METAL-ORGANIC COMPOUNDS

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Sodium Bis[1,2-ethanediolato(2−)](hydroxyethoxo)silicate(1−) Acetonitrile Solvate, $Na[Si(C_2H_4O_2)_2(C_2H_5O_2)].0.25C_2H_3N$

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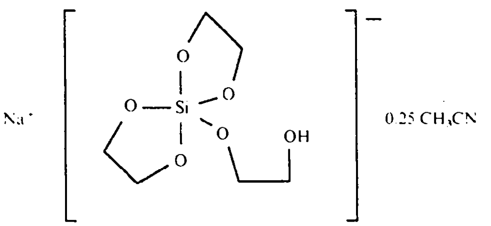
Abstract

The title compound was prepared by the dissolution of silicic acid in alkaline glycol solution, using NaOH. The structure of the five-coordinate Si anion is similar to that found in the potassium salt with one glycolate oxygen not bound to the Si. One hydrogen bond utilizing the H atom of the unbound glycolate hydroxyl and the O atom of an adjacent molecule causes the formation of a tetramer of anions around the fourfold axis. Six glycolate-O···Na-cation interactions complete the intermolecular binding into layers perpendicular to the tetragonal axis. The acetonitrile solvent is bound between these layers in the one cavity of sufficient size, created by the anionic tetramer.

Comment

Despite the fact that 1,2-diols must be highly substituted to form monomeric tetrahedral spirosilicates (Frye, 1969), hypervalent silicon is readily formed with ethylene glycolate ligands (Frye, 1970). The reductions in the bite angles which occur when increasing the coordination number allow the unsubstituted ethylene glycolate ligands to chelate effectively and stabilize the hypervalent silicon. von Schomburg (1982) reported a neutral pentacoordinate silane containing a chelating glycolate ligand and, more recently, Laine *et al.* (1991) reported the crystal structure of the potassium salt of a pentacoordinate silicate anion (hereafter KSA). In addition, Hoppe, Laine, Kampf, Gordon & Burggraf (1993) reported the crystal structure of a hexacoordinate silicate anion, again containing chelating ethylene glycolate ligands. We report here the sodium salt analogue of the pentacoordinate ethylene glycolate silicate anion, (I), and describe its crystal packing.



(I)

The structure consists of independent Si(glycolate)$_3$ anions and Na^+ cations bound intermolecularly by $Na^+\cdots O$ interactions, and one hydrogen bond. The geometry about the silicon is five-coordinate, with one glycolate ligand bound through only one O atom (see Fig. 1). The distortion from a trigonal bipyramid towards a rectangular pyramid is around 27%, similar to that found in KSA, with the dihedral δ_{24} angles 40.3 and 44.0°, respectively, according to the dihedral angle method (see Holmes & Deiters, 1977; Muetterties & Guggenberger, 1974). The equatorial and axial Si—O bond lengths average 1.769 and 1.690 Å, respectively, compared with the values of 1.761 and 1.688 Å for KSA.

There are six normal $Na^+\cdots O$ contacts (2.33–2.51 Å) (*cf.* Hosmane *et al.*, 1991; Rudert, Buschmann, Luger & Trummlitz, 1992) compared with seven found for K^+ in KSA. In both these structures, the one glycolate O atom not involved in an ionic interaction with a cation is hydrogen bonded to the proton on the O atom of the free glycolate [O(6)] of a neighbouring anion [O(4)···H(O6) = 1.74 (4) here, O(2)···H(O6) = 1.95 Å in KSA].

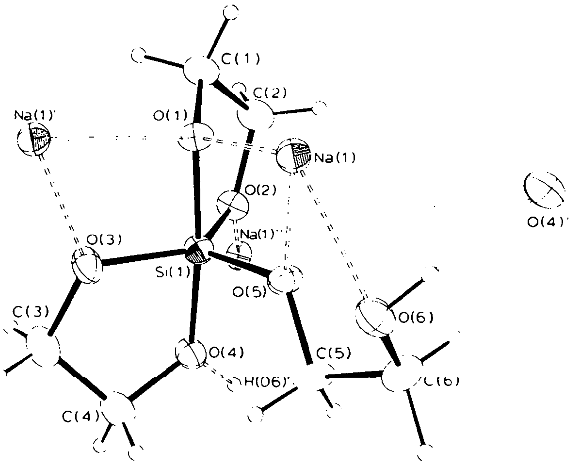


Fig. 1. *ORTEP* (Johnson, 1971) view of the ions of the title compound. Intermolecular contacts are shown by broken lines; primed atoms are symmetry-related to unprimed atoms; displacement ellipsoids are shown at the 50% probability level.

