O(*W*2)· · ·O(*W*1)	2.868 (5)	O(*W*2)· · ·O(21)	2.775 (5)
O(*W*4)· · ·O(11)	2.878 (7)	O(*W*2)· · ·O(12^{i})	2.761 (5)
O(*W*3)· · ·O(*W*1^{i})	2.841 (6)	O(*W*1)· · ·O(12^{i})	2.885 (5)
O(*W*1)· · ·O(32^{i})	2.888 (5)	O(*W*1)· · ·O(22^{iv})	2.776 (5)
O(*W*2)· · ·O(13^{ii})	2.866 (7)	O(*W*3)· · ·O(*W*2^{v})	2.761 (6)
O(*W*4)· · ·O(*W*3^{iii})	2.736 (9)		

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

Intensity data were corrected for Lp factors. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares. All non-H atoms were refined anisotropically. H atoms on the benzene rings were located by theoretical calculation. All calculations were performed using the *SHELXTL* program system (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters and bond angles have been deposited with the IUCr (Reference: AB1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Mixed-Ligand Cadmium(II) Complex of Xanthic Acid and *N*,*N*′-Bis(4-methoxyphenyl)thiourea

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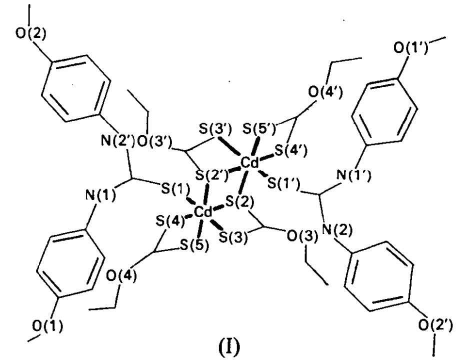
Abstract

The X-ray analysis reveals that the title compound, bis(μ-*O*-ethyl dithiocarbonato)-1κS,1:2$\kappa^2 S'$;2κS,-1:2$\kappa^2 S'$-bis{(*O*-ethyl dithiocarbonato-$\kappa^2 S,S'$)[*N*,*N*′-bis(4-methoxyphenyl)thiourea-κS]cadmium(II)}, $[Cd_2(C_3H_5OS_2)_4(C_{15}H_{16}N_2O_2S)_2]$, is a dimer of distorted octahedral Cd ions each coordinated to six S atoms: one non-bridging S atom of the thiourea ligand at a distance of 2.641 (1) Å, four non-bridging S atoms of the chelating/chelating–bridging xanthato (*O*-ethyl dithiocarbonato) ligands at distances of 2.606 (2)–2.765 (1) Å, and one bridging S atom of the chelating–bridging xanthato ligand at a much longer distance of 2.831 (2) Å. The shortest metal–sulfur distances involve the S atoms of one of the chelating moieties, while the S atoms of the chelating–bridging moiety form one of the shorter and the longest '2.831 Å' metal–sulfur distances. The other 'short' bond is subtended to an S atom of a symmetry-related bridging–chelating ligand. Cd, S(2), S(2^{i}) and Cd^{i} are coplanar [symmetry code: (i) $-x, -y, -z$].

Comment

Cadmium thiourea and xanthato derivative complexes have aroused considerable interest in recent years in view of their nonlinear optical properties (Xing, Jiang, Shao & Xu, 1987; Tao, Jian, Xu & Shao, 1987). Cd has a variety of coordination environments. In previous papers it appears that the coordination of Cd is most frequently tetrahedral or trigonal bipyramidal (Castineiras, Arguero, Masaguer, Ruiz-Amil, Martinez-Carrera & Garcia-Blanco, 1985; Casas, Sanchez, Bravo, Garcia-Fontan, Castellano & Jones, 1989). To study the Cd coordination environments and to determine the precise conditions which favour selective synthesis of asymmetric complexes, the crystal structure of a Cd^{II} complex, (I), of mixed ligands of xanthic acid and *N*,*N*′-bis(4-methoxyphenyl)thiourea is reported here.



