

A new binding mode for thiosulfate in six-coordinate poly[[*(1,10-phenanthroline-κ²N,N')*cadmium(II)]-μ-thio-sulfato]

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In the novel title six-coordinate cadmium complex, $[\text{Cd}(\text{S}_2\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)]_n$, the anion binds to three different six-coordinate cationic centres through all four external atoms, an unprecedented coordination mode for thiosulfate metal-organic complexes. This connectivity leads to strongly linked dimers, connected to form interleaved double chains, which in turn interact through remarkably short π - π bonds between their phenanthroline groups.

Comment

Complexes of group XII metals containing sulfur oxoanions have been of interest to us for many years, and as a result we have prepared a number of compounds having thiosulfate, sulfate, peroxodisulfate and, to a lesser extent, sulfite as ligands. Many of these complexes exhibit novel modes of coordination, as expected from the characteristics of the cations (Zn^{2+} , Cd^{2+} and Hg^{2+}) and the versatility of the anions involved. The use of less common sulfur oxoanions, such as dithionite and pyrosulfite, though highly desirable as a natural continuation of this line of work, appeared to be impaired by the instability of these anions in solution. Transformation products can be expected when interacting with transition metal ions and organic ligands (Remy, 1956). As an example, sodium dithionite, though basically stable in the solid state, decomposes easily in solution, giving thiosulfate and pyrosulfite. On the other hand, the chemistry in solution of the latter is essentially the chemistry of SO_3^{2-} and HSO_3^- ions, even though the formal oxidation numbers S^{III} and S^{V} are those that would be expected in the solid state.

This high anionic instability, which makes the chemistry of these anions so difficult, also makes them attractive as precursors in the synthesis of sulfite and thiosulfate complexes. Some previously unintentional outcomes in our synthetic attempts (Harvey *et al.*, 2004) strongly suggested that sulfur

oxoanions could provide feasible alternative routes where direct syntheses had previously proven unsuccessful, or provide a way to produce crystallographic phases that differ from those already obtained either by conventional methods or by similar decomposition procedures. We present here one such case, a novel anhydrous six-coordinate cadmium phenanthroline thiosulfate, *viz.* the title compound, (I), which is crystallographically different from a recently published five-coordinate form with the same formula [hereafter (II); Harvey *et al.*, 2004]. Both forms were obtained by essentially the same procedure, under slightly different conditions (See *Experimental*).

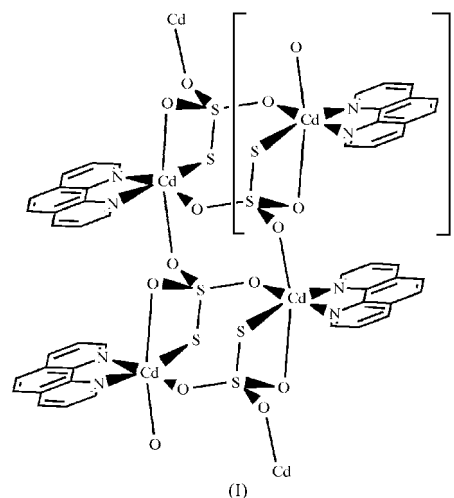
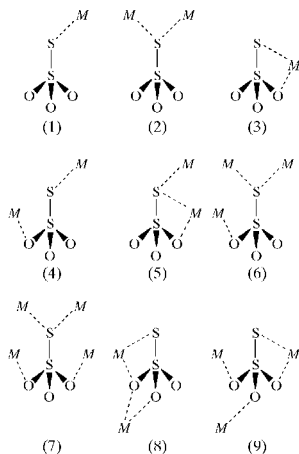


