

Sample Preparation:

Sodium triphenylcyanoborate (Apolda, Germany) was in a hydrated crystalline form, $\text{NaPh}_3\text{BCN} \times 2.5 \text{H}_2\text{O}$. Cesium, rubidium and potassium triphenylcyanoborates were prepared by addition of corresponding metal chlorides to an aqueous solution of sodium triphenylcyanoborate; a concentrated KCl solution was employed in case of potassium. Rubidium and cesium precipitates were rinsed with cold water; no washing was in the case of potassium salt. Potassium triphenylcyanoborate is well soluble in water, while rubidium and cesium compounds have limited solubility. All these compounds are well soluble in alcohols, acetonitrile, and dimethylsulfoxide. Various solvents were tried for crystallization. For potassium triphenylcyanoborate, all alcohols afford the same water-containing crystals (this is supported by FTIR and X-ray data); all rubidium crystals contain no solvent molecules. Relatively large cesium triphenylcyanoborate crystals grow from methanol; they are quickly becoming opaque on open air. Similar behavior was observed for the same compound from aqueous solutions. Crystals suitable for X-ray study were grown from methanol solutions and were sealed with epoxy resin on a glass fiber (Rb, Cs) or on a loop (K) immediately after removal from the mother liquor.

Bruker X2S diffractometer equipped with Breeze CCD detector and Rigaku AFC-7S diffractometer were used for crystal structure determination. $\text{MoK}\alpha$ radiation (0.71073 \AA) was used in all experiments. Crystal structures were solved by direct methods using SHELXS-97¹⁷ or SIR-2004¹⁶; all refinement was performed by SHELXL-97¹⁷. All non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. The H atoms of water molecule for **1** were found from difference map and refined with O-H distance restraint (0.85 \AA) and $U(\text{H})=1.2U_{\text{eq}}(\text{O})$; all other hydrogen atoms in **1** were refined using riding model resulting in C-H distances of $0.94\text{-}0.96 \text{ \AA}$. Non-crystallographic symmetry in **2** resulted in lower quality of refinement: therefore, thermal parameters of triphenylcyanoborate ions were restrained. Restrained were also parameters of poorly defined disordered methanol molecule in structure **3**.

Bruker XP, Mercury 2.4 and CorelDraw X5 were used for graphics preparation.

Spectral Data:

NMR spectra were recorded at Bruker DPX-300 spectrometer; IR spectra both as ATR and in mineral oil mulls were measured on Thermo-Nicolet Nexus 470, Raman spectra of solid crystals were recorded at RamanSystems 2.0 instrument. NMR spectra of dimethylsulfoxide solutions of alkali metal triphenylcyanoborates show only phenyl proton signals, with a visible increase of the water signal intensity in the case of cesium, sodium, and potassium compounds.

FT-IR spectra of neat triphenylcyanoborates (corrected ATR on ZnSe) and mineral oil mulls both show intense signal at 2176 cm^{-1} ($\nu(\text{C}\equiv\text{N})$), along with group of strong signals at $3060, 2995, 1583, 1483, 1429, 1155, 760, 739, 704, \text{ and } 615 \text{ cm}^{-1}$. Raman spectra show a very strong peak at $993\text{-}996 \text{ cm}^{-1}$, with weaker peaks at $1579, 1180, 1147, 1114, 614, \text{ and } 255\text{-}260 \text{ cm}^{-1}$ and weak CN vibration band at around 2160 cm^{-1} .

Methanol peaks at $3350 \text{ and } 2832, 1031$ were observed in CsPh_3BCN crystals grown from methanol; these peaks quickly disappear on drying the sample. Potassium compound shows a peak at 1606 cm^{-1} attributed to a bridged water molecule. Similar peaks for water were observed for sodium compound¹³.

Table S1 - Crystal Data and Details of the Structure Determination

	I	II	III
Formula	C ₃₈ H ₃₂ B ₂ K ₂ N ₂ O	C ₃₈ H ₃₀ B ₂ N ₂ Rb ₂	C ₃₈ H ₃₀ B ₂ N ₂ Cs ₂ xCH ₃ OH
Formula Weight	632.48	707.20	834.12
Crystal System	Tetragonal	Orthorhombic	Monoclinic
Space group	P-421c (No.114)	Pbca (No. 61)	C2/c (No. 15)
a, Å	17.1789(16)	27.406(6)	23.317(5)
b, Å	17.1789(16)	15.760(3)	18.586(4)
c, Å	11.4979(10)	15.649(3)	9.2090(18)
β, °			106.36(3)
V, Å ³	3393.2(5)	6759(2)	3829.3(15)
Z	4	8	4
D _{calc} , g/cm ³	1.238	1.390	1.447
μ(MoKα), mm ⁻¹	0.311	2.924	1.934
F(000)	1320	2848	1640
Crystal Size, mm	0.6 x 0.3 x 0.13	0.3 x 0.12 x 0.07	0.2 x 0.15 x 0.15
Temperature (K)	297	294	293
Radiation, Å	0.71073 MoKa	0.71073 MoKa	0.71073 MoKa
θ _{min} , θ _{max} , °	2.4, 25.0	2.6, 25.0	2.8, 25.3
Dataset	-17: 20 ; -20: 20 ; -13: 12	0: 32 ; -18: 0 ; -18: 0	0: 27 ; -22: 22 ; -11: 10
Total, Unique Data, R(int)	21626, 3004, 0.04	5982, 5982, 0.05	3452, 3452, 0.04
Observed data [I > 2.0 sigma(I)]	2706	2407	2868
Nref, Npar	3004, 222	5982, 398	3452, 220
R, wR2, S	0.0310, 0.0767, 1.03	0.0548, 0.1151, 0.85	0.0360, 0.0946, 1.06
Max. and Av Shift/Error	0.00, 0.00	0.00, 0.00	0.00, 0.00
Min. and Max.	-0.11, 0.19	-0.33, 0.39	-1.10, 0.70