Each Na^+ cation interacts with three oxygens of one anion [O(1), O(5) and O(6)], two of an inversion-related anion [O(1) and O(3)] and O(2) of a glide-plane-related anion. The combined covalent and ionic bonding in the structure results in a 'zeolite-like' layer in the *ab* plane (see Fig. 2). There are two 'cavities' in the layer, centred on the twofold and the fourfold inversion axes. Into the larger of the two, which is surrounded by the anionic 'tetramer', fit the two molecules of acetonitrile per cell; molecular modelling indicates that the smaller cavity is of insufficient size to accommodate this solvate molecule.

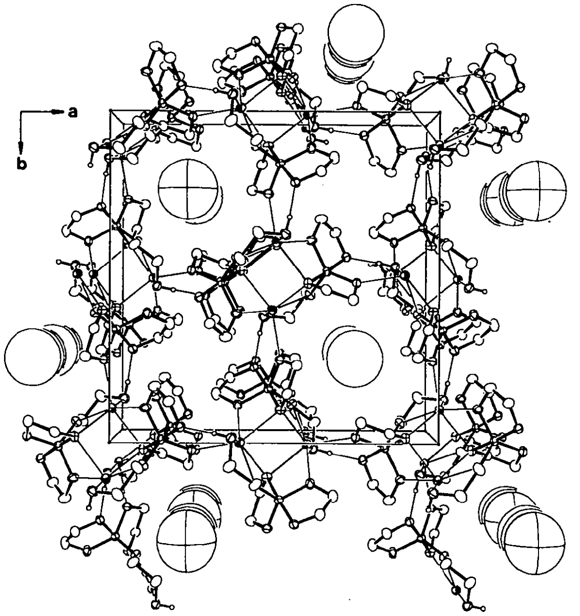


Fig. 2. Crystal packing viewed down the tetragonal axis, showing the solvate acetonitrile atoms with enlarged atomic radii. Ionic contacts between Na and O and hydrogen bonding are shown as thinner lines.

Experimental

The title compound was prepared by the dissolution of silicic acid in alkaline glycol solution, using NaOH. Crystals were grown by slow vapour diffusion of acetonitrile into a solution of the silicate in ethylene glycol, over a period of three weeks.

Crystal data

$Na[Si(C_2H_4O_2)_2(C_2H_5O_2)].0.25C_2H_3N$
$M_r = 242.6$
Tetragonal
$P4/n$
$a = 15.963$ (4) Å
$c = 8.525$ (3) Å
$V = 2172$ (1) Å^3
$Z = 8$
$D_x = 1.48$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 4.9$–$13.9°$
$\mu = 0.25$ mm^{-1}
$T = 124$ K
Approximately cubic
0.26 × 0.22 × 0.22 mm
Colourless

Data collection

Nicolet *P*4 diffractometer
ω scans
Absorption correction: none
2286 measured reflections
2214 independent reflections
1211 observed reflections [$I \geq 2.5\sigma(I)$]
$R_{int} = 0.012$

$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 97 reflections intensity variation: <2%

Refinement

Refinement on *F*
$R = 0.028$
$wR = 0.033$
$S = 0.93$
1211 reflections
189 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.0005|F_o|^2]^2$
$(\Delta/\sigma)_{max} = 0.025$

