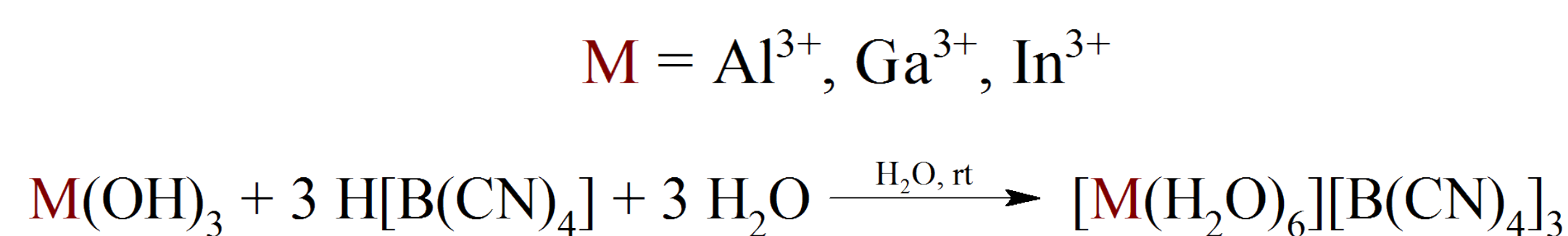


Tetracyanidoborate salts with the trivalent cations Al^{3+} , Ga^{3+} , and In^{3+}

Antje Siegesmund and Martin Köckerling

synthesis

The borat-based weakly coordinating anion $[\text{B}(\text{CN})_4]^-$ shows exceptional characteristics such as low nucleophilicity, chemical inertness, and high solubility resulting in applications in organic or inorganic chemistry.^[1]



In this study we report three new $[\text{B}(\text{CN})_4]^-$ salts which were synthesized using either acid-base reactions of freshly precipitated metal-hydroxides and the tetracyanidoborate acid.^[2] All prepared salts are easily synthesized in bulk and finally stable under air and sunlight.

analysis

vibration spectroscopy

The IR spectrum of $[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$ shows as expected one band at 2354 cm^{-1} , which originates from the $\nu_6(\text{CN})$ stretching mode. Because of the higher charge of the Al^{3+} cation. This frequency is found at much higher wavenumber than for example $\text{K}[\text{B}(\text{CN})_4]$ (2234 cm^{-1}).^[3] Furthermore the shift in this high wavenumber correlates nicely with a small CN-distance ($d = 1,140(1) \text{ Å}$). Peaks around the wavenumber 3150 cm^{-1} indicate weak hydrogen bonds.

