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Di-μ-aqua-bis({*N*-[(2-dimethylamino-κN)ethyl]-*N*,*N*′,*N*′-trimethylethane-1,2-diamine-$\kappa^2 N,N'$}-sodium(I)) diiodide

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.011 Å
R factor = 0.040
wR factor = 0.091
Data-to-parameter ratio = 12.9

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

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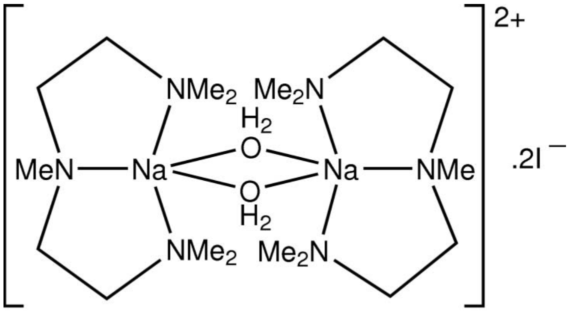
The title compound comprises centrosymmetric dimeric units, $[Na_2(PMDTA)_2(H_2O)_2]^{2+}$ (PMDTA is *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, $C_9H_{23}N_3$), where two Na cations are bridged by two water molecules. Each Na^+ cation is also coordinated by three N atoms of a PMDTA molecule to give a five-coordinate distorted square-pyramidal geometry. Polymeric chains are then obtained through weak interactions between the water molecules and the I^- anions that provide the charge balance. The cations and anions lie on a mirror plane.

Comment

Each of the Na^+ ions in the title compound, (I) (Fig. 1 and Table 1), is coordinated by two O atoms from water molecules and three N atoms from a single PMDTA molecule (PMDTA is *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). The charge balance is provided by iodide anions and the entire assembly is disposed about a position with site symmetry 2/*m*.



(I)

This N_3O_2 donor set defines a five-coordinate polyhedron that is a distorted square pyramid, which is the usual five-coordinate geometry encountered together with the trigonal bipyramid (Reglinski *et al.*, 1999; Shen & Jing, 2002). However, the coordination number found for the Na^+ cation is quite rare. Indeed, sodium usually forms six-coordinate complexes (Albada *et al.*, 1999; Goher & Mautner, 1994), and significantly fewer five- and seven-coordinated geometries have been reported (Aukauloo *et al.*, 1999; Barnhart *et al.*, 1995; Bishop *et al.*, 2000; Gibney *et al.*, 1996). This structure can be related to the previously reported anhydrous complex $[Na_2I_2(PMDTA)_2]$, which is a μ,μ'-diiodo-bridged dimer with the tridentate PMDTA molecules providing the five-coordinate environment around the Na cations (Raston *et al.*, 1989). Unlike this compound, where the Na cations are connected through iodide anions [Na—I = 3.081 (2) Å], compound (I) achieves dimerization through water O atoms [mean Na—O =

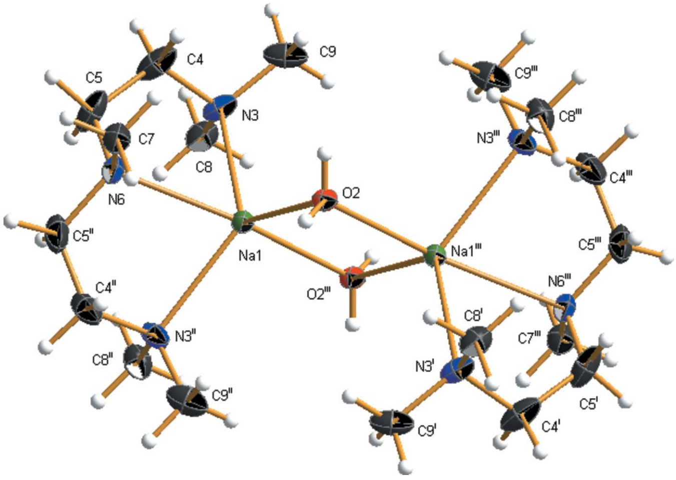


Figure 1
The structure of the cation (30% probability displacement ellipsoids). [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, -y, z$; (iii) $1 - x, y, -z$.]

