

Tetraethylammonium bis(*N,N*-diethylthiocarbamate- κ^2 *S,S'*)iodocadmate(II)

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The title compound, $(C_8H_{20}N)[Cd(C_5H_{10}NS_2)_2I]$, containing a heteroleptic five-coordinate mononuclear anionic cadmium complex, crystallizes in orthorhombic form in the space group *Pnma*. Both anion and cation lie about mirror planes. Unlike other known $[Cd(dtc)_2X]$ -type complexes (where *dtc* is dithiocarbamate and *X* is a halogen or pseudohalogen), the central CdS_4I core shows a square-pyramidal configuration, with a basal plane defined by four S atoms from two chelating dithiocarbamate ligands related by a symmetry plane. The central Cd atom is displaced from the basal S_4 plane towards the apical I atom of the square pyramid.

Comment

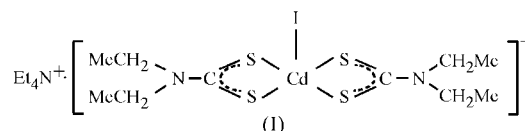
Only a few mixed cadmium–halide–dithiocarbamate complexes are known. A neutral polymeric $[Cd(S_2CNET_2)_n]$ complex was obtained by oxidation of dimeric cadmium bis(*N,N*-diethylthiocarbamate) (Domenicano *et al.*, 1968) with a limited amount of elemental iodine (Duhme *et al.*, 1990). The crystal structure of this complex is built up from $[Cd(S_2CNET_2)_2CdI_2]$ repeat units and can be regarded as an alternating copolymer of cadmium *N,N*-diethylthiocarbamate and cadmium iodide. A group of $[Cd(S_2CNET_2)_2X]^-$ (*X* = Cl, Br, I or NCS) species have been prepared by reacting tetraalkylammonium salts of respective monodentate X^- ligands with dimeric cadmium bis(*N,N*-diethylthiocarbamate) (Baggio *et al.*, 1992). All complexes but one, *viz.* $(NBu_4)[Cd(S_2CNET_2)_2I]$, were isolated as $[NEt_4]^+$ salts. The crystal and molecular structures were determined only for the isothiocyanate adduct. It was found to be mononuclear with strongly distorted trigonal-bipyramidal CdS_4N coordination geometry and an N atom occupying one of the equatorial positions. IR and Raman data allowed the authors to suggest monometallic character (but nothing more) also for related Cl-, Br- and I-containing complexes.

This suggestion was later confirmed by the synthesis and structure determination by X-ray crystallography of two

complexes, *viz.* $(PPh_4)[Cd(S_2CNET_2)_2Cl]$ and $(PPh_4)[Cd(S_2CNET_2)_2Br]$ (Baggio *et al.*, 1996). These compounds were found to be not only monometallic but also isomorphous, with the central Cd atom linked to the halide and four S atoms from two chelating dithiocarbamate ligands. The geometry of the resulting CdS_4X kernel was described as exactly halfway between trigonal-bipyramidal and square-pyramidal. The iodine-containing complex, $[Cd(S_2CNET_2)_2I]^-$, was not mentioned.

It is generally accepted that even minor modifications to a material (*e.g.* the exchange of one alkyl group for another) can have a profound effect on the structure and hence the properties of the compound (Miller, 2005). This also means that any predictions of unknown structures, such as, for example, that of the $[Cd(S_2CNET_2)_2I]^-$ complex anion, should be treated cautiously. The small number of complexes that may be used for comparisons and the different cations that they are bonded to made such predictions even less reliable.

We report here the synthesis, isolation of single crystals and X-ray analysis of the title compound, $(NEt_4)[Cd(S_2CNET_2)_2I]$, (I). The compound was formed during the reaction of dimeric cadmium bis(tri-*tert*-butoxysilanethiolate) (Wojnowski *et al.*, 1992) with sodium *N,N*-diethylthiocarbamate in the presence of tetraethylammonium iodide in a toluene/water mixture.