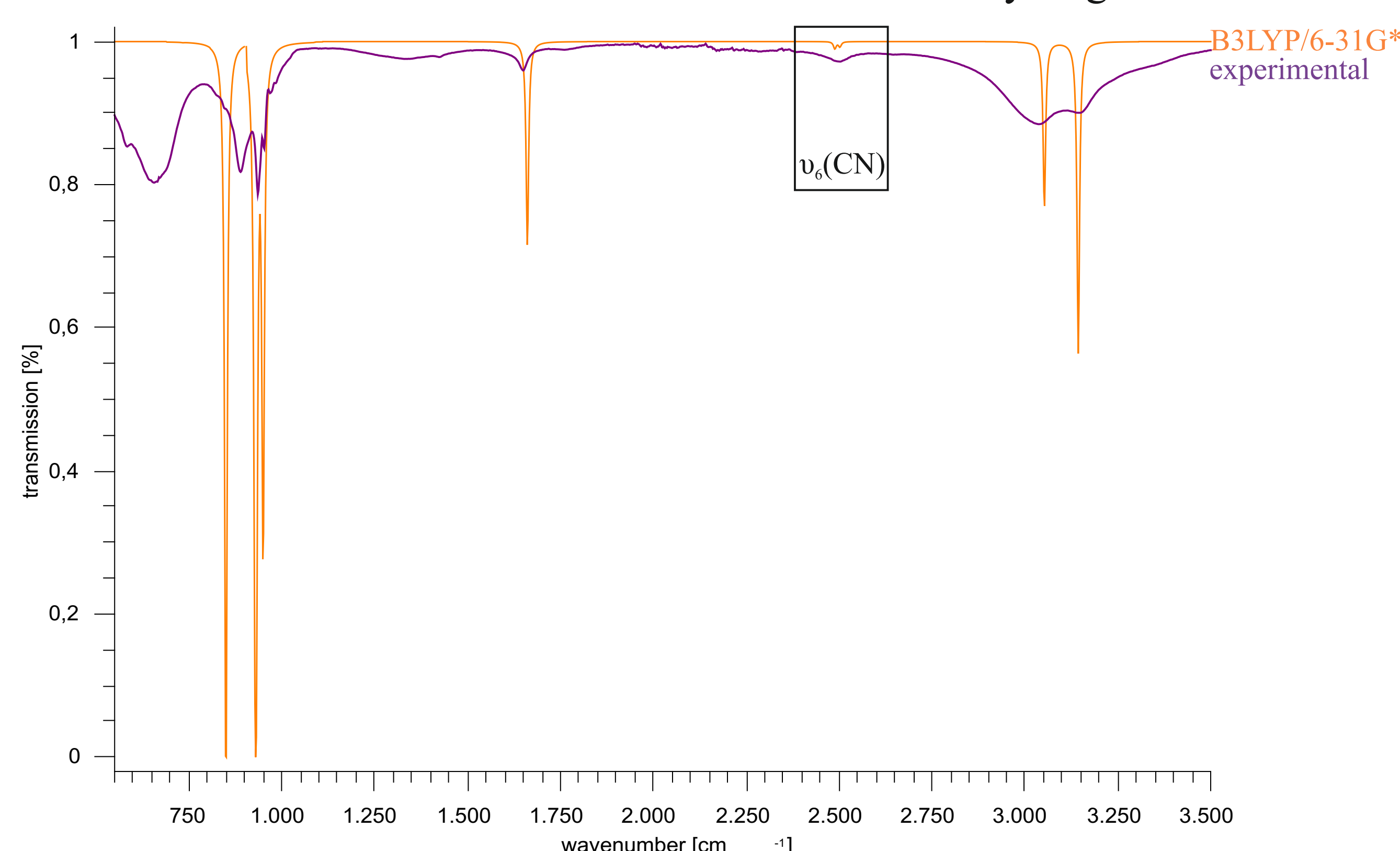


Figure 1: IR spectrum and calculated spectrum (DFT-calculation curve for B3LYP/6-31G*) for $[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$.

	$\nu_6(\text{CN})$ [cm^{-1}]	$d(\text{CN})$ [Å]
$[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	2354	1,140 (1)
$[\text{Ga}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	2364	1,141 (1)
$[\text{In}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	2385	1,145 (2)

Table 1: $\nu_6(\text{CN})$ stretching mode and CN distance.

X-RAY crystallography

The salt $[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$ crystallizes in the trigonal space group $R\bar{3}c$ with 3 formula units in the unit cell.

