Acta Cryst. (1997). C**53**, 727–729

(2,2′-Bipyridine-*N*,*N*′)(μ-thiosulfato)-cadmium(II)

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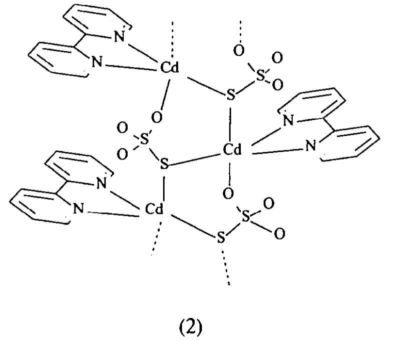
(*Received 27 August 1996; accepted 31 January 1997*)

Abstract

The title Cd^{II} complex, [Cd(S_2O_3)($C_{10}H_8N_2$)], consists of polymeric chains running along the monoclinic symmetry axis. The elementary units are defined by pentacoordinated Cd^{II} atoms bonded to three different thiosulfate groups and a bidentate bipyridine ligand. The bridging thiosulfates bind metal centres through two different sequences, Cd1—S1—Cd1′ and Cd1—O1′—S2′—S1′—Cd1′, thus defining a six-membered ring. Individual chains are held together solely *via* van der Waals interactions.

Comment

Few structures of complexes containing ions of group IIB, coordinated to thiosulfate anions, have been reported so far. In the case of Cd, we have recently described the structure of [Cd(dmph)(S_2O_3)] (dmph is dimethylphenanthroline), (1) (Baggio, Baggio, Pardo & Garland, 1996), in which the S_2O_3 group presents an unusual type of coordination, acting both as a bridging and bidentate ligand. As is well known, in this type of metal ion, even small modifications in the nature of the starting ligands can produce large differences in the structure of the final complexes. In this paper, we describe the structure of [Cd(bipy)(S_2O_3)] (bipy is bipyridine), (2), in order to compare the structural effects of changing the organic ligand.



(2)

The asymmetric unit contents, with the labelling scheme used, are shown in Fig. 1. Two symmetry-related thiosulfate groups have been added in order to complete the Cd coordination sphere. The structure of the complex consists of chains parallel to the *b* axis, loosely connected by pure van der Waals interactions (Fig. 2). The pentacoordinated Cd atoms are interconnected through thiosulfate groups, which act as bridging ligands in a very versatile fashion, bonding simultaneously to three neighbouring metal atoms through S (in a bifurcated manner) and O atoms. As a result, a six-membered Cd—O—S—S—Cd—S— ring is formed.

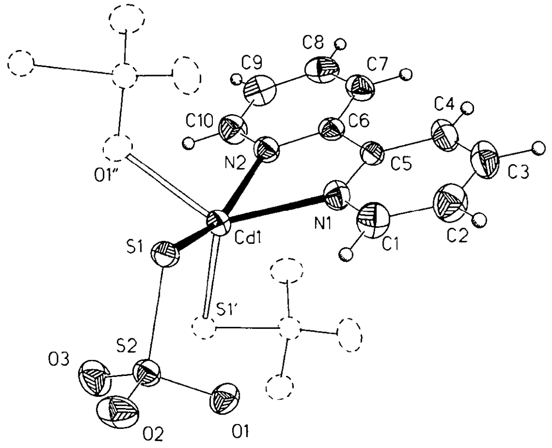


Fig. 1. View of the title molecule showing the numbering scheme used, with displacement ellipsoids drawn at the 50% probability level. Dashed ellipsoids correspond to symmetry-related units, included to complete the Cd coordination sphere. [Symmetry codes: (′) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (″) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.]

