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Key indicators

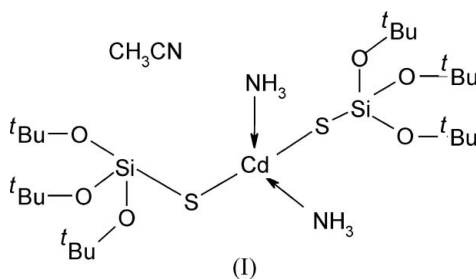
Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.036
 wR factor = 0.090
Data-to-parameter ratio = 22.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diamminebis(tri-*tert*-butoxysilanethiolato)-
cadmium(II) acetonitrile solvate

The title compound, $[\text{Cd}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{NH}_3)_2] \cdot \text{C}_2\text{H}_3\text{N}$, is a molecular heteroleptic cadmium thiolate with two ammine ligands and contains a tetrahedrally coordinated Cd^{II} ion with an S_2N_2 environment. All ammine H atoms and one of the H atoms of the acetonitrile methyl group participate in the formation of intra- and intermolecular hydrogen bonds, which link adjacent molecules into infinite chains.

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Comment

We have been interested in the synthesis of low molecular weight cadmium complexes having $N_x\text{S}(\text{thiolate})_y\text{O}_z$ ligand sets, intended as useful ^{113}Cd NMR spectroscopic models of cadmium-substituted protein sites (Summers, 1988; Coleman, 1993; Öz *et al.*, 1998). We report here the crystal structure of the title compound, (I).



Compound (I) is closely related to the zinc analog, diammine[bis(tri-*tert*-butoxysilanethiolato)]zinc(II) acetonitrile solvate (Becker *et al.*, 2001), reported previously. Cadmium in (I) is tetrahedrally coordinated by two thiolate S atoms and two ammonia N atoms (Fig. 1). The resulting tetrahedron is distorted, with the $\text{S1}-\text{Cd1}-\text{S2}$ angle being the widest and $\text{N1}-\text{Cd1}-\text{N2}$ the smallest, which is usual for compounds with a CdS_2N_2 kernel (Corwin & Koch, 1988; Santos *et al.*, 1990; Otto *et al.*, 1999; Sun *et al.*, 1999).

Initially we expected that Cd^{II} would expand its coordination environment compared with Zn^{II} . Among group 12 elements only cadmium was several times reported to form octahedral hexaammine complexes (Yamaguchi & Ohtaki, 1979; Himmel & Jansen, 1998; Paul *et al.*, 2004) and in general it is more likely to form octahedral than tetrahedral complexes (CSD; Version 5.27 of November 2005; Allen, 2002). We suppose that the geometry of the metal environment and crystal structure of (I) is determined first by the network of hydrogen bonds, and then by the size of the central ion.

Seven different hydrogen bonds can be recognized in (I): three intramolecular and four intermolecular (Table 2, Figs. 2 and 3). The structure of (I) is supported by three intra-

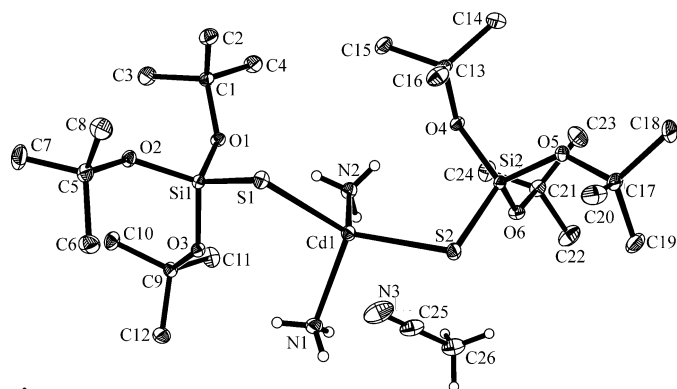


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms of *tert*-butyl groups have been omitted for clarity.

