catena-Poly[[aqua(3,4,7,8-tetramethyl-1,10-phenanthroline-$\kappa^2 N,N'$)cadmium(II)]-μ_3-thiosulfato-$\kappa^3 S{:}S{:}O$]

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The title compound, $[Cd(S_2O_3)(C_{16}H_{16}N_2)(H_2O)]_n$, presents a polymeric one-dimensional structure running along the $P2_1/c$ glide direction, with elementary units defined by six-coordinate Cd^{II} atoms bonded to three symmetry-related thiosulfate groups, a bidentate tetramethylphenanthroline ligand and one aqua ligand. The bridging thiosulfates bind metal centers through two different sequences, *viz.* Cd—S—Cd′ and Cd′—S′—S′—O′—Cd, defining a closed six-membered ring. Individual chains are held together *via* π–π interactions to generate two-dimensional networks parallel to the (100) plane. These, in turn, are connected by much weaker van der Waals interactions.

Comment

As part of a general study of metal complexes incorporating sulfur oxoanions, we describe here the structure of $[Cd(S_2O_3)(tmph)(H_2O)]$, (I) (tmph is 3,4,7,8-tetramethyl-1,10-phenanthroline). The metal atom has a distorted six-coordinate environment (Fig. 1), provided by the two N atoms of a chelating tmph ligand, one O atom from an aqua molecule and three atoms of three different symmetry-related thiosulfate anions, through one O atom and the terminal S atoms acting in a bridging mode.

The distorted coordination polyhedron can be described as an asymmetrically elongated octahedron, having atoms N1, N2, O1*W* and S1 as the basal plane [the mean deviation from the plane is 0.08 (1) Å], with atom Cd1 deviating by 0.44 (1) Å towards the apical site S1[ii] and with O3[i]—Cd1—S1[ii] as the slightly deformed apical axis [177.15 (8)°; symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]. The Cd1—S1[ii]/O3[i] vectors

subtend angles of 4.5 (1) and 6.3 (1)°, respectively, to the plane normal.

Tmph has been previously reported as a ligand with Ti, W and Mo [refcodes LASDUE, MELGIT, MELGOZ, MELGUF and MELHAM in the November 2004 release of the Cambridge Structural Database (CSD; Allen, 2002)], and we have recently presented (Díaz de Vivar *et al.*, 2004) a close Zn relative of (I), *viz.* $Zn(tmph)(H_2O)_4](S_2O_3)$, where the anion does not coordinate but acts as a charge-balancing counter-ion. No structures containing the Cd(tmph) group have been reported. The tmph ligand appears planar within experimental error [the mean deviation from the least-squares plane is 0.011 (6) Å] and binds to the cation in a slightly slanted way, the CdN_2 group subtending an angle of 5.2 (1)° to the ligand mean plane.

(I)
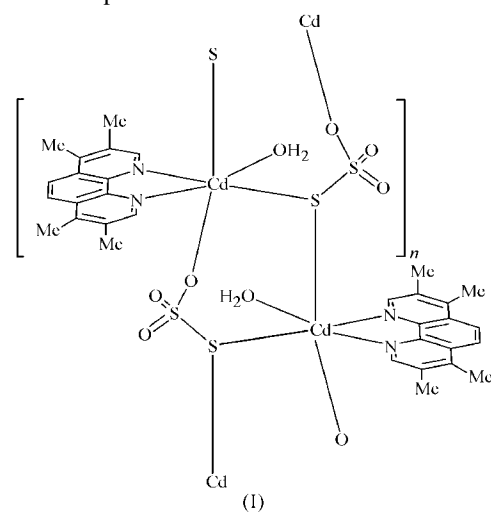
The $Cd-N_{tmph}$ bonds are slightly asymmetric (2.1% difference; Table 1), and this percentage is somewhat larger than the mean value found for the 244 other cadmium complexes with aromatic amines reported in the CSD [$\Delta(\%) = 0.4 (4)$]. The remaining parameters of the tmph coordination fall well within the reported range [*viz.* mean Cd—N = 2.36 (4) and 2.32 (2) Å, and mean N—Cd—N = 70.4 (4) and 71.66 (14)°, for the CSD and this work, respectively].