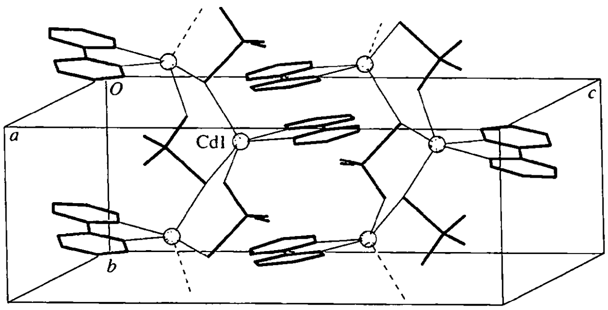


Fig. 2. Simplified packing diagram (H atoms removed) showing the way a chain is built up. For clarity, only one of the parallel, non-interacting chains running along the *b* axis has been drawn.

Each Cd atom binds to two S, one O and two N atoms from the bidentate bipy ligand. To our knowledge, no other pentacoordinate Cd complex containing bipy as a ligand has been reported. The environment around the central atom differs from any of the ideal pentacoordinate geometries, mainly as a result of the severe constraints imposed by the bipyridine bite.

Distances in the Cd coordination sphere are normal. The Cd—O distance of 2.365 (2) Å resembles that found in the pentacoordinate $[Cd(thiourea)_3(SO_4)]$ complex [2.34 (1) Å; Corao & Baggio, 1969], more so than the one found in $[Cd(dmph)(S_2O_3)]$ [2.478 (3) Å; Baggio *et al.*, 1996]. This can probably be ascribed to some steric limitations imposed in the latter by the chelating character of the ligand. The mean Cd—N distance [2.315 (4) Å] in this five-coordinate environment lies at the lower end of the wide range displayed by reported Cd—$N_{\rm bipy}$ distances, *e.g.* 2.334 (6) Å in (bipyridyl-*N*,*N*′)bis(2,4,6-tri-isopropylbenzenethiolato-*S*,*S*′)cadmium(II) (Santos, Gruff, Koch & Harbison, 1990) and 2.535 (14) Å in (2,2′-bipyridyl-*N*,*N*′)dimethylcadmium(II) (Almond, Beer, Drew & Rice, 1991)

The thiosulfate group presents a distorted tetrahedral geometry and bond lengths clearly correlate with the degree of bonding of individual atoms. Thus, the S—S bond [2.084 (1) Å, which is much longer than the one found in the free ion, 1.987 (3)–2.031 (4) Å; Teng, Fuess & Bats, 1984, and references therein] and S—O values are clearly split between the shorter ones involving uncoordinated O atoms and the longer S—O··· contacts corresponding to the bridging moieties.

Even though the coordination spheres around the metal centre in the present compound and in its dmph homologue are similar, the actual structures are quite dissimilar, the main difference being in the polymeric character of the former in contrast with the dimeric nature of the latter. Also, the binding behaviour of the thiosulfate group is different, being only bridging in (2) compared with the coexisting bridging/bidentate character displayed in (1). This confirms the previously mentioned fact that small modifications in the ligand type can have a large influence on the geometry of the complexes.

Experimental

The title compound was obtained by allowing a methanol solution of bipyridine to diffuse into an aqueous solution of sodium thiosulfate and cadmium acetate, in an equimolar ratio. On standing, two well differentiated phases crystallized from the mother liquours, *i.e.* an early one, which appeared in a few days in the shape of well developed elongated plates, but which proved to be hopelessly unstable when withdrawn from the solution and were therefore discarded, and some tiny colourless prisms, which after a period of only 6–8 weeks of unperturbed standing of the solution grew to a size suitable for X-ray analysis. These were the crystals finally used for data collection.

