Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Investigation of commercial sodium cacodylate trihydrate: penta-μ-aqua-disodium(I) bis(dimethylarsenate) and di-μ-aqua-bis[triaquasodium(I)] bis(dimethylarsenate)

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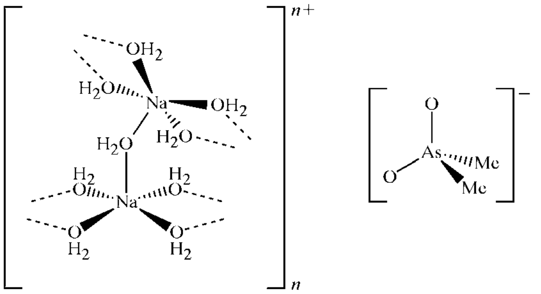
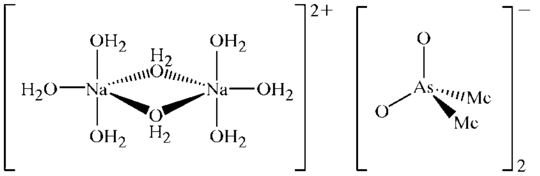
Received 11 October 2007
Accepted 1 November 2007
Online 14 December 2007

Crystals from commercial samples of sodium cacodylate trihydrate, $NaO_2As(CH_3)_2 \cdot 3H_2O$, were analyzed by single-crystal X-ray diffraction and two phases were identified, *viz*. penta-μ-aqua-disodium(I) bis(dimethylarsenate), $\{[Na_2(H_2O)_5](C_2H_6AsO_2)_2\}_n$, (I), and di-$\mu$-aqua-bis[triaquasodium(I)] bis(dimethylarsenate), $[Na_2(H_2O)_8](C_2H_6AsO_2)_2$, (II). Both (I) and (II) form layered structures in which hydrated Na^+ ions form layers in the *ab* plane, the cacodylate ions being located in between the layers. In (I), the two non-equivalent Na^+ ions (located at twofold axes) and the three non-equivalent aqua ligands (one of which also lies on a twofold axis) form infinite polymeric layers, but in (II), layers of discrete centrosymmetric $[Na_2(H_2O)_8]^{2+}$ ions are present. One of the commercial samples analyzed contained almost exclusively crystals of the tetrahydrate (II), while another sample consisted of a mixture of the two phases.

Comment

The first salts of cacodylic acid were prepared by Robert Bunsen in 1842 during his famous studies on the cacodyl radical in 1837–1843 (Bunsen, 1891). Bunsen informed Berzelius, who wrote an account of the results in his annual report on the progress of chemistry (Berzelius, 1842), which is the first publication on the subject. Although more than 160 years have passed, none of the salts are found in the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen 2002). Sodium cacodylate trihydrate is today commercially available; one important use is in buffer solutions, which find use in protein crystallization (Ericsson *et al.*, 2006; Izaac *et al.*, 2006). Examination of a commercial sample showed that it contained crystals of two distinct morphologies, *viz*. round irregularly shaped crystals (some of which displayed well developed faces) and a few crystal plates. It was possible to select crystals suitable for single-crystal X-ray diffraction, and the plates were identified as the expected trihydrate, $[\{Na(H_2O)_3\}_\infty][O_2As(CH_3)_2]_\infty$, (I), but the irregular crystals were identified as a tetrahydrate, $[Na_2(H_2O)_8][O_2As(CH_3)_2]_2$, (II). Another commercial sample was shown by powder X-ray diffraction to consist almost exclusively of the tetrahydrate, (II). The weight loss on drying this sample at 433 K overnight is also consistent with the expected weight loss on dehydratization of the tetrahydrate. A tetrahydrate of sodium cacodylate does not appear to be officially available on a commercial basis. *SciFinder Scholar* (American Chemical Society, 2005) lists 29 commercial sources for sodium cacodylate; of these, 11 are identified simply as 'sodium cacodylate' and may be the anhydrous product, six are identified as 'sodium cacodylate hydrate' and 12 as the trihydrate. Care should be taken on using sodium cacodylate, when molar mass is a matter of importance.


