

Pentaaquadisodium bis(triphenylcyanoborate)
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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$ R factor = 0.048 wR factor = 0.140

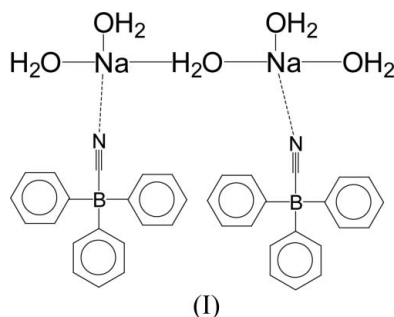
Data-to-parameter ratio = 16.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the crystal structure of the title compound, $[\text{Na}_2(\text{H}_2\text{O})_5]-(\text{C}_{19}\text{H}_{15}\text{BN})_2$, the Na atom is octahedrally coordinated by three water molecules and three N atoms of triphenylcyanoborate anions. The basic structural unit is composed of two octahedra sharing a common face, and this unit is connected by a common edge with the next unit, forming an infinite chain along the crystallographic c axis.

Comment

The triphenylcyanoborate anion (as a sodium salt, 'caesignost') has been used as a gravimetric reagent for the determination of caesium, thallium and large organic cations (Havir, 1961; Bauman, 1968). The goal of this study was the investigation of the crystal structure of the hydrated sodium salt of triphenylcyanoborate, (I), using X-ray structure analysis and vibrational spectroscopy.



The environment of the sodium ion is a distorted octahedron, with three water molecules (O1, O2, O3) and one N atom of a cyano group in the equatorial plane, while two cyano groups are axially positioned (Fig. 1 and Table 1). Two such octahedra share a common face defined by water molecule O2 (located on a twofold axis) and atoms N1 and N1B, forming a basic structural unit that is repeated by an inversion operation through a common edge (of two N atoms) generating an infinite chain along the c axis (Figs. 2 and 3). The resulting structure is additionally stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{C}(\text{aromatic})$ hydrogen bonds (Table 2).

The high level of hydration of the sodium salt explains its good solubility in water, which makes it a suitable reagent for caesium precipitation from aqueous solutions.

Experimental

Sodium triphenylcyanoborate was received from Apolda (Germany) and recrystallized from water. Karl Fischer titration results: H_2O calculated 13.4%; found 13.2%. Two groups of $\text{O}-\text{H}$ vibrations for bridging and terminal water molecules are observed in the IR spectrum.

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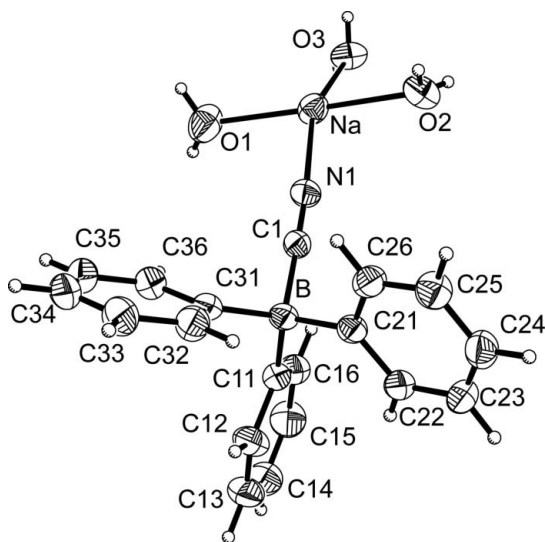


Figure 1
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

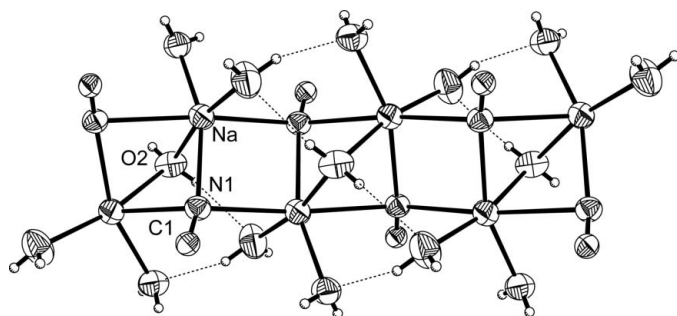


Figure 2
The coordination polyhedra around the Na⁺ ions, with hydrogen bonds (dashed lines) between coordinated water molecules. For clarity, the triphenylborate units of the anions have been omitted.

