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Two new dimeric cadmium(II) and zinc(II) sulfate complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine and 2,2:6′,2″-terpyridine

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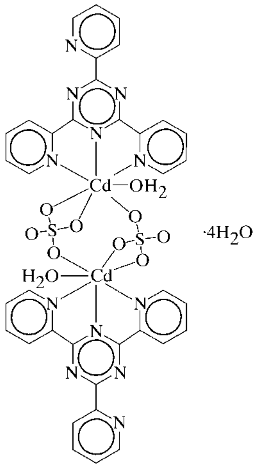
The structures of two new sulfate complexes are reported, namely di-μ-sulfato-$\kappa^3O,O':O''$-bis{aqua[2,4,6-tris(2-pyridyl)-1,3,5-triazine-κ^3N^1,N^2,N^6]cadmium(II)} tetrahydrate, $[Cd_2(SO_4)_2(C_{16}H_{12}N_6)_2(H_2O)_2]\cdot 4H_2O$, and di-$\mu$-sulfato-$\kappa^2O:O'$-bis[(2,2′:6′,2″-terpyridine-$\kappa^3N^1,N^{1'},N^{1''}$)zinc(II)] dihydrate, $[Cd_2(SO_4)_2(C_{15}H_{11}N_3)_2]\cdot 2H_2O$, the former being the first report of a Cd(tpt) complex [tpt is 2,4,6-tris(2-pyridyl)-1,3,5-triazine]. Both compounds crystallize in the space group $P\overline{1}$ and form centrosymmetric dimeric structures. In the cadmium complex, the metal center is heptacoordinated in the form of a pentagonal bipyramid, while in the zinc complex, the metal ion is in a fivefold environment, the coordination geometry being intermediate between square pyramidal and trigonal bipyramidal. Packing of the dimers leads to the formation of planar structures strongly linked by hydrogen bonding.

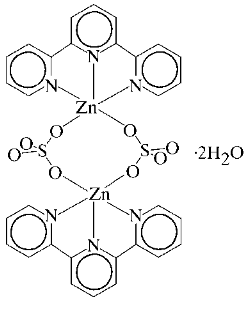
Comment

The study of Cd^{II} and Zn^{II} coordination compounds with sulfur oxoanions as ligands has been ongoing for many years. A number of structures, interesting from a stereochemical point of view, have been synthesized, as many of these anions (sulfite, sulfate, thiosulfate, tetrathionate, *etc.*) behave as versatile ligands when coordinating to d^{10} metal centers. The sulfate ion, in particular, is quite attractive in this respect; it has been reported as coordinating to transition metals through one, two or three O atoms, giving rise to monomeric, dimeric or polymeric structures. In spite of extensive studies, the full binding capability of the anion does not seem to be exhausted.

A search in the November 2002 version of the Cambridge Structural Database (CSD; Allen, 2002) returned 33 organometallic complexes in which the sulfate group is attached either to Zn^{II} or Cd^{II}. The 16 Zn^{II} complexes reported in the CSD are almost equally distributed between compounds displaying monomeric monodentate ($M—O—SO_3$) and polymeric bridging ($M—O—SO_2—O—M$) modes, with only three exceptions, which we will refer to by their CSD refcodes, *viz*. a dimer (MASVUX; Harvey *et al.*, 2000), a one-dimensional polymeric $M—O—SO_2—O—M$ structure (LOPNIN; Plater *et al.*, 2000), where the sulfate group binds through three O atoms, two to the same metal center in a chelate fashion, and a polynuclear monomeric structure (VABMEK; Ali *et al.*, 1998), in which the sulfate group binds to three different Zn^{II} ions. Complexes with Cd^{II}, in contrast, show only a few examples of monomeric structures, the preferred coordination being polymeric of the $M—O—SO_2—O—M$ type. The only two exceptions [TIRXAT (Rahmani *et al.*, 1996) and COXQUB (Huang *et al.*, 1999)] organize as polymers built up by three O atoms, binding to three different metal centers. Continuing our research on this type of compound, we report herein the structures of two new sulfate complexes, namely