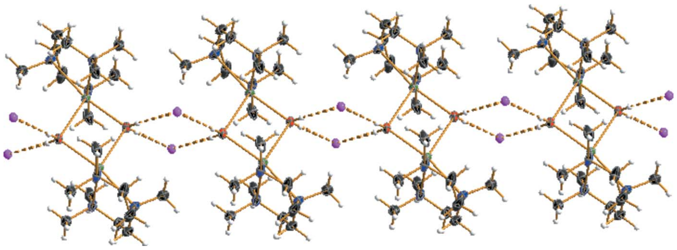


Figure 2
View of one of the polymeric chains running along the *c* axis. The broken lines indicate hydrogen bonds.

2.37 (2) Å]. It is noteworthy that the overall topology of both dimers is identical. In contrast, the three-dimensional arrangement is different. In the anhydrous compound, the dimeric units are discrete, whereas in the hydrated compound, the dimeric units form chains running along the *c* axis of the unit cell through a network of weak interactions between the I^- anions and the water molecules [O2—H7 = 0.82 (5) Å, I10$\cdots$H7 = 2.69 (5) Å and O—H$\cdots$I = 176 (4)°; see Fig. 2]. The *ac* planes containing these chains stack along the *b* axis in a step-like manner with an *a*/2 shift (see Fig. 3). The mean Na—O [2.37 (2) Å] and Na—N distances [2.482 (4) Å] are in good agreement with those reported in similar compounds (Raston *et al.*, 1989; Cole *et al.*, 2002). Within the PMDTA ligand, all distances agree well with expected C—C and C—N bond lengths (Ellermann *et al.*, 1998).

Experimental

The title compound was obtained as a by-product from the reaction of $BaI_2\cdot2H_2O$ with $NaOCH(CF_3)_2$ (1:1 stoichiometry) in a solution of tetrahydrofuran and dimethoxyethane (1:1 in volume) in the presence of PMDTA. Small colorless crystals of (I) grew overnight from the concentrated mother liquor at 253 K, together with the related anhydrous compound and two barium derivatives (which remain to be characterized).

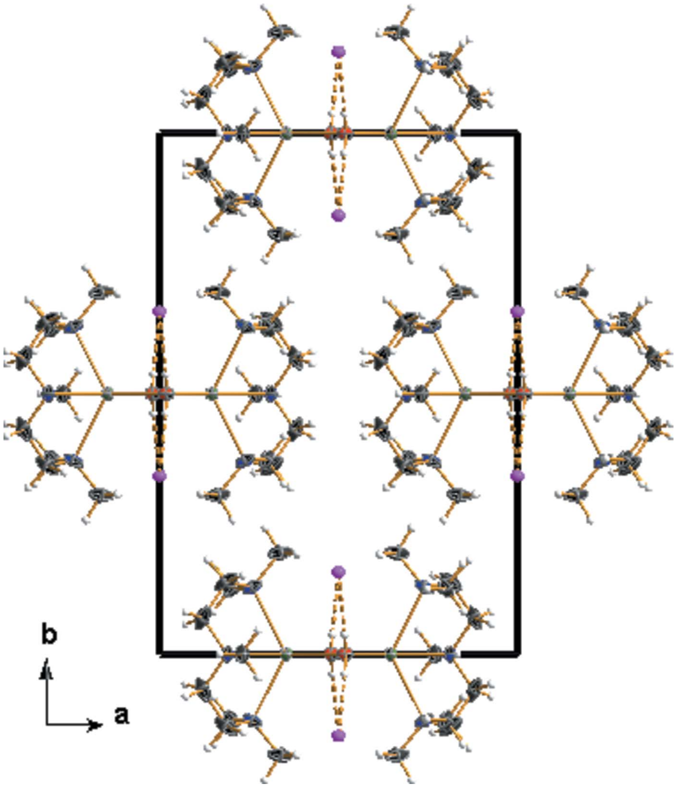


Figure 3
Projection of the unit-cell contents along the *c* axis. The broken lines indicate hydrogen bonds.

