) of $Na[B(CN)_4]$ were transferred into a 500 mL round-bottom flask equipped with a valve and a PTFE-coated magnetic stirring bar. Under an argon atmosphere the flask was charged with 150 mL of concentrated ammonia solution (25 wt %) and the suspension was stirred vigorously for 2 h. Approximately 25 mL of the colorless solution was transferred under an argon atmosphere into a 50 mL round-bottom flask, and all volatiles were removed under reduced pressure. The obtained colorless solid residue was washed with 10% hydrochloric acid and dried in a vacuum. The yield was not determined.

Anal. Calcd for C_4BCuN_4 ($M_r = 178.428$): C, 26.93; N, 31.40. Found: C, 26.40; N, 31.76.

(iv) Preparation of Single Crystals. Colorless single crystals of $Li[B(CN)_4]$ were prepared from an aqueous solution containing a small amount of tri-*n*-propylamine through slowly evaporating the solvent at room temperature. Colorless single crystals of $Na[B(CN)_4]$, $[NH_4][B(CN)_4]$, $Rb[B(CN)_4]$, and $Tl[B(CN)_4]$ have been

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Table 1. Crystal Data and Structure Refinement Parameters for $M[B(CN)_4]$ ($M = Li^+, Na^+, Rb^+, Cs^+, Tl^+, [NH_4]^+, Cu^+$) and $M[B(CN)_4]\cdot THF$ ($M = Na^+, [NH_4]^+$)

	$Na[B(CN)_4]$	$Li[B(CN)_4]$	$Cu[B(CN)_4]$	$Rb[B(CN)_4]$	$Cs[B(CN)_4]$	$[NH_4]$-$[B(CN)_4]$	$Tl[B(CN)_4]$	$Na[B$-$(CN)_4]\cdot THF$	$[NH_4][B$-$(CN)_4]\cdot THF$
formula	C_4BNaN_4	C_4BLiN_4	C_4BCuN_4	C_4BN_4Rb	C_4BCsN_4	$C_4H_4BN_5$	C_4BN_4Tl	$C_8H_8BN_4NaO$	$C_8H_{12}BN_5O$
fw	137.88	121.83	178.43	200.36	247.80	132.93	319.26	209.98	205.04
T, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
cryst sys	cubic	cubic	cubic	tetragonal	tetragonal	tetragonal	tetragonal	orthorhombic	orthorhombic
space group	$Fd\bar{3}m$	$P\bar{4}3m$	$P\bar{4}3m$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$Pnma$	Pnma
a, Å	11.680(1)	5.4815(1)	5.4314(7)	7.1354(2)	7.300(2)	7.132(1)	7.0655(2)	13.908(3)	8.831(1)
b, Å								9.288(1)	9.366(2)
c, Å				14.8197(6)	15.340(5)	14.745(4)	14.6791(4)	8.738(1)	15.061(3)
V, Å^3	1593.4(9)	164.70(1)	160.2(1)	754.53(4)	817.6(6)	750.0(3)	732.55(5)	1128.8(3)	1245.7(4)
Z	8	1	1	4	4	4	4	4	4
ρ_{calcd}, $g\cdot cm^{-1}$	1.150	1.228	1.849	1.764	2.013	1.177	2.895	1.236	1.093
μ, mm^{-1}	0.12	0.08	3.31	6.48	4.46	0.08	21.97	0.12	0.08
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
$R1(F)^a$	0.0242	0.0417	0.0165	0.0250	0.0397	0.0446	0.0520	0.0496	0.0692
$wR2(F^2)^b$	0.0639	0.1212	0.0346	0.0523	0.1053	0.1203	0.1399	0.1584	0.2179
weighting^c	0.0162, 0.37	0.0864, 0	0.0, 0	0.0169, 0.44	0.0773, 1.26	0.0500, 0	0.0840, 0	0.0912, 0.12	0.1193, 0.16
GOF	1.112	1.076	1.026	1.082	1.063	1.066	1.057	1.047	1.079

^{a} $R1 = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_c\rvert$. ^{b} $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$. ^{c} $w = 1/[(\sigma^2(F_o^2) + (0.0162P)^2 + 0.37P]$; $P = (F_o^2 + 2F_c^2)/3$.

grown from aqueous solutions at room temperature by slow evaporation of water. In addition the solvated single crystals $Na[B(CN)_4]\cdot THF$ and $[NH_4][B(CN)_4]\cdot THF$ were crystallized from THF solutions.

Colorless single crystals of $Cu[B(CN)_4]$ were prepared in a small glass U-tube, separated at the bottom by a small glass frit (D4). The U-tube was charged under argon atmosphere on one side with a saturated aqueous $Li[B(CN)_4]$ solution and on the other side with a saturated copper(I) chloride solution in aqueous ammonia (25 wt %). Crystals formed on the surface of the glass frit while the U-tube was kept at 2 °C for 6 weeks.

(B) Characterization. (i) Vibrational Spectroscopy. (a) Infrared spectra were recorded at room temperature on a Bruker Tensor 27 FTIR spectrometer (Bruker, Karlsruhe, Germany) equipped with a DTGS detector and a KBr/Ge beam splitter operating in the region 4000−400 cm^{-1}. For each spectrum 128 scans were coadded with an apodized resolution of 2 cm^{-1}. The crystalline samples were measured as Nujol mulls between KBr disks.

