

A novel heterocyclic compound: *catena*-poly[[[diaquasodium(I)]-di- μ - aqua] hemi(1,5-dihydroxy-4,8,9- trioxa-2,6-diazabicyclo[3.3.1]nona- 2,6-diene-3,7-diolate)]

Rui-Qin Fang,^a Zhu-Ping Xiao,^{a,b} Ping Cao,^a Da-Hua Shi^a
and Hai-Liang Zhu^{a*}

^aSchool of Life Sciences, State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing 210093, People's Republic of China, and ^bDepartment of Chemistry, Shangrao Normal College, Jiangxi, People's Republic of China
Correspondence e-mail: zhuhl@nju.edu.cn

Received 6 January 2007

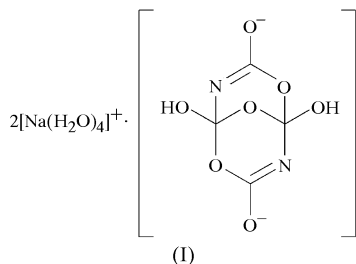
Accepted 15 January 2007

Online 14 April 2007

In the title compound, $\{[\text{Na}(\text{H}_2\text{O})_4]_2(\text{C}_4\text{H}_2\text{N}_2\text{O}_7)\}_n$, the 1,5-dihydroxy-4,8,9-trioxa-2,6-diazabicyclo[3.3.1]nona-2,6-diene-3,7-diolate anion lies across a twofold axis in the space group $C2/c$; there are two independent Na sites, one on a twofold axis and the other on a centre of inversion. Hydrogen bonds link the $\{[\text{Na}(\text{H}_2\text{O})_4]^+\}_n$ chains and diolate anions into a three-dimensional framework.

Comment

The synthesis of organic compounds from common inorganic materials has long attracted attention because of its potential significance in pharmacology, agriculture and the chemical industry (Gleix, 1954; Achille *et al.*, 1998). To our knowledge, however, there have been no reports of the formation of heterobicyclic compounds from a metal carbonate with ammonia in a single-step process. Recently, we have synthesized from sodium carbonate and aqueous ammonia by a hydrothermal method the novel heterocyclic title compound, (I), whose structure is reported here.



The title compound crystallizes in the centrosymmetric space group $C2/c$ with two independent Na sites, one on a twofold axis and the other on an inversion centre, and a 1,5-dihydroxy-4,8,9-trioxa-2,6-diazabicyclo[3.3.1]nona-2,6-diene-

3,7-diolate anion located across a twofold axis (Fig. 1). Both Na sites are six-coordinated by O atoms from water molecules, forming distorted octahedra with Na—O distances in the range 2.395 (3)–2.458 (3) Å, which are comparable to those observed in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (El Saffar, 1968) and $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (Betzler *et al.*, 1982). Neighbouring sodium octahedra share edges *via* two water molecules, forming infinite chains parallel to [001] (Fig. 1). Similar arrangements of hydrated sodium ions are found in $\text{Na}_2\text{C}_4\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Ranganathan & Kulkarni, 2002) and $\text{NaHC}_4\text{O}_4 \cdot \text{H}_2\text{O}$ (Petrova *et al.*, 2006).

The 1,5-dihydroxy-4,8,9-trioxa-2,6-diazabicyclo[3.3.1]nona-2,6-diene-3,7-diolate anion contains a novel heterocyclic skeleton. All the bond lengths are in their normal ranges. The C—O single-bond lengths [C1—O1, C1—O2, C2—O3, C2—O4 and C2—O1A; the suffix *A* denotes the symmetry code ($-x + 1, y, -z + \frac{3}{2}$)] are between 1.366 (5) and 1.495 (4) Å,

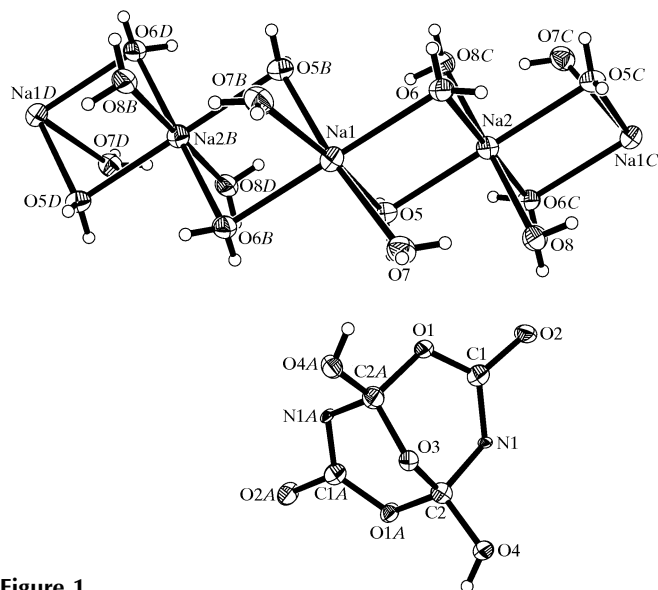


Figure 1
The crystal structure of (I), shown with 35% probability displacement ellipsoids. [Symmetry codes: (A) $-x + 1, y, -z + \frac{3}{2}$; (B) $-x, y, -z + \frac{3}{2}$; (C) $-x, -x, -y, -z + 1$; (D) $x, -y, \frac{1}{2} + z$.]

