

Bis(diisobutylammonium) tris(naphthalene-2,3-diolato)silicate acetonitrile trisolvate

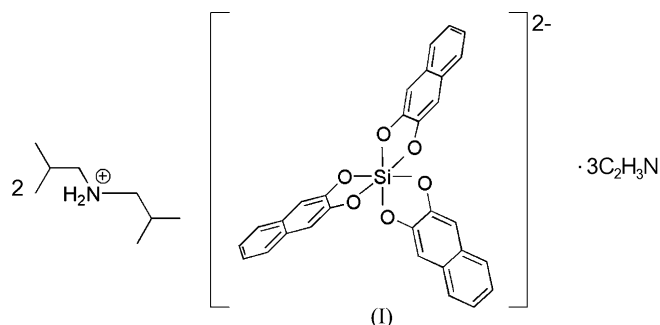
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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.058
wR factor = 0.202
Data-to-parameter ratio = 16.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.In the title compound, $2\text{C}_8\text{H}_{20}\text{N}^+ \cdot \text{C}_{30}\text{H}_{18}\text{O}_6\text{Si}^{2-} \cdot 3\text{C}_2\text{H}_3\text{N}$, the oxygen coordination around silicon is slightly distorted octahedral. $\text{N}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds are effective in stabilizing the molecular structure.

Comment

Single-crystal X-ray structures of dianionic six-coordinate silicates with ligands such as citric, malic and salicylic acids were reported recently (Tacke *et al.*, 2004; Seiler *et al.*, 2002). Among aromatic diols only tris(catecholato)silicates with different ammonium counter-cations were known (Bindu *et al.*, 2003; Sackerer & Nagorsen, 1977). For 2,3-dihydroxynaphthalene, a structural study of five-coordinate silicon complexes has been reported (Tacke *et al.*, 1995). The title compound, (I), is the first example of a dianionic six-coordinate silicate of 2,3-dihydroxynaphthalene.

Diffraction quality crystals were obtained by cooling a concentrated acetonitrile solution of the title compound, (I), in a refrigerator for a period of seven days. The sample was mounted with mother liquor in a Lindemann capillary tube as the crystal was found to be unstable in air. The asymmetric unit consists of a tris(2,3-dihydroxynaphthalato)silicate anion with two diisobutylammonium cations and three molecules of acetonitrile (Fig. 1).

The oxygen coordination around silicon is slightly distorted octahedral, with ligand bite angles $\text{O}1-\text{Si}1-\text{O}2 = 87.93(10)^\circ$, $\text{O}3-\text{Si}1-\text{O}4 = 87.79(9)^\circ$ and $\text{O}5-\text{Si}1-\text{O}6 = 88.83(10)^\circ$. The counter-cations form $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds with O atoms of the anion. One of the solvent acetonitrile molecules forms an $\text{N}-\text{H} \cdots \text{N}$ hydrogen bond with the cation (Table 1). However, there is no extended hydrogen bonding running through the crystal structure (Fig. 2). The six-coordination of Si was also confirmed spectroscopically, using ^{29}Si NMR, which gave a peak at -143.9 p.p.m. ESI-MS spectra gives m/z corresponding to a molecular ion peak ($M + 1$) at 763 (100%), which corresponds to the unsolvated complex.

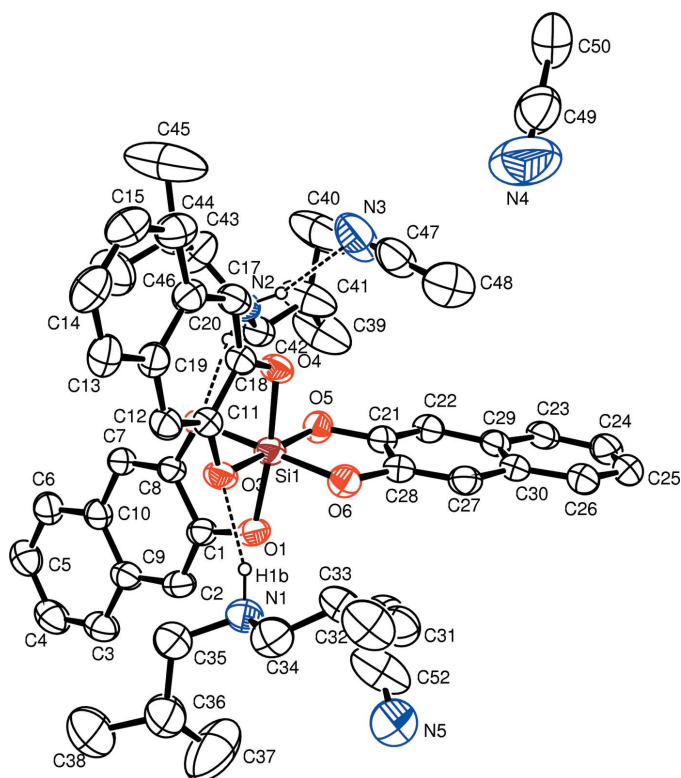


Figure 1
The molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted. Only one disorder component is shown.