Compound (I) consists of the common tetraethylammonium cation and the complex $[Cd(S_2CNET_2)_2I]^-$ anion, where the central Cd^{II} ion is coordinated by iodide and two bidentate *N,N*-diethylthiocarbamate ligands (Fig. 1). The

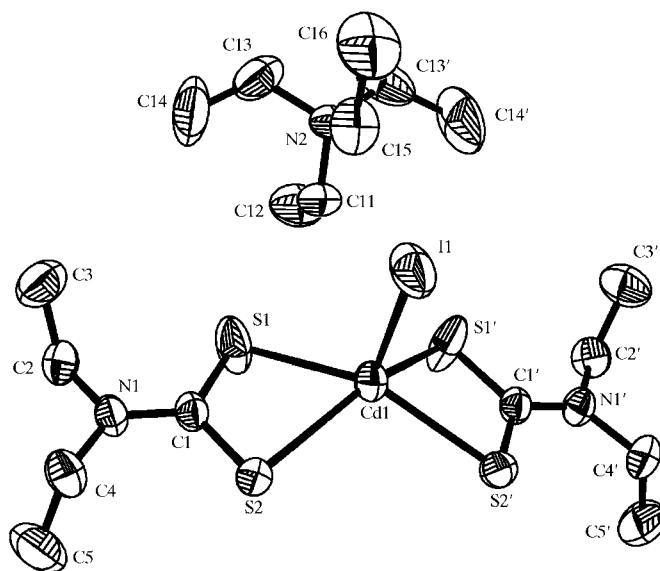


Figure 1

A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level (ORTEP-3; Farrugia, 1997). H atoms have been omitted. Primed atoms are related by a mirror plane (symmetry code: $x, \frac{1}{2} - y, z$).

whole assembly is symmetrical, with atoms Cd1 and I1 (from the anion), as well as atoms N2, C11, C12, C15 and C16 (from the cation), lying on the mirror plane. Fig. 2 shows the packing diagram viewed along the *c* axis. Selected geometric parameters are collected in Table 1.

The structure of the $[\text{NET}_4]^+$ cation is very typical and does not require any discussion. The most notable structural feature of the anion is its square-pyramidal geometry, with atoms S1, S1', S2 and S2' defining the basal plane (Fig. 3). Some deviations are imposed by the bite angle of two symmetry-related chelating dithiocarbamate ligands and the non-equivalence of the necessarily wider S1—Cd1—S1' and S2—Cd1—S2' angles. Further distortion is demonstrated by atom Cd1 being displaced from the basal plane towards the apical I atom of the square pyramid and the apical-to-basal bond angles being greater than 90° . These deviations, however, by no means favor a trigonal-bipyramidal config-

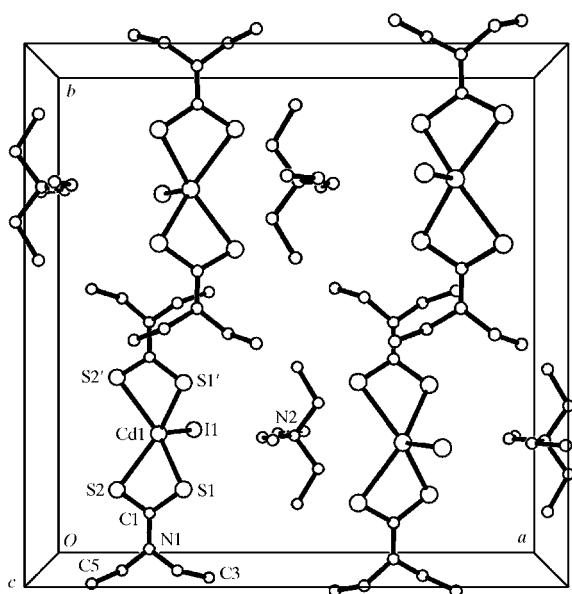


Figure 2
A packing diagram of (I), viewed along the *c* axis. H atoms have been omitted.