(I)

The dimeric molecule is located on a centre of inversion. The Cd atom is octahedrally coordinated to one xanthato group functioning as a bidentate ligand, one bridging–bidentate xanthato and one monodentate *N*,*N*′-bis(4-methoxyphenyl)thiourea. The sixth coordination site around the Cd atom is

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occupied by the symmetry-related bridging–chelating xanthato ligand. The Cd—S(4) [2.606 (2) Å] and Cd—S(5) [2.710 (2) Å] bond distances indicate that the xanthate acts as a bidentate chelating ligand. The Cd—S bond lengths vary from 2.606 (2) Å for the non-bridging chelate ligand to 2.831 (1) Å for the bridging–chelating ligand. Two of the shortest metal–sulfur distances are formed by the S atoms of one of the chelating moieties [S(4) and S(5)] while the S atoms of the other chelating–bridging moiety produce the longest [Cd—S(2)] and a shorter [Cd—S(3)] metal–sulfur distances. The sharing of an S atom gives rise to a dimeric unit in which one of the ligands forms a four-membered chelate ring and the other is coordinated to two different Cd^{2+} ions while at the same time it completes a chelate ring with a long approach distance [2.831 (1) Å]. This situation is similar to that in cadmium bis(*n*-butyl)dithiocarbamate (Casas *et al.*, 1989) in spite of the fact that the title compound possesses a different coordination number.

The Cd—S(1) bond length, which is longer than that of a bridging thiourea (Thanmaniwong, Akimov, Andrianov, Struchkov & Molodkin, 1984), indicates that the *N*,*N*′-bis(4-methoxyphenyl)-thiourea is a neutral monodentate ligand.

The N—C and C—S bond lengths of the thiourea correspond with those of other thiourea derivatives (Reid, 1963). On the basis of the bond angles at the central atom, the complex may be described as having distorted octahedral coordination.

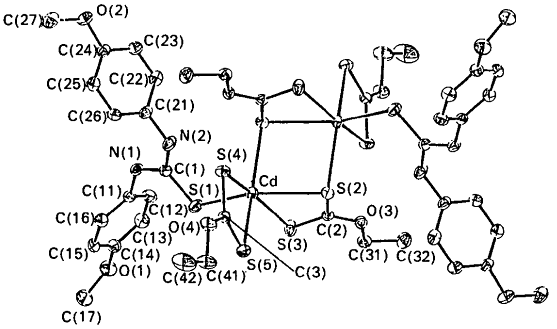

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) plot of the title complex.

Experimental

The title compound was synthesized by refluxing cadmium bromide with stoichiometric quantities of carbon disulfide, sodium ethoxide and 4-methoxyaniline in ethanol for 2 h. The single crystals were obtained by slow evaporation of the solvent.

Crystal data

$[Cd_2(C_3H_5OS_2)_4$-
$(C_{15}H_{16}N_2O_2S)_2]$
$M_r = 1286.27$
Triclinic
$P\bar{1}$
$a = 9.430$ (4) Å
$b = 11.826$ (3) Å
$c = 12.044$ (7) Å
$\alpha = 92.23$ (3)°
$\beta = 96.31$ (4)°
$\gamma = 91.94$ (3)°
$V = 1333$ (2) Å^3

$Z = 1$
$D_x = 1.60$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13$-15°
$\mu = 1.22$ mm^{-1}
$T = 296$ K
Cubic
0.45 × 0.35 × 0.30 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans [1-10° min^{-1}; width (0.85 + 0.35tanθ)° in ω]
Absorption correction: empirical (ψ scan)
$T_{min} = 0.73$, $T_{max} = 1.24$
4920 measured reflections
4675 independent reflections
4069 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.038$
$\theta_{max} = 25°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 90 min
intensity variation: −2.7%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.063$
$S = 1.94$
4069 reflections
299 parameters
Unit weights applied