(b) Raman spectra were recorded at room temperature with a Bruker RFS100/S FT Raman spectrometer (Bruker, Karlsruhe, Germany) using the 1064 nm exciting line (500 mW) of a Nd:YAG laser.

Crystalline samples contained in large melting point capillaries (2 mm o.d.) were used for recording spectra in the region 3000−80 cm^{-1} with a resolution of 2 cm^{-1}. For each spectrum 256 scans were coadded, and the Raman intensities were corrected by calibration of the spectrometer with a tungsten halogen lamp.

(ii) Single-Crystal X-ray Diffraction. For the measurement of X-ray diffraction data colorless single crystals of the above-mentioned tetracyanoborates were mounted either inside thin-wall capillaries or fixed with glue on the tip of thin glass rods. Data were recorded at room temperature for $M[B(CN)_4]$ with $M = Na^+$, $[NH_4]^+$, Cs^+ and $M[B(CN)_4]\cdot THF$ with $M = Na^+$ and $[NH_4]^+$ on a Siemens-Bruker P4 four-circle diffractometer employing Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The cell parameters were obtained from least-squares fits to the angular coordinates of 25 reflections. Intensities were measured by standard $\omega\angle 2\theta$ scans. Empirical absorption corrections were applied by using the results from ψ scans on selected reflections.

Crystallographic data for $M[B(CN)_4]$ with $M = Li^+, Rb^+, Tl^+$, and Cu^+ were collected at 293(2) K with the aid of a Bruker-Nonius APEX-X8 Platform CCD diffractometer utilizing graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Absorption corrections were performed using SADABS.[16]

All structures were solved via direct methods and refined by full-matrix least-squares methods on F^2 using the SHELX-97 program package.[17] All atoms (except hydrogen) were treated anisotropically. Hydrogen atoms in $Na[B(CN)_4]\cdot THF$ and $[NH_4][B(CN)_4]\cdot THF$ were fixed on idealized positions and refined with isotropic thermal parameters based on the bonded carbon atom. Only in $[NH_4][B(CN)_4]$ the hydrogen atoms of the $[NH_4]^+$ ion were located from the difference Fourier map and refined with isotropic thermal parameters. Crystal data, data collection, and refinement parameters for all compounds are given in Table 1. Table 2 lists important interatomic distances.

More detailed crystallographic information, atomic positional and equivalent isotropic displacement parameters, and the anisotropic displacement parameters are available in the Supporting Information.

(iii) Powder X-ray Diffraction. Powder X-ray diffraction patterns were recorded with a Siemens D500 powder diffractometer utilizing monochromatized Cu Kα radiation. Flat powder samples were used. Measurements were performed with 0.03 deg steps, 1 s measuring time/step, and a scan range from $10° \leq 2\theta \leq 70°$.

(iv) DSC Measurements. Thermoanalytical measurements were performed with a Netzsch DSC 204 (Netzsch GmbH, Selb, Germany) instrument. Temperature and sensitivity calibrations in the temperature range of 20−600 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 5−10 mg of the solid samples was weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 20−600 °C with a heating rate of 10 K min^{-1}; throughout this process the furnace was flushed with dry nitrogen. For the evaluation of the output, the Netzsch Protens 4.0 software was employed.

(v) Elemental Analysis. The elemental analyses were accomplished by microanalytical combustion methods at the Euro

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Table 2. Selected Structural Data of the Tetracyanoborate Salts with Singly Charged Cations[a]