The thiosulfate unit binds to three different Cd centers; atom S1 acts as a direct bridge between two of them, and the third is linked *via* atom O3. This coordination mode for thiosulfate corresponds to type 6 in the classification presented by Freire *et al.* (2000), and this seems to be the preferred coordination mode for the anion in Cd complexes, as it has been found to coordinate this way in four out of seven other Cd–thiosulfate complexes reported in the CSD (Baggio *et al.*, 1997, 1998; Freire *et al.*, 2001; Harvey *et al.*, 2004). In contrast to the general trend of internal S—O distances bearing an inverse relationship to the degree of coordination involvement displayed by the corresponding O atom, O2 (not directly bound to cadmium, though an acceptor of two strong hydrogen bonds; see Table 2) does present a longer S—O distance than the (weakly) bound atom O3.

The result of the multiple coordination of the thiosulfate anion is the formation of chains parallel to the *c*-glide direction through two different bridging sequences, *viz.* Cd1—S1—
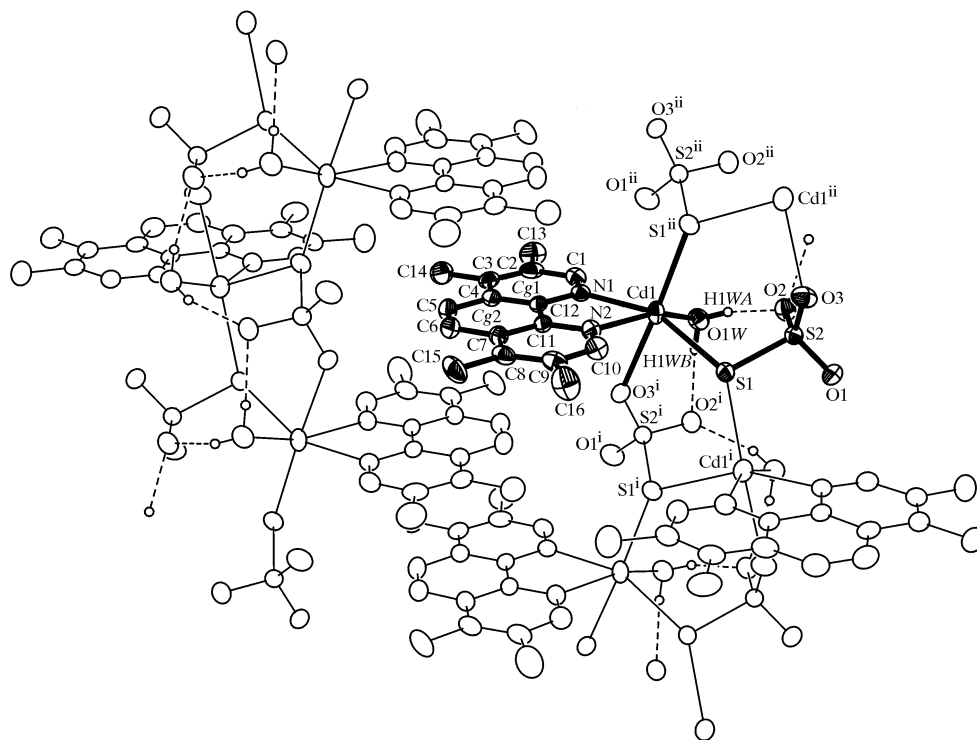
Figure 1
A displacement ellipsoid plot (40% probability level) of the dimeric units in (I). Only the independent moiety is drawn in full ellipsoids. Internal hydrogen bonds are shown as broken lines. The way in which planar tmph groups interdigitate is suggested. Symmetry codes are as in Table 1.
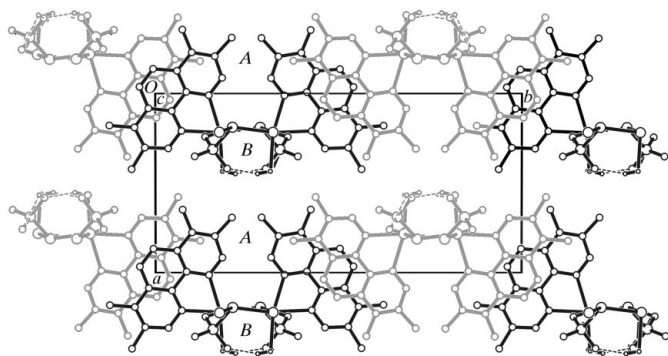

