

Bis(O-methyldithiocarbonato)cadmium(II)

Victor G. Young Jr^a and Edward R. T. Tiekink^{b*}^aDepartment of Chemistry, University of Minnesota, 160 Kolthoff Hall, 207 Pleasant Street S.E., Minneapolis, MN 55455, USA, and^bDepartment of Chemistry, National University of Singapore, Singapore 117543

Correspondence e-mail: chmert@nus.edu.sg

Key indicators

Single-crystal synchrotron study

T = 123 K

Mean $\sigma(\text{O}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.030

wR factor = 0.073

Data-to-parameter ratio = 18.1

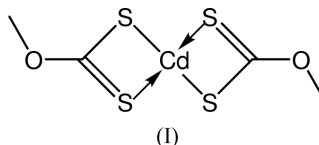
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

To a first approximation, the cadmium centre in the centrosymmetric title compound, $[\text{Cd}(\text{S}_2\text{COCH}_3)_2]$, exists within an S_4 donor set which defines a distorted square planar geometry. Molecules associate in the crystal structure *via* Cd—S interactions above and below the square plane, so as to form stacks that might be considered as edge-shared, tetragonally distorted octahedra.

Comment

As highlighted in a bibliographic review of the zinc-triad binary 1,1-dithiolates, *e.g.* with dithiocarbamate ($^-\text{S}_2\text{CNR}_2$), xanthate ($^-\text{S}_2\text{COR}$), and dithiophosphate [$^-\text{S}_2\text{P}(\text{OR})_2$] anions, the structural chemistry of this class of ligands is extraordinarily diverse (Cox & Tiekink, 1997). Particularly interesting is the observation that very different structural types may be found, even when there has only been a minor change in the nature of the organic substituent. Pertinent to the present paper are the structures of the cadmium bis-(xanthate)s.

The structure of the butylxanthate, *i.e.* $\text{Cd}(\text{S}_2\text{CONBu})_2$, features tetrahedral cadmium centres and bridging xanthate ligands, so that a layer structure is formed (Rietveld & Maslen, 1965). A similar motif is found for the ethyl- (Iimura *et al.*, 1972) and isopropylxanthates (Iimura, 1973; Tomlin *et al.*, 1999; Tiekink, 2000). Incredibly, exchanging the γ -methylene group in $\text{Cd}(\text{S}_2\text{CONBu})_2$ for an O atom, giving $\text{Cd}(\text{S}_2\text{COCH}_2\text{CH}_2\text{OMe})_2$, leads to an entirely different motif based on a square planar geometry (Abrahams *et al.*, 1988). The challenge remains to rationalize the diverse structures found in the solid state.



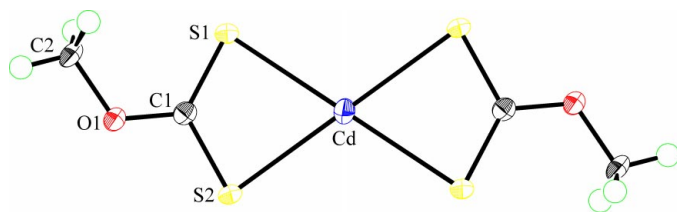
Systematic studies in this field have been hampered by the inability to grow suitable crystals for X-ray analysis. In the case of the title compound, $\text{Cd}(\text{S}_2\text{COMe})_2$, (I), this difficulty has been overcome by the utilization of synchrotron radiation, enabling a full structure determination on a microcrystal with dimensions $0.01 \times 0.025 \times 0.025 \text{ mm}$. As described, the structure of (I) resembles that reported earlier for $\text{Cd}(\text{S}_2\text{COCH}_2\text{CH}_2\text{OMe})_2$ (Abrahams *et al.*, 1988).

The molecular structure of (I) (Fig. 1 & Table 1) is centrosymmetric and features two almost symmetrically chelating xanthate ligands that define an S_4 donor set leading, to a first approximation, to a square planar geometry. The

Received 2 September 2002

Accepted 4 September 2002

Online 13 September 2002


Figure 1

The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 70% probability level (Johnson, 1976). Symmetry operator for generating equivalent atoms: $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$.

variation of the parameters associated with the independent xanthate ligand are as expected; see Table 1. Molecules associate in the crystal structure to form stacks between translationally related molecules aligned along b ; one such stack is illustrated in Fig. 2. These are held in place by close $\text{Cd} \cdots \text{S}$ interactions occurring above and below the square plane. The $\text{Cd} \cdots \text{S1}^i$ ($i: x, y - 1, z$) distance of 2.8881 (6) Å is at least 0.24 Å longer than the weaker of the $\text{Cd}-\text{S}$ bonds defining the square plane. The comparable intermolecular $\text{Cd}-\text{S}$ interaction in the structure of $\text{Cd}(\text{S}_2\text{COCH}_2\text{CH}_2\text{OMe})_2$ was reported to be significantly longer at 3.0225 (8) Å (Abrahams *et al.*, 1988). If the $\text{Cd}-\text{S1}^i$ interaction in (I) was considered significant, the coordination geometry could be considered as tetragonally distorted octahedral and the crystal structure thought of being comprised of edge-shared octahedra.

Experimental

Pale-yellow crystals were obtained from the slow evaporation of an acetone solution of the compound, which had been prepared following the literature procedure (Abrahams *et al.*, 1988).

