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Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.040
wR factor = 0.098
Data-to-parameter ratio = 17.6

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

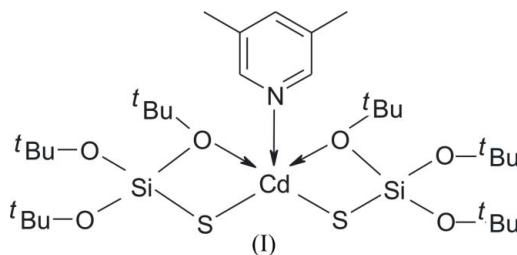
(3,5-Dimethylpyridine)bis(tri-*tert*-butoxy- silanethiolato)cadmium(II)

The title compound, $[\text{Cd}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_7\text{H}_9\text{N})]$, is a molecular heteroleptic cadmium thiolate containing an additional 3,5-dimethylpyridine ligand. The Cd^{II} ion is located at the centre of the trigonal bipyramid formed by five atoms, *viz.* two S, two O and one N. Molecules pack as discrete units, with no short intermolecular contacts.

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Comment

It is well established that cadmium can replace zinc in metal-binding domains of proteins, *e.g.* transcription factors (South *et al.*, 1989; Huang *et al.*, 2004; Kopera *et al.*, 2004). Arising from this, for the past 30 years ^{113}Cd and ^{111}Cd NMR techniques have been used to study the coordination environment of the metal in zinc-containing proteins (Summers, 1988; Chen *et al.*, 2000; Klein *et al.*, 2000). Whether the structures of Cd proteins are the same as those of zinc-bound molecules is less certain (Ramalho & Figureoa-Villar, 2002; Kopera *et al.*, 2004). On the other hand, cadmium is a toxic and carcinogenic metal (Waalkes, 2003). The explanation of its toxicity also involves probable interaction with typical zinc-binding amino acids such as cysteine and histidine. This may subsequently lead to a variety of responses at a cellular level; one of the recently proposed mechanisms of cadmium toxicity is connected with inhibition of the DNA repair pathway (Jin *et al.*, 2003; Banerjee & Flores-Rozas, 2005). For the reasons presented above, structural studies on S- and N-complexes of zinc and their cadmium analogues seem to be justified as they provide information on possible geometric distortions or even more dramatic changes in coordination environment, forced by metal replacement.



The thiolate function in the title compound, (I), is supplied by tri-*tert*-butoxysilanethiol, which was first described by Piękoś & Wojnowski (1962). Over 20 papers describing the structures of various metal tri-*tert*-butoxysilanethiolates, including zinc, cadmium and mercury compounds, have been published by our group. Zinc complexes are most widely represented among them (Becker, Dołęga *et al.*, 2001; Dołęga, Ciborska *et al.*, 2005; Dołęga, Konitz *et al.*, 2005, and refer-

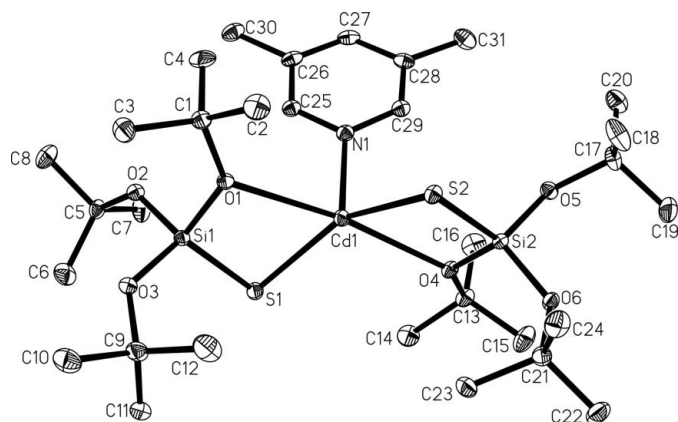


Figure 1
ORTEP (Johnson, 1976) view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

ences therein). Only three tri-*tert*-butoxysilanethiolates of cadmium and mercury have been structurally characterized so far (Wojnowski *et al.*, 1985, 1992; Chojnacki *et al.* 2003). In these complexes, tri-*tert*-butoxysilanethiol serves both as an S-only and as an O,S ligand. Additionally, N-complexation in (I) is provided by 3,5-dimethylpyridine.

The crystal structure of the title compound consists of discrete molecules. The central Cd atom is coordinated by five atoms: two S (S1 and S2), one N (N1) and two O atoms (O1 and O4) (Fig. 1). The geometry of the coordinating atoms may be approximated to a distorted trigonal bipyramid. The equatorial trigonal plane is formed by atoms S1, S2 and N1; atom Cd1 deviates from the plane on the O1 side by 0.0016 (5) Å. The S1–Cd1–S2, S1–Cd1–N1 and S2–Cd1–N1 angles strongly deviate from the ideal value of 120°, with the S1–Cd1–S2 angle being the widest [147.29 (3)°]. We discussed the reasons for the distortion in a previous paper describing the analogous zinc complex (Dołęga, Konitz *et al.*, 2005). Atoms O1 and O4 occupy the two axial positions. The distance from O1 to the S1/S2/N1 plane is 2.4857 (19) Å; the corresponding distance for O4 is 2.4729 (19) Å and the O1–Cd1–O4 angle is 169.43 (7)°. Complexation of O1 and O4 with cadmium is reflected in the Si–O bond lengths. Si1–O1 and Si2–O4 are on average 0.028 Å longer than the rest of the Si–O bonds (Table 1). The effect has also been observed for other silanethiolates (*e.g.* Becker, Zalewska *et al.*, 2001). The arrangement of the Cd, N and S atoms has C_{2v} symmetry but the overall symmetry of the molecule is reduced by the alkoxy substituents on the Si atoms.

