

Compound (I)					
N11—H111...O22 ⁱ	2.17 (1)	3.017 (10)	147.8 (6)	84.1 (3)	inter
N11—H111...O23	2.83 (1)	3.050 (15)	94.3 (7)		intra
N11—H112...O11 ⁱⁱ	2.32 (1)	3.035 (10)	132.0 (7)	75.4 (2)	inter
N11—H112...O12 ⁱⁱⁱ	2.73 (1)	3.513 (10)	139.9 (6)	75.2 (2)	intra
N11—H112...S2 ⁱⁱⁱⁱ	3.05 (1)	3.636 (11)	121.6 (7)	94.1 (2)	intra
N12—H121...O14 ^v	2.60 (1)	3.079 (10)	111.5 (6)	97.0 (3)	inter
N12—H121...O22 ⁱ	2.12 (1)	2.983 (12)	149.7 (5)		inter
N12—H122...S2	2.98 (1)	3.716 (12)	135.7 (8)	85.8 (1)	intra
N12—H122...S2 ^v	2.92 (1)	3.684 (9)	138.4 (8)		inter
N21—H211...O13 ^v	2.06 (1)	2.942 (9)	153.6 (5)	85.2 (3)	inter
N21—H211...O23 ⁱ	2.44 (1)	2.941 (13)	112.4 (6)		inter
N21—H212...O21	1.95 (1)	2.898 (9)	175.0 (6)		intra
N22—H221...O13 ^v	2.31 (1)	3.104 (10)	140.8 (5)	86.4 (3)	inter
N22—H221...O24 ^{vi}	2.19 (1)	2.852 (11)	125.7 (6)		inter
N22—H222...S1 ^{vii}	2.70 (1)	3.543 (9)	147.9 (6)		inter

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x - 1, y, z$; (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, -y, -z$; (v) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ for compound (I), (i) $2 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 1 + y, z$; (iv) $2 - x, -y, 1 - z$; (v) $1 + x, y, z - 1$; (vi) $1 + x, y - 1, z$ for compound (II).

Thiourea H atoms were calculated in a riding geometry with fixed $U_{\text{iso}} = 0.506 \text{ \AA}^2$.

For both compounds, data collection: *CAD-4 User's Manual* (Enraf-Nonius, 1988); data reduction: *SDP/PDP* (Enraf-Nonius, 1985). Program(s) used to solve structures: *MULTAN11/82* (Main *et al.*, 1982) for (I); *SHELXS86* (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *SDP/PDP*; molecular graphics: *ORTEPII* (Johnson, 1976), *STRUPLO84* (Fischer, 1985); software used to prepare material for publication: *KAPPA* (Macíček, unpublished) in *SDP/PDP*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1939–1942

Bis(μ -thiosulfato)- $1\kappa\text{O}, 1:2\kappa^2\text{S}; 2\kappa\text{O}, 1:2\kappa^2\text{S}$ -bis[(2,9-dimethyl-1,10-phenanthroline- N, N')cadmium(II)]

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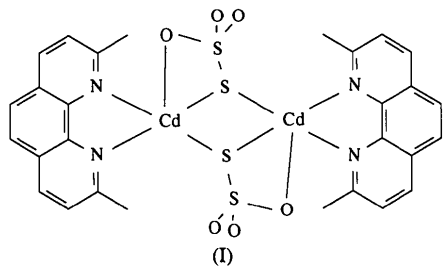
Abstract

The title complex, $[\text{Cd}_2(\text{S}_2\text{O}_3)_2(\text{C}_{14}\text{H}_{12}\text{N}_2)_2]$, presents a dimeric structure with the novel feature of having the thiosulfate group acting as both a bridging and a bidentate ligand. This unusual coordination mode leads to an S—S bond length in the mid-range of those found in the S-bridging thiosulfates, but longer than those observed in monodentate S-bonded complexes. The pentacoordinate Cd^{II} center exhibits a distorted environment.

Comment

As a part of a general study of metal complexes incorporating sulfur oxyanions, we describe here the structure of $[\text{Cd}(\text{dmph})(\text{S}_2\text{O}_3)]$, (I) (where dmph is

2,9-dimethyl-1,10-phenanthroline), which is, to our knowledge, the first reported crystal structure of a complex in which a thiosulfate group is coordinated to a Cd^{II} atom.



