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A novel five-coordinate cadmium phenanthroline thiosulfate

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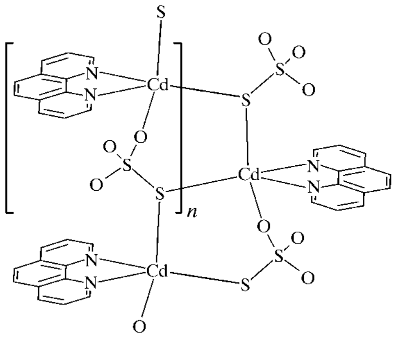
The structure of the novel cadmium phenanthroline thiosulfate poly[[(1,10-phenanthroline-κ^2N,N')cadmium(II)]-μ_3-thiosulfato-κ^3S:S:O], $[Cd(S_2O_3)(C_{12}H_8N_2)]_n$, with a pentacoordinated Cd centre, is reported. It forms linear chains built up around a 2_1 axis and is isostructural with the known bipyridine homologue. The structure is also compared with a previously reported closely related monoaqua monohydrated phase, where the Cd^{2+} cation is hexacoordinated. The incidence of weak C—H···O interactions in the determination of its general packing properties is discussed.

Comment

The dithionite anion is quite unstable even in the absence of air and it can gradually decompose, breaking up easily into thiosulfate plus pyrosulfite (Remy, 1956). During an exploration of the Cd^{+2}–dithionite–phenanthroline system, and as part of a search for a synthetic route to the elusive cadmium dithionite complexes, we unwittingly obtained the title novel anhydrous five-coordinate cadmium phenanthroline thiosulfate, (I). The compound is polymeric and crystallizes in the form of double chains, or strips, built up around the 2_1 axis running along **a**. This motif is not unusual, being shared by a number of related compounds, *viz*. the aqua monohydrated six-coordinate cadmium phenanthroline (phen) thiosulfate, (II) (Baggio *et al.*, 1998), and the anhydrous cadmium bipyridine (bpy) thiosulfate, (III) (Baggio *et al.*, 1997). In spite of belonging to an enantiomorphic class (222), no definite handedness could be ascribed to the structure of (I), the best model for refinement being a racemic twin with a 0.43 (7):0.57 (7) ratio.

A displacement ellipsoid plot of the ensemble (I) is shown in Fig. 1. The bonds to the five-coordinate Cd centre are provided by two N atoms from the chelating dinitrogenated base, and two S atoms and one O atom from three different thiosulfate groups. The anion acts in two different bridging modes: (i) as a short bridge through the terminal S1 atom (shared by two different Cd centres) and (ii) as a long bridge through the whole S1—S2—O3 arm. The geometry of the anion is normal for this type of coordination. Comparison of (I) with the closely related structures (II) and (III) reveals that, beyond the overall similarities, there are some minor subtle points differentiating them.



(I)

Structure (II) presents a six-coordinate Cd centre surrounded by the same ligands as in (I), but with the sixth coordination position occupied by one aqua molecule and with a stabilizing hydration water molecule. In spite of the obvious differences which the larger coordination number introduces, the general structural trend is the same in both compounds, namely that one-dimensional chains are built up along one of the crystallographic axes, the axial length along the chains being defined by the doubling of the motif through the 2_1 axis, and with interleaving of the phen groups normal to this axis in the usual gear-like mode. As expected, the larger coordination number in (II) results in an elongation of the coordination bonds (Table 2). The effect is reflected in the concomitant enlargement of the associated cell parameter, which in (II) is ~8% larger than in (I) [7.051 (2) *versus* 6.520 (1) Å]. The relative weakening of the coordination bonds can be quantitatively analyzed in terms of the 'bond valence' (Brown & Altermatt, 1985) associated with each of these interactions, those corresponding to bonds in (II) being consistently smaller than their homologues in (I) (Table 2). In both cases, the sum around the cation (2.013 and 2.045) is consistent with the divalent character of cadmium. These differences in coordination strength propagate to the thiosulfate group; the larger involvement in coordination of atom S1 in structure (I) slightly weakens the S1—S2 bond in the anion, and this is reflected in its consequent enlargement and the associated evenness of the S—O bond lengths compared with those in (II) (Table 2).