			dists (Å) and no. of occurrences/formula unit			angles (deg)		
compd[a]	cryst sys	space group	M−N	B−C	C−N	C−B−C	B−C−N	M−N−C
Na[B(CN)$_4$]	cubic	$Fd\bar{3}m$	2.352(2) (4×)	1.575(2) (4×)	1.130(3) (4×)	109.47 (6×)	180	180
Li[B(CN)$_4$]	cubic	$P\bar{4}3m$	2.0213(8) (4×)	1.5842(8) (4×)	1.142(1) (4×)	109.47 (6×)	180	180
Cu[B(CN)$_4$]	cubic	$\mathrm{P}\bar{4}3m$	1.976(2) (4×)	1.588(2) (4×)	1.140(3) (4×)	109.47 (6×)	180	180
Rb[B(CN)$_4$]	tetragonal	$I4_1/a$	3.065(1) (4×) 3.226(2) (4×)	1.590(1) (4×)	1.136(2) (4×)	108.79(5) (4×) 110.8(1) (2×)	178.4(2)	116.6(1) 124.5(1)
Cs[B(CN)$_4$]	tetragonal	$I4_1/a$	3.232(5) (4×) 3.340(5) (4×)	1.582(5) (4×)	1.127(7) (4×)	109.1(2) (4×) 110.3(4) (2×)	178.5(5)	117.6(4) 125.2(4)
[NH$_4$][B(CN)$_4$]	tetragonal	$I4_1/a$	3.012(2) (4×) 3.265(2) (4×)	1.592(2) (4×)	1.133(2) (4×)	108.90(7) (4×) 110.6(1) (2×)	179.5(2)	114.8(1) 126.8(2)
Tl[B(CN)$_4$]	tetragonal	$I4_1/a$	3.029(6) (4×) 3.190(6) (4×)	1.581(5) (4×)	1.139(7) (4×)	109.0(2) (4×) 110.5(4) (2×)	178.3(6)	116.1(5) 123.7(5)
Na[B(CN)$_4$]·THF	orthorh	$Pnma$	2.484(2) (2×) 2.475(3) 2.477(3) M−O: 2.341(2)	1.590(3) (2×) 1.588(4) 1.589(4)	1.133(2) (2×) 1.135(4) 1.141(3)	109.4(1) (2×) 109.9(1) (2×) 108.8(2) 109.4(2)	178.7(2) 179.1(3) 179.3(3)	158.9(2) 166.6(3) 178.5(2)
[NH$_4$][B(CN)$_4$]·THF	orthorh	$Pnma$	2.969(2) (2×) 2.995(4) 3.008(4) M−O: 2.832(3)	1.589(2) (2×) 1.589(4) 1.588(4)	1.142(3) (2×) 1.125(4) 1.142(4)	109.4(2) (2×) 109.6(2) (2×) 109.0(2) 109.8(2)	178.4(2) 179.4(3) 179.5(3)	163.6(3) 167.4(2) 171.4(3)
K[B(CN)$_4$][b]	tetragonal	$I4_1/a$	2.895(1) (4×) 3.133(1) (4×)	1.595(1) (4×)	1.142(1) (4×)	108.83(4) (4×) 110.77(7) (2×)	178.68(9)	114.94(8) 123.78(8)
Ag[B(CN)$_4$][b]	cubic	$P\bar{4}3m$	2.244(2) (4×)	1.589(2) (4×)	1.131(3)	109.47 (6x)	180	180
[Bu$_4$N][B(CN)$_4$][b]	orthorh	$Pnma$		1.582(3) (2×) 1.590(3) (2×)	1.135(3) 1.141(3)	108.5(1) (2×) 109.0(1) (2×) 110.5(3) 111.5(3)	177.6(3) 178.8(3)	

[a] All structure determinations were performed at room temperature except for K[B(CN)$_4$], Ag[B(CN)$_4$], and [Bu$_4$N][B(CN)$_4$], which were done at 150 K. [b] Reference 5.

Table 3. Properties of Tetracyaborate Salts with Singly Charged Cations

	solubility					
compd	g/100 g of H$_2$O	mol/L	mp (°C)	dec (°C)	Raman ν(CN), A$_1$/T$_2$ (cm^{-1})	IR ν(CN), T$_2$ (cm^{-1})
Li[B(CN)$_4$]	14.06	1.03		500[a]	2263[a]	2262
Na[B(CN)$_4$]	92.10	3.89	520[a]	540[a]	2252[a]	2252
K[B(CN)$_4$]	5.83	0.365	430[a]	510[a]	2233[b]	2234[b]
Rb[B(CN)$_4$]	2.01	0.100	430	510	2232	2232
Cs[B(CN)$_4$]	1.77	0.071	420[a]	510[a]	2230[a]	2230
Tl[B(CN)$_4$]	6.21	0.190	370	470	2224	2225
Cu[B(CN)$_4$]	<0.02	$<1 \times 10^{-3}$		470[a]	2259/2253	2252
Ag[B(CN)$_4$]	6×10^{-5}	3×10^{-5}		440[a]	2256[b]	2257[b]
[NH$_4$][B(CN)$_4$]	17.43	1.13		300[a]	2233[a]	2234
[Bu$_4$N][B(CN)$_4$]	insol	insol	80[a]	350[a]	2222[b]	2222[b]
[1-Bu-3-Me-imidazolium][B(CN)$_4$][c]	insol	insol	<−50	400	2224	2223

[a] Reference 15. [b] Reference 5. [c] Reference 14.

EA3000 instrument (HEKA-Tech GmbH, Wegberg, Germany). The error margins for the determination of the elements were C ± 0.3%, H ± 0.51%, and N ± 0.2%.

(vi) Solubilities. The solubilities of the tetracyanoborate salts in water were determined at 22 °C (Table 3). Saturated solutions of Li[B(CN)$_4$], Na[B(CN)$_4$], K[B(CN)$_4$], Rb[B(CN)$_4$], Cs[B(CN)$_4$], and Tl[B(CN)$_4$] were prepared in small glass containers with a snap-on lid. About 1.0 mL of the saturated solutions was transferred into a weighed empty glass container. After the mass differences were measured, the solutions were evaporated to dryness at 65 °C at atmospheric pressure and weighed again. All measurements were repeated several times, and the results were averaged.

The solubility of Ag[B(CN)$_4$] was determined by potentiometry. The potential of the saturated solution of Ag[B(CN)$_4$] was measured against a saturated silver chloride solution.