(I)


(II)

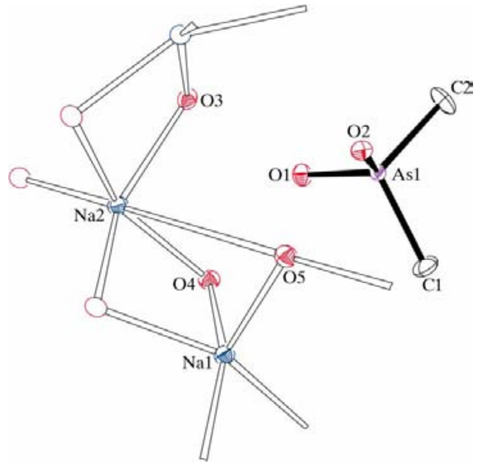


Figure 1
The structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

DOI: 10.1107/S0108270107055151

There are two non-equivalent Na^+ ions in the structure of (I), Na1 and Na2, both located on twofold axes (Fig. 1 and Table 1). All of the three water molecules in (I) are coordinated to Na^+ ions and give rise to infinite layers in the *ab* plane. Both Na1 and Na2 are five-coordinate, with coordination geometries intermediate between trigonal bipyramidal and square pyramidal. The coordination geometry around atom Na1 is perhaps closer to square pyramidal, while Na2 is perhaps closer to trigonal bipyramidal coordination geometry. The aqua ligands are bridging between atoms Na1 and Na2. Atom O5 forms a single bridge between atoms Na1 and Na2; atoms O3 and O3(x, y, $-z + \frac{1}{2}$) form two bridges between atoms Na2 and Na1($-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$), and atoms O4 and O4($x, y, -z + \frac{1}{2}$) form two bridges between atoms Na2 and Na1(x + 1, y, z). The resulting layer is depicted in Fig. 2. The cacodylate anions are located in between the Na/H_2O layers and form hydrogen bonds to the layers. Atom O2 interacts with atoms H3, H5 and H7($-x + 1$, $y - \frac{1}{2}$, z), and atom O1 interacts with atoms H4($x - 1, y, z$) and H6($x - 1, y, z$) (Table 2). All of these H atoms are in the same layer. There

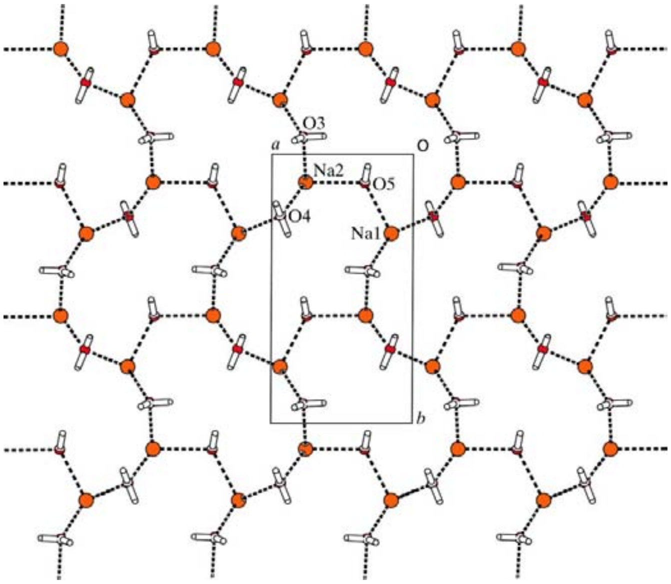


Figure 2
Na^+ ions and water molecules form infinite layers in (I). The layer is viewed along the *c* axis. The appearance of double μ_2-bridges in the structure cannot be seen in the figure since the water molecules giving rise to them are superimposed. The cacodylate ions have been omitted.

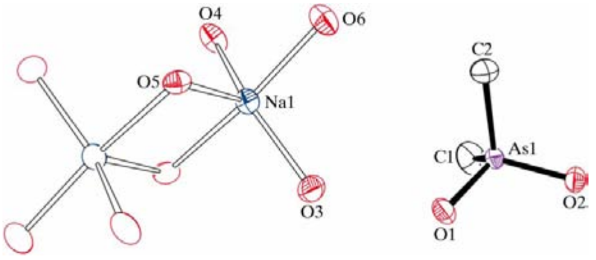


Figure 3
The structure of (II), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted.

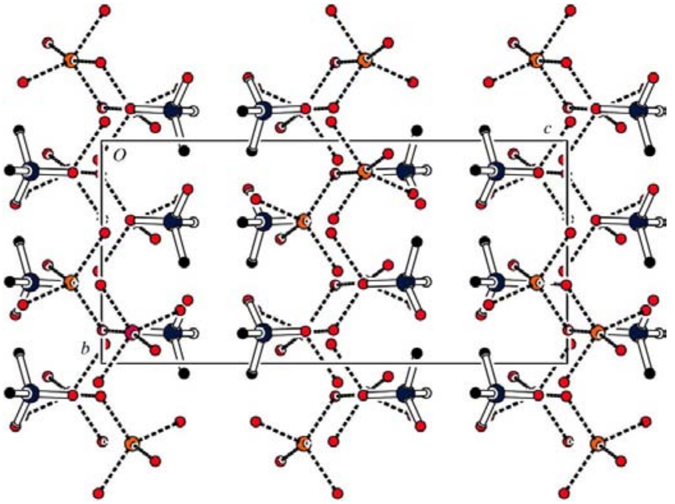


Figure 4
The unit cell of (II), viewed along the *a*-axis direction. All H atoms have been omitted. Three layers run vertically in the figure. Layers of hydrated Na^+ ions are separated by cacodylate ions.