Compound (III) is the bpy homologue of (I). Although it presents an almost exactly isostructural double chain (see Fig. 2 for an overlap view) and a very similar density [2.16 *versus* 2.15 Mg m^{-3} in (I)], it crystallizes in a different space group ($P2_1/n$). Even though all the strips run in a unique crystallographic 2_1 screw-axis direction in both unit cells [the *a* axis in (I) and the *b* axis in (III)], two different orientations for

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the strip widths appear in the former (Fig. 3), while a single orientation appears in the latter, due to the different symmetry-element dispositions. This enables different modes of interaction between neighbouring chains. In fact, the weak C—H···O bonds present in the structures (Table 3) involve some H atoms which exist in just one of the ligands but not in the other. Thus, atom H4 in bpy has no counterpart in phen and atom H5*A* (C5) in phen has no counterpart in bpy, both H atoms being actively engaged in C—H···O bonds. Thus it seems that it is the different geometry (and, accordingly, the external hydrogen 'shield' of each ligand) which favours one packing mode or the other. This is not a novel fact; we have recently reported (Harvey *et al.*, 2003) a very similar situation where the presence (or absence) of some H atoms in the bpy or phen ligands in two otherwise absolutely isostructural compounds determined differences in weak interactions, leading to measurable effects on some crystallographic properties, *viz*. the cell dimensions. In the present case, these modifications are more extensive, involving not only the cell parameters but also the crystal system and space group as well. The planar aromatic groups stack in the usual gear-like mode, leading to the classical 6.5 Å spacing. Here, however, the offset is rather large (Fig. 3), with almost no overlapping areas along the normal to the aromatic planes.

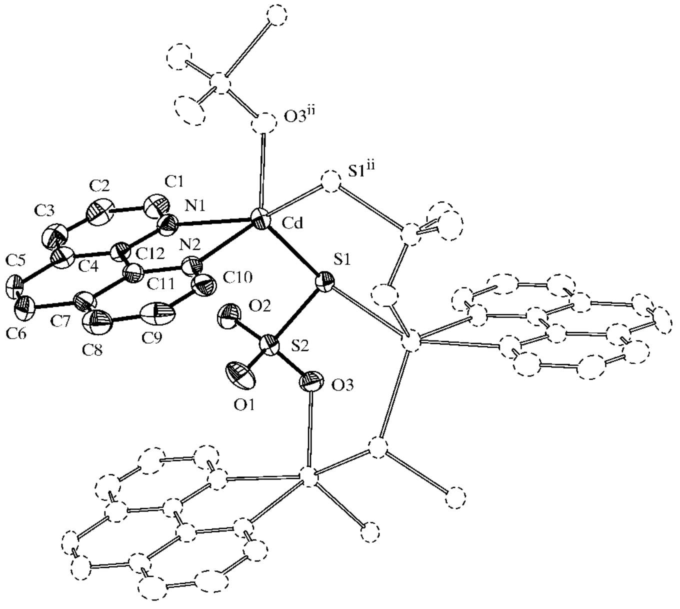

Figure 1

A view of the polymeric unit of (I). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity. The independent part of the structure is shown with full ellipsoids. For symmetry codes, refer to Table 1.

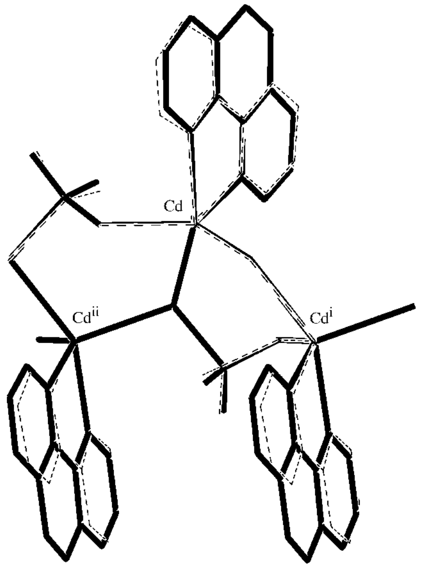

Figure 2

A comparison of (I) and (III) through the overlap of the corresponding double chains. Structure (I) is denoted by solid lines and (III) by dashed lines. Note the almost perfect match between the chain cores. For symmetry codes, refer to Table 1.

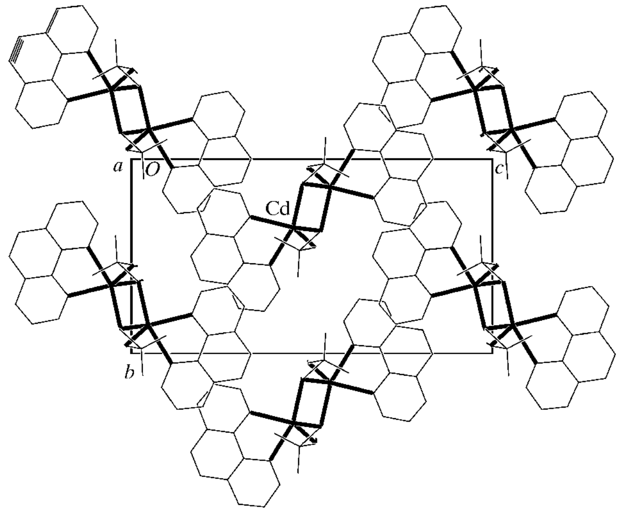

Figure 3

A schematic packing view of (I) down the chain direction.