Figure 2
A packing diagram of (I), viewed down the *c* axis, showing the way in which planes parallel to (100) build up. Adjacent interdigitated columns have been drawn in alternating colors (black/grey) for clarity.

$Cd1^i$ and $Cd1^i$—$S1^i$—$S2^i$—$O3^i$—$Cd1$, defining a six-membered closed loop (see Fig. 1). The symmetry element responsible for the repetition scheme is the *c*-glide plane, which bisects the sequence.

Chains in transition metal complexes with thiosulfate ligands are not unusual, and translational operations promoting them are diverse; in some cases they are built up along a short cell axis through a unit-cell translation (*viz*. CSD refcodes WIPNEP and XORWOQ), sometimes with imbedded symmetry centers (as in PAHTAU); chains may evolve along a twofold screw axis (as in INIZEK, NUTLUV and RAVLUV) or have glide planes as generators (as in ETUZNT, MIPWAJ and the present structure).

The fact that the C13···C16 transversal axis in tmph is not parallel but oblique to the *c*-glide plane, with one of its outermost methyl groups almost 'touching' the plane [atom C16 lies at 0.87 (1) Å] has the effect of clustering symmetry-related tmph groups at one side of the chain, defining some kind of a 'hydrophobic column' (a non-active zone for hydrogen-bonding interactions, zone '*A*' in Fig. 2). The thiosulfate groups and the aqua ligands, on the other hand, pile themselves at the opposite side, in a contrasting hydrophilic, or hydrogen-bonding active, region (zone '*B*' in Fig. 2). In fact, the two hydrogen bonds (Table 2) present in the structure, both of them internal to the chain, evolve in this zone, joining symmetry-related water molecules and O2 atoms in the thiosulfate groups in a sort of continuous threading (Fig. 1).

The 'double-column' chains are related to one another by external inversion centers; those symmetry elements at $x = 0$ and 1 promote the nearest approach of (inverted) neighboring chains, with the effect that consecutive 'type *B*' columns slide sideways into each other along the *b* axis, with their bulky tmph groups filling neighboring voids in a classical 'gear-like' fitting. As a result, parallel aromatic cycles lie at a graphitic distance from one another, thus giving rise to the π–π interactions that link the chains together (Fig. 2 and Table 3). The result is a two-dimensional structure parallel to (100). These broad planes are repeated along the *a* axis in such a way as to confront 'type *A*' zones with 'type *B*' zones, at a rather long non-interacting distance (typical values $H_{methyl}···O_{thiosulfate} > 2.70$ Å; Fig. 2)

Experimental

The title compound was obtained by allowing a 96% ethanol solution of 3,4,7,8-tetramethyl-1,10-phenanthroline to diffuse into an equimolar aqueous solution containing cadmium acetate and sodium thiosulfate (5 ml of each solution, all concentrations being 0.025 M). After two months, a few colorless needles suitable for X-ray analyses were obtained.

