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catena-Poly[[diaqua(1,10-phenanthroline-*N*,*N*′)cadmium(II)]-μ-(sulfato-*O*:*O*′)] and *catena*-poly[[diaqua(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)-cadmium(II)]-μ-(sulfato-*O*:*O*′)]

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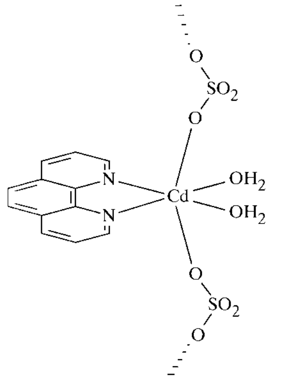
Both title compounds, $[Cd(SO_4)(C_{12}H_8N_2)(H_2O)_2]_n$ and $[Cd(SO_4)(C_{14}H_{12}N_2)(H_2O)_2]_n$, respectively, are polymeric and present the Cd atoms in very similar octahedral environments, provided by the bidentate organic ligand (phenanthroline/dimethylphenanthroline), two aqua molecules and two O atoms from two translationally related sulfate groups, which thus act as links in the resulting polymeric chains.

Comment

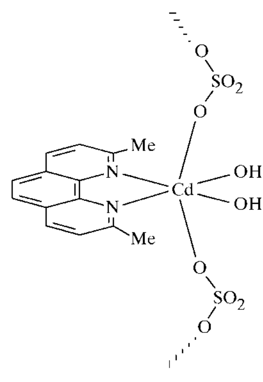
Cadmium(II) complexes have been extensively studied from a chemical and structural point of view, mainly due to the capability of cadmium(II) (shared by most d^{10} metal ions) to adopt different modes of coordination determined by considerations of size, as well as electrostatic and covalent bonding forces. The presence of sulfate as a ligand introduces some additional degrees of freedom, due to its versatility in acting as a monodentate, bidentate or bridging ligand.

This latter mode of coordination has been reported so far in four Cd–sulfate complexes, as revealed by a search of the Cambridge Structural Database (Allen & Kennard, 1993). In three of these complexes, namely bis(μ-sulfato)tetraaquabis(μ-cyanoguanidine)dicadmium(II) (Hubberstey & Falshaw, 1982), *catena*-[(μ-sulfato-*O*,*O*′)aqua(2,2′-bipyridyl-*N*,*N*′)(2-imidazolinethione-*S*)cadmium(II)] monohydrate (Rodesiler *et al.*, 1987) and bis(thiosemicarbazide)cadmium(II) sulfate (Larsen & Trinderup, 1975), the bridging sulfates are in *trans* positions. However, in the fourth complex, *catena*-[*cis*-(μ-sulfato)aquatris(imidazole)cadmium(II)] (Caira *et al.*, 1976), the anionic ligands are located in *cis* positions.

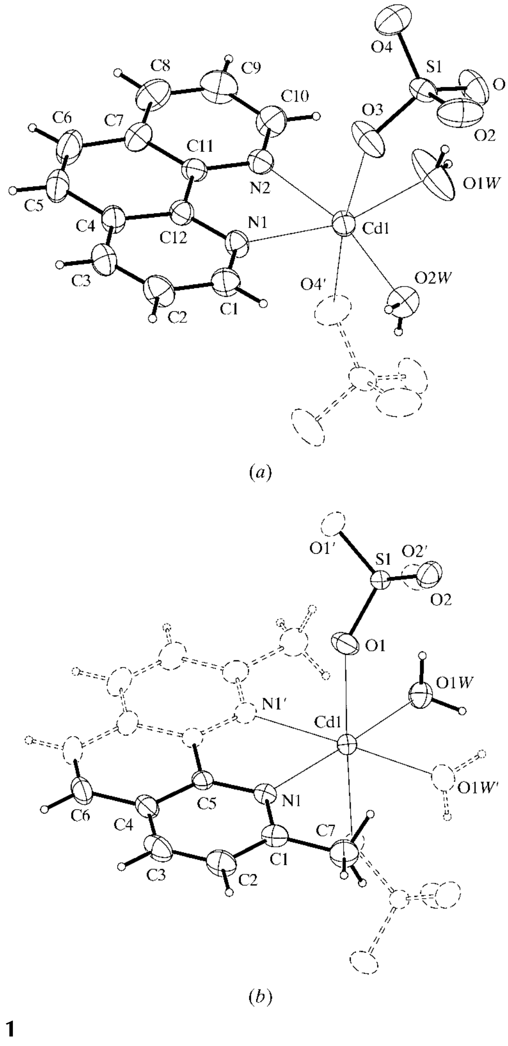
The two polymeric structures presented herein, [Cd(phen)-$(SO_4)(H_2O)_2$], (I), and [Cd(dmph)$(SO_4)(H_2O)_2$], (II) (Figs. 1*a* and 1*b*, respectively), where phen is 1,10-phenanthroline and dmph is 2,9-dimethyl-1,10-phenanthroline, are examples of the former bridging case (*trans* ligands). In spite of crystallizing in quite different space groups and displaying different degrees of local symmetry, the structures have many features