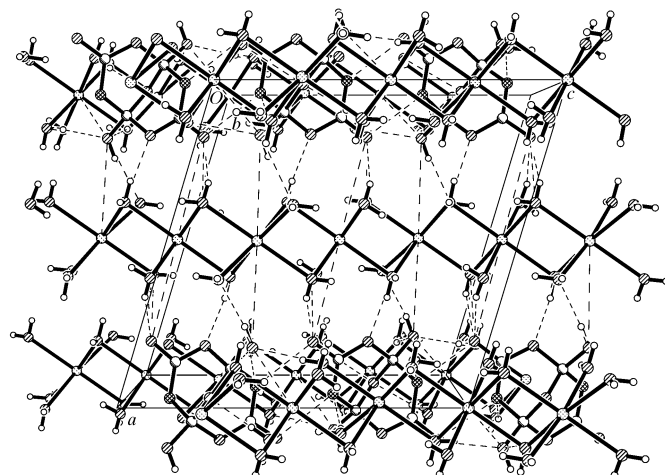


Figure 2
The crystal packing of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

while the C1=N1 and C2–N1 bond lengths are 1.384 (4) and 1.507 (4) Å, respectively. The O2–C1–O1, O2–C1–N1 and O1–C1–N1 angles are close to 120°, while the O3–C2–O4 and O1A–C2–N1 angles are 111.8 (3) and 108.3 (3)°, respectively. In the diolate anion, atoms N1, O1, N1A and O1A constitute an equatorial plane, with a mean deviation from the mean plane of 0.0781 Å. Atoms O3, O4 and C2 are located above the plane at distances of 1.7111, 1.6691 and 0.8775 Å, and atoms O2 and C1 atoms are below the plane at distances of 0.9588 and 0.3207 Å, respectively.

All the H atoms of hydroxy groups and water molecules contribute to the formation of a hydrogen-bond network (Table 1), and O–H···O and O–H···N hydrogen bonds link the diolate anions and the {[Na(H₂O)₄]⁺}_n chains into a three-dimensional framework (Fig. 2).

Experimental

Anhydrous sodium carbonate (0.318 g) and 18% aqueous ammonia (0.6 ml) in a 3:5 molar ratio were dissolved in water (5 ml) with stirring at room temperature for 10 min. The solution was then transferred to a 15 ml Teflon-lined bomb and heated at 413 K for 4 d. Colourless crystals were obtained in 42% yield after cooling to room temperature. Analysis found: C 12.64, H 4.77, N 7.37%; calculated for C₄H₁₈N₂Na₂O₁₅: C 12.61, H 4.80, N 7.35%. IR (KBr, cm⁻¹): 3442 (s), 1795 (w), 1254 (m), 1106 (m), 873 (w), 816 (w).

Crystal data

[Na(H ₂ O) ₄] ₂ (C ₄ H ₂ N ₂ O ₇)	Z = 4
<i>M_r</i> = 380.18	<i>D_x</i> = 1.680 Mg m ⁻³
Monoclinic, <i>C2/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 11.935 (7) Å	<i>μ</i> = 0.22 mm ⁻¹
<i>b</i> = 10.709 (6) Å	<i>T</i> = 298 (2) K
<i>c</i> = 12.277 (7) Å	Block, colourless
<i>β</i> = 106.634 (8)°	0.33 × 0.25 × 0.18 mm
<i>V</i> = 1503.5 (16) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	3719 measured reflections
<i>φ</i> and <i>ω</i> scans	1333 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1998)	1146 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.932, <i>T_{max}</i> = 0.962	<i>R_{int}</i> = 0.026
	<i>θ_{max}</i> = 25.0°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1475P)^2 + 3.8784P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.225$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.08	Δρ _{max} = 0.96 e Å ⁻³
1333 reflections	Δρ _{min} = -0.81 e Å ⁻³
116 parameters	
Only H-atom displacement parameters refined	

Table 1

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>
O4–H4···O7 ⁱ	0.82	2.11	2.897 (4)	160
O5–H5A···O4 ⁱⁱ	0.83	2.19	2.970 (4)	157
O5–H5B···O1	0.85	1.99	2.833 (4)	171
O6–H6A···O2 ⁱⁱⁱ	0.81	2.10	2.869 (4)	157
O6–H6B···O4 ^{iv}	0.85	2.05	2.888 (4)	169
O7–H7A···O8	0.85	2.12	2.943 (4)	161
O7–H7B···N1 ^v	0.84	2.33	3.118 (4)	157
O8–H8A···O3 ^{iv}	0.82	1.99	2.810 (3)	179
O8–H8B···O2	0.83	2.40	3.171 (4)	155

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

All H atoms were located in difference maps and then treated as riding atoms (O–H = 0.81–0.86 Å). The *U*_{iso}(H) values were refined freely. The highest residual peak is located 0.98 Å from O2, 1.77 Å from N1 and 1.98 Å from C1.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXL97.

This work was supported by the Measurement Foundation of Nanjing University. HLZ is grateful for the support of the National Natural Science Foundation of China (No. 30672516).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3082). Services for accessing these data are described at the back of the journal.

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