Experimental

Diisobutylamine (0.3 ml, 1.88 mmol) was added to a stirred acetonitrile solution of 2,3-dihydroxynaphthalene (0.45 g, 2.85 mmol) under a nitrogen atmosphere. To this solution, tetraethoxysilane (0.2 ml, 0.94 mmol) was added as neat liquid over a period of 5 min at room temperature. The mixture was stirred for 5 h and then the precipitate was filtered and washed with diethyl ether to yield the title compound as a white powder (ca 70%). Some more of the compound was recovered by cooling the concentrated filtrate to 273 K for 1 d (yield 0.64 g, 80%; m.p. 550 K). Analysis calculated (MW 762.0): C 72.4, H 7.61, N 3.67%; found: C 73.94, H 7.71, N 3.33%. IR (KBr, cm^{-1}): 2962, 2931, 2868, 1587, 1472, 1261, 1167, 1108, 871, 739, 693, 638, 586, 485. ^1H NMR (p.p.m.): δ 0.90 (*d*, 6H), 2.13 (*sep*, 1H), 2.98 (*d*, 2H), 6.75 (*s*, 2H), 7.05 (*m*, 2H), 7.44 (*m*, 2H); ^{13}C NMR (p.p.m.): δ 20.3, 26.1, 56.2, 104.7, 122.3, 126.3, 130.6, 153.5; ^{29}Si NMR (p.p.m.): δ -143.9.

Crystal data

$2\text{C}_8\text{H}_{20}\text{N}^+ \cdot \text{C}_{30}\text{H}_{18}\text{O}_6\text{Si}^{2-} \cdot 3\text{C}_2\text{H}_3\text{N}$
 $M_r = 886.20$
 Triclinic, $P\bar{1}$
 $a = 9.919$ (4) Å
 $b = 12.701$ (9) Å
 $c = 21.568$ (14) Å
 $\alpha = 104.74$ (6)°
 $\beta = 94.24$ (4)°
 $\gamma = 99.59$ (5)°
 $V = 2572$ (3) Å³

$Z = 2$
 $D_x = 1.144$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 20$ –25°
 $\mu = 0.81$ mm⁻¹
 $T = 296$ (2) K
 Block, colorless
 $0.3 \times 0.2 \times 0.2$ mm

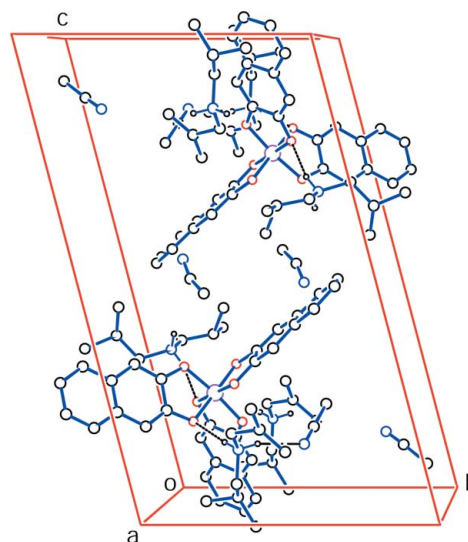


Figure 2
A packing diagram of (I). The hydrogen bonds are shown by dashed lines. H atoms not involved in hydrogen bonding have been omitted. Only one disorder component is shown.

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.825$, $T_{\max} = 0.851$
 9945 measured reflections
 9358 independent reflections
 5541 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 68.0^\circ$
 $h = 0 \rightarrow 11$
 $k = -15 \rightarrow 15$
 $l = -25 \rightarrow 25$
 2 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.202$
 $S = 1.04$
 9358 reflections
 577 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.125P)^2 + 0.0791P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.38 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0012 (3)

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N1---H1B}\cdots\text{O3}$	0.90	1.90	2.778 (3)	164
$\text{N2---H2A}\cdots\text{O2}^{\ddagger}$	0.90	1.97	2.857 (3)	171
$\text{N2---H2B}\cdots\text{N3}^{\ddagger}$	0.90	2.18	3.056 (5)	163

Symmetry code: (i) $x - 1, y, z$.

H atoms were positioned geometrically [$\text{N---H} = 0.90$ Å, and $\text{C---H} = 0.93$ and 0.98 (CH), 0.97 (CH₂), and 0.96 Å (CH₃)] and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The N atom of one of the acetonitrile molecules was twofold disordered. The occupancies of the disordered positions were refined keeping their sums as unity. As the refinement showed the occupancies to be 0.5, the occupancies were fixed at 0.5 in the final refinement.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SIR92* (Altomare

et al., 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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