The structure consists of isolated dinuclear molecules, which lie across a center of inversion (Fig. 1). The metal atom has a distorted five-coordinate environment, bonding to the two N atoms of a bidentate dmph molecule and to one thiosulfate O and two thiosulfate S atoms. S atoms constitute the bridge in the dimeric moiety.

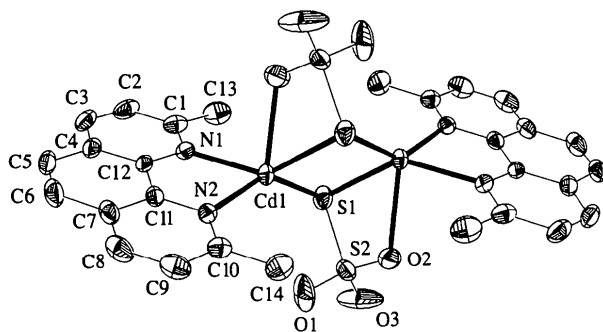


Fig. 1. A view of the dimeric unit showing the numbering scheme used for the independent moiety. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms have been omitted for clarity.

The central Cd₂S₂ ring is a strictly planar parallelogram, with a short and a long Cd—S bond [2.5307 (11) and 2.6950 (12) Å, respectively]. Similar features are observed for the same ring in [Cd(thiourea)₃(SO₄)], in which the bridging ligand is thiourea. In this case, however, the distances are somewhat longer than those reported here [2.627 (7) and 2.870 (7) Å; Corao & Baggio, 1969].

The coordination around the metal atom is distorted and far from the ideal regular geometries expected (trigonal bipyramid or square pyramid) for five-coordinate compounds, mainly due to the acute bite angles of the bidentate ligands.

The Cd—N distances [2.286 (3) and 2.295 (3) Å] are slightly longer than the sum of the covalent radii (2.18 Å), but shorter than those reported in octahedral

or tetrahedral Cd complexes with phenanthroline as N-atom donor (range 2.35–2.38 Å; Clegg & Wheatley, 1974; Bustos, Green, Hencher, Khan & Tuck, 1983).

The thiosulfate group presents an unusual coordination mode, acting as a bidentate (through S and O) and bridging (through S) ligand simultaneously. The Cd—O bond distance [2.480 (3) Å] is rather long compared with similar bonds found in complexes involving other O-atom donors, *e.g.* 2.34 (1) Å in five-coordinate [Cd(thiourea)₃(SO₄)] (Corao & Baggio, 1969), and 2.224 (2) and 2.274 (2) Å in octahedral [Cd(acac)₂(phen)] (Bustos, Green, Hencher, Khan & Tuck, 1983).

When the geometry of the thiosulfate group is compared with that of the free anion, a considerable lengthening of the S—S bond is observed [2.090 (2) *versus* 1.99–2.02 Å; Teng, Fuess & Bats, 1984] and a concomitant shortening of the S—O bond length takes place. In the present case, the endocyclic S—O distance is slightly longer than the exocyclic one [1.445 (4) *versus* 1.422 (3) Å].

It is interesting to contrast the characteristics of the anion when acting as a bidentate or as a bridging ligand through sulfur. In many compounds of the first type, *e.g.* [Co(en)₂(S₂O₃)]⁺ (Murdoch, Tyree, Otterbein, Kinney, Carreras, Copper & Elder, 1985), [Ni(thiourea)₄(S₂O₃)]·H₂O (Fava Gasparri, Mangia, Musatti & Nardelli, 1969) and [(C₅H₅)Mo(O)(μ-S)₂Mo(O)(S₂O₃)]⁻ (Kim & Coucouvanis, 1993), the S—S bond length is practically the same as that in the free anion, but a considerable lengthening of the coordination S—O bond is observed [1.533 (8) *versus* 1.45 (3), 1.50 (1) *versus* 1.45 (2) and 1.51 (1) *versus* 1.43 (1) Å, respectively, in the compounds cited above]. On the other hand, in complexes of the second type, modifications in bonds and angles are observed, but they are not easily rationalized, *e.g.* in [Fe(S₂O₃)₂(NO)₄]²⁻, the S₂O₃ group is a bridging ligand with a very long S—S bond length of 2.173 (3) Å (Glidewell, Lambert, Hursthouse & Motevalli, 1989) and short S—O lengths, while in [Cu_n(S₂O₃)_{2n}]³ⁿ⁻ (Ferrari, Braibanti & Tiripicchio, 1966), very small modifications in the S—S and S—O bond lengths were observed.