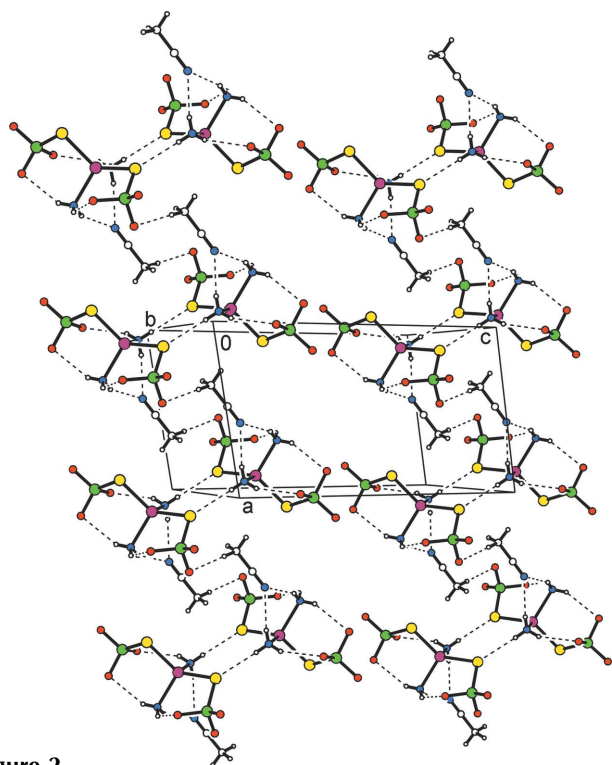


Figure 2
A packing diagram of (I). Cd atoms are purple, S atoms are yellow, Si atoms are green, O atoms are red, C and H atoms are white, N atoms are blue. Dashed lines indicate hydrogen bonds. *tert*-Butyl groups have been omitted.

molecular N—H \cdots O hydrogen bonds formed between ammonia ligands and ether O atoms from *tert*-butoxy groups. The intermolecular aggregation in (I) is determined by a combination of N—H \cdots S, C—H \cdots O and N—H \cdots N hydrogen bonds. The molecules of (I) are linked into dimers *via* intermolecular N—H \cdots S bonds. Acetonitrile is held in position by three intermolecular hydrogen bonds: two N—H \cdots N bonds linking solvent acetonitrile with ammonia ligands and one C—H \cdots O bond formed between asymmetric units. The C—H \cdots O contact was not recognized in the case of the previously described zinc compound (Becker *et al.*, 2001). Very weak hydrogen bonds such as C—H \cdots O may easily be missed by application of van der Waals cut-off criteria

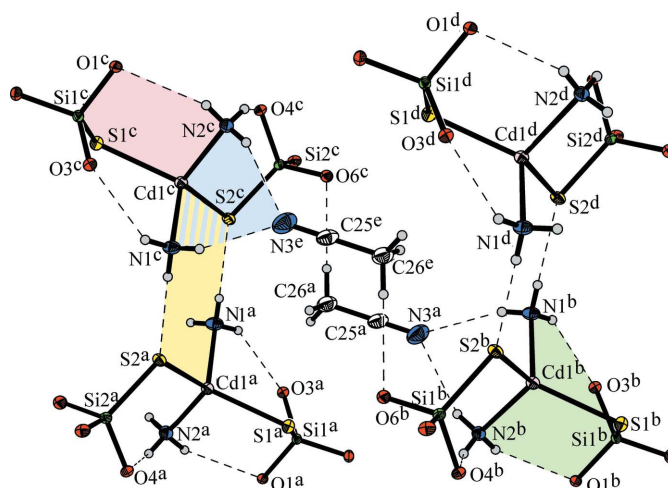


Figure 3
Hydrogen-bonding (dashed lines) patterns in (I). Colouring scheme as in Fig. 2, except for grey H atoms. [Symmetry codes: (a) x, y, z ; (b) $1+x, y, z$; (c) $-x, 1-y, -z$; (d) $1-x, 1-y, -z$; (e) $-x, 1-y, 1-z$.]

(Desiraju & Steiner, 2001). If this interaction is included the molecules form infinite zigzag chains along the *a* axis (Fig. 2).