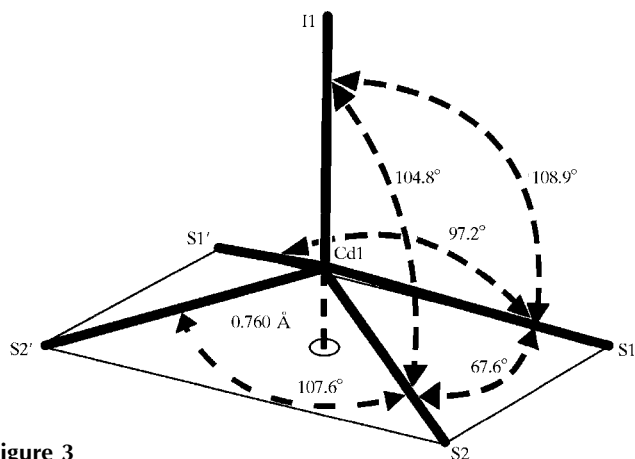


Figure 3
The central square-pyramidal CdS_4I core.

uration of the CdS_4I kernel. The index parameter τ (Addison *et al.*, 1984), conveniently describing the changes on going from ideal square-pyramidal ($\tau = 0.0$) to ideal trigonal-bipyramidal geometry ($\tau = 1.0$), calculated for the structures of four different $[\text{Cd}(\text{S}_2\text{CNET}_2)_2\text{X}]^-$ -type anions is 0.5 when *X* is Cl and Br (Baggio *et al.*, 1996), 0.27 when *X* is NCS (Baggio *et al.*, 1992), and 0.0 when *X* is I (this paper). It is unlikely that any 'special' property of homologous Cl, Br or I ligands (or even the NCS ligand) determines the complex anion geometry. Instead, we conclude that it is the cation and, more precisely, its steric requirements (namely $[\text{NET}_4]^+$ versus $[\text{PPh}_4]^+$) that significantly influence the structure. In the somewhat similar complex anion $[\text{Cd}(\text{S}_2\text{P}(\text{OEt})_2)_2\text{I}]^-$, when accompanied by a very large cation such as $[\mu_3\text{-oxo-tri-}\mu_2\text{-sulfido-tris}(\text{diethyl-dithiophosphonato})(\text{pyridine})\text{molybdenum}]^+$ [Cambridge Structural Database (CSD; Version 5.27 of 2006; Allen, 2002) refcode MAJGIN (Lu *et al.*, 1997)], the geometry of the central CdS_4I kernel is slightly distorted, but nevertheless it easily qualifies as trigonal-bipyramidal ($\tau = 0.7$).

The dithiocarbamate ligand in the $[\text{Cd}(\text{S}_2\text{CNET}_2)_2\text{X}]^-$ complex anion with *X* = I is bonded to cadmium much more symmetrically (the Cd—S bond lengths differ by only 0.01 Å) than the same ligand in the cases where *X* = NCS (0.07 Å; Baggio *et al.*, 1992) and *X* = Cl or Br (*ca* 0.16 Å; Baggio *et al.*, 1996). This property seems to be related to the magnitude of advancement of the CdS_4X kernel geometry towards trigonal-bipyramidal where the discrimination in bond lengths formed by the same donor atoms in equatorial and axial positions is usually observed. The mean Cd—S bond length remains, however, the same in all complexes discussed (2.65 Å) and does not differ from that in the neutral dimeric cadmium bis(*N,N*-diethyldithiocarbamate) complex (Domenicano *et al.*, 1968). Again, the data reported for $[\text{Cd}(\text{S}_2\text{P}(\text{OEt})_2)_2\text{I}]^-$ (Lu *et al.*, 1997) support this conclusion (Cd— S_{eq} = 2.531 and 2.545 Å, although Cd— S_{ax} = 2.766 and 2.952 Å).

Finally, the Cd—I bond length of 2.7919 (8) Å seems unexceptional as it falls roughly within the upper limit of Cd—I bond lengths reported for different complexes where non-bridging I and S atoms are bonded to five-coordinated cadmium (2.70–2.80 Å; CSD).