Fig. 1 shows a molecular diagram of the structure with the atom-labelling scheme; the bonds to the six-coordinate Cd centre come from four different ligands, *viz.* atoms N1 and N2 from the chelating phenanthroline (phen) ligand, atom O2' from the thiosulfate anion at $(-x + 1, -y + 1, -z + 1)$, atom O'' from the thiosulfate anion at $(x + 1, y, z)$, and atoms S1 and O1 from the reference anion, acting in a chelating mode. The latter Cd—O bond is worth analysing. It is far longer than average [Cd—O1 = 2.788 (4) Å *versus* a mean of 2.317 (4) Å for the other two Cd—O bonds; Table 1], but though unusual it is not unprecedented; a number of such long Cd—O bonds have been reported, and a search of the Cambridge Structural Database (CSD; Allen, 2002) produced 32 cases of Cd—O bonds longer than 2.788 Å out of a total of *ca* 5000 bonds spanning the range 1.959–3.052 Å. To clarify definitively the coordinating character of this interaction, we carried out a bond valence calculation (Brown & Altermatt, 1985) comparing (I) with its five-coordinate isomer (II). The valence sum around the cation in the latter gave 2.012 electrons, while the same calculation for (I) gave 1.925 electrons when atom O1 was excluded from the calculation and 2.016 electrons when it was included. Although rather weak, the involvement of atom O1 in coordination is therefore confirmed. The highly distorted coordination polyhedron could be described as an asymmetrically elongated octahedron, having atoms S1, N1, O1 and O3'' as the basal plane [the mean deviation from the plane is 0.24 (1) Å, with the Cd atom deviating by 0.06 (1) Å] and N2—Cd—O2' as the apical axis [the deviations from the

plane normal are $17.2 (1)^\circ$ for $N2-Cd$ and $16.8 (1)^\circ$ for $O2'-Cd$. The phen unit is slightly concave in shape, the central ring subtending angles of $4.3 (1)$ and $2.2 (1)^\circ$ with the lateral rings, the deformation resulting in an average deviation from planarity of $0.047 (1) \text{ \AA}$.

Uniquely, the thiosulfate ligand binds through its four external atoms to three different metal centres in a new coordination mode in transition metal thiosulfate complexes (see entry 9 in the scheme below), which thus adds to the eight different modes already known [see entries 1–8 in the scheme below; Freire *et al.* (2000) give references for the corresponding structures]. Another peculiarity of the anion in (I) is that the terminal S atom is singly coordinated and does not enter into the formation of any direct $M-S-M$ bridge; this behaviour is unprecedented for cadmium thiosulfates, irrespective of character (metal-organic or inorganic) or coordination number (five- or six-coordinate). In all previous examples, *e.g.* the five-coordinate isomer (II) (Harvey *et al.* (2004), $[Cd(S_2O_3)(C_{10}H_8N_2)]$), (III) (Baggio, Pardo, Baggio & Garland, 1997), $[Cd_2(S_2O_3)_2(C_{14}H_{12}N_2)_2]$, (IV) (Baggio *et al.*, 1996), $[Cd(S_2O_3)(C_{10}H_9N_3)(H_2O)] \cdot H_2O$, (V) (Freire *et al.*, 2001), $[Cd(S_2O_3)(C_{12}H_8N_2)(H_2O)] \cdot H_2O$, (VI) (Baggio *et al.*, 1998), and $CdS_2O_3 \cdot 2H_2O$, (VII) (Baggio, Pardo, Baggio & González, 1997), the terminal S1 atom bridges two different metal centres. The thiosulfate ion exhibits an almost ideal C_{3v} geometry, the S–O distances and S–S–O angles being indistinguishable within experimental errors. The coordination mode of atom S1 results in the expected lengthening of the S–S bond with respect to that of the free anion [$2.0462 (19) \text{ \AA}$ versus $1.99\text{--}2.02 \text{ \AA}$; Teng *et al.*, 1984, and references therein].