(I)



(II)

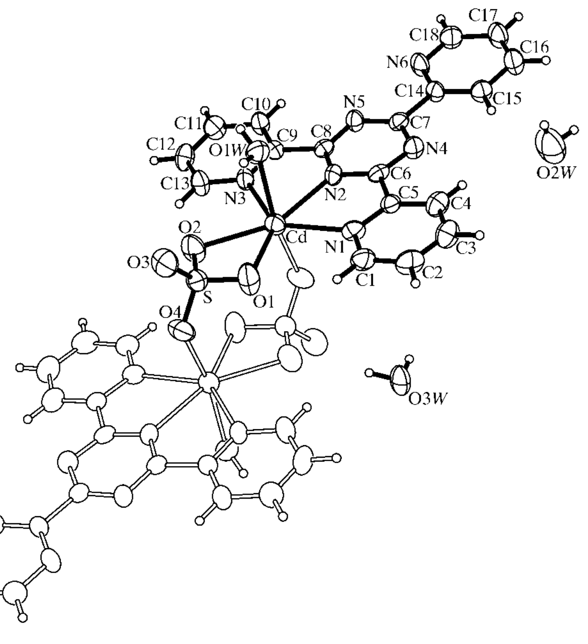


Figure 1
Ellipsoid plot (50% probability level) showing the dimeric unit of (I).

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$[Cd(SO_4)(tpt)(H_2O)\cdot2H_2O]_2$, (I), and $[Zn(SO_4)(tpy)\cdot H_2O]_2$, (II) [tpt is 2,4,6-tris(2-pyridyl)-1,3,5-triazine and tpy is 2,2′:6′,2″-terpyridine]. The former is the first report of a Cd(tpt) complex.

Both title compounds crystallize in the space group $P\overline{1}$ and form dimeric centrosymmetric structures. In complex (I), the metal ion is heptacoordinated by three N atoms from the tridentate tpt ligand, one aqua O atom and three O atoms from two symmetry-related sulfate ions, each of which binds to two metal centers, thus generating the dimeric structure (Fig. 1). In the two other Cd complexes incorporating tridentate sulfate ligands reported previously (TIRXAT and COXQUB), the anion binds to three different metal centers, generating polymeric structures. The coordination polyhedra in (I) can be described as a distorted pentagonal bipyramid, with the equatorial plane formed by atoms N1, N2, N3, O1 and O2 [maximum deviation of 0.04 (1) Å for N2], and angles subtended at the Cd site ranging from 58.6 (3) to 83.6 (3)° (ideal 72°). The axial sites are occupied by atoms O1*W* and O4($-x$, $-y$, $-z$), which subtend an angle of 166.1 (3)° to the cation.

The ligand is almost planar and acts in a tridentate manner, with the central Cd—N distance [2.337 (4) Å] being considerably shorter than the lateral Cd—N distances [2.437 (4) and 2.415 (4) Å]. Comparison with similar cases in the literature becomes difficult since there are no other reports of heptacoordinated cadmium(II) complexes with tpt or related tridentate ligands. There are, however, some examples where the heptacoordinated cation binds to a similar base [*viz*. 2,4-bis(4-pyridyl)-1,3,5-triazine], acting in a bridging manner, which display Cd—N distances in the range 2.28–2.32 Å (XESHOS, XESHUY and XESJAG; Barnett *et al.*, 2001). The larger values in (I) could be attributed to the steric hindrance introduced by the planar tridentate bite.