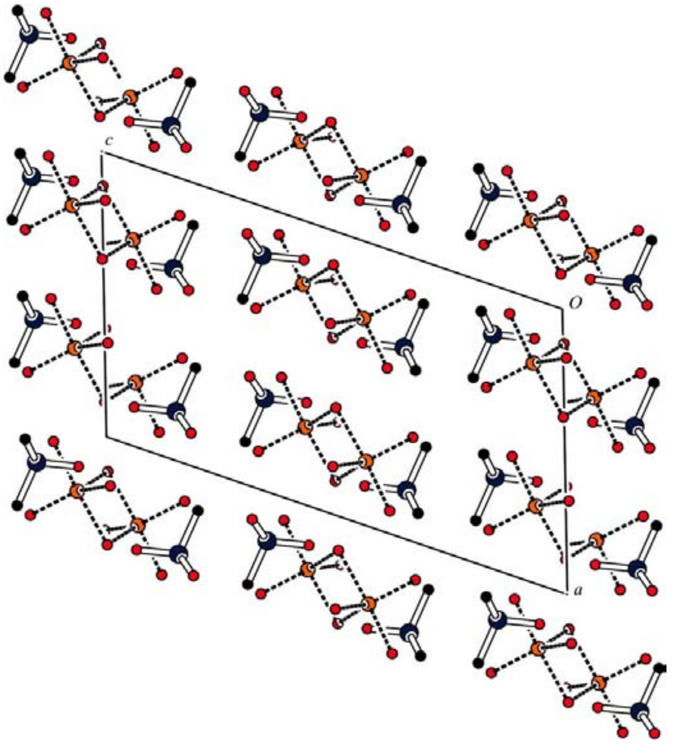


Figure 5
The unit cell of (II), viewed along the *b*-axis direction. All H atoms have been omitted. Three layers of di-μ_2-aqua-hexaquadisodium ions run vertically in the figure, the layers being separated by cacodylate ions.

are no directed attractive forces between the anions; one reason is that only relatively weak C—H···O interactions could form. The geometry of the cacodylate anion is unremarkable, with only a slight degree of distortion from ideal tetrahedral coordination geometry around the central As atom.

In the crystal structure of (II), the Na^+ ions and water molecules give rise to discrete dinuclear cations (Fig. 3) rather than the infinite layers present in (I). As in (I), atom Na1 is five-coordinate, and the coordination geometry is best described as trigonal bipyramidal distorted towards square-pyramidal geometry. Atoms Na1 and Na1^{vii} [symmetry code: (vii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$] are linked by two μ_2-aqua ligands, corresponding to atoms O5 and O5^{vii}. One of the two bridging aqua ligands is in an equatorial position and the other is in an axial position in the coordination environment of atom Na1. The resulting di-μ_2-aqua-hexaquadisodium ion appears to be very rare in combination with organic counter-ions; there is only one further example in the CSD (Laborda *et al.*, 2004). A number of similar ions are, however, found in the CSD, where the Na atoms are six-coordinate.

As in the structure of (I), the crystal structure of (II) is built up by layers of Na^+ ions and water molecules in the *ab* plane {although in the form of discrete $[Na_2(H_2O)_8]^{2+}$ ions}, with the anions appearing between the layers, the components being linked by hydrogen bonds. Within the asymmetric unit, there is one short contact between the anion and the cation (O1—H3*A*; Table 3). In addition, atom O1 forms two short intermolecular contacts, to H3*B*^{i} and H6^{iv}, and atom O2 forms four short intermolecular contacts, to H5*B*^{viii}, H4*B*^{iv}, H5*A*^{iii} and H4*A*^{ix} [Table 3; symmetry codes: (viii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ix) $x, -y+2, z-\frac{1}{2}$]. The cation forms four equivalent short contacts (2.10 Å), besides those involving O1 and O2, *viz.* O4···H6*B*^{vi}, H6*B*···O4^{vi}, O4^{vii}···H6*B*^{x} and O4^{x}···H6*B*^{vii} [symmetry codes: (x) $x-\frac{1}{2}, y-\frac{1}{2}, z$]. The crystal structure of (II) is depicted in Fig. 4 (along the *a* axis) and in Fig. 5 (along the *b* axis). The formation of layers in the *ab* plane is most easily seen from Fig. 4.