It seems that the novel coordination mode reported here leads to an S—S bond length intermediate between those found in the S-bridging thiosulfates studied so far, but longer than those observed in monodentate S-bonded complexes (Baggio, Baggio, Pardo & Garland, 1996). As far as S—O bonds are concerned, the differences between endocyclic and exocyclic distances are not as pronounced as in solely bidentate thiosulfate compounds.

The dmph molecule presents no unusual features, being best described as formed by three planar C₆ rings tilted by less than 2° with respect to one another into a very shallow boat-like conformation. A similar effect was reported for the free ligand (Britton, Thompson & Holz, 1991).

Interdimeric interactions are weak, as suggested by the estimated lengths of the H...S and H...O contacts, which are never shorter than the corresponding sum of the van der Waals radii (2.85 and 2.40 Å, respectively).

Experimental

The crystalline title compound was obtained by allowing a methanol solution of dmph to diffuse into an aqueous solution of sodium thiosulfate and cadmium acetate (molar ratio 1:1:1). After several days, small colorless plates suitable for X-ray analysis appeared.

Crystal data

[Cd₂(S₂O₃)₂(C₁₄H₁₂N₂)₂]

$M_r = 865.5$

Monoclinic

$P2_1/n$

$a = 8.439$ (1) Å

$b = 16.864$ (2) Å

$c = 11.010$ (1) Å

$\beta = 109.56$ (1)°

$V = 1476.5$ (3) Å³

$Z = 2$

$D_x = 1.947$ Mg m⁻³

D_m not measured

Data collection

Siemens R3m diffractometer

$\omega/2\theta$ scans

Absorption correction:

semi-empirical via ψ scan

(XEMP in SHELXTL/PC;

Sheldrick, 1991)

$T_{\min} = 0.78$, $T_{\max} = 0.82$

2089 measured reflections

1938 independent reflections

1692 observed reflections

$[I > 2\sigma(I)]$

Refinement

Refinement on F^2

$R(F) = 0.0252$

$wR(F^2) = 0.0638$

$S = 1.056$

1935 reflections

199 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2$

$+ 2.3937P]$

where $P = (F_o^2 + 2F_c^2)/3$

Mo K α radiation

$\lambda = 0.71073$ Å

Cell parameters from 25

reflections

$\theta = 7.5$ – 12.5 °

$\mu = 1.77$ mm⁻¹

$T = 293$ (2) K

Plate

$0.24 \times 0.12 \times 0.10$ mm

Colorless

$R_{\text{int}} = 0.010$

$\theta_{\text{max}} = 22.54$ °

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = -11 \rightarrow 11$

2 standard reflections

monitored every 98

reflections

intensity decay: <2%

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.543$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.375$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{eq}
Cd1	0.54946 (4)	0.00518 (2)	0.66817 (2)	0.03412 (13)
S1	0.26695 (13)	-0.00201 (7)	0.49042 (10)	0.0414 (3)
S2	0.27291 (14)	-0.12535 (7)	0.47380 (10)	0.0430 (3)
O1	0.3566 (5)	-0.1564 (2)	0.5991 (3)	0.0788 (12)
O2	0.3687 (6)	-0.1377 (2)	0.3885 (4)	0.092 (2)
O3	0.1048 (5)	-0.1512 (2)	0.4188 (5)	0.110 (2)
C1	0.4527 (5)	0.1414 (2)	0.8425 (4)	0.0398 (10)