Crystal data

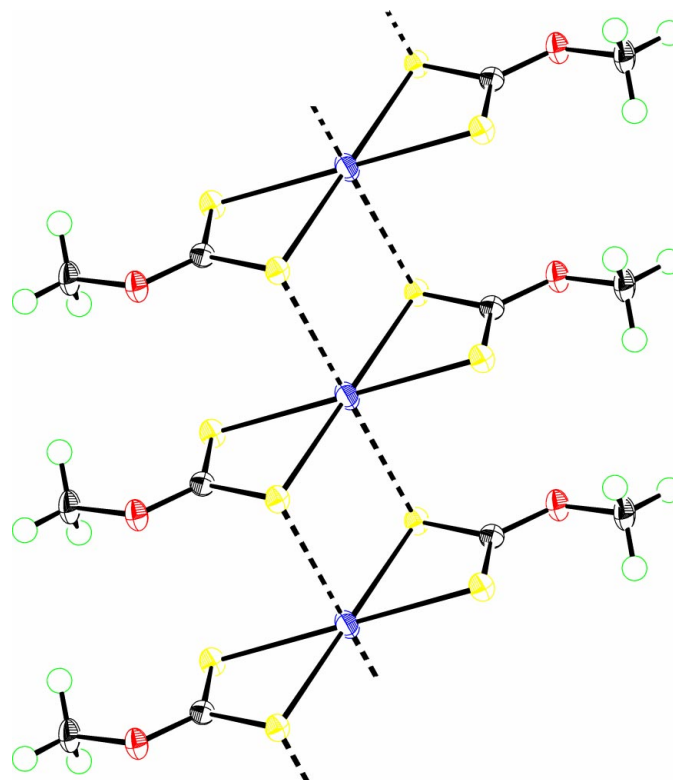
$[\text{Cd}(\text{C}_2\text{H}_3\text{OS}_2)_2]$	Synchrotron radiation
$M_r = 326.73$	$\lambda = 0.56357$ Å
Monoclinic, $C2/c$	Cell parameters from 2655 reflections
$a = 19.006$ (2) Å	$\theta = 2.7-21.4^\circ$
$b = 3.9728$ (3) Å	$\mu = 1.72$ mm $^{-1}$
$c = 12.5126$ (14) Å	$T = 123$ (2) K
$\beta = 107.993$ (4) $^\circ$	Plate, yellow
$V = 898.59$ (17) Å 3	$0.025 \times 0.025 \times 0.01$ mm
$Z = 4$	
$D_x = 2.415$ Mg m $^{-3}$	

Data collection

Bruker Mosaic CCD κ -geometry diffractometer	1031 independent reflections
φ scans	992 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{\text{int}} = 0.084$
$T_{\text{min}} = 0.958$, $T_{\text{max}} = 0.998$	$\theta_{\text{max}} = 21.4^\circ$
6696 measured reflections	$h = -24 \rightarrow 23$
	$k = 0 \rightarrow 5$
	$l = 0 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.72$ e Å $^{-3}$
1031 reflections	$\Delta\rho_{\text{min}} = -1.22$ e Å $^{-3}$
57 parameters	Extinction correction: <i>SHELXL</i>
H atoms: see text	Extinction coefficient: 0.0301 (16)


Figure 2

View of the molecular aggregation in (I).

Table 1

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

$\text{Cd}-\text{S1}$	2.6364 (6)	$\text{S2}-\text{C1}$	1.6871 (19)
$\text{Cd}-\text{S2}$	2.6413 (5)	$\text{C1}-\text{O1}$	1.322 (3)
$\text{Cd}-\text{S1}^i$	2.8881 (6)	$\text{O1}-\text{C2}$	1.454 (3)
$\text{S1}-\text{C1}$	1.7307 (18)		
$\text{S1}-\text{Cd}-\text{S2}$	69.373 (17)	$\text{S1}-\text{C1}-\text{O1}$	113.84 (14)
$\text{S1}-\text{Cd}-\text{S2}^{\text{ii}}$	110.627 (17)	$\text{S2}-\text{C1}-\text{O1}$	123.17 (14)
$\text{S2}-\text{Cd}-\text{S1}^i$	90.679 (16)	$\text{S1}-\text{C1}-\text{S2}$	122.99 (11)
$\text{Cd}-\text{S1}-\text{C1}$	82.94 (7)	$\text{C1}-\text{O1}-\text{C2}$	118.87 (17)
$\text{Cd}-\text{S2}-\text{C1}$	83.57 (6)		

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

The H atoms were placed in ideal geometry, with $\text{C}-\text{H} = 0.98$ Å, with the aid of a toroidal Fourier synthesis. Refinement includes one additional parameter for the torsional refinement of the methyl plus three isotropic displacement parameters for the H atoms. The maximal residual electron density peak was located 0.78 Å from the Cd atom

Data collection: *SMART-KAPPA* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The National University of Singapore is thanked for the award of a research grant (R-143-000-151-112). Use of the ChemMatCARS sector 15 at the Advanced Photon Source was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program.

ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under grant number CHE0087817 and by the Illinois Board of Higher Education. The Advanced Photon Source is supported by the US Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. Special thanks go to D. Cookson, T. Graber, and J. Gebhardt at ChemMatCARS, for providing exceptional assistance at 15-ID.

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