Cu[B(CN)$_4$] is also poorly soluble in water. Because the preparation of copper tetracyanoborate can be performed in a metathesis reaction with copper(I) chloride, the solubility of Cu[B(CN)$_4$] in water must be lower than that of CuCl (1×10^{-3} mol L^{-1}).[18]

Results and Discussion

(A) Synthetic Aspects. The most efficient synthesis of tetracyanoborates is based on a sintering reaction of a solid mixture of K[BF$_4$], LiCl, and KCN at 300 °C.[15] The role of the LiCl is to lower the melting point of the reaction mixture below the decomposition temperature of the [B(CN)$_4$]$^-$ anion at about 450 °C. After extraction of the solid reaction with water, the excess of cyanide is removed by treatment with H$_2$O$_2$. Subsequently the solution is acidified with HCl(aq) and N^{n}Pr$_3$ is added. In this manner sparingly water soluble [N^{n}Pr$_3$H][B(CN)$_4$] is formed, which is extracted with

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(18) Meyer, R. J., Pietsch, E. H. E., Eds. *Gmelins Handbook of Inorganic Chemistry*, 8th ed.; Verlag Chemie GmbH: Weinheim/Bergstr., Germany, 1958; Vol. 60.

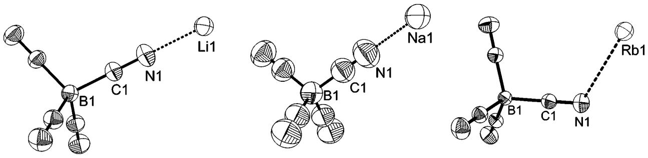

Figure 1. Structures of the tetracyanoborate anions together with the cation in Li[B(CN)$_4$] (left), Na[B(CN)$_4$] (middle), and Rb[B(CN)$_4$] (right). Thermal ellipsoids are shown with 50% probability.

CH_2Cl_2. This *n*-propylammonium salt is the starting material for all alkali metal salts according to:

$$[N^nPr_3H][B(CN)_4] + MOH \xrightarrow{H_2O} M[B(CN)_4] + H_2O + N^nPr_3 \tag{1}$$

The amine is removed by washing with CH_2Cl_2, and the excess of MOH, by extracting the tetracyanoborate with an organic solvent (e.g. CH_3CN or THF).

Also less basic carbonates, like Tl_2CO_3, are able to displace the amine, if the amine is volatile enough. Thallium tetracyanoborate is synthesized by treating the triethylammonium salt with commercial available Tl_2CO_3:

$$2[NEt_3H][B(CN)_4] + Tl_2CO_3 \xrightleftharpoons{H_2O} 2Tl[B(CN)_4] + 2NEt_3 + H_2O + CO_2 \tag{2}$$

This equilibrium is shifted to the product side by repeated heating and evaporating of added water. In this manner volatile NEt_3 and CO_2 are removed.

The ammonium salt is prepared by a metathesis reaction[15]

$$2K[B(CN)_4] + [NH_4]_2[SiF_6] \xrightarrow{H_2O} 2[NH_4][B(CN)_4] + K_2[SiF_6]\downarrow \tag{3}$$

as well as ionic liquids, e.g.[14]:

$$[\text{1-Bu-3-Me-imidazolium}]Cl + K[B(CN)_4] \xrightarrow{H_2O} [\text{1-Bu-3-Me-imidazolium}][B(CN)_4]\downarrow + KCl \tag{4}$$

Cu[B(CN)$_4$] can be prepared either from CuCl and K[B(CN)$_4$] in water[15] or by comproportionation of copper and copper(II) sulfate in the presence of sodium tetracyanoborate in concentrated ammonia solution:

$$Cu + CuSO_4 + Na[B(CN)_4] \xrightarrow{NH_3(aq)} 2Cu[B(CN)_4] + Na_2SO_4 \tag{5}$$

Cu[B(CN)$_4$] precipitates from the colorless solution by removing NH_3 in a vacuum.

(B) Structural Aspects. All the title compounds contain tetracyanoborate anions, $[B(CN)_4]^-$, which have the boron atoms tetrahedrally surrounded by cyano groups. The structures of the tetracyanoborate anions together with their corresponding cations for all the nine compounds are shown as thermal ellipsoid plots with 50% probability in Figures 1−3.

As expected, the boron atom is always connected to the carbon atom of the cyano group,[7] as is verified by smaller R-values for the M−N−C−B arrangement compared to M−C−N−B. The shortest B−C bond is found in the cubic Na[B(CN)$_4$] (1.575(2) Å), whereas the upper limit is found in the potassium salt (1.595(1) Å) (although such a comparison seems difficult, because of differently sized thermal ellipsoids).[5] Structural details for the nine compounds under investigation are compiled in Table 2 together with the literature values of K[B(CN)$_4$], Ag[B(CN)$_4$], and [Bu$_4$N][B(CN)$_4$] for comparison. The C−N distances range from 1.125(4) Å in [NH$_4$][B(CN)$_4$]·THF to 1.142(1) Å in Li[B(CN)$_4$], values consistent with the description as a C−N triple bond. In the cubic structures of Li[B(CN)$_4$],[6] Na[B(CN)$_4$], and Cu[B(CN)$_4$] the B−C−N units are exactly linear and the $[B(CN)_4]^-$ ions show full T_d symmetry (site symmetry for B: $\bar{4}3m$). Li[B(CN)$_4$] is isostructural with the copper(I) as well as with the silver(I) salt.[5] A view of this structure is presented in Figure 4 emphasizing the tetrahedral units. In all the other structures, only small deviations from the full tetrahedral symmetry are found. In the tetragonal structures which are found for the Rb^+, Cs^+, $[NH_4]^+$, and Tl^+ salts, the boron atom is located on a site with $\bar{4}$ symmetry. The $[B(CN)_4]^-$ ions with the tetragonal structure are slightly compressed along the $\bar{4}$ axis with the deviations of the C−B−C angle from 109.47° not exceeding 1.33° (in the Rb salt). In the two compounds which contain cocrystallized THF the boron atoms of the $[B(CN)_4]^-$ ions are located on mirror planes, allowing for even larger distortions from tetrahedral symmetry (see Table 2).