The special coordination mode of the anion results in five long different three-atom-length bridges ($O2-S2-S1$, $O2-S2-O1$, $O3-S2-S1$, $O3-S2-O1$ and $O2'-S2'-O3'$; Fig. 1), which, along with their symmetry-related bridges, connect the cation to its four nearest neighbours. Those bridges in which atom O3 does not take part lead to the formation of strongly linked dimers through a 'cage' built up around the symmetry centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (upper half of Fig. 1). The sharing of atom O3 by these dimers shifted by one unit cell along $\langle 100 \rangle$ generates eight-membered loops, which serve to join dimers together into polymeric structures in the shape

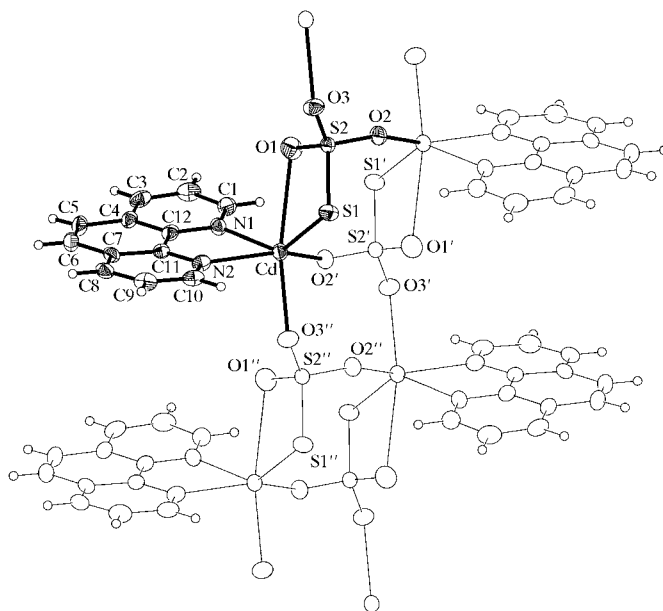


Figure 1

A displacement ellipsoid plot (50% probability level) showing the polymeric unit of (I). The independent part of the structure is shown with full displacement ellipsoids. [Symmetry codes: (') $-x + 1, -y + 1, -z + 1$; (") $x + 1, y, z$.]

of double chains. In spite of the structure core being different from those previously reported in metal-organic thiosulfates, the outermost part is essentially similar, with the aromatic amines protruding outwards and interleaving into each other in a gear-like fashion (Fig. 2), and with an important partial overlap of neighbouring rings. The π – π interactions arising from this setup are relatively strong, leading to interplanar distances (distances from a ring centre to the plane of the opposite ring) of $3.20 (1)$ and $3.27 (1) \text{ \AA}$, with slippage angles (angles subtended by the vector joining a ring centre to one of the planes of the ring) of $24 (1)$ and $21 (1)^\circ$, respectively. This contact appears to be unusually short for this type of intermolecular interaction without other enhancing interactions. To evaluate this situation, we searched the CSD for structures containing strong 'intermolecular' interactions, characterized by having nearly parallel aromatic cycles (the maximum allowed interplanar dihedral angle was 5°), with a maximum centre-to-plane distance of 3.40 \AA and a maximum slippage angle of 30° . The search provided a total of 340 such cases, of which fewer than 5% of the total were shorter than the $3.20 (1) \text{ \AA}$ found in (I) [the minimum values found were 3.17 \AA and 26° for CSD refcode HUPZIB (Kingston *et al.*, 2003)]. When the same search was performed allowing any type of interaction (either intra- or intermolecular), this fraction rose to 25% of the total.

In summary, complex (I), synthesized through non-conventional methods, exhibits a new coordination scheme for the thiosulfate anion. It serves as an efficient connector between cationic centres and, as a result, strongly linked two-dimensional structures can be built up. These interact with one another through π – π contacts that are found to be among the strongest intermolecular contacts of this type reported.