$\Delta\rho_{max} = 0.360$ e Å^{-3}
$\Delta\rho_{min} = -0.260$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.67 (10)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Si(1)	0.83886 (5)	0.01606 (5)	0.12221 (9)	1.50 (3)
Na(1)	1.00598 (6)	−0.10193 (6)	0.08441 (1)	1.70 (4)
O(1)	0.89720 (11)	−0.01969 (12)	−0.0423 (2)	1.67 (8)
O(2)	0.74907 (11)	−0.01829 (11)	0.0362 (2)	1.69 (8)
O(3)	0.88689 (12)	0.11043 (11)	0.1000 (2)	2.20 (8)
O(4)	0.77727 (12)	0.06052 (11)	0.2721 (2)	1.80 (8)
O(5)	0.88880 (12)	−0.05440 (12)	0.2326 (2)	1.74 (8)
O(6)	1.03154 (12)	−0.12351 (13)	0.3638 (3)	2.01 (8)
N(1)	3/4	−1/4	0.5790 (9)	5.4 (3)
C(1)	0.84469 (19)	−0.0386 (2)	−0.1722 (3)	1.93 (12)
C(2)	0.76223 (19)	−0.0678 (2)	−0.1022 (4)	2.20 (12)
C(3)	0.8558 (2)	0.1775 (2)	0.1952 (4)	2.84 (14)
C(4)	0.8102 (2)	0.1373 (2)	0.3310 (4)	2.36 (13)
C(5)	0.8992 (2)	−0.0527 (2)	0.3995 (3)	2.17 (13)
C(6)	0.9534 (2)	−0.1274 (2)	0.4449 (4)	2.40 (13)
C(7)	3/4	−1/4	0.4434 (11)	4.0 (3)
C(8)	3/4	−1/4	0.2684 (9)	5.0 (3)

Table 2. *Selected geometric parameters* (Å, °)

Si(1)—O(1)	1.777 (2)	O(1)—C(1)	1.422 (3)
Si(1)—O(2)	1.701 (2)	O(2)—C(2)	1.436 (3)
Si(1)—O(3)	1.701 (2)	O(3)—C(3)	1.432 (4)
Si(1)—O(4)	1.762 (2)	O(4)—C(4)	1.424 (4)
Si(1)—O(5)	1.669 (2)	O(5)—C(5)	1.433 (3)
Na(1)—O(1)	2.430 (2)	O(6)—C(6)	1.428 (4)
Na(1)—O(1^{i})	2.508 (2)	N(1)—C(7)	1.156 (12)
Na(1)—O(2^{ii})	2.416 (2)	C(1)—C(2)	1.519 (4)
Na(1)—O(3^{i})	2.327 (2)	C(3)—C(4)	1.511 (5)
Na(1)—O(5)	2.381 (2)	C(5)—C(6)	1.522 (4)
Na(1)—O(6)	2.441 (3)	C(7)—C(8)	1.492 (12)
O(1)—Si(1)—O(2)	89.89 (9)	O(2^{ii})—Na(1)—O(3^{i})	86.92 (7)
O(1)—Si(1)—O(3)	87.73 (9)	O(2^{ii})—Na(1)—O(5)	105.90 (7)
O(1)—Si(1)—O(4)	173.76 (10)	O(2^{ii})—Na(1)—O(6)	93.18 (7)
O(1)—Si(1)—O(5)	88.75 (9)	O(3^{i})—Na(1)—O(5)	162.62 (8)
O(2)—Si(1)—O(3)	128.13 (10)	O(3^{i})—Na(1)—O(6)	121.88 (8)
O(2)—Si(1)—O(4)	88.40 (9)	O(5)—Na(1)—O(6)	70.04 (7)
O(2)—Si(1)—O(5)	115.35 (10)	Si(1)—O(1)—C(1)	111.97 (17)
O(3)—Si(1)—O(4)	88.61 (9)	Si(1)—O(2)—C(2)	114.11 (16)

O(3)—Si(1)—O(5)	116.38 (10)	Si(1)—O(3)—C(3)	116.26 (18)
O(4)—Si(1)—O(5)	97.41 (10)	Si(1)—O(4)—C(4)	113.35 (17)
O(1)—Na(1)—O(1^i)	87.62 (7)	Si(1)—O(5)—C(5)	127.05 (17)
O(1)—Na(1)—O(2^{ii})	109.58 (7)	O(1)—C(1)—C(2)	105.7 (2)
O(1)—Na(1)—O(3^i)	104.86 (8)	O(2)—C(2)—C(1)	106.3 (2)
O(1)—Na(1)—O(5)	60.15 (7)	O(3)—C(3)—C(4)	106.5 (3)
O(1)—Na(1)—O(6)	129.00 (8)	O(4)—C(4)—C(3)	105.9 (3)
O(1^i)—Na(1)—O(2^{ii})	145.82 (7)	O(5)—C(5)—C(6)	107.7 (2)
O(1^i)—Na(1)—O(3)	59.68 (6)	O(6)—C(6)—C(5)	109.9 (3)
O(1^i)—Na(1)—O(5)	108.27 (7)	N(1)—C(7)—C(8)	180.0
O(1^i)—Na(1)—O(6)	98.40 (7)		