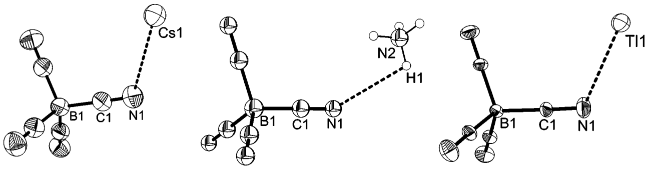

Figure 2. Structures of the tetracyanoborate anions together with the cation in Cs[B(CN)$_4$] (left), [NH$_4$][B(CN)$_4$] (middle), and Tl[B(CN)$_4$] (right). Thermal ellipsoids are shown with 50% probability, and hydrogen atoms, with arbitrary size.

As can be seen from Tables 1 and 2, the solvent free tetracyanoborates with monocations crystallize in three different structure types.

As can be seen from Table 4, these cubic structures are formed with small singly charged cations. The low coordination numbers and relatively short M−N distances might indicate some covalent bonding. Since the MN$_4$ tetrahedra compose the vertexes of the [B(CN)$_4$] units, two identical and interpenetrating three-dimensional networks exist in the structures of M[B(CN)$_4$] with M = Li^+, Cu^+, and Ag^+ as shown in Figure 4. Each network is displaced by one lattice translation from the other. Replacing the [B(CN)$_4$] units by S and M by Zn for one of the independent networks gives the sphalerite (cubic ZnS) structure of a ccp arrangement of anions with the cations occupying half of the tetrahedral holes.[19] This of course is related to the diamond structure.[19] The two interpenetrating tetrahedral networks show also a close structural relation to the cuprite (Cu_2O) structure.[19] Further compounds which are found to exist in this tetra-

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(19) Wells, A. F. *Structural Inorganic Chemistry*, 3rd ed.; Clarendon Press: Oxford, U.K., 1962.

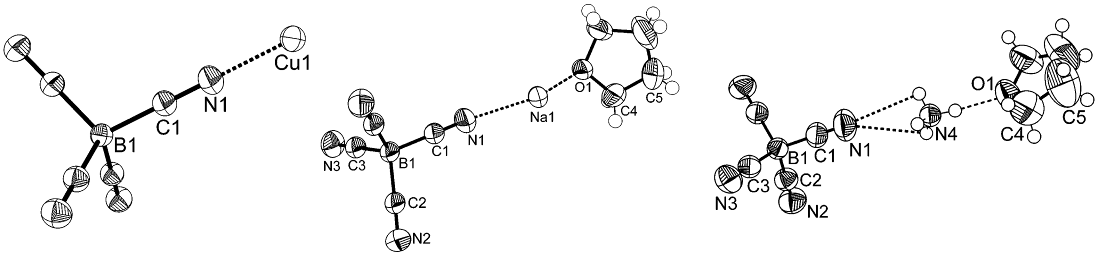

Figure 3. Structures of the tetracyanoborate anions together with the cation in Cu[B(CN)$_4$] (left), Na[B(CN)$_4$]·THF (middle), and [NH$_4$][B(CN)$_4$]·THF (right). Thermal ellipsoids are shown with 50% probability, and hydrogen atoms, with arbitrary size.

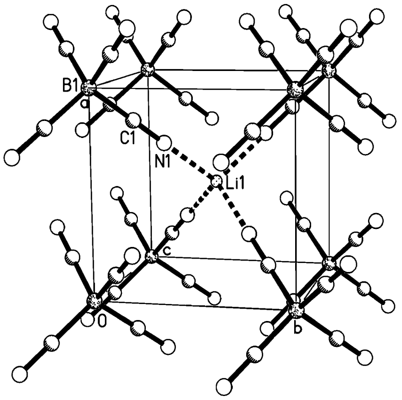

Figure 4. Perspective view of the primitive cubic structure of Li[B(CN)$_4$], which is also adopted by Cu[B(CN)$_4$] and Ag[B(CN)$_4$].

Table 4. Cation Radii in pm[a]

cation	radii	ref	cation	radii	ref
Li$^+$ (4)	59	*b*	K$^+$ (8)	151	*b*
Cu$^+$ (4)	60	*b*	Tl$^+$ (8)	159	*b*
Na$^+$ (4)	99	*b*	Rb$^+$ (8)	161	*b*
Ag$^+$ (4)	100	*b*	Cs$^+$ (8)	174	*b*
[NH$_4$]$^+$ (8)	136	*c*			

[a] Coordination number in parentheses. [b] Reference 25. [c] Reference 26.

cyanoborate structure type are Li[Co(CO)$_4$][20] and Li[Al(CN)$_4$].[21] Contrary to the tetracyanoborates with M = Li$^+$, Cu$^+$, and Ag$^+$ (space group $P\bar{4}3m$) the sodium salt is found to crystallize in the cubic space group $Fd\bar{3}m$. The lattice constants and crystal system were confirmed by X-ray powder diffraction. Again linear M−N−C units exist resulting in a network structure. A view of this structure is shown in Figure 5.