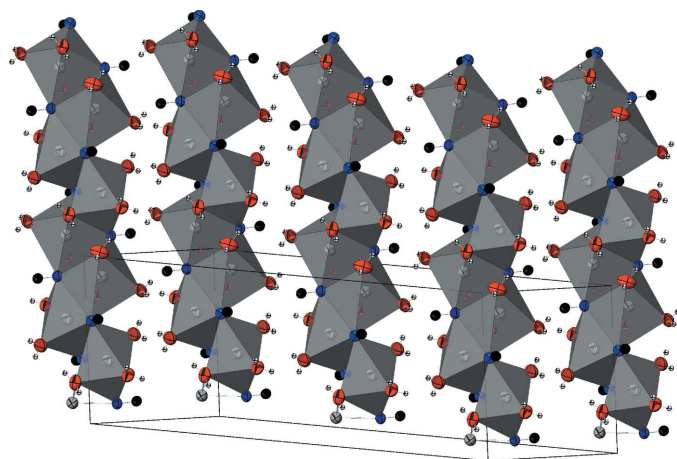


Figure 3
The three-dimensional arrangement of octahedra running along the *c* axis. Each Na⁺ ion is surrounded by three water molecules (shown in red) and three N atoms (shown in blue) from triphenylcyanoborate anions (omitted for clarity).

Crystal data

[Na₂(H₂O)₅](C₁₉H₁₅BN)₂
M_r = 672.32
 Monoclinic, *C*2/*c*
a = 26.200 (5) Å
b = 14.719 (3) Å
c = 9.5537 (19) Å
 β = 96.12 (3)°
V = 3663.4 (13) Å³
Z = 4

D_x = 1.219 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 30–35°
 μ = 0.10 mm⁻¹
T = 293 (2) K
 Prism, colourless
 0.50 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-7S diffractometer
 ω scans
 Absorption correction: ψ scan
 (TEXSAN; Molecular Structure Corporation, 1999)
T_{min} = 0.95, *T_{max}* = 0.98
 4207 measured reflections
 4206 independent reflections
 3134 reflections with *I* > 2σ(*I*)

R_{int} = 0.03
 θ_{max} = 27.5°
h = 0 → 34
k = −19 → 19
l = −12 → 12
 3 standard reflections
 every 150 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.140
S = 1.02
 4206 reflections
 253 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0735*P*)² + 0.6203*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.25 e Å⁻³
 Δρ_{min} = −0.18 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0052 (8)

Table 1

Selected geometric parameters (Å, °).

Na—O1	2.3118 (18)	Na—N1	2.5455 (15)
Na—O3	2.3488 (16)	Na—N1 ⁱ	2.7034 (16)
Na—O2	2.3869 (17)	Na—N1 ⁱⁱ	2.7097 (16)
O1—Na—O3	103.87 (7)	O2—Na—N1 ⁱ	91.46 (5)
O1—Na—O2	169.03 (6)	N1—Na—N1 ⁱ	97.99 (5)
O3—Na—O2	85.43 (5)	O1—Na—N1 ⁱⁱ	107.39 (6)
O1—Na—N1	89.83 (7)	O3—Na—N1 ⁱⁱ	83.51 (5)
O3—Na—N1	161.17 (6)	O2—Na—N1 ⁱⁱ	79.11 (5)
O2—Na—N1	82.52 (5)	N1—Na—N1 ⁱⁱ	80.05 (6)
O1—Na—N1 ⁱ	81.79 (6)	N1 ⁱ —Na—N1 ⁱⁱ	170.53 (5)
O3—Na—N1 ⁱ	96.73 (5)		

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O3 ⁱⁱⁱ	0.85 (2)	2.04 (2)	2.858 (2)	160 (2)
O1—H1B...C16 ⁱⁱ	0.83 (2)	2.65 (3)	3.352 (3)	143 (2)
O2—H2...O1 ^{iv}	0.82 (2)	2.28 (2)	3.001 (2)	146 (2)
O3—H3A...C26 ⁱⁱ	0.81 (2)	2.37 (2)	3.142 (2)	159 (2)
O3—H3B...C31 ⁱ	0.82 (2)	2.42 (2)	3.214 (2)	161 (2)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $x, -y + 1, z + \frac{1}{2}$; (iv) $x, -y + 1, z - \frac{1}{2}$.

All H atoms of phenyl groups were located in a difference map and allowed to ride on their parent C atoms, with C—H = 0.91–1.02 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C). Water H atoms were located in a Fourier map and refined with restrained bond lengths [O—H = 0.83 (2) Å and *U*_{iso}(H) = 1.3*U*_{eq}(O)].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

The packing diagram given in Fig. 3 was prepared by the program *ATOMS* (Dowty, 2004) kindly provided by Dr B Perić, Rudjer Boskovic Institute, Zagreb, Croatia.

References

- Bauman, A. (1968). *Talanta*, **15**, 185–188.
Dowty, E. (2004). *ATOMS*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Havir, J. (1961). *Collect. Czech. Chem. Commun.* **26**, 1775–1783.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.