O(1)—Si(1)—O(2)—C(2)	9.2 (1)
O(4)—Si(1)—O(2)—C(2)	−176.8 (2)
O(1)—Si(1)—O(3)—C(3)	171.5 (2)
O(4)—Si(1)—O(3)—C(3)	−3.4 (2)
O(1)—Si(1)—O(4)—C(4)	−70.7 (2)
O(3)—Si(1)—O(4)—C(4)	−16.7 (1)
Si(1)—O(1)—C(1)—C(2)	−30.9 (11)
Si(1)—O(2)—C(2)—C(1)	−27.8 (11)
Si(1)—O(3)—C(3)—C(4)	20.7 (1)
Si(1)—O(4)—C(4)—C(3)	30.4 (2)
Si(1)—O(5)—C(5)—C(6)	−176.7 (3)
O(1)—C(1)—C(2)—O(2)	36.1 (1)
O(3)—C(3)—C(4)—O(4)	−30.8 (1)
O(5)—C(5)—C(6)—O(6)	57.4 (2)
O(2)—Si(1)—O(1)—C(1)	13.8 (2)
O(3)—Si(1)—O(1)—C(1)	−114.3 (2)
O(4)—Si(1)—O(1)—C(1)	−60.3 (2)
O(5)—Si(1)—O(1)—C(1)	129.2 (2)
O(3)—Si(1)—O(2)—C(2)	96.2 (2)
O(5)—Si(1)—O(2)—C(2)	−79.4 (2)
O(2)—Si(1)—O(3)—C(3)	83.5 (2)
O(5)—Si(1)—O(3)—C(3)	−101.0 (2)
O(2)—Si(1)—O(4)—C(4)	−144.9 (2)
O(5)—Si(1)—O(4)—C(4)	99.7 (2)
O(1)—Si(1)—O(5)—C(5)	158.5 (2)
O(2)—Si(1)—O(5)—C(5)	−112.3 (2)
O(3)—Si(1)—O(5)—C(5)	71.6 (2)
O(4)—Si(1)—O(5)—C(5)	−20.5 (1)

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

The crystal selected was mounted rapidly under a cold nitrogen stream on the diffractometer. Data were collected with a fixed background time and a scan speed of 5.0° $\min^{-1}$. The crystal decomposed by reaction with atmospheric moisture within minutes of its removal from the cold nitrogen stream.

The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement was by a full-matrix least-squares method (Gabe *et al.*, 1992). All H atoms were refined with isotropic displacement parameters. The H atoms on the acetonitrile solvate were not located. No features of significance were noted in the final difference map.

Figures were produced by the *NRCVAX* version (Gabe *et al.*, 1992) of *ORTEP*II (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and mean-plane data have been deposited with the IUCr (Reference: OH1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorotris(trimethylsilylcyclopentadienyl)zirconium

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Abstract

The title compound, $[ZrCl(C_8H_{13}Si)_3]$, is a bent metallocene with two η^5-cyclopentadienyl ligands and one η^1-cyclopentadienyl ligand, *i.e.* chloro(3-trimethylsilylcyclopentadienyl-κC^1)bis(η^5-trimethylsilylcyclopentadienyl)zirconium. The Zr—C bond length to the η^1-cyclopentadienyl ligand is 2.396 (5) Å and the Zr—Cl bond length is 2.442 (1) Å.

Comment

The title compound (I) was synthesized as part of a study of zirconium compounds having several cyclopentadienyl rings. Zirconium compounds are known to possess up to three η^5-cyclopentadienyl rings as seen in the crystal structures of tetrakis(cyclopentadienyl)zirconium (Rogers, Vann Bynum & Atwood, 1978) and tris(cyclopentadienyl)zirconium triethylaluminium hydride (Kopf, Vollmer & Kaminsky, 1980); tris(cyclopentadienyl)zirconium chloride is also reported to possess three η^5-cyclopentadienyl rings (Strittmatter & Bursten, 1991). The *ansa*-bridged tris(cyclopentadienyl)zirconium and tris(cyclopentadienyl)hafnium chlorides also possess