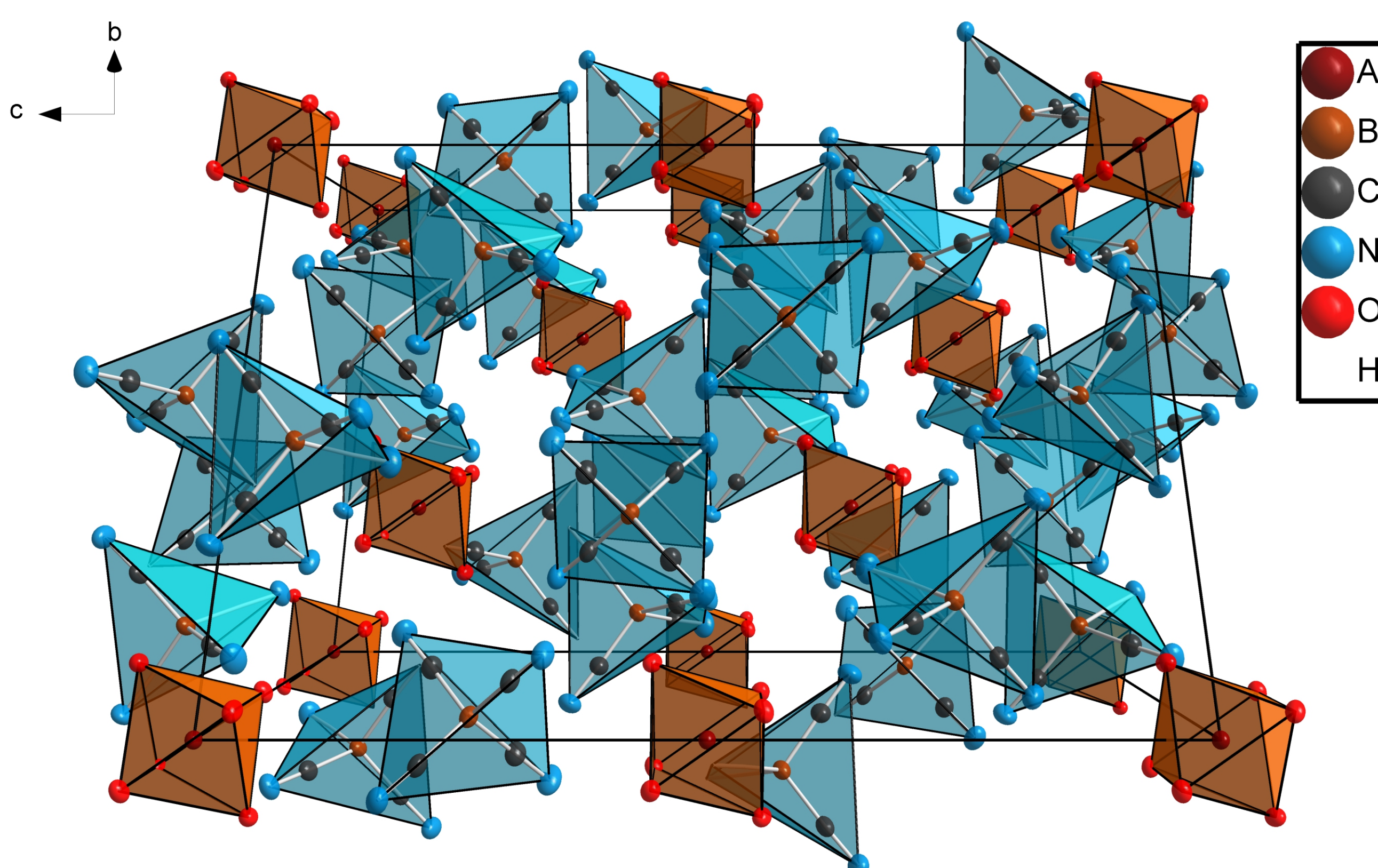


Figure 2:

View of the structure of $[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$ along the crystallographic a direction, showing the stacking of anion and cation layers.

The structure consists of discrete cations and anions units.

The Al^{3+} cation is bonded to (water) O atoms forming an octahedral coordination environment with an $\text{Al}-\text{O}$ distance of $1.878(2) \text{ Å}$.

property

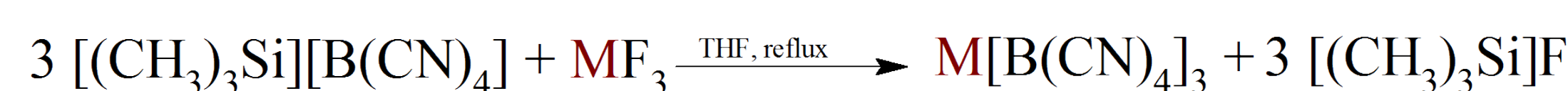
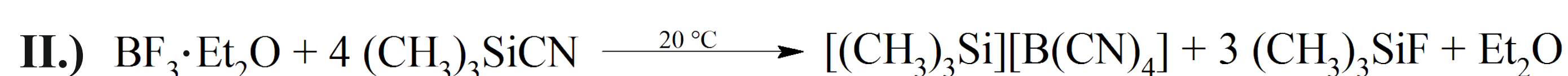
All compounds are soluble in polar solvents. They also show good solubilities in unpolar solvents such as THF (but not in hexane). This feature makes the substances suitable starting materials for organometallic chemistry.

Table 2: Solubilities in mg/100mL.

	water	ethanol	acetonitrile	acetone	THF
$[\text{Al}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	5.4	1.1	7.1	3.9	12.6
$[\text{Ga}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	4.0	1.3	8.0	3.1	8.6
$[\text{In}(\text{H}_2\text{O})_6][\text{B}(\text{CN})_4]_3$	4.5	1.6	4.3	4.8	10.6

RAMAN- and IR-results show, that water molecules can be partially replaced by acetonitrile molecules.

reaction mechanism for solventless metal tetracyanidoborate salts



In corresponding anhydrous compounds cavities may arise, which could be used for gas absorption and for catalytic purposes.

references

- [1] a.) C. Nitschke, M. Köckerling, *Inorg. Chem.* **2011**, 50, 4313–4321. b.) G. Kopplin, A. Bernsdorf, M. Köckerling, *Eur. J. Inorg. Chem.* **2014**, 319–325. c.) F. Falk, L. Hackbarth, S. Lochbrunner, H. Marciniak, M. Köckerling, *Eur. J. Inorg. Chem.* **2016**, 469–476. d.) M. Marszałek, Z. Fei, D.-R. Zhu, R. Scopelliti, P. J. Dyson, S. M. Zakeeruddin, M. Grätzel, *Inorg. Chem.* **2011**, 50, 11561–11567.
- [2] a.) T. Küppers, E. Bernhardt, C. W. Lehmann and H. Willner, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1666–1672. b.) E. Bernhardt, M. Finze and H. Willner, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1229–1234.
- [3] E. Bernhardt, G. Henkel, H. Willner, *Z. Anorg. Allg. Chem.*, 2000, 626, 560.
- [4] Gaussian 03, Revision B.03, M. J. Frisch et al. Gaussian, Inc., Pittsburgh PA, 2003.
- [5] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.