Coordination does not affect the dimensions of the sulfate moiety; moreover, no significant differences are observed among the S—O distances involving either coordinated or uncoordinated O atoms. In fact, the mean S—O distance [1.463 (3) Å] is similar to that reported for the free anion [a search in the CSD gave a mean value of 1.472 (8) Å for 118 structures with $R < 0.05$]. The tpt ligand does not show any abnormal characteristics, with its three bound rings being basically coplanar; the atoms deviate from an ideal plane on average by less than 0.02 (1) Å. The terminal pyridyl ring deviates from planarity by less than 0.01 (1) Å and subtends an angle of 3.6 (1)° to the ideal plane. The structure is stabilized by hydrogen bonding involving the two independent hydrate molecules (see Table 2).

The structure of (II) is also dimeric. The coordination is such that three N atoms from tpy and two O atoms from two symmetry-related sulfate ions complete a distorted fivefold environment around the metal ion (Fig. 2). The geometry lies midway between square pyramidal and trigonal bipyramidal. As in the case of (I), a considerable difference is observed in the Zn—N distances, that to the central N atom of tpy being the shortest [2.074 (3) *versus* 2.167 (3) and 2.201 (3) Å]. Similar results have been observed in other pentacoordinated Zn–tpy complexes, *viz*. 2.209, 2.115 and 2.170 Å in DOLVIJ (Harrison *et al.*, 1986), 2.181, 2.097 and 2.155 Å in OFABOM (Finn & Zubieta, 2002), and 2.169, 2.066 and 2.164 Å, and 2.158, 2.062 and 2.172 Å in XEZZIL (two independent molecules; Hagrman & Zubieta, 2001).

As the zinc complex is pentacoordinated, larger valence bond values (Brown & Altermatt, 1985) for the Zn—O bonds are expected compared to those in the heptacoordinated cadmium complex and, accordingly, a larger effect on the corresponding S—O$_{\rm coord}$ distances of the sulfate group is predicted. In fact, the regular geometry displayed by the anion in (I) is lost in (II), where a clear difference is observed

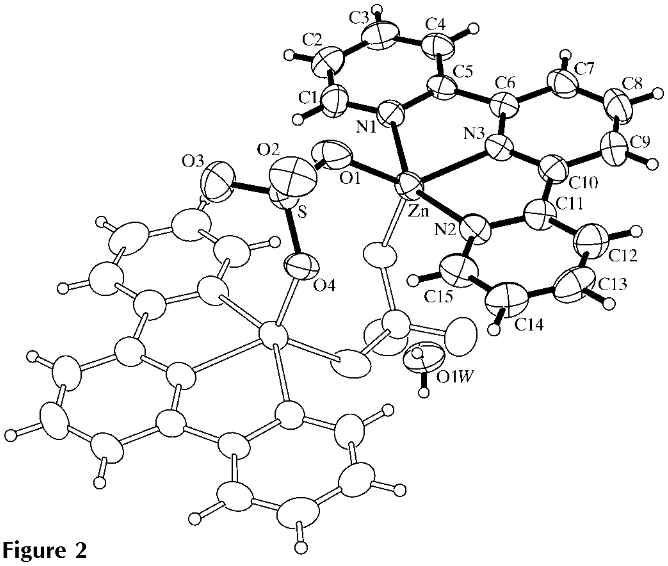

Figure 2
Ellipsoid plot (50% probability level) showing the dimeric unit of (II).