So far, Na[B(CN)$_4$] is the only compound found in this structure type. It is interesting to note that this is one of the very few compounds which contain Na cations with such a low coordination number. It usually prefers a coordination number of 6. Similar to the Li$^+$ (and Cu$^+$, Ag$^+$) salt, both the Na$^+$ cation and the boron atom are perfect tetrahedrally surrounded. As above, a relation exists similar to that of the diamond structure but with a slightly different replacement mode of one network relative to the other.[19] The third structural type of the solvent-free tetracyanoborates is found for the compounds with the larger cations Rb$^+$, Cs$^+$, [NH$_4$]$^+$, and Tl$^+$. They are isostructural with the potassium salt K[B(CN)$_4$][5] and crystallize in the tetragonal space group $I4_1/a$. A view of the unit cell is shown in Figure 6.

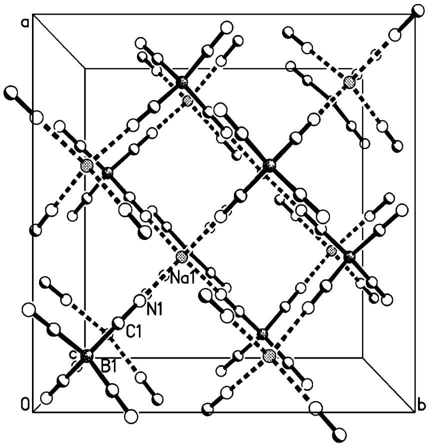

Figure 5. Perspective view of the *F*-centered cubic structure of Na[B(CN)$_4$], showing the tetrahedral environment of both the B and the Na atoms.

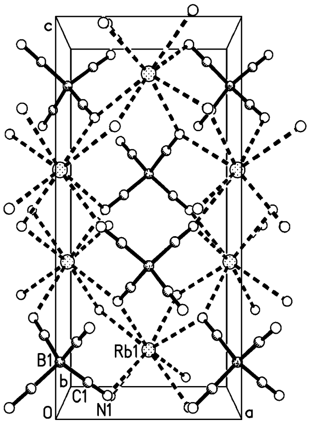

Figure 6. Perspective view of the tetragonal structure of Rb[B(CN)$_4$], showing the environment of the boron as well as the Rb atoms. The cesium, ammonium, and thallium salts have essentially the same structure.

In this structure the three-dimensional arrangement of the cations and tetracyanoborate anions leads to a coordination of eight nitrogen atoms for the cations. This MN$_8$ unit has $\bar{4}$ symmetry, as does the [B(CN)$_4$]$^-$ anion. Contrary to the linear arrangement of neighboring atoms in the cubic structures, the nitrogen atoms have a trigonal environment which is almost planar in the tetragonal tetracyanoborates (see Figure 6).[5] Structural relations exist to compounds with the Scheelite (CaWO$_4$) structure,[19] compounds with the general formula ABX$_4$ (with A = Na, K, Rb, Ag, NH$_4$, Ca, Sr, Ba, ..., B = I, Tc, Ru, Re, ..., X = O, N, F, Cl).[22,23]

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(20) Klüfers, P. *Z. Kristallogr.* **1984**, *167*, 275−286.

(21) Wittig, G.; Bille, H. *Z. Naturforsch.* **1951**, *6b*, 226.

(22) de Waal, D.; Range, K.-J. *Z. Naturforsch.* **1996**, *51b*, 1365 and references therein.

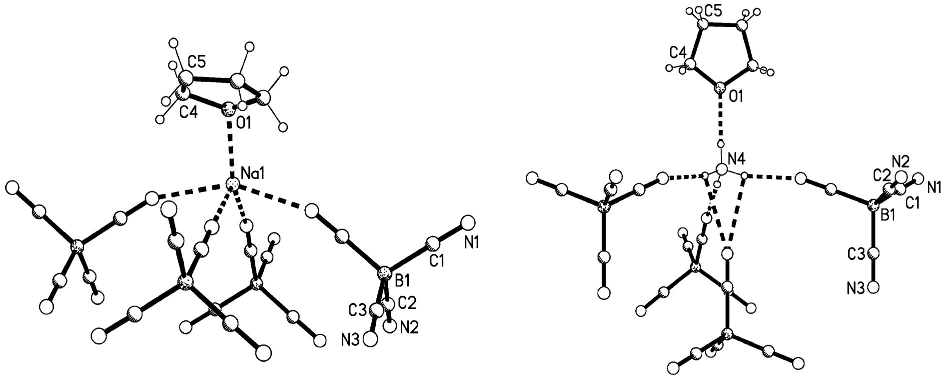

Figure 7. View of the coordination environments of the monocations in crystals of Na[B(CN)$_4$]·THF (left) and [NH$_4$][B(CN)$_4$]·THF (right).