Experimental

Crystals were carefully selected from a commercial sample of 'sodium cacodylate trihydrate'.

Compound (I)

Crystal data

$[Na_2(H_2O)_5](C_2H_6AsO_2)_2$
$M_r = 410.04$
Orthorhombic, *Pbcm*
$a = 6.1299$ (11) Å
$b = 10.7515$ (18) Å
$c = 23.901$ (4) Å
$V = 1575.2$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.32$ mm^{-1}
$T = 100$ (2) K
0.3 × 0.2 × 0.2 mm

Data collection

Rigaku R-AXIS-IIC image-plate system diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.255$, $T_{max} = 0.420$
10364 measured reflections
1585 independent reflections
1493 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.067$
$S = 1.18$
1585 reflections
115 parameters
Only H-atom coordinates refined
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—As1	1.920 (3)	Na1—O3^{i}	2.370 (2)
C2—As1	1.918 (3)	Na1—O4^{ii}	2.409 (2)
As1—O1	1.6725 (19)	Na2—O4	2.316 (2)
As1—O2	1.6840 (18)	Na2—O5	2.364 (3)
Na1—O5	2.317 (3)	Na2—O3	2.422 (2)
O1—As1—O2	112.69 (9)	O3^{i}—Na1—O4^{ii}	154.01 (10)
O1—As1—C2	109.97 (12)	O4^{iv}—Na1—O4^{ii}	81.67 (11)
O2—As1—C2	107.66 (11)	O4—Na2—O4^{v}	85.70 (11)
O1—As1—C1	109.67 (12)	O4—Na2—O5	115.49 (8)
O2—As1—C1	107.84 (12)	O4—Na2—O3^{v}	151.08 (10)
C2—As1—C1	108.91 (15)	O4—Na2—O3	88.95 (7)
O5—Na1—O3^{i}	111.66 (9)	O4^{v}—Na2—O3	151.08 (10)
O3^{iii}—Na1—O3^{i}	84.37 (11)	O5—Na2—O3	92.43 (8)
O5—Na1—O4^{ii}	93.80 (9)	O3^{v}—Na2—O3	82.15 (11)
O3^{iii}—Na1—O4^{ii}	91.19 (7)		

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

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.83 (4)	1.92 (4)	2.742 (3)	172 (3)
O3—H4···O1^{vi}	0.75 (4)	2.01 (4)	2.757 (3)	171 (3)
O5—H5···O2	0.86 (3)	1.87 (3)	2.714 (3)	170 (3)
O4—H6···O1^{vi}	0.94 (4)	1.81 (3)	2.743 (3)	171 (3)
O4—H7···O2^{iii}	0.74 (4)	1.96 (4)	2.693 (3)	172 (3)

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

Compound (II)

Crystal data

$[Na_2(H_2O)_8](C_2H_6AsO_2)_2$
$M_r = 464.08$
Monoclinic, $C2/c$
$a = 11.516$ (3) Å
$b = 8.838$ (2) Å
$c = 19.635$ (5) Å
$\beta = 109.907$ (8)°
$V = 1879.1$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.65$ mm^{-1}
$T = 303$ (2) K
0.25 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS-IIc image-plate system diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.373$, $T_{max} = 0.696$
5714 measured reflections
1652 independent reflections
1517 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.044$
$S = 1.00$
1652 reflections
125 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

The H atoms in (II) were included in calculated positions (C—H = 0.96 Å) and refined using a riding model, with U_{iso}(H) values 1.5 times U_{eq}(C).

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1	0.75 (3)	2.10 (3)	2.842 (2)	169 (3)
O3—H3B···O1$^{\rm i}$	0.75 (3)	2.04 (4)	2.788 (2)	169 (3)
O4—H4A···O2$^{\rm ii}$	0.78 (3)	2.05 (4)	2.835 (2)	172 (3)
O4—H4B···O2$^{\rm iii}$	0.82 (3)	2.00 (3)	2.823 (2)	175 (3)
O5—H5A···O2$^{\rm iv}$	0.78 (2)	2.07 (3)	2.849 (2)	175 (3)
O5—H5B···O2$^{\rm v}$	0.76 (2)	2.06 (2)	2.810 (2)	169 (3)
O6—H6A···O1$^{\rm iii}$	0.71 (2)	2.05 (3)	2.758 (2)	176 (3)
O6—H6B···O4$^{\rm vi}$	0.84 (3)	2.10 (3)	2.939 (2)	173 (3)

Symmetry codes: (i) $-x, y, -z+\frac{1}{2}$; (ii) $x, -y+2, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (vi) $-x+1, -y+2, -z+1$.

For both compounds, data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Financial support from the Swedish Research Council (VR) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3063). Services for accessing these data are described at the back of the journal.

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