Crystal data

$[Na_2(C_9H_{23}N_3)_2(H_2O)_2]I_2$
$M_r = 682.42$
Monoclinic, $C2/m$
$a = 13.7534$ (6) Å
$b = 17.1348$ (8) Å
$c = 7.6723$ (3) Å
$\beta = 120.997$ (2)°
$V = 1549.87$ (12) Å^3
$Z = 2$
$D_x = 1.462$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1809 reflections
$\theta = 1$–28°
$\mu = 2.08$ mm^{-1}
$T = 150$ K
Block, colorless
0.05 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)
$T_{\min} = 0.901$, $T_{\max} = 0.901$
3361 measured reflections
1899 independent reflections
1629 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 27.9°$
$h = -17 \rightarrow 18$
$k = -22 \rightarrow 20$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.091$
$S = 0.87$
1629 reflections
126 parameters
Only H-atom coordinates refined
Weighting scheme: see below
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Na1—O2^{i}	2.356 (5)	N3—C8	1.453 (7)
Na1—N3^{ii}	2.480 (4)	N3—C9	1.452 (8)
Na1—O2	2.385 (5)	C4—C5	1.461 (10)
Na1—N3	2.480 (4)	C5—N6	1.468 (7)
Na1—N6	2.485 (6)	N6—C7	1.450 (10)
N3—C4	1.476 (7)		
O2^{i}—Na1—N3^{ii}	101.39 (12)	C4—N3—C8	114.4 (5)
O2^{i}—Na1—O2	85.87 (16)	Na1—N3—C9	114.5 (4)
N3^{ii}—Na1—O2	115.45 (13)	C4—N3—C9	106.2 (5)
O2^{i}—Na1—N3	101.39 (12)	C8—N3—C9	108.3 (5)
N3^{ii}—Na1—N3	125.1 (3)	N3—C4—C5	113.8 (5)
O2—Na1—N3	115.45 (13)	C4—C5—N6	114.0 (5)
O2^{i}—Na1—N6	167.9 (2)	C5^{ii}—N6—C5	107.6 (7)
N3^{ii}—Na1—N6	73.71 (13)	C5^{ii}—N6—Na1	107.7 (3)
O2—Na1—N6	106.2 (2)	C5—N6—Na1	107.7 (3)
N3—Na1—N6	73.71 (13)	C5^{ii}—N6—C7	112.2 (4)
Na1^{i}—O2—Na1	94.13 (16)	C5—N6—C7	112.2 (4)
Na1—N3—C4	106.0 (3)	Na1—N6—C7	109.2 (4)
Na1—N3—C8	107.6 (3)		

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x, -y, z$.

A Chebychev polynomial (Watkin, 1994; Prince, 1982) was used in the weighting scheme, [weight] = $1.0/[A_0T_0(x) + A_1T_1(x) \cdots + A_{n-1}T_{n-1}(x)]$, where A_i are the Chebychev coefficients 25.3, 38.1, 24.1, 10.0 and 3.69, and $x = F/F_{\rm max}$; robust weighting (Prince, 1982) W = [weight] $[1 - (\delta F/6\sigma F)^2]^2$. The H-atom positions and $U_{\rm iso}$(H) values were refined using soft restraints on the bond lengths and angles to regularize their geometry [C—H = 0.95 (4) to 0.98 (2) Å, O—H = 0.82 (5) Å, and $U_{\rm iso}$(H) = $1.2U_{\rm equiv}$(C) and $1.5U_{\rm equiv}$(O)]. The maximum residual electron density is located 0.98 Å from atom Na1.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

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