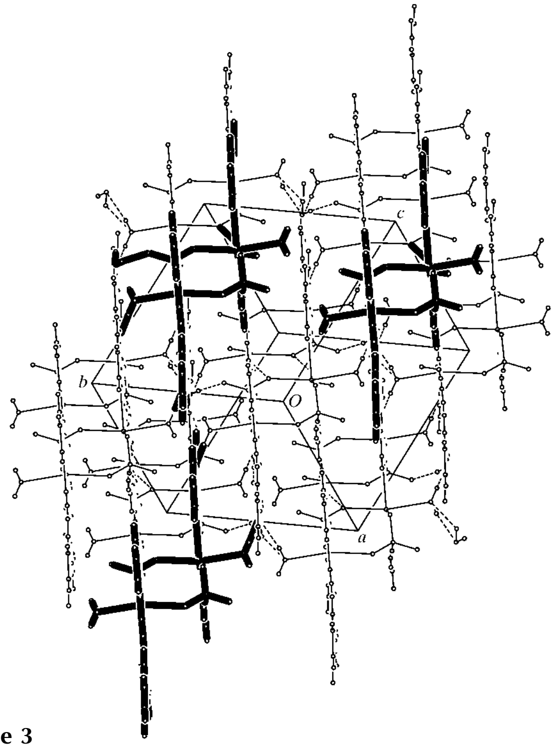

Figure 3
Schematic packing view of (II) along the planes, which are shown as horizontal lines. Selected dimers are drawn in heavy full lines so as to distinguish them from the background.

between the mean S—O$_{coord}$ and S—O$_{uncoord}$ distances [1.490 (6) and 1.427 (6) Å, respectively]. Since (II) is the first reported structure containing pentacoordinated Zn cations bridged by sulfate anions in a Zn—O—SO$_2$—O—Zn mode, it was not possible to make a fair comparison with other Zn complexes displaying analogous cation environments. We could trace, however, both tetra- and hexacoordinated Zn structures with a similar sulfate coordination. These structures clearly confirm the effect of bond valence; in the only tetracoordinated case of this sort reported so far (MASVUX; Harvey *et al*., 2000), the difference between the two types of S—O bonds is enhanced, being even larger than in the present pentacoordinated case [1.506 (6) and 1.439 (2) Å, respectively]. In the five hexacoordinated structures reported, in contrast, there is almost no trend differentiating the two kinds of bonds, their mean values being 1.47 (2) and 1.48 (3) Å, respectively, indistinguishable from each other and from the already mentioned average for the free ligand [1.472 (8) Å]. The geometry of the tpy ligand and the internal parameters are unexceptional. There is one hydrogen-bonded crystallization water molecule in the structure (Table 4).

The packing is rather similar in both structures. As the dimers build up around a symmetry center, the planar molecules [tpt in (I) and tpy in (II)] are aligned parallel to each other. Cell symmetry preserves the orientation of the dimeric units, which stack with sets of parallel planes sharing one part of the dimer units. This distribution (illustrated in Fig. 3) consists of a set of interleaved planar arrays at a nearly graphitic distance (3.4 Å). The linking agent is the extensive hydrogen-bonding network involving all the available water molecules acting as donors and, together with some N atoms of the organic ligand and sulfate O atoms, as acceptors, in some cases. The most important of these interactions are reported in Tables 2 and 4.

Experimental

Both compounds were obtained by direct mixing of an aqueous solution of the cation sulfate ($3CdSO_4 \cdot 8H_2O$ or $ZnSO_4 \cdot 7H_2O$) with a methanol solution of the corresponding organic ligand (tpt or tpy), both in a concentration of 0.025 *M*. A crop of tiny crystals appeared readily, but they were not adequate for X-ray diffraction and were dissolved in hot water [for compound (I)] or in a 1:1 mixture of hot water and dimethylformamide [for compound (II)]. On standing, small specimens of both compounds suitable for structure analysis were collected.

Compound (I)

Crystal data

$[Cd_2(SO_4)_2(C_{16}H_{12}N_6)_2(H_2O)_2] \cdot 4H_2O$
$M_r = 1149.68$
Triclinic, $P\overline{1}$
$a = 8.870$ (2) Å
$b = 10.640$ (2) Å
$c = 12.685$ (2) Å
$\alpha = 103.36$ (2)°
$\beta = 98.79$ (2)°
$\gamma = 110.45$ (2)°
$V = 1055.0$ (4) Å^3
$Z = 1$
$D_x = 1.810$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 28 reflections
$\theta = 7.5$–15°
$\mu = 1.19$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.20 × 0.12 × 0.05 mm

Table 1
Selected interatomic distances (Å) for (I).