Experimental

In a trial aimed at obtaining a cadmium dithionite, a methanol solution of phenanthroline monohydrate was allowed to diffuse into a water solution of cadmium acetate dihydrate and sodium dithionite (all concentrations being 0.025 *M*). Due to the unplanned dithionite decomposition, colourless needles of the title thiosulfate, (I), suitable for X-ray diffraction analysis appeared after a few days.

Crystal data

[$Cd(S_2O_3)(C_{12}H_8N_2)$]
$M_r = 404.72$
Orthorhombic, $P2_12_12_1$
$a = 6.5200$ (13) Å
$b = 10.172$ (2) Å
$c = 18.871$ (4) Å
$V = 1251.6$ (4) Å^3
$Z = 4$
$D_x = 2.148$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–15°
$\mu = 2.09$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.50 × 0.15 × 0.15 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MSC/AFC Diffractometer Control Software*; Molecular Structure Corporation, 1988)
$T_{\min} = 0.35$, $T_{\max} = 0.73$
2276 measured reflections
2093 independent reflections
2013 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 24$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.140$
$S = 1.01$
2093 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 7.6222P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 1.21$ e Å^{-3}
$\Delta\rho_{\min} = -1.04$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.43 (7)

Table 1
Selected bond angles (°).

N1—Cd—S1$^{\rm i}$	150.7 (2)	N1—Cd—O3$^{\rm ii}$	85.5 (3)
N2—Cd—S1$^{\rm i}$	91.91 (18)	N2—Cd—O3$^{\rm ii}$	132.4 (2)
O3$^{\rm ii}$—Cd—S1$^{\rm i}$	87.55 (18)	N1—Cd—S1	100.6 (2)
S1—Cd—S1$^{\rm i}$	108.66 (5)	N2—Cd—S1	117.5 (2)
N1—Cd—N2	72.4 (2)	O3$^{\rm ii}$—Cd—S1	107.52 (17)

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

Table 2
Coordination bond lengths (Å) and bond valences for compounds (I), (II) and (III).

	Bond lengths			Bond valences		
	(I)	(II)	(III)	(I)	(II)	(III)
S1—Cd	2.559 (2)	2.595 (2)	2.5744 (9)	0.502	0.455	0.482
S1$^{\rm i}$—Cd	2.593 (2)	2.698 (2)	2.5866 (8)	0.458	0.345	0.466
O3$^{\rm ii}$—Cd	2.364 (7)	2.549 (4)	2.365 (2)	0.288	0.175	0.288
N1—Cd	2.307 (7)	2.351 (4)	2.311 (3)	0.391	0.348	0.386
N2—Cd	2.324 (7)	2.346 (4)	2.310 (3)	0.374	0.352	0.378
O1*W*—Cd		2.272 (4)			0.370	
Sums of the coordination bond valences:				2.013	2.045	2.000
S1—S2	2.0825 (3)	2.054 (2)	2.0840 (11)			
S2—O1	1.455 (6)	1.463 (4)	1.445 (2)			
S2—O2	1.455 (7)	1.469 (4)	1.454 (2)			
S2—O3	1.474 (7)	1.466 (4)	1.478 (2)			

Symmetry codes: see Table 1.

Table 3
Hydrogen-bond geometry (Å, °) in (I) and (III).

	D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
Compound (I)					
	C1—H1*A*⋯O2$^{\rm i}$	0.93	2.65	3.323 (12)	130
	C5—H5*A*⋯O1$^{\rm ii}$	0.93	2.45	3.357 (12)	166
	C8—H8*A*⋯O2$^{\rm iii}$	0.93	2.34	3.195 (13)	154
	C9—H9*A*⋯O1$^{\rm iii}$	0.93	2.71	3.526 (12)	147
Compound (III)					
	C4—H4*A*⋯O2$^{\rm iv}$	0.93	2.66	3.587 (9)	179
	C7—H7*A*⋯O2$^{\rm iv}$	0.93	2.49	3.413 (9)	171
	C8—H8*A*⋯O3$^{\rm v}$	0.93	2.61	3.435 (8)	148
	C9—H9*A*⋯O1$^{\rm vi}$	0.93	2.68	3.601 (9)	169

Symmetry codes: (i) $x - \frac{3}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; (ii) $2 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (iii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x - 1, -y - 1, -z - 2$; (v) $x - \frac{1}{2}, -y - \frac{3}{2}, z - \frac{1}{2}$; (vi) $-x - 2, -y - 1, -z - 2$. Codes (i)–(iii) correspond to compound (I) (space group $P2_12_12_1$) and codes (iv)–(vi) correspond to compound (III) (space group $P2_1/n$).

All H atoms in (I) were defined by the stereochemistry and they were accordingly located at their calculated positions riding on their host atoms, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection, cell refinement and data reduction: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1040). Services for accessing these data are described at the back of the journal.

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