Experimental

All commercially available reagents were of analytical or reagent grade purity and were used as received. Cadmium bis(tri-*tert*-butoxysilanethiolate) (0.135 g, 0.11 mmol), prepared according to a previously reported procedure (Wojnowski *et al.*, 1992), was dissolved in toluene (15 ml). Sodium *N,N*-diethyldithiocarbamate trihydrate (0.49 g, 0.22 mmol) and tetraethylammonium iodide (0.056 g, 0.22 mmol) were dissolved in hot water (7 ml each). The aqueous solutions were mixed, and to the resulting mixture a solution of the cadmium complex in toluene was added. The mixture was shaken vigorously for *ca* 3 h and the layers separated. The organic layer was washed with three 15 ml portions of water, dried over anhydrous magnesium sulfate and finally evaporated to dryness. The solid was dissolved in a minimum amount of toluene and the solution was left for crystallization at room temperature. After a few days, the

deposited small yellow crystals were collected and recrystallized from toluene, giving single crystals of quality sufficient for X-ray measurement. The yield was *ca* 40% and was not optimized.

Crystal data

(C₈H₂₀N)[Cd(C₅H₁₀NS₂)₂I]
M_r = 666.07
 Orthorhombic, *Pnma*
a = 17.859 (2) Å
b = 17.994 (2) Å
c = 8.692 (1) Å
V = 2793.3 (5) Å³
Z = 4
D_x = 1.584 Mg m⁻³

Mo *Kα* radiation
 Cell parameters from 11478 reflections
 $\theta = 2.5\text{--}32.5^\circ$
 $\mu = 2.19\text{ mm}^{-1}$
T = 293 (2) K
 Prism, pale yellow
 0.24 × 0.14 × 0.08 mm

Data collection

Kuma KM-4 diffractometer with Sapphire-2 CCD detector
 ω scans
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)
 19561 measured reflections

2827 independent reflections
 2675 reflections with *I* > 2 σ (*I*)
R_{int} = 0.038
 $\theta_{\text{max}} = 26^\circ$
h = -22 → 22
k = -22 → 20
l = -10 → 10

Table 1

Selected geometric parameters (Å, °).

I1—Cd1	2.7919 (8)	C4—C5	1.488 (9)
Cd1—S1	2.6450 (16)	C2—C3	1.503 (8)
Cd1—S2	2.6571 (12)	N2—C15	1.502 (9)
S2—C1	1.723 (5)	N2—C13	1.506 (7)
S1—C1	1.711 (5)	N2—C11	1.518 (9)
N1—C1	1.334 (6)	C11—C12	1.492 (12)
N1—C2	1.475 (6)	C13—C14	1.554 (13)
N1—C4	1.476 (6)	C15—C16	1.532 (15)
S1—Cd1—S1 ⁱ	97.23 (7)	C1—N1—C4	122.6 (4)
S1—Cd1—S2	67.63 (4)	C2—N1—C4	114.8 (4)
S1 ⁱ —Cd1—S2	146.09 (6)	N1—C1—S1	120.1 (4)
S2—Cd1—S2 ⁱ	107.56 (5)	N1—C1—S2	121.4 (4)
S1—Cd1—I1	108.91 (5)	S1—C1—S2	118.4 (3)
S2—Cd1—I1	104.76 (4)	C15—N2—C13	110.2 (5)
C1—S2—Cd1	85.96 (15)	C13—N2—C13 ⁱ	107.8 (8)
C1—S1—Cd1	86.58 (16)	C15—N2—C11	106.6 (6)
C1—N1—C2	122.5 (4)	C13—N2—C11	111.0 (4)

Symmetry code: (i) *x*, -*y* + $\frac{1}{2}$, *z*.

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.054
wR(*F*²) = 0.118
S = 1.06
 2827 reflections
 138 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 12.9136P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.65\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.5\text{ e \AA}^{-3}$

All H atoms were refined as riding (C—H = 0.96 and 0.97 Å), with their *U*_{iso}(H) values constrained to be 1.5*U*_{eq}(C) of the pivot atoms for CH₃ groups or 1.3*U*_{eq}(C) for CH₂ groups.

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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3001). Services for accessing these data are described at the back of the journal.

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