Cd—O4^i	2.278 (3)	Cd—N3	2.437 (4)
Cd—N2	2.337 (4)	S—O3	1.465 (3)
Cd—O2	2.354 (3)	S—O2	1.463 (3)
Cd—O1*W*	2.387 (4)	S—O1	1.464 (3)
Cd—O1	2.407 (3)	S—O4	1.465 (3)
Cd—N1	2.417 (4)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*W*—H3*WA*···O3^i	0.89 (2)	1.90 (2)	2.784 (5)	170 (4)
O3*W*—H3*WB*···O3^{ii}	0.90 (2)	1.91 (2)	2.800 (4)	171 (4)
O2*W*—H2*WB*···O4^{iii}	0.80 (2)	2.34 (3)	2.956 (5)	134 (3)
O2*W*—H2*WA*···O3^{iii}	0.89 (2)	2.50 (3)	3.206 (5)	137 (3)
O1*W*—H1*WA*···N6^{iv}	0.84 (2)	2.21 (3)	2.881 (5)	136 (4)
O1*W*—H1*WB*···O3*W*^{v}	0.86 (2)	1.96 (3)	2.791 (5)	162 (4)

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

Data collection

Rigaku AFC-7*S* diffractometer
ω/2*θ* scans
Absorption correction: *ψ* scan (*MSC*/*AFC Diffractometer Control Software*; Molecular Structure Corporation, 1988)
$T_{min} = 0.83$, $T_{max} = 0.90$
5842 measured reflections
4010 independent reflections
1996 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 26.0°$
$h = -5 \rightarrow 10$
$k = -13 \rightarrow 12$
$l = -15 \rightarrow 13$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.056$
$S = 0.88$
4010 reflections
319 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2))^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Compound (II)

Crystal data

$[Cd_2(SO_4)_2(C_{15}H_{11}N_3)_2] \cdot 2H_2O$
$M_r = 825.43$
Triclinic, $P\overline{1}$
$a = 9.700$ (2) Å
$b = 9.755$ (2) Å
$c = 10.324$ (2) Å
$\alpha = 110.34$ (2)°
$\beta = 116.59$ (2)°
$\gamma = 98.83$ (2)°
$V = 761.4$ (4) Å^3
$Z = 1$
$D_x = 1.800$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 30 reflections
$\theta = 7.5$–15°
$\mu = 1.79$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.24 × 0.16 × 0.10 mm

Data collection

Rigaku AFC-7*S* diffractometer
ω/2*θ* scans
Absorption correction: *ψ* scan (*MSC*/*AFC Diffractometer Control Software*; Molecular Structure Corporation, 1988)
$T_{min} = 0.79$, $T_{max} = 0.86$
4216 measured reflections
2890 independent reflections
2008 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 4$
$l = -11 \rightarrow 12$
2 standard reflections every 98 reflections intensity decay: <2%

Table 3
Selected interatomic distance (Å) for (II).

Zn—O4^{i}	1.952 (2)	S—O3	1.422 (3)
Zn—O1	1.970 (3)	S—O2	1.434 (3)
Zn—N3	2.074 (3)	S—O1	1.483 (3)
Zn—N2	2.166 (3)	S—O4	1.496 (2)
Zn—N1	2.201 (3)		

Symmetry code: (i) $2-x, 2-y, 2-z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WB\cdots$O1^{i}	0.81 (3)	2.17 (3)	2.957 (4)	166 (4)
O1W—H1$WA\cdots$O2^{ii}	0.81 (3)	2.04 (3)	2.834 (4)	169 (4)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.073$
$S = 0.85$
2890 reflections
234 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

For both compounds, H atoms were located at calculated positions, riding on their host atoms. Water H atoms were found in a difference Fourier synthesis and were refined with restrained O—H (0.80 Å) and H$\cdots$H (greater than 1.30 Å) distances, and $U_{\rm iso} = 1.2U_{\rm eq}$(O).

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: *XP* in *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1011). Services for accessing these data are described at the back of the journal.

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