It is worth noting that the Cd1–S1 and Cd1–S2 bonds are relatively short, implying strong interactions between cadmium and sulfur in (I). They are comparable to Cd–S bonds in four-coordinate cadmium complexes or even three-coordinate homoleptic cadmium thiolates. It is not surprising, however, as the terminal thiolate groups in homoleptic cadmium tri-*tert*-butoxysilanethiolate, which served as a substrate in the synthesis of (I), form very short Cd–S bonds (Wojnowski *et al.*, 1992). There is only one compound listed in

the Cambridge Structural Database (CSD; Version 5.27 of November 2005; Allen, 2002) that contains shorter Cd–S bonds; these are formed by terminal thiolate ligands in $[\text{Cd}(\text{SC}_6\text{H}_2\text{Bu}_3)_2]_2$ (Bochmann *et al.*, 1990). A certain degree of double bond character in Cd–S in $[\text{Cd}(\text{SC}_6\text{H}_2\text{Bu}_3)_2]_2$ has been suggested. Usual Cd–S bond distances in complexes of tetrahedral, trigonal bipyramidal and octahedral geometry fall within the range 2.5–2.9 Å (García-Vázquez *et al.* 1999; Fleischer *et al.*, 2005) with an average Cd–S distance of 2.60 (11) Å (calculated from all Cd–S data in the CSD). The Cd1–N1 bond of 2.297 (3) Å is also relatively short in opposition to the Cd1–O1 bond of 2.6165 (19) Å and the Cd1–O4 bond of 2.5978 (19) Å, which are longer than average Cd–O bonds in related compounds. The average Cd–N and Cd–O bond lengths (Allen, 2002) are 2.35 (8) Å and 2.36 (12) Å, respectively (from all data in CSD). Selected data on Cd–S and Cd–N distances are compared in Table 2. The selection has been made with the respect to bond lengths and the nature of the reported complexes; mainly molecular, monomeric or dimeric species were included.

Complex (I) is a close analogue of the recently published (3,5-dimethylpyridine)bis(tri-*tert*-butoxysilanethiolato)zinc(II) (Dołęga, Konitz *et al.*, 2005). This supports the assumption that cadmium can replace zinc in biological systems preserving the direct environment of binding ligands.

Experimental

Compound (I) was synthesized from dimeric cadmium bis(tri-*tert*-butoxysilanethiolate) (Wojnowski *et al.*, 1992). Cadmium bis(tri-*tert*-butoxysilanethiolate) (0.675 g, 0.5 mmol) was dissolved in toluene (10 ml). 3,5-Dimethylpyridine (3,5-lutidine) (0.114 ml, 0.107 g, 1 mmol) was subsequently added to the solution and the mixture was gently stirred. The solvent was evaporated to half its volume and the contents placed in a refrigerator (273 K). The colourless crystals that crystallized after 24 h were suitable for X-ray analysis. Elemental analysis found: C 47.85, H 8.23, N 1.75, S 7.97%; calculated: C 47.82, H 8.16, N 1.80, S 8.24%. Melting point 440–445 K.

Crystal data

$[\text{Cd}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_7\text{H}_9\text{N})]$
 $M_r = 778.05$
 Monoclinic, $P2_1/c$
 $a = 14.5499$ (6) Å
 $b = 12.8873$ (6) Å
 $c = 23.9692$ (9) Å
 $\beta = 114.167$ (3)°
 $V = 4100.5$ (3) Å³
 $Z = 4$

$D_x = 1.26$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 18919 reflections
 $\theta = 2.8$ – 32.5°
 $\mu = 0.73$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.21 \times 0.15 \times 0.09$ mm

Data collection

Kuma KM-4 four-axis diffractometer with SAPPHERE2 CCD detector
 ω scans
 Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2005)
 $T_{\min} = 0.807$, $T_{\max} = 0.871$
 18919 measured reflections