The structures of the two tetracyanoborates which contain cocrystallized THF molecules are built up of three-dimensional networks as well. As in all the other tetracyanoborates, they contain tetrahedral [B(CN)$_4$]$^-$ anions. They are located on mirror planes; thereby 3 symmetry-independent CN groups exist per tetracyanoborate unit. Average distances within the anions are 1.589 Å (BC) and 1.136 Å (CN) in Na[B(CN)$_4$]·THF and 1.589 Å (BC) and 1.138 Å (CN) in [NH$_4$][B(CN)$_4$]·THF, values which compare well with those in the other tetracyanoborates. Deviations from an ideal tetrahedral arrangement of the cyano groups are marginal (see Table 2). Both the THF-containing compounds crystallize in the orthorhombic space group *Pnma* with the lattice constants given in Table 1. In both structures the THF molecules coordinate to the cations. Figure 7 shows the cation environment for both structures.

The sodium coordination in Na[B(CN)$_4$]·THF can be described as trigonal bipyramidal with the trigonal basis being constructed from 2 N(cyanide) and the O(THF) atoms. Because of the higher coordination number the average NaN(cyanide) distances are longer in Na[B(CN)$_4$]·THF (2.480 Å (average) compared to 2.352(2) Å in Na[B(CN)$_4$]). In the two ammonium salts we find just the opposite situation. Whereas in the THF free salt the N(ammonium) coordination number of the nearest neighbors is 8, we find 5 (as in the sodium salt·THF) for [NH$_4$][B(CN)$_4$]·THF. Contrary to the sodium salt the coordination environment of the cation in [NH$_4$][B(CN)$_4$]·THF is better described as tetragonal pyramidal with the pyramidal basis being formed by the 4 N(cyanide) atoms (see Figure 7).

As can be seen already from these differences, the two compounds are not isostructural, even though they crystallize in the same space group. This becomes clear from the arrangement within the unit cell for the different parts which are depicted in Figure 8 for comparison.

(C) Vibrational Spectroscopy. The vibrational spectrum of the tetracyanoborate anion has already been completely analyzed in our first report about its synthesis.[5] In all yet studied tetracyanoborate salts only one CN stretching mode in the region 2220−2270 cm^{-1} could be observed in the Raman spectra, because the A$_1$ and T$_2$ modes are accidentally degenerate. The reason can be seen in a lack of coupling between the CN stretching modes as no π back-bonding between the boron atom and the CN ligands occurs.

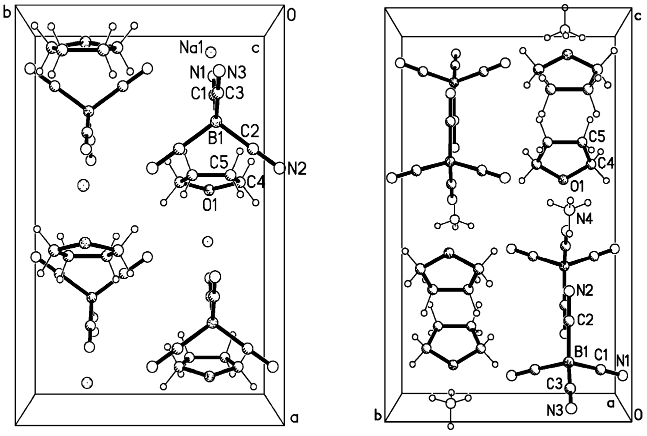

Figure 8. Comparison of the crystal structures of Na[B(CN)$_4$]·THF (left) and [NH$_4$][B(CN)$_4$]·THF (right): view of the content of the unit cells.

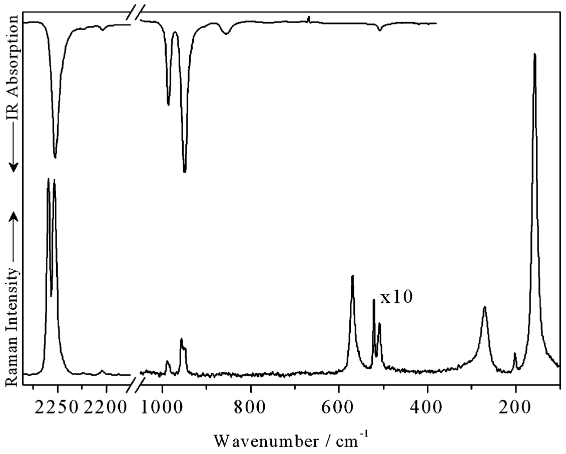

Figure 9. Raman spectrum (bottom) and IR spectrum (top) of Cu[B(CN)$_4$].

A first exception is the copper tetracyanoborate in which both CN stretching modes (2259 and 2253 cm^{-1}) are well separated into two bands in the Raman spectrum with the T$_2$ mode coinciding with the IR band (see Figure 9). Responsible for the existence of two CN stretching modes is a significant π back-bonding from copper to CN. Only the copper ion offers filled d-orbitals high enough in energy to interact with the empty π* CN orbitals, and in turn vibrational coupling in the two symmetry classes by different π electron flow can occur. In contrast, the alkali metal and

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(23) Krebs, B.; Hasse, K. *Acta Crystallogr., Sect. B: Struct. Sci.* **1976**, *32*, 1334−1337.