Crystal data

$[Cd(S_2O_3)(C_{16}H_{16}N_2)(H_2O)]$	$D_x = 1.894$ Mg m^{-3}
$M_r = 478.84$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1520
$a = 11.086$ (2) Å	reflections
$b = 21.846$ (5) Å	$\theta = 5.3–47.4°$
$c = 7.2000$ (15) Å	$\mu = 1.57$ mm^{-1}
$\beta = 105.615$ (4)°	$T = 297$ (2) K
$V = 1679.4$ (6) Å^3	Plate, colorless
$Z = 4$	$0.27 \times 0.09 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	3818 independent reflections
	2868 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.064$
Absorption correction: multi-scan [$SADABS$ (Sheldrick, 1996) in $SAINT\text{-}NT$ (Bruker, 2000)]	$\theta_{max} = 28.1°$
	$h = -14 \rightarrow 13$
	$k = -28 \rightarrow 28$
$T_{min} = 0.82$, $T_{max} = 0.94$	$l = -9 \rightarrow 9$
13727 measured reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.058$	
$wR(F^2) = 0.110$	
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3818 reflections	
238 parameters	$(\Delta/\sigma)_{max} = 0.002$
	$\Delta\rho_{max} = 0.82$ e Å^{-3}
	$\Delta\rho_{min} = -0.64$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.292 (4)	Cd1—S1^{ii}	2.6521 (14)
Cd1—O1W	2.327 (4)	S1—S2	2.0719 (18)
Cd1—N2	2.340 (4)	S2—O1	1.438 (4)
Cd1—O3^i	2.583 (4)	S2—O3	1.454 (4)
Cd1—S1	2.6394 (14)	S2—O2	1.468 (4)
N1—Cd1—O1W	96.15 (14)	N2—Cd1—S1	94.46 (11)
N1—Cd1—N2	71.66 (14)	O3^i—Cd1—S1	86.07 (9)
O1W—Cd1—N2	156.96 (15)	N1—Cd1—S1^{ii}	103.97 (10)
N1—Cd1—O3^i	73.21 (12)	O1W—Cd1—S1^{ii}	104.12 (10)
O1W—Cd1—O3^i	76.81 (13)	N2—Cd1—S1^{ii}	97.89 (11)
N2—Cd1—O3^i	80.89 (13)	O3^i—Cd1—S1^{ii}	177.15 (8)
N1—Cd1—S1	156.44 (10)	S1—Cd1—S1^{ii}	96.60 (3)
O1W—Cd1—S1	89.76 (10)	Cd1—S1—Cd1^i	129.47 (5)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WB\cdots$O2^i	0.85 (3)	1.98 (3)	2.831 (5)	172 (6)
O1W—H1$WA\cdots$O2	0.86 (4)	1.89 (3)	2.701 (5)	157 (6)

Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 3
π–π contacts (Å, °) for (I).

$Cg1$ and $Cg2$ are the centroids of the C1–C4/C12/N1 and C4–C7/C11/C12 rings, respectively.

Contact	cc (Å)	sa (°)	cp (Å)
$Cg1\cdots Cg2^{iii}$	3.707 (3)	20.03 (9)	3.483 (2)
$Cg2\cdots Cg2^{iii}$	3.810 (3)	23.88 (1)	3.484 (1)
$Cg2\cdots Cg2^{iv}$	3.697 (3)	18.16 (1)	3.512 (1)

Notes: cc is the center-to-center distance; sa is the (mean) slippage angle, subtended by cc vectors and the plane normals; cp is the (mean) center-to-plane distance. Symmetry codes: (iii) $-x, -y, -z$; (iv) $-x, -y, -z + 1$.

H atoms attached to C atoms were placed at calculated positions (aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å) and allowed to ride. Methyl groups were also allowed to rotate around the C—C axis. H atoms of water molecules were located from difference Fourier maps and refined with restrained O—H distances [0.85 (2) Å]. U_{iso}(H) values were set at xU_{eq}(host), with $x = 1.2$ for aromatic and water H atoms and $x = 1.5$ for methyl H atoms.

Data collection: $SMART\text{-}NT$ (Bruker, 2001); cell refinement: $SAINT\text{-}NT$ (Bruker, 2000); data reduction: $SAINT\text{-}NT$; program(s) used to solve structure: $SHELXS97$ (Sheldrick, 1997); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 1997); molecular graphics: XP in $SHELXTL\text{-}PC$ (Sheldrick, 1994); software used to prepare material for publication: $SHELXL97$.

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