(I)



(II)



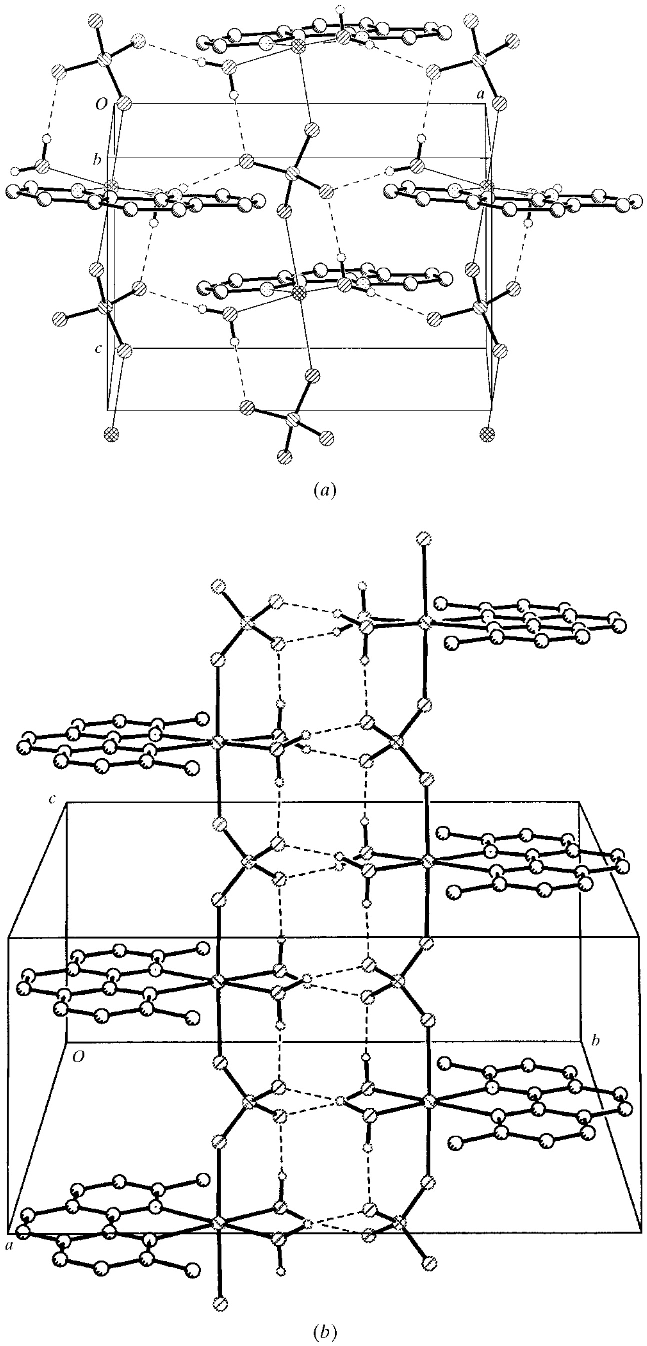
(*a*)

(*b*)

Figure 1
Molecular diagrams of (*a*) compound (I) and (*b*) compound (II) showing the numbering schemes used. Displacement ellipsoids are drawn at the 50% level. Note the twofold axis across the molecule in (*b*).

in common. The main similarities are that both compounds form polymeric chains constituted by the stacking of Cd octahedra, the equatorial planes of which are defined by the close bidentate bite of the organic ligand plus two coordinated water molecules. The apical sites, in turn, are occupied by two O atoms of the sulfate anion, which thus acts as the bridging link of the chains.

For the four cadmium sulfate bridging complexes reported in the literature, the Cd—O(SO_3) distances vary in an ample range (2.259 to 2.525 Å), with the values found in (I) [2.320 (3) and 2.326 (3) Å] and (II) [2.370 (2) Å], being in the lower half of the range reported.



(*a*)

(*b*)

Figure 2
Simplified packing diagrams showing hydrogen-bonding interactions for (*a*) compound (I) and (*b*) compound (II).

Among the differences between the two structures is the effect of the two bulky methyl groups on the geometry of the equatorial plane in (II), pushing the two water molecules into each other and stretching the O*W*—Cd—O*W* angle [81.6 (1)°] to a much smaller value than in the unconstrained case [97.8 (2)° in (I)]. This effect will be discussed further when describing the packing. The angle contraction is accompanied by a small but perceptible lengthening of the Cd—O*W* bond lengths, of *ca* 3.5%. Another difference is to be found in the local symmetry of the polyhedra, which in (I) lie in general positions (space group $P2_12_12_1$), but in (II) (space group *C*2/*c*), the cation as well as the S atom lie in special positions of type *e*, on two different twofold axis, thus rendering only half of the molecule independent. In both structures, the two aqua molecules attached to each cation are fully involved in hydrogen bonding, each one making one 'intra-chain' bond, in the direction of, and reinforcing, the link determined by the bridging sulfate, and a second one connecting neighbouring chains (Figs. 2*a* and 2*b*). The similarities end here, as the differences which both polyhedra exhibit in the O*W*—Cd—O*W* angle determine the way in which the chains pack; the close approach of both water molecules in (II) determines that they can interact with one and only one of the neighbouring chains, due to steric hindrance. As a consequence, a ribbon made up of two parallel chains results. In the case of (I), instead, the much more open geometry permits the approach of two parallel chains, one at each side, interacting with one water molecule each and thus defining an infinite two-dimensional structure parallel to (010). Both structures [planes in (I) and ribbons in (II)] share the usual gear-like appearance with the organic ligands protruding outwards and fitting into the hollows left by adjacent homologous groups in the neighbouring structures. The thus interleaved ligands give rise to a 'dovetail' structure, with the planar groups parallel to each other at the characteristic graphitic distance of *ca* 3.40 Å.

