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Two routes to new anhydrous alkaline earth metal tetracyanidoborate salts

Antje Siegesmund, Gereon Behrendt, Martin Köckerling

Inorganic Solid State Chemistry, UNIVERSITY OF ROSTOCK, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany

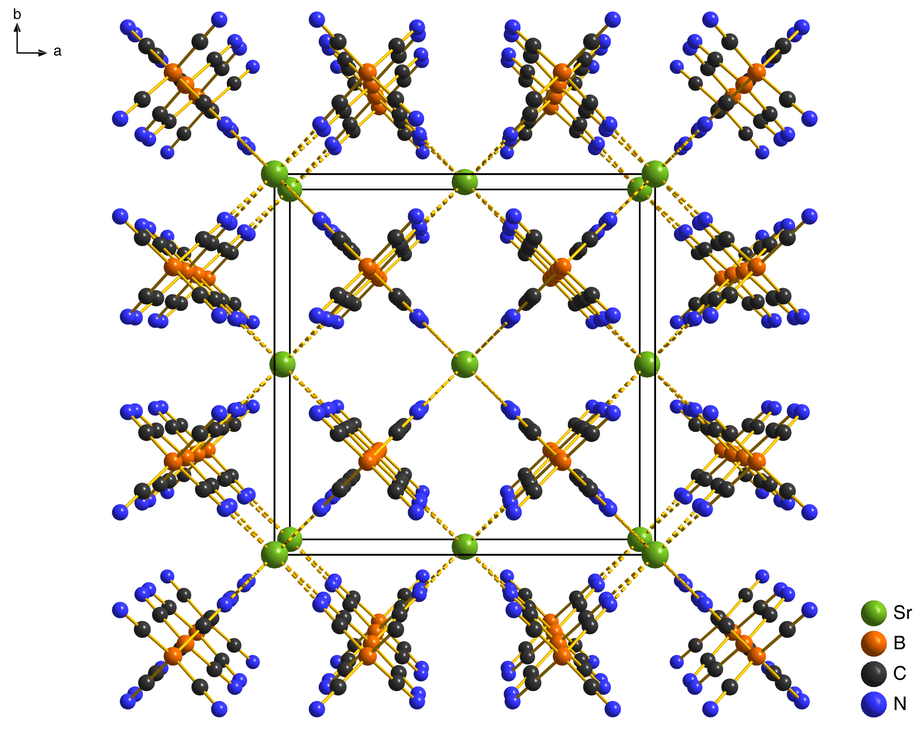

Fig. 1: View of the cubic structure of $Sr[B(CN)_4]_2$ along the *c* axis.

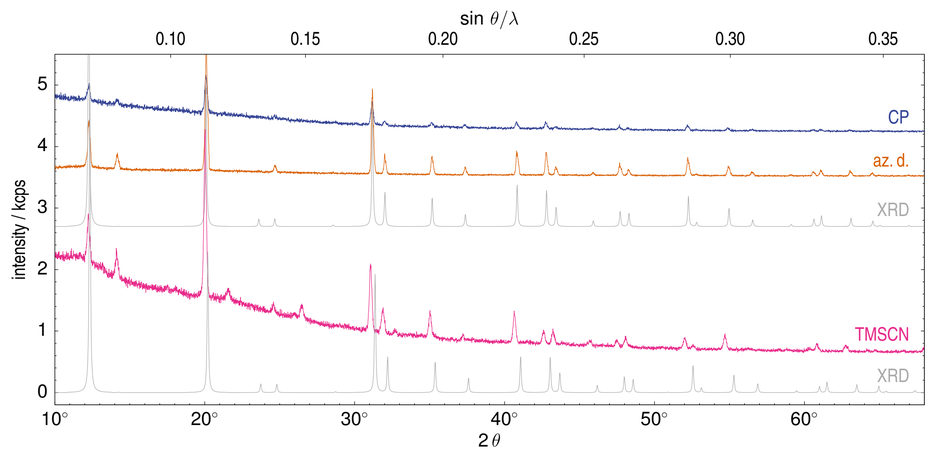

Fig. 2: X-ray powder diffraction patterns of $Sr[B(CN)_4]_2$ obtained by different methods: crystallization preparation (CP), azeotropic distillation (az. d.), calculated pattern from XRD dataset solved in $Fm\bar{3}m$, and drying with TMSCN: powder and calculated pattern from crystal; $\lambda = 154.06$ pm (Cu).