C2	0.4712 (6)	0.1831 (3)	0.9569 (5)	0.0490 (12)
C3	0.5805 (6)	0.1573 (3)	1.0703 (5)	0.0466 (12)
C4	0.6770 (5)	0.0899 (3)	1.0741 (4)	0.0387 (10)
C5	0.7959 (6)	0.0593 (3)	1.1909 (4)	0.0497 (13)
C6	0.8837 (6)	-0.0061 (3)	1.1909 (4)	0.0500 (12)
C7	0.8627 (5)	-0.0494 (3)	1.0753 (4)	0.0391 (10)
C8	0.9486 (5)	-0.1200 (3)	1.0728 (5)	0.0492 (12)
C9	0.9207 (6)	-0.1589 (3)	0.9600 (5)	0.0492 (12)
C10	0.8061 (5)	-0.1288 (2)	0.8445 (4)	0.0366 (10)
C11	0.7483 (5)	-0.0219 (2)	0.9575 (4)	0.0295 (9)
C12	0.6537 (5)	0.0497 (2)	0.9572 (3)	0.0281 (9)
C13	0.3301 (6)	0.1688 (3)	0.7175 (5)	0.0572 (13)
C14	0.7763 (6)	-0.1723 (3)	0.7202 (5)	0.0539 (13)
N1	0.5427 (4)	0.0762 (2)	0.8432 (3)	0.0306 (7)
N2	0.7231 (4)	-0.0614 (2)	0.8444 (3)	0.0292 (7)

Table 2. Selected geometric parameters (Å, °)

Cd1—N1	2.286 (3)	C3—C4	1.391 (6)
Cd1—N2	2.295 (3)	C4—C12	1.409 (5)
Cd1—O2 ¹	2.480 (3)	C4—C5	1.436 (6)
Cd1—S1	2.5307 (11)	C5—C6	1.329 (7)
Cd1—S1 ¹	2.6950 (12)	C6—C7	1.426 (6)
S1—S2	2.090 (2)	C7—C8	1.399 (6)
S1—Cd1 ¹	2.6950 (12)	C7—C11	1.411 (5)
S2—O3	1.412 (4)	C8—C9	1.353 (7)
S2—O1	1.422 (3)	C9—C10	1.410 (6)
S2—O2	1.445 (4)	C10—N2	1.334 (5)
O2—Cd1 ¹	2.480 (3)	C10—C14	1.498 (6)
C1—N1	1.334 (5)	C11—N2	1.365 (5)
C1—C2	1.405 (6)	C11—C12	1.447 (5)
C1—C13	1.492 (6)	C12—N1	1.366 (5)
C2—C3	1.353 (7)		
N1—Cd1—N2	74.51 (11)	C3—C4—C12	117.7 (4)
N1—Cd1—O2 ¹	80.06 (11)	C3—C4—C5	123.1 (4)
N2—Cd1—O2 ¹	120.06 (14)	C12—C4—C5	119.2 (4)
N1—Cd1—S1	113.21 (8)	C6—C5—C4	121.3 (4)
N2—Cd1—S1	143.10 (8)	C5—C6—C7	121.5 (4)
O2 ¹ —Cd1—S1	96.79 (12)	C8—C7—C11	117.4 (4)
N1—Cd1—S1 ¹	137.60 (8)	C8—C7—C6	122.9 (4)
N2—Cd1—S1 ¹	101.25 (8)	C11—C7—C6	119.6 (4)
O2 ¹ —Cd1—S1 ¹	65.54 (8)	C9—C8—C7	119.9 (4)
S1—Cd1—S1 ¹	95.46 (3)	C8—C9—C10	120.6 (4)
S2—S1—Cd1	94.09 (5)	N2—C10—C9	120.6 (4)
S2—S1—Cd1 ¹	83.55 (5)	N2—C10—C14	119.3 (4)
Cd1—S1—Cd1 ¹	84.54 (3)	C9—C10—C14	120.1 (4)
O3—S2—O1	113.8 (3)	N2—C11—C7	121.9 (4)
O3—S2—O2	112.2 (3)	N2—C11—C12	119.2 (3)
O1—S2—O2	111.9 (3)	C7—C11—C12	118.9 (3)
O3—S2—S1	107.2 (2)	N1—C12—C4	121.6 (4)
O1—S2—S1	107.5 (2)	N1—C12—C11	119.0 (3)
O2—S2—S1	103.64 (15)	C4—C12—C11	119.4 (3)
S2—O2—Cd1 ¹	107.3 (2)	C1—N1—C12	119.3 (3)
N1—C1—C2	121.0 (4)	C1—N1—Cd1	127.0 (3)
N1—C1—C13	118.5 (4)	C12—N1—Cd1	113.5 (2)
C2—C1—C13	120.5 (4)	C10—N2—C11	119.6 (3)
C3—C2—C1	120.2 (4)	C10—N2—Cd1	127.1 (3)
C2—C3—C4	120.2 (4)	C11—N2—Cd1	113.2 (2)

Symmetry code: (i) 1 - x, -y, 1 - z.

