

# Structural variety of rare earth metal tetracyanidoborate salts

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# Introduction

Tetracyanidoborates are salts containing the  $[B(CN)_4]^-$  anion. The chemistry of these salts has been intensively developed in the last fifteen years because of their interesting and unique properties.<sup>[1]</sup> Investigations have been carried out regarding useful applications of the tetracyanidoborate salts, for example, for use in ionic liquids, as membranes, or as battery electrolytes.<sup>[2,3]</sup> Lately, the first tetracyanidoborate salts with a triple charged metal cation have been described, e.g.  $[Fe(H_2O)_6][B(CN)_4]_3$ .<sup>[1]</sup>

To improve the knowledge about tetracyanidoborate salts with trivalent metal cations, here we present the syntheses and structures of rare earth metal (RE) tetracyanidoborate hydrates. Three groups of compounds were obtained by crystallization from aqueous solutions, namely,  $[RE(H_2O)_8][B(CN)_4]_3 \cdot nH_2O$  (structure I),  $[RE(H_2O)_7[\kappa^1N-B(CN)_4]][B(CN)_4]_2$  (structure II) for RE = Y, Tb, Dy, Ho, Er, Tm, Yb, Lu and  $n \leq 3$  and  $[RE\{\mu^2 - B(CN)_4\}\{\kappa^1 N - B(CN)_4\}_2(H_2O)_5] \cdot nH_2O$  for  $RE = Ce, La, Pr, Nd, Sm, Eu, Gd and n \leq 0.5$  (structure III).<sup>[4,5]</sup>

### Structures

structure I	[ <i>RE</i> <sup>III</sup> (H <sub>2</sub> O) <sub>8</sub> ][B(CN) <sub>4</sub> ] <sub>3</sub> *3H <sub>2</sub> O
	mulhum munum
Multhurn	RE = Tb

The X-ray powder diffraction patterns indicate that tetracyanidoborates of the rare earth metals crystallize in at least three different structures, which correspond to three different chemical compositions. For the light rare earth metal tetracyanidoborates one structure was found. All heavy rare earth metal tetracyanidoborates exist in at least two structures. The corresponding powder patterns of two randomly selected examples for each structure type are shown in Figure 1.

# Preparation

The tetracyanidoboronic acid was obtained through a cation-exchange process according to ref.<sup>[6]</sup>. The hydroxides Ce(OH)<sub>3</sub>, Pr(OH)<sub>3</sub>, Ho(OH)<sub>3</sub>,  $Er(OH)_3$  and  $Yb(OH)_3$  were precipitated from aqueous solutions of chlorides with concentrated NH<sub>3</sub> and were used directly.

Samples of rare earth oxides (*RE* = Nd, Sm, Eu, Gd, Tb, Dy, Tm, Lu, Y, La) or hydroxides (*RE* = Ce, Pr, Ho, Er, Yb) were added to an equivalent amount of H[B(CN)<sub>4</sub>] •  $nH_2O$  in small portions. The mixtures were stirred and heated with a water bath. The reactions were complete at pH 7.0. After filtration the solvents were slowly evaporated at room temperature to afford clear single crystals for X-ray structure determinations. The colors of the crystals correlate with the colors of the rare earth cations.

Three groups of compounds differerent in their amount of coordinated and cocrystallized water molecules were obtained. After crystallization, a slow structure reorganization of structure I with the loss of water molecules finally forms structure II.





**Figure 1.** X-ray powder patterns of two examples of structure I (Tb, Y), structure II (Er, Lu) and structure III (Eu, Gd).

(structure II).

cation in **1** (structure I).

Suitable crystals for single-crystal X-ray structure determination were obtained from aqueous solutions of the Tb (1), Dy, Er (2), Y and Ce compound (3). Structure I (Tb, Dy and Y) contains isolated  $[RE(H_2O)_8]^{3+}$  cations for RE = Tb, Dy and Y, discrete  $[B(CN)_{4}]^{-}$  anions and cocrystallized solvent molecules. Similarly, structure II (Er) contains isolated erbium cations coordinated by the O atoms of seven water molecules and the N atom of one  $[B(CN)_4]^-$  anion. In structure III (Ce) the cerium cations are not discrete, but form 1D-chains with bridging  $[B(CN)_4]^-$  anions.

15 20 25 30 35 40 45 50 55 60 65 70 All three structures have monoclinic symmetry, structure I of the space group C2/c, structure II and III of the space group  $P2_1/n$ . In all structures the asymmetric unit contains two formula units shown in Figure 2 (1), 3 (2) and 4 (3). In the structures I and II, the coordination number of the rare earth metal cations is eight, whereas in structure III, the

(structure III).

coordination number is nine. The O5N4 coordination environment of the cerium cations can be described as a distorted tricapped trigonal prism (see Figure 5). Similarly the coordination environment of compound 2 can be described as a distorted bicapped trigonal prism (see Figure 6), whereas in compound **1** as distorted square antiprismatic (see Figure 7).





Figure 2. View of the molecular structure of 1 (structure I). Figure 3. View of the molecular structure of 2 (structure II). Figure 4. View of the molecular structure of 3 (structure III).

## Reference

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