Table 1: Crystallographic data of $Sr[B(CN)_4]_2$, $\lambda = 71.073$ pm (Mo).

Crystal system	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
Cubic	$Fm\bar{3}m$ (no. 225)	12.487(2)	12.487(2)	12.487(2)	90.00	90.00	90.00	1947.0(9)
Temperature	**Crystal size (mm)**	**Z**	**2θ range**	**R_{int}**	**R_1**	**wR_2**	**Goodness of fit**	
123 K	0.30×0.30×0.30	1	5.42 – 65.3 °	0.049	0.025	0.11	0.88	

Tetracyanidoborate salts

- compound class intensely investigated since 2001[1]
- $[B(CN)_4]^-$ anion relatively large, chemically robust, and weakly coordinating: is able to stabilise unusual cations, can be used for ionic liquids
- large electrochemical windows and low viscosities: potential applications in solar cells,[2] as components of membranes,[3] and battery electrolytes[4]
- anhydrous alkaline earth metal tetracyanidoborates might possess significantly large voids potentially suitable for applications, e. g. gas absorption
- various $[E(H_2O)_x][B(CN)_4]_2$ known, first anhydrous $E[B(CN)_4]_2$ (E = Mg, Ca) characterised by infrared spectroscopy only,[5] since crystalline material difficult to obtain
- $Eu^{2+/3+}$ doped tetracyanidoborates currently tested for photoluminescence

1. Drying agent trimethylsilyl cyanide

- $4\ (CH_3)_3SiCN + [Sr(H_2O)_2][B(CN)_4]_2 \longrightarrow Sr[B(CN)_4]_2 + 2\ (CH_3)_3Si{-}O{-}Si(CH_3)_3 + 4\ HCN$
- $Sr[B(CN)_4]_2$ has CaF_2 structure type and ~12 times the volume of CaF_2 (Fig. 1, Table 1)
- similar experiments with $[Mg(H_2O)_2][B(CN)_4]_2$ and $[Ca(H_2O)_2][B(CN)_4]_2$ often polymerise out, no crystalline products

2. Azeotropic distillation with pyridine

- $[Sr(H_2O)_2][B(CN)_4]_2$: pyridine as entraining agent (water – pyridine azeotrope: $T_b = 92.6$° C) gives the same anhydrous product as above (Figs. 1, 2, Table 1)
- $[Mg(H_2O)_2][B(CN)_4]_2 \xrightarrow[\text{pyridine}]{\text{azeotr. dist.}} [Mg(H_2O)_4(Py)_2][B(CN)_4]_2 \cdot H_2O$ (Figs. 3, 4, Table 2)

Table 2: Crystallographic data of $[Mg(H_2O)_4(Py)_2][B(CN)_4]_2 \cdot H_2O$, $\lambda = 71.073$ pm (Mo).

Crystal system	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
Monoclinic	$C2/c$ (no. 15)	18.143(4)	8.969(2)	17.332(3)	90.00	95.32(1)	90.00	2808.0(17)
Temperature	**Crystal size (µm)**	**Z**	**2θ range**	**R_{int}**	**R_1**	**wR_2**	**Goodness of fit**	
123 K	10×30×40	8	2.26 – 21.1 °	0.202	0.061	0.17	0.90	