Crystal data

$[Cd(S_2O_3)(C_{10}H_8N_2)]$
$M_r = 380.71$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Monoclinic
$P2_1/n$
$a = 10.199\ (2)$ Å
$b = 6.543\ (1)$ Å
$c = 18.145\ (3)$ Å
$\beta = 104.77\ (1)°$
$V = 1170.8\ (3)$ Å^3
$Z = 4$
$D_x = 2.16$ Mg m^{-3}
D_m not measured
Cell parameters from 25 reflections
$\theta = 7.5$–$12.5°$
$\mu = 2.22$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.26 × 0.22 × 0.12 mm
Colourless

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
$T_{\rm min} = 0.58$, $T_{\rm max} = 0.72$
2555 measured reflections
2062 independent reflections
1812 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 12$
$k = -1 \rightarrow 7$
$l = -21 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.0220$
$wR(F^2) = 0.0534$
$S = 1.067$
2062 reflections
164 parameters
H atoms riding on host atoms
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.8289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.002$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0053 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cd1—N1	2.311 (3)	N1—C1	1.343 (4)
Cd1—N2	2.319 (3)	N2—C6	1.341 (4)
Cd1—O1$^{\rm i}$	2.365 (2)	N2—C10	1.346 (4)
Cd1—S1$^{\rm ii}$	2.5744 (9)	C1—C2	1.382 (5)
Cd1—S1	2.5866 (8)	C2—C3	1.375 (6)
S1—S2	2.0840 (11)	C3—C4	1.376 (5)
S1—Cd1$^{\rm i}$	2.5744 (9)	C4—C5	1.398 (4)
S2—O2	1.445 (2)	C5—C6	1.490 (4)
S2—O3	1.454 (2)	C6—C7	1.393 (4)
S2—O1	1.478 (2)	C7—C8	1.387 (5)
O1—Cd1$^{\rm ii}$	2.365 (2)	C8—C9	1.374 (5)
N1—C5	1.343 (4)	C9—C10	1.372 (5)
N1—Cd1—N2	71.55 (10)	C5—N1—C1	119.1 (3)
N1—Cd1—O1$^{\rm i}$	130.59 (9)	C5—N1—Cd1	117.2 (2)
N2—Cd1—O1$^{\rm i}$	82.79 (9)	C1—N1—Cd1	123.7 (2)
N1—Cd1—S1$^{\rm ii}$	116.96 (7)	C6—N2—C10	118.9 (3)
N2—Cd1—S1$^{\rm ii}$	97.91 (7)	C6—N2—Cd1	117.3 (2)
O1$^{\rm i}$—Cd1—S1$^{\rm ii}$	107.69 (6)	C10—N2—Cd1	123.8 (2)
N1—Cd1—S1	95.94 (7)	N1—C1—C2	122.9 (3)
N2—Cd1—S1	152.27 (7)	C3—C2—C1	117.8 (4)
O1$^{\rm i}$—Cd1—S1	87.65 (6)	C2—C3—C4	120.4 (3)
S1$^{\rm ii}$—Cd1—S1	109.80 (2)	C3—C4—C5	118.9 (3)
S2—S1—Cd1$^{\rm i}$	106.02 (4)	N1—C5—C4	120.9 (3)
S2—S1—Cd1	99.13 (4)	N1—C5—C6	117.2 (3)
Cd1$^{\rm i}$—S1—Cd1	113.60 (3)	C4—C5—C6	121.9 (3)
O2—S2—O3	114.5 (2)	N2—C6—C7	121.3 (3)
O2—S2—O1	112.92 (14)	N2—C6—C5	116.8 (3)

O3—S2—O1	110.57 (15)	C7—C6—C5	121.9 (3)
O2—S2—S1	107.07 (11)	C8—C7—C6	119.1 (3)
O3—S2—S1	108.26 (11)	C9—C8—C7	119.1 (3)
O1—S2—S1	102.62 (10)	C10—C9—C8	119.1 (3)
S2—O1—Cd1^{ii}	110.41 (12)	N2—C10—C9	122.5 (3)

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The title structure was solved by direct methods and completed by difference Fourier. It was refined by full-matrix least squares. H atoms were added at their expected positions and not refined, but were allowed to ride.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB SHELXL*93, *PARST* (Nardelli, 1983) and CSD (Allen, Kennard & Taylor, 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 atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1303). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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