Experimental

The direct mixing of a 0.075 *M* aqueous solution of $3CdSO_4{\cdot}8H_2O$ and an ethanolic solution of phenanthroline gave a white precipitate, which when recrystallized from boiling water yielded well developed colourless needles of (I) suitable for X-ray studies. Slow diffusion of a 0.025 *M* alcoholic solution of dimethylphenanthroline into an aqueous solution of $3CdSO_4{\cdot}8H_2O$ developed thin colourless needles of (II). After a week, the specimens had the appropriate size for X-ray analysis.

Compound (I)

Crystal data

$[Cd(SO_4)(C_{12}H_8N_2)(H_2O)_2]$
$M_r = 424.70$
Orthorhombic, $P2_12_12_1$
$a = 10.352\ (1)$ Å
$b = 20.083\ (2)$ Å
$c = 6.828\ (4)$ Å
$V = 1419.5\ (9)$ Å^3
$Z = 4$
$D_x = 1.987$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 7.5$–$15.0°$
$\mu = 1.72$ mm^{-1}
$T = 293\ (2)$ K
Needle, colourless
0.40 × 0.15 × 0.12 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.57$, $T_{\max} = 0.80$
2536 measured reflections
1894 independent reflections (plus 454 Friedel-related reflections)
2084 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.016$
$\theta_{\max} = 27.49°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 26$
$l = -1 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.076$
$S = 0.995$
2348 reflections
217 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0042 (5)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (4)

Table 1
Selected bond lengths (Å) for (I).

Cd1—O1*W*	2.243 (3)	Cd1—N1	2.341 (3)
Cd1—O2*W*	2.243 (3)	S1—O2	1.466 (3)
Cd1—N2	2.312 (3)	S1—O4	1.466 (3)
Cd1—O4$^{\text{i}}$	2.320 (3)	S1—O3	1.468 (3)
Cd1—O3	2.326 (3)	S1—O1	1.472 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1*W*—H1*WA*$\cdots$O1	0.77 (4)	1.87 (4)	2.650 (6)	178 (4)
O1*W*—H1*WB*$\cdots$O2$^{\text{i}}$	0.77 (4)	1.92 (4)	2.681 (5)	165 (4)
O2*W*—H2*WB*$\cdots$O1$^{\text{ii}}$	0.75 (3)	1.91 (4)	2.652 (4)	166 (3)
O2*W*—H2*WA*$\cdots$O2$^{\text{iii}}$	0.76 (3)	1.89 (3)	2.647 (5)	172 (3)

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

Compound (II)

Crystal data

$[Cd(SO_4)(C_{14}H_{12}N_2)(H_2O)_2]$
$M_r = 452.75$
Monoclinic, $C2/c$
$a = 15.384$ (3) Å
$b = 14.826$ (3) Å
$c = 6.926$ (1) Å
$\beta = 107.54$ (3)°
$V = 1506.3$ (5) Å^3
$Z = 4$
$D_x = 1.996$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–$15.0°$
$\mu = 1.62$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.28 × 0.12 × 0.12 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.69$, $T_{\max} = 0.82$
1787 measured reflections
1727 independent reflections
1622 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = -8 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.073$
$S = 1.050$
1727 reflections
120 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.887P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.98$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Cd1—O1*W*	2.308 (2)	S1—O1	1.4751 (18)
Cd1—N1	2.340 (2)	S1—O2	1.4804 (18)
Cd1—O1	2.370 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1*W*—H1*WA*$\cdots$O2$^{\text{i}}$	0.92 (3)	1.82 (3)	2.726 (3)	165 (3)
O1*W*—H1*WB*$\cdots$O2$^{\text{ii}}$	0.93 (3)	1.76 (3)	2.686 (3)	171 (3)

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

H atoms attached to carbon were idealized; those unambiguously determined by the stereochemistry were allowed to ride, while those in the methyl groups were allowed to rotate as a rigid ideal group as well. Finally, those attached to oxygen were found in the difference Fourier map and refined with softly restrained O—H and H$\cdots$H distances and individual isotropic displacement parameters.

For both compounds, 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, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1526). Services for accessing these data are described at the back of the journal.

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