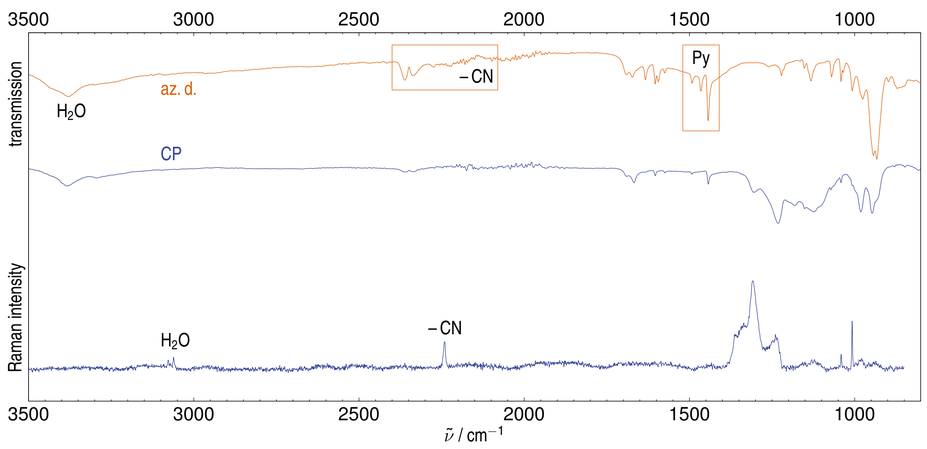

Fig. 3: Infrared and Raman spectrum of $[Mg(H_2O)_4(Py)_2][B(CN)_4]_2 \cdot H_2O$ obtained through a crystallization preparation (CP) and by azeotropic distillation (az. d.), respectively.

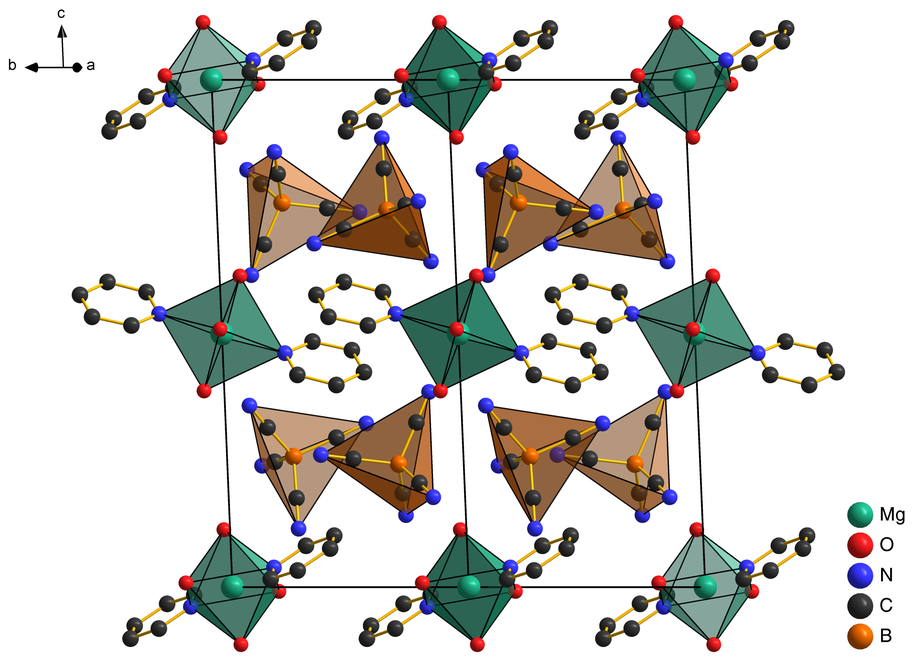

Fig. 4: Representation of the structure of $[Mg(H_2O)_4(Py)_2][B(CN)_4]_2 \cdot H_2O$ along the direction $[\bar{1}\bar{1}0]$, octahedral coordination of Mg sites and tetrahedral $[B(CN)_4]^-$ anions highlighted with polyhedra, hydrogen atoms and additional water molecules omitted for clarity.

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(3) P. Izák, M. Köckerling, U. Kragl, *Green Chem.*, 2006, **8**, 947 – 948.
(4) J.-D. Decoppet, T. Moehl, S. S. Babkair, R. A. Alzubaydi, A. A. Ansari, S. S. Habib, S. M. Zakeeruddin, H.-W. Schmidt, M. Grätzel, *J. Mater. Chem. A*, 2014, **2**, 15972 – 15977.
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