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 1.50$ e Å^{-3}
$\Delta\rho_{min} = -1.06$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cd	0.06490 (4)	0.16879 (3)	−0.00149 (3)	3.26 (2)
S(1)	0.2862 (1)	0.2656 (1)	−0.0819 (1)	4.56 (6)
S(2)	−0.1929 (1)	0.0359 (1)	−0.0320 (1)	3.19 (5)
S(3)	−0.0399 (1)	0.1286 (1)	−0.2128 (1)	4.19 (5)
S(4)	0.0994 (1)	0.2308 (1)	0.2100 (1)	3.73 (5)
S(5)	−0.0789 (1)	0.3574 (1)	0.0411 (1)	3.94 (5)
O(1)	0.6581 (5)	0.4570 (4)	−0.4332 (3)	5.6 (2)
O(2)	0.8841 (4)	0.0924 (3)	0.4138 (3)	4.8 (2)
O(3)	−0.2661 (3)	−0.0092 (3)	−0.2405 (3)	3.3 (1)
O(4)	−0.0120 (4)	0.4163 (3)	0.2543 (3)	4.5 (2)
N(1)	0.5648 (4)	0.2786 (4)	−0.0259 (3)	3.8 (2)
N(2)	0.4360 (4)	0.1975 (5)	0.1009 (4)	5.1 (2)
C(1)	0.4389 (5)	0.2452 (4)	0.0026 (4)	3.6 (2)
C(2)	−0.1695 (5)	0.0492 (4)	−0.1701 (4)	2.9 (2)
C(3)	−0.0007 (5)	0.3426 (4)	0.1710 (4)	3.4 (2)
C(11)	0.5860 (5)	0.3274 (4)	−0.1305 (4)	3.4 (2)
C(12)	0.5720 (6)	0.2603 (4)	−0.2277 (5)	4.3 (2)
C(13)	0.5960 (6)	0.3065 (5)	−0.3277 (5)	4.4 (2)
C(14)	0.6351 (5)	0.4192 (4)	−0.3301 (4)	4.0 (2)
C(15)	0.6517 (6)	0.4855 (4)	−0.2326 (5)	4.2 (2)
C(16)	0.6256 (5)	0.4392 (4)	−0.1331 (4)	4.0 (2)
C(17)	0.6749 (8)	0.5756 (6)	−0.4418 (6)	6.5 (3)
C(21)	0.5566 (5)	0.1747 (5)	0.1784 (4)	4.0 (2)
C(22)	0.6044 (5)	0.0661 (5)	0.1855 (4)	4.0 (2)

C(23)	0.7129 (6)	0.0411 (5)	0.2644 (4)	4.0 (2)
C(24)	0.7770 (5)	0.1257 (4)	0.3368 (4)	3.6 (2)
C(25)	0.7309 (6)	0.2338 (5)	0.3306 (5)	4.4 (2)
C(26)	0.6211 (6)	0.2583 (5)	0.2502 (5)	4.5 (2)
C(27)	0.9602 (7)	0.1762 (6)	0.4846 (4)	5.2 (3)
C(31)	−0.2537 (6)	−0.0060 (4)	−0.3602 (4)	3.7 (2)
C(32)	−0.3611 (7)	−0.0911 (5)	−0.4172 (5)	5.0 (3)
C(41)	−0.0903 (8)	0.5180 (5)	0.2324 (6)	6.1 (3)
C(42)	−0.068 (1)	0.5904 (7)	0.3313 (8)	9.3 (5)

Table 2. *Selected geometric parameters* (Å, °)