The title structure was solved through a combination of direct methods and difference Fourier synthesis, using the SHELXTL/PC package (Sheldrick, 1991). Refinement was performed with SHELXL93 (Sheldrick, 1993) on F^2 , using the whole data set. H atoms were placed at their expected positions and allowed to ride with a fixed overall isotropic displacement parameter $U(\text{H}) = 0.08$ Å². Distances and angles involving H atoms were calculated using corrected values after Jeffrey & Lewis (1978).

Data collection: P3/PA-PC Diffractometer Program (Siemens, 1991). Cell refinement: P3/PA-PC Diffractometer Program. Data reduction: XDISK in SHELXTL/PC. Molecular graphics: XP in SHELXTL/PC. Software used to prepare material for publication: CIFTAB in SHELXL93 and PARST (Nardelli, 1983).

The authors would like to thank Fundación Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1942–1943

trans-Di- μ -chloro-bis[chloro(trimethylphosphine-*P*)platinum(II)]

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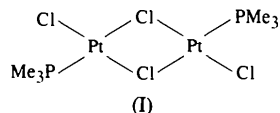
Abstract

The title compound, [Pt₂Cl₄(C₃H₉P)₂], is shown to have a *trans* conformation.

Comment

Although the title compound, (I), has been used extensively in the synthesis of mononuclear (trimethyl-

phosphine)platinum compounds *via* cleavage of the bridging Pt—Cl bonds, the structure has not been reported previously. Previous structure analyses of related dimers (Black, Mais & Owston, 1969; Simms, Shang, Lu, Youngs & Ibers, 1987; Blake, Gould, Marr, Rankin & Schröder, 1989) have shown them to be centrosymmetric, necessitating a *trans* configuration, now shown to be a feature of the structure of [Pt₂(μ -Cl)₂Cl₂{P(CH₃)₃}]₂.



The relative *trans* influences of the chloride and trimethylphosphine ligands would suggest this to be the thermodynamically favourable isomer and result in some asymmetry in the Pt₂(μ -Cl)₂ unit; the Pt— μ -Cl distance *trans* to Pt—P is 2.423 (3) Å and that *trans* to Pt—Cl is 2.309 (3) Å. The orientation of the PMe₃ group is such that the C2 atom is within 0.038 Å of the plane defined by atoms Cl1, Cl2, Pt and P1. The resulting steric interference is presumably the reason for the observed widening of the Cl1—Pt1—P1 angle to 95.10(10)° (Black, Mais & Owston, 1969).

Details of the synthesis and NMR data (³¹P{¹H} and ¹⁹⁵Pt{¹H}) for the title compound and related chloro-bridged dimers have already been presented previously (Boag & Ravetz, 1995).

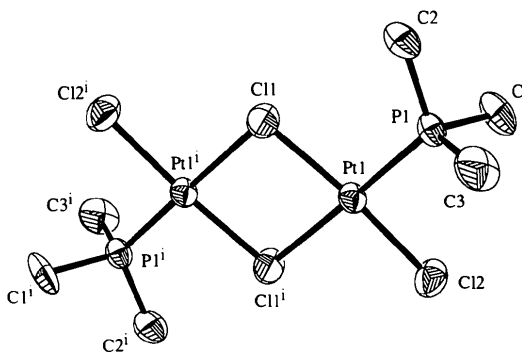


Fig. 1. The molecular structure of [Pt₂(μ -Cl)₂Cl₂{P(CH₃)₃}]₂. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The crystal of the title complex used for analysis was grown by slow evaporation of a saturated CDCl₃ solution of [Pt₂(μ -Cl)₂Cl₂{P(CH₃)₃}]₂.

Crystal data

[Pt₂Cl₄(C₃H₉P)₂]
M_r = 684.12

Mo K α radiation
 λ = 0.71073 Å