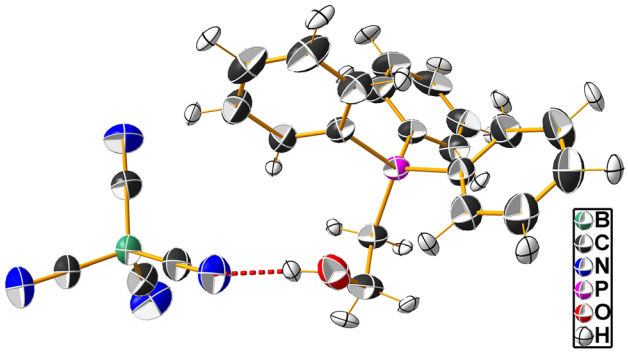
Anke Topp, Lukas Konstantin and Martin Köckerling*

Crystal structure of 2-hydroxyethyl-triphenylphosphonium tetracyanidoborate, $C_{24}H_{20}BN_4OP$



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Abstract

$C_{24}H_{20}BN_4OP$, monoclinic, $P2_1/n$ (no. 14), a = 14.1418(2) Å, b = 10.5821(1) Å, c = 15.4684(2) Å, β = 94.622(1)°, V = 2307.32(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0203, wR_{ref} = 0.0408, T = 293(2) K.

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The molecular structure is shown in the figure[12]. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

Equivalent amounts of $K[B(CN)_4]$ (250 mg, 1.624 mmol) and commercial [nPrPh$_3$P]Br (626 mg), which was shown after the X-ray structure determination to contain a larger amount of 2-hydroxyethyl-triphenyl-phosphonium bromide as "impurity", have been separately dissolved in acetonitrile (15 ml). Both colourless solutions were combined and stirred for approximately 5 min. The precipitated KBr was removed by centrifugation. The solvent of the decanted liquid was evaporated under reduced pressure by using a rotary evaporator. A colourless solid remained, which has been washed with diethylether (20 ml) and dried under reduced pressure. The recrystallization from CH_3CN resulted in the growth of single crystals.

Table 1: Data collection and handling.

Crystal:	Colourless irregular block
Size:	0.42 × 0.37 × 0.31 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.14 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	27.0°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	33743, 4994, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4,120
$N(param)_{refined}$:	460
Programs:	Bruker,[1] SHELX,[2] Olex2[5]

2 Experimental details

X-ray diffraction data were collected on a Bruker–Nonius Apex-II diffractometer. The Multi-scan method (SADABS) was used for absorption correction.[1] The structure solution and first structure refinements were carried out using the SHELX suite of programs (version 2014-2).[2] The final refinement of the structure were done applying the Hirshfeld atom refinement (HAR) method[3] via the NoSpherA2 procedure[4] within Olex2 (vers. 1.5).[5] The full asymmetric unit as obtained from the Shelx refinements was used as the initial fragment for HAR refinements. The ORCA quantum chemistry program package (vers. 6.0.1)[6] was used for wave function calculations. According to this procedure the hydrogen atoms were refined anisotropically.

3 Comment

Salts with the tetracyanidoborate anion, $[B(CN)_4]^-$, have attracted significant scientific and commercial interest

***Corresponding author: Martin Köckerling**, Anorganische Festkörperchemie, Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, D-18059, Rostock, Germany, E-mail: martin.koeckerling@uni-rostock.de. https://orcid.org/0000-0001-7666-6990
Anke Topp and Lukas Konstantin, Anorganische Festkörperchemie, Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, D-18059, Rostock, Germany, E-mail: anke.topp@biotronik.com (A. Topp), lukas.konstantin@uni-rostock.de (L. Konstantin)

due to their extraordinary properties.[7,8] These include high thermal and electrochemical stability as well as weak coordination abilities, making them useful e.g. in supercapacitors or dye-sensitive solar cells.[9,10] High temperature stability has been reported especially for tetracyanidoborates with phosphonium-based cations.[11]

This contribution reports about the so far not published room-temperature structure of 2-hydroxyethyl-triphenyl-phosphonium tetracyanidoborate. The asymmetric unit of the title structure contains one 2-hydroxyethyl-triphenyl-phosphonium cation and one tetracyanidoborate anion, i.e. one molecular formula. The bond lengths and angles within the two ions are within the expected ranges. The arrangement of the C atoms around B1 deviates from ideal T_d with C–B1–C angles ranging from 108.33(7)° to 111.20(7)°. The H atom attached to O1 is involved in a hydrogen bond to one of the N atoms of the anion shown as red dashed line in the figure. The O1···N1 distance is 2.9147(9) Å. The ions are arranged within the unit cell, such that chains of anions and cations exist, which are arranged in rows running along the crystallographic *b* direction.

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