7190 independent reflections
 6733 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25^\circ$
 $h = -14 \rightarrow 17$
 $k = -15 \rightarrow 8$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.099$
 $S = 1.08$
 7190 reflections
 408 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 9.2291P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.016$
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Cd1—N1	2.297 (3)	Si1—O1	1.653 (2)
Cd1—S1	2.4337 (7)	Si1—O2	1.627 (2)
Cd1—S2	2.4351 (7)	Si1—O3	1.627 (2)
Cd1—O1	2.6165 (19)	Si2—O4	1.656 (2)
Cd1—O4	2.5978 (19)	Si2—O5	1.626 (2)
Si1—S1	2.0841 (10)	Si2—O6	1.626 (2)
Si2—S2	2.0847 (10)		
N1—Cd1—S1	107.09 (6)	S2—Cd1—O1	104.47 (5)
N1—Cd1—S2	105.62 (6)	N1—Cd1—O4	94.37 (7)
S1—Cd1—S2	147.29 (3)	S1—Cd1—O4	105.33 (5)
N1—Cd1—O1	96.18 (7)	S2—Cd1—O4	72.10 (5)
S1—Cd1—O1	71.90 (4)	O4—Cd1—O1	169.43 (7)

Table 2
 Comparison of Cd—S and Cd—N bond lengths (\AA) and geometry for selected cadmium thiolates.

Compound	Cd—X	Complex geometry
(I) ^a	X = S 2.4337 (7) 2.4351 (7)	Trigonal bipyramidal
KIKHAN ^b	2.417 (2) 2.436 (2)	Tetrahedral
KIKHER ^b	2.454 (3) 2.474 (4)	Trigonal bipyramidal
FIKYAZ10 ^b	2.471 (3) 2.451 (3)	Tetrahedral
KELWAZ ^c	2.419 (3) 2.421 (3) 2.428 (3)	Trigonal
TABXAV ^d	2.377 (6) 2.583 (7)	Trigonal (tS) ^f Trigonal (bS) ^f
PAGBAA ^e	2.409 (2) 2.548 (2)	Trigonal (tS) ^f Trigonal (bS) ^f
ZOJLAL ^f	2.433 (3) 2.440 (3)	Tetrahedral
DILHAH ^g	2.453 (3) 2.459 (3)	Tetrahedral
GUFFUI ^h	2.466 (1) 2.467 (1)	Tetrahedral
JUKYAV ⁱ	2.4806 (8) 2.4536 (8)	Tetrahedral Tetrahedral
HOKFUI ^j	2.460 (3) 2.474 (3)	Square pyramidal
I ^a	X = N 2.297 (3)	Trigonal bipyramidal
RAGDIM ^k	2.340 (3)	Tetrahedral
FIKYAZ10 ^b	2.259 (9) 2.268 (9)	Tetrahedral
DILHAH ^g	2.286 (8) 2.261 (8)	Tetrahedral
GUFFUI ^h	2.275 (4) 2.296 (4)	Tetrahedral
JUQYAV ⁱ	2.261 (2) 2.245 (2)	Tetrahedral

Notes: (a) this work; (b) Santos *et al.* (1990) {KIKHAN is bis(2,4,6-tri-isopropylbenzenethiolato)(bipyridyl-*N,N'*)cadmium(II), KIKHER is bis[(μ_2 -2,4,6-tri-isopropylbenzene-

thiolato-*S,S'*)(1,10-phenanthroline-*N,N'*)cadmium(II)], FIKYAZ10 is bis(2,4,6-triisopropylbenzenethiolato)bis(*N*-methylimidazol-3-yl)cadmium(II)); (c) Gruff & Koch (1990) [KELWAZ is tetraphenylphosphonium tris[(2,4,6-tri-isopropyl)benzenethiolato]cadmium(II) dimethylformamide isopropanol solvate]; (d) Bochmann *et al.* (1990) [TABXAV is bis[(μ_2 -2,4,6-tri-*tert*-butylbenzenethiolato-*S,S'*)(2,4,6-tri-*tert*-butylbenzenethiolato-*S*)cadmium(II)]; (e) Wojnowski *et al.* (1992) [PAGBAA is bis[(μ_2 -tri-*tert*-butoxysilanethiolato) (tri-*tert*-butoxysilanethiolato)cadmium(II)]; (f) Edwards *et al.* (1996) [ZOJLAL is (tetramethylethylenediamine)bis(tritylthiolato)cadmium(II)]; (g) Mugesh *et al.* (1999) [DILHAH is bis[2-(4,4-dimethyl-2-oxazolonyl)phenylthiolato-*N,S*]cadmium(II)]; (h) Otto *et al.* (1999) [GUFFUI is bis(*N*-methylimidazole)bis[*N*-(2-thiophenyl)-2,5-dimethylpyrrole]cadmium(II)]; (i) Sun *et al.* (1999) [JUQJAV is bis[(2-(benzoylamino)benzenethiolato)(*N*-methylimidazole)cadmium(II) hemihydrate]; (j) Pérez-Lourido *et al.* (1999) [HOKFUI is bis(2-diphenyl(oxo)phosphanyl-6-trimethylsilylphenylthiolato)(methanol)cadmium(II)]; (k) Nyman *et al.* (1997) [RAGDIM is bis(3,5-dimethylpyridine)bis(thiopivaloato)cadmium(II)]; (l) tS denotes terminal S; bS denotes bridging S.

All H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.95–0.98 \AA and with isotropic displacement parameters of 1.2 times U_{eq} of their attached atoms. The highest density peak is located 1.41 \AA from atom S1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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