Cd—S(4)	2.606 (2)	N(1)—C(1)	1.323 (6)
Cd—S(1)	2.641 (2)	N(1)—C(11)	1.437 (6)
Cd—S(3)	2.646 (2)	N(2)—C(1)	1.334 (6)
Cd—S(5)	2.710 (2)	N(2)—C(21)	1.430 (6)
Cd—S(2^{i})	2.765 (1)	C(11)—C(16)	1.365 (7)
Cd—S(2)	2.831 (2)	C(11)—C(12)	1.380 (8)
S(1)—C(1)	1.699 (5)	C(12)—C(13)	1.380 (8)
S(2)—C(2)	1.714 (5)	C(13)—C(14)	1.373 (7)
S(3)—C(2)	1.655 (5)	C(14)—C(15)	1.378 (8)
S(4)—C(3)	1.701 (5)	C(15)—C(16)	1.380 (7)
S(5)—C(3)	1.673 (5)	C(21)—C(26)	1.369 (8)
O(1)—C(14)	1.373 (6)	C(21)—C(22)	1.378 (8)
O(1)—C(17)	1.415 (8)	C(22)—C(23)	1.367 (7)
O(2)—C(24)	1.373 (5)	C(23)—C(24)	1.379 (7)
O(2)—C(27)	1.405 (7)	C(24)—C(25)	1.366 (7)
O(3)—C(2)	1.329 (5)	C(25)—C(26)	1.384 (7)
O(3)—C(31)	1.461 (6)	C(31)—C(32)	1.495 (8)
O(4)—C(3)	1.319 (6)	C(41)—C(42)	1.43 (1)
O(4)—C(41)	1.451 (6)		
S(1)—Cd—S(2)	150.85 (5)	N(2)—C(1)—S(1)	121.3 (4)
S(1)—Cd—S(3)	85.87 (6)	O(3)—C(2)—S(3)	122.7 (3)
S(1)—Cd—S(5)	98.68 (5)	O(3)—C(2)—S(2)	114.0 (3)
S(3)—Cd—S(2)	65.46 (5)	S(3)—C(2)—S(2)	123.3 (3)
S(3)—Cd—S(5)	98.56 (6)	O(4)—C(3)—S(5)	123.2 (3)
S(4)—Cd—S(1)	103.96 (6)	O(4)—C(3)—S(4)	113.0 (3)
S(4)—Cd—S(2)	105.26 (6)	S(5)—C(3)—S(4)	123.8 (3)
S(4)—Cd—S(3)	164.28 (5)	C(16)—C(11)—C(12)	119.9 (5)
S(4)—Cd—S(5)	68.09 (5)	C(16)—C(11)—N(1)	119.9 (5)
S(5)—Cd—S(2)	91.04 (5)	C(12)—C(11)—N(1)	120.1 (4)
S(1)—Cd—S(2^{i})	94.66 (5)	C(11)—C(12)—C(13)	120.1 (5)
S(2)—Cd—S(2^{i})	84.63 (5)	C(14)—C(13)—C(12)	119.8 (5)
S(3)—Cd—S(2^{i})	97.71 (5)	C(13)—C(14)—O(1)	115.5 (5)
S(4)—Cd—S(2^{i})	93.82 (5)	C(13)—C(14)—C(15)	120.0 (5)
S(5)—Cd—S(2^{i})	159.63 (4)	O(1)—C(14)—C(15)	124.5 (5)
Cd—S(2)—Cd	95.37 (5)	C(14)—C(15)—C(16)	119.9 (5)
C(1)—S(1)—Cd	110.5 (2)	C(11)—C(16)—C(15)	120.3 (5)
C(2)—S(2)—Cd	98.8 (1)	C(26)—C(21)—C(22)	119.2 (4)
C(2)—S(2)—Cd	81.9 (2)	C(26)—C(21)—N(2)	120.8 (5)
C(2)—S(3)—Cd	89.0 (2)	C(22)—C(21)—N(2)	119.9 (5)
C(3)—S(4)—Cd	85.3 (2)	C(23)—C(22)—C(21)	120.7 (5)
C(3)—S(5)—Cd	82.5 (2)	C(22)—C(23)—C(24)	119.8 (5)
C(14)—O(1)—C(17)	116.7 (5)	C(25)—C(24)—O(2)	124.3 (5)
C(24)—O(2)—C(27)	118.1 (4)	C(25)—C(24)—C(23)	120.1 (4)
C(2)—O(3)—C(31)	118.4 (4)	O(2)—C(24)—C(23)	115.6 (4)
C(3)—O(4)—C(41)	119.0 (4)	C(24)—C(25)—C(26)	119.7 (5)
C(1)—N(1)—C(11)	124.3 (4)	C(21)—C(26)—C(25)	120.5 (5)
C(1)—N(2)—C(21)	126.6 (4)	O(3)—C(31)—C(32)	106.8 (4)
N(1)—C(1)—N(2)	117.6 (4)	C(42)—C(41)—O(4)	107.6 (6)
N(1)—C(1)—S(1)	121.0 (4)		

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

The structure was solved by the Patterson method and Fourier syntheses and refined by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. H-atom coordinates were refined with fixed bond distances. All calculatios were performed on a MicroVAX 3100 using *TEXSAN* (Molecular Structure Corporation, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: AL1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[*meso*-5,10,15,20-Tetrakis(4-methoxyphenyl)porphinato]bis(trimethyl phosphito)iron(II)

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Abstract

The structure determination of the title compound, {2,7,12,17-tetrakis(4-methoxyphenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{16,17}]tetracosa-1(21),2,4,6,8(23),9,11,13,15,17,19-undecaenediido-*N*,*N*′,*N*″,*N*‴}bis(trimethyl phosphito-*P*)iron(II), $[Fe(C_{48}H_{36}N_4)(C_3H_9O_3P)_2]$, is the first example of a

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