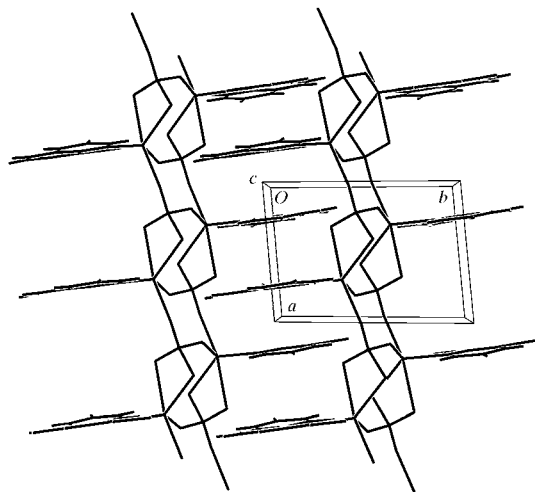


Figure 2
The packing of the structure, showing the interleaving of the phenanthroline groups.

Experimental

The title compound was obtained by dissolving cadmium acetate and phenanthroline (molar ratio 1:1) in ethanol (96%) and allowing this solution to diffuse slowly into an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{S}_2\text{O}_5$ (molar ratio 1:2). After two months, small colourless prisms suitable for X-ray analysis had developed.

Crystal data

$[\text{Cd}(\text{S}_2\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)]$	$Z = 2$
$M_r = 404.72$	$D_x = 2.191 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.4860 (13) \text{ \AA}$	Cell parameters from 25 reflections
$b = 9.2530 (19) \text{ \AA}$	$\theta = 7.5\text{--}15^\circ$
$c = 10.621 (2) \text{ \AA}$	$\mu = 2.13 \text{ mm}^{-1}$
$\alpha = 76.58 (3)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 83.52 (3)^\circ$	Prism, colourless
$\gamma = 83.50 (3)^\circ$	$0.35 \times 0.12 \times 0.10 \text{ mm}$
$V = 613.6 (2) \text{ \AA}^3$	

Data collection

Rigaku AFC-6S diffractometer	$R_{\text{int}} = 0.035$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 28.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.74$, $T_{\text{max}} = 0.80$	$k = -12 \rightarrow 0$
3025 measured reflections	$l = -13 \rightarrow 13$
2853 independent reflections	3 standard reflections
1913 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 0.9%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} = 0.008$
2853 reflections	$\Delta\rho_{\text{max}} = 0.98 \text{ e \AA}^{-3}$
181 parameters	$\Delta\rho_{\text{min}} = -1.20 \text{ e \AA}^{-3}$

H atoms were all defined by the stereochemistry and were accordingly placed at calculated positions and treated as riding on their host atoms ($\text{C-H} = 0.93 \text{ \AA}$), with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

Table 1
Selected geometric parameters (\AA , $^\circ$).

Cd-O^{i}	2.282 (4)	Cd-O1	2.788 (4)
Cd-N1	2.308 (5)	S1-S2	2.0462 (19)
Cd-O^{ii}	2.353 (4)	S2-O1	1.453 (4)
Cd-N2	2.368 (5)	S2-O2	1.459 (4)
Cd-S1	2.5207 (16)	S2-O3	1.466 (4)
$\text{O}^{\text{i}}-\text{Cd-N1}$	82.45 (15)	$\text{O}^{\text{ii}}-\text{Cd-S1}$	108.18 (11)
$\text{O}^{\text{i}}-\text{Cd-O}^{\text{ii}}$	85.51 (14)	N2-Cd-S1	100.00 (12)
$\text{N1-Cd-O}^{\text{ii}}$	113.41 (15)	$\text{O}^{\text{i}}-\text{Cd-O1}$	89.40 (14)
$\text{O}^{\text{i}}-\text{Cd-N2}$	146.44 (15)	N1-Cd-O1	76.14 (14)
N1-Cd-N2	71.52 (16)	$\text{O}^{\text{ii}}-\text{Cd-O1}$	168.38 (13)
$\text{O}^{\text{ii}}-\text{Cd-N2}$	85.80 (15)	N2-Cd-O1	104.03 (15)
$\text{O}^{\text{i}}-\text{Cd-S1}$	113.51 (11)	S1-Cd-O1	64.46 (9)
N1-Cd-S1	136.50 (12)		

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

Data collection, cell refinement and data reduction: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1075). Services for accessing these data are described at the back of the journal.

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