Table 5. Solubilties in Water of Salts with Tetrahedral Singly Charged Anions in mol·L^{-1} at Room Temperature

cation	$[B(CN)_4]^-$	$[BF_4]^-$	$[ClO_4]^-$	$[IO_4]^-$
Li^+	1.03	high[a]	>3.5[b]	
Na^+	3.89	>4.5[c]	>0.6[b]	high[a]
K^+	0.365	0.045[a]	0.1[a]	0.03[a,d]
Rb^+	0.100	0.035[a]	0.04[a]	0.02[a,d]
Cs^+	0.071	0.075[a]	0.05[a]	0.07[d]
Tl^+	0.190	high[e]	>0.4[b]	
$[NH_4]^+$	1.13	>2.0[f]	>1.7[b]	0.13[d]
Cu^+	$<1 \times 10^{-3}$			
Ag^+	3×10^{-5}	high[g]	>10[b]	

[a] Reference 27. [b] Reference 28. [c] Reference 29. [d] Reference 30. [e] Reference 31. [f] Reference 32. [g] Reference 33.

also the thallium and the silver ions do not interact because their p- or d-type orbitals are too low in energy.

A consideration of the vibrational data in Table 3 shows that the wavenumbers of the CN stretching mode increases with decreasing radii of the ammonium and alkali metal cations, because the lone pair (σ-CN orbital) is lowered in energy by the M···N−C interaction, causing a strengthening of the CN bond. Hence, the CN stretching frequency increases with the strength of the interionic contacts (Table 3) and the highest CN stretching frequency shows the lithium salt, because lithium is a good σ-acceptor and weak π-donor.

Although the cation radii of thallium and rubidium are very similar, the CN stretching frequency in $Tl[B(CN)_4]$ is 8 wavenumbers lower than in $Rb[B(CN)_4]$. The reason is seen in the repulsion of the inert $6s^2$ electron pair of Tl^+.

(D) Solubilites. The highest solubility in water of the studied tetracyanoborates is exhibited by $Na[B(CN)_4]$, and it shows the maximum within the series of alkali metal salts (Table 3). The lowest solubility of the tetracyanoborates is found for the copper and silver salts.

In the series Cs^+ to Li^+ the hydration enthalpy (kJ mol^{-1}) of the cations becomes more negative (Cs^+, −264; Rb^+, −293; K^+, −322; Na^+, −406; Li^+, −519).[24] The increase in lattice energy in the same row from Cs^+ to Li^+ is lower than the increase in hydration enthalpies; hence, the solubility is expected to rise. The observed discontinuity within the solubilities may be caused by the changing of the crystal structures and the related lattice energy (see above).

The potassium salt and ammonium salt are isostructural, and although both cation radii are close,[25,26] the ammonium salt shows a significant better solubility. This is due to the increased solvation energy by hydrogen bonding of the ammonium cation with the solvating water molecules.

Although the ionic radii of Rb^+ and Tl^+ for the coordination number 8 are very similar (161 and 159 pm),[25] the solubility of the thallium salt in water is significant higher. This can be rationalized by a weak repulsion between the inert $6s^2$ electron pair of Tl^+ and the $[B(CN)_4]^-$ ion resulting in a reduced lattice energy.

An interesting comparison of the solubilities of tetracyanoborates with salts of other tetrahedral monoanions is shown in Table 5.

The tetracyanoborates with cubic structures $Li[B(CN)_4]$, $Cu[B(CN)_4]$, and $Ag[B(CN)_4]$ are less soluble then the corresponding tetrafluoroborates, perchlorates, and periodates. The solubilities of $Cu[BF_4]$ and $Cu[ClO_4]$ are unknown, because hydrated Cu^+(aq) ions disproportionate. In the series from $K[B(CN)_4]$ to $Cs[B(CN)_4]$, the solubility decreases in the same order as observed for the comparable $[BF_4]^-$, $[ClO_4]^-$, and $[IO_4]^-$ salts but the solubilities of the tetracyanoborates are higher in general.

In general the lithium and sodium salts of the listed anions are more soluble than the other alkali metal salts. Also all ammonium salts are more soluble than the potassium salts due to hydrogen bonding in water.

(E) Thermal Stability of Tetracyanoborates. Table 3 presents the thermal properties of the tetracyanoborates with singly charged cations. They are thermally stable up to 500 °C, where the anion starts to decompose. The lower decomposition temperatures of the tetracyanoborate with organic cations are due to the decomposition of the cations.

As a first approximation, the melting points correlate with the estimated lattice energies, which has a maximum for the lithium salt and a minimum for the tetrabutylammonium salt. The repulsion of the inert $6s^2$ electron pair of Tl^+ ion is responsible for the low melting point of its salt in comparison to that of the rubidium salt.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, complete structure reports are available from the Fachinformationszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany (E-mail, crystdata@fiz-karlsruhe.de; fax, int. 49-7247-808-132; deposit nos. CSD 414556 for $Cs[B(CN)_4]$, CSD 414557 for $Cu[B(CN)_4]$, CSD 414558 for $Li[B(CN)_4]$, CSD 414559 for $Na[B(CN)_4]$, CSD 414560 for $Na[B(CN)_4]$·THF, CSD 414561 for $[NH_4][B(CN)_4]$, CSD 414562 for $[NH_4][B(CN)_4]$·THF, CSD 414563 for $Rb[B(CN)_4]$, and CSD 414564 for $Tl[B(CN)_4]$).

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