Pentaaquadisodium bis(triphenylcyanoborate) (caesignost)

Alexander Y. Nazarenko[a]* and Victor Nemykin[b]

[a]Chemistry Department, State University of New York, College at Buffalo, 1300 Elmwood Ave, Buffalo, NY 14222-1095, USA, and [b]Department of Chemistry, University of Minnesota Duluth, Minnesota 55812-2496, USA

Correspondence e-mail:
nazareay@buffalostate.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
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, $[Na_2(H_2O)_5]$-$(C_{19}H_{15}BN)_2$, 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.

(I)
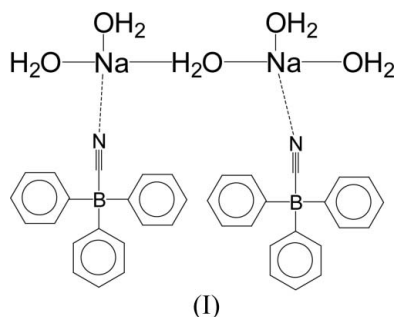
The environment of the sodium ion is a distorted octahedron, with three water molecules (O1, O2, O3) and one N atom of a cyano group in the equatorial plane, while two cyano groups are axially positioned (Fig. 1 and Table 1). Two such octahedra share a common face defined by water molecule O2 (located 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 O—H$\cdots$O and O—H$\cdots$C(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 O—H vibrations for bridging and terminal water molecules are observed in the IR spectrum.
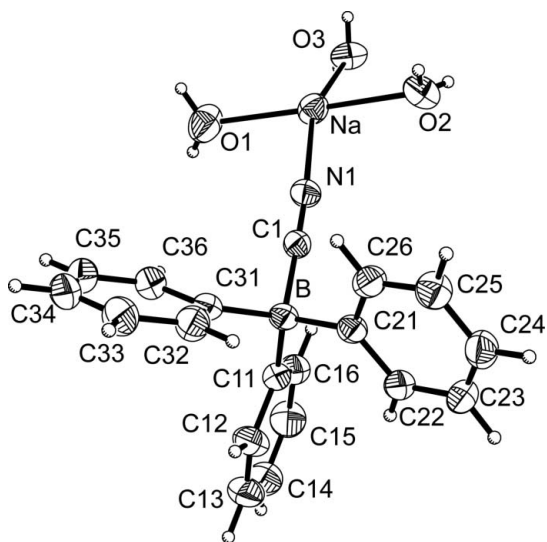
Figure 1
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
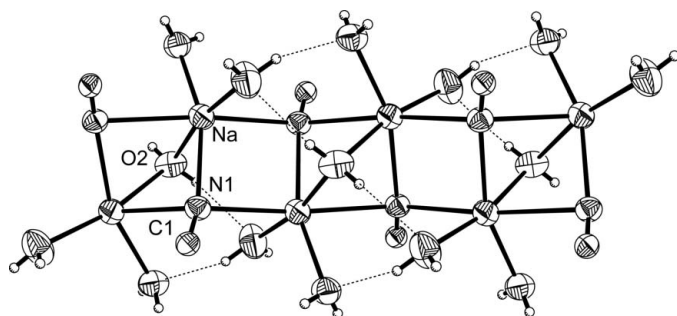

Figure 2
The coordination polyhedra around the Na^I ions, with hydrogen bonds (dashed lines) between coordinated water molecules. For clarity, the triphenylborate units of the anions have been omitted.
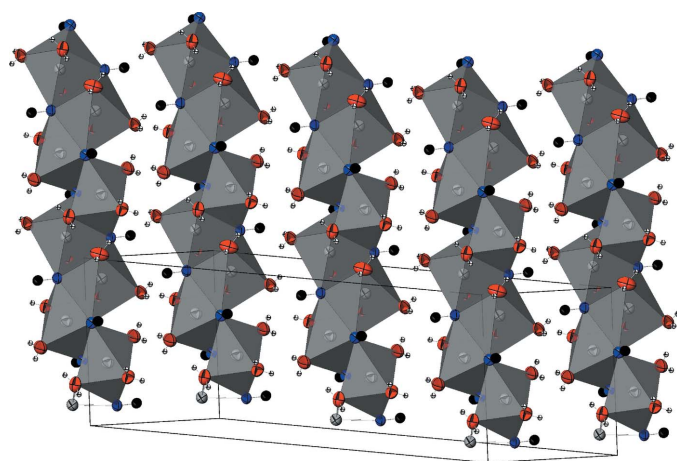

Figure 3
The three-dimensional arrangement of octahedra running along the c axis. Each Na^I ion is surrounded by three water molecules (shown in red) and three N atoms (shown in blue) from triphenylcyanoborate anions (omitted for clarity).

Crystal data

$[Na_2(H_2O)_5](C_{19}H_{15}BN)_2$
$M_r = 672.32$
Monoclinic, $C2/c$
$a = 26.200 (5)$ Å
$b = 14.719 (3)$ Å
$c = 9.5537 (19)$ Å
$\beta = 96.12 (3)°$
$V = 3663.4 (13)$ Å^3
$Z = 4$

$D_x = 1.219$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 30–35°$
$\mu = 0.10$ mm^{-1}
$T = 293 (2)$ K
Prism, colourless
$0.50 \times 0.30 \times 0.25$ 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 $I > 2\sigma(I)$

$R_{int} = 0.03$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 34$
$k = -19 \rightarrow 19$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: none

Refinement

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

$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 0.6203P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ 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, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O3^{iii}	0.85 (2)	2.04 (2)	2.858 (2)	160 (2)
O1—H1$B\cdots$C16^{ii}	0.83 (2)	2.65 (3)	3.352 (3)	143 (2)
O2—H2$\cdots$O1^{iv}	0.82 (2)	2.28 (2)	3.001 (2)	146 (2)
O3—H3$A\cdots$C26^{ii}	0.81 (2)	2.37 (2)	3.142 (2)	159 (2)
O3—H3$B\cdots$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 $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were located in a Fourier map and refined with restrained bond lengths [O—H = 0.83 (2) Å and $U_{iso}(H) = 1.3U_{eq}(O)$].

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.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.