Application of graph theory to (I) results in a variety of possible hydrogen-bonding patterns (Etter, 1990; Bernstein *et al.*, 1995), as presented in Fig. 3: three different $S(6)$ rings formed by N2—H2E \cdots O4, N2—H2F \cdots O1 and N1—H1C \cdots O3 (shown in red) hydrogen bonds, an intramolecular $R_2^2(8)$ ring (green), a typical intermolecular $R_2^2(8)$ motif (Etter & Adson, 1990; Etter *et al.*, 1990; Harkema *et al.*, 1984; van Hummel & Helmholdt, 1991; Leiserowitz & Nader, 1977; Wiedenfeld & Knoch, 1990) (yellow), an intermolecular $R_1^1(6)$ ring, in which N3 acts as bifurcated acceptor (blue), and an $R_4^1(18)$ motif incorporating C26—H26 \cdots O6ⁱⁱ bonds (not shown).

We suppose that, due to the variety of hydrogen-bonding patterns, (I) and its zinc precedent may be useful models for testing the correctness of computational procedures applied to the characterization of metal binding regions within proteins (Zimmer, 1995; Hemmingsen & Ryde, 1996; Noodleman *et al.*, 2004).

Experimental

Bis(*tri-tert*-butoxysilanethiolate) cadmium(II) (Wojnowski *et al.*, 1992) (0.675 g, 0.5 mmol) was dissolved in toluene (10 ml) and placed in a closed box filled with ammonia vapour. The colourless needles that crystallized after several days were recrystallized from a mixture acetonitrile–toluene (3:2) giving colourless prisms suitable for X-ray analysis.

Crystal data

$[\text{Cd}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{NH}_3)_2] \cdot \text{C}_2\text{H}_3\text{N}$	$V = 1983.2 (2) \text{ \AA}^3$
$M_r = 746.49$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.25 \text{ Mg m}^{-3}$
$a = 9.5244 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.0693 (8) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$c = 16.8974 (9) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\alpha = 82.035 (5)^\circ$	Prism, colourless
$\beta = 75.877 (5)^\circ$	$0.30 \times 0.17 \times 0.08 \text{ mm}$
$\gamma = 77.502 (5)^\circ$	

Data collection

Kuma KM-4-CCD κ geometry diffractometer	16404 measured reflections
ω scans	9049 independent reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	8483 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.767$, $T_{\max} = 0.89$	$R_{\text{int}} = 0.028$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 2.0571P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.13 \text{ e } \text{\AA}^{-3}$
9049 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$
404 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cd1—S1	2.4820 (5)	Si1—O1	1.6422 (15)
Cd1—S2	2.4647 (5)	Si1—O2	1.6353 (15)
Cd1—N1	2.282 (2)	Si1—O3	1.6470 (15)
Cd1—N2	2.2898 (19)	Si2—O4	1.6407 (14)
S1—Si1	2.0810 (7)	Si2—O5	1.6339 (15)
S2—Si2	2.0849 (7)	Si2—O6	1.6338 (15)
N1—Cd1—N2	98.10 (8)	N1—Cd1—S1	107.08 (6)
N1—Cd1—S2	105.57 (6)	N2—Cd1—S1	105.12 (5)
N2—Cd1—S2	114.54 (5)	S2—Cd1—S1	123.312 (18)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B \cdots S2 ⁱ	0.84 (3)	2.65 (3)	3.479 (2)	173 (3)
N1—H1A \cdots N3	0.86 (4)	2.39 (4)	3.204 (4)	158 (3)
N1—H1C \cdots O3	0.82 (3)	2.42 (3)	3.115 (3)	143 (3)
N2—H2F \cdots O1	0.85 (3)	2.48 (3)	3.246 (3)	151 (3)
N2—H2E \cdots O4	0.83 (3)	2.60 (3)	3.248 (3)	137 (3)
N2—H2D \cdots N3	0.86 (4)	2.47 (4)	3.271 (4)	155 (3)
C26—H26C \cdots O6 ⁱⁱ	0.98	2.54	3.519 (3)	173

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

The H atoms of the NH_3 groups were located in a difference map and refined freely [$N-H = 0.82$ (3)– 0.86 (4) \AA]. The methyl H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.98 \AA and with isotropic displacement parameters of $1.2U_{\text{eq}}$ of their attached atoms [1.5 times for those attached to

C26]. The highest residual density peak is located 0.02 \AA from atom Cd1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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