metal-organic compounds

Diaqua(sulfato-κO)[2,4,6-tris(2-pyridyl)-1,3,5-triazine-$\kappa^3 N^1,N^2,N^6$]-zinc(II) dihydrate

Miguel Angel Harvey,[a,c] Sergio Baggio[b,c] and Ricardo Baggio[d]*

[a]Universidad Nacional de la Patagonia, Sede Trelew, 9100 Trelew, Chubut, Argentina, [b]Universidad Nacional de la Patagonia, Sede Puerto Madryn, 9120 Puerto Madryn, Chubut, Argentina, [c]CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, and [d]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

In the title compound, [Zn(SO$_4$)(C$_{18}$H$_{12}$N$_6$)(H$_2$O)$_2$]·2H$_2$O, the metal complex is monomeric, with an octahedral Zn^{II} centre coordinated by the tridentate ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt), two aqua molecules and a monodentate sulfate ion. A complex hydrogen-bonding scheme is built up out of the profuse availability of donors and acceptors (O—H···O/N and C—H···O) which, in addition to π–π interactions between tpt groups, define a three-dimensional assembly.

Comment

Sulfate–metal complexes have been extensively studied over the years and their appeal appears to be still maintained; one third of all structural research on the subject has been performed in the last three years [Cambridge Structural Database (CSD), April 2004 release; Allen, 2002]. There are good reasons for this appeal: in addition to the important role played by the anion in metal–organic chemistry, in recent times some biology-related roles have been reported, *viz.* participation in the biosynthesis of cysteine and other S-containing molecules in biological systems. Another focus of our interest in the present work on Zn–sulfate complexes arises as a result of findings from X-ray analyses that the cation may be present in enzyme systems where the sulfate anion is a substrate (Tamasi & Cini, 2003). Finally, to give examples of some applied investigations in which the anion is involved, it can be mentioned that metal–sulfate compounds have been studied in relation to porous-framework materials (Khan *et al.*, 2001) and in the chemistry relating to the chemotherapeutic drug cisplatin (Reedijk, 1992).

To this broad span of interests it can added, as a bonus, that sulfate complexes having polycyclic aromatic ligands (and, additionally, aqua molecules) in their coordination polyhedra have been shown to be extremely prolific in generating crystal

structures with a variety of non-covalent interactions. These may be through conventional hydrogen bonds and/or through medium-range contacts linking aromatic rings, either in a parallel-displaced arrangement (hereinafter π–π) or in an edge-to-face (or point-to-face) T-shaped conformation (C—H···π) (Janiak, 2000).

It can be concluded that sulfate complexes very often produce interesting crystal structures. Confirming this assertion, we report here a crystallographic study of the title compound, (I), which is a zinc(II) complex containing the tridentate ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt).
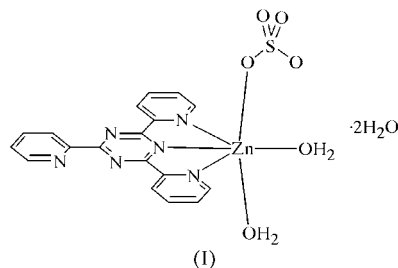
In (I), the metal complex is monomeric, and a distorted octahedral Zn centre is coordinated by three N-atom donors from the tridentate tpt ligand, two *cis*-related aqua ligands and an O atom of a monodentate sulfate group (Fig. 1).

Several factors might affect the regular geometry of the coordination polyhedron, *e.g.* the Jahn–Teller effect typical of a d^{10} metal atom, but the main distortion of (I) is certainly due to the steric limitations imposed by the tpt ligand. The bond lengths to the central metal atom are clearly differentiated into two groups, with three shorter distances to an aqua O atom (O1W), a sulfate O atom (O1) and the central tpt N atom (N2), and three longer ones to the second aqua O atom (O2W) and the two outermost N atoms in the organic ligand (N1 and N3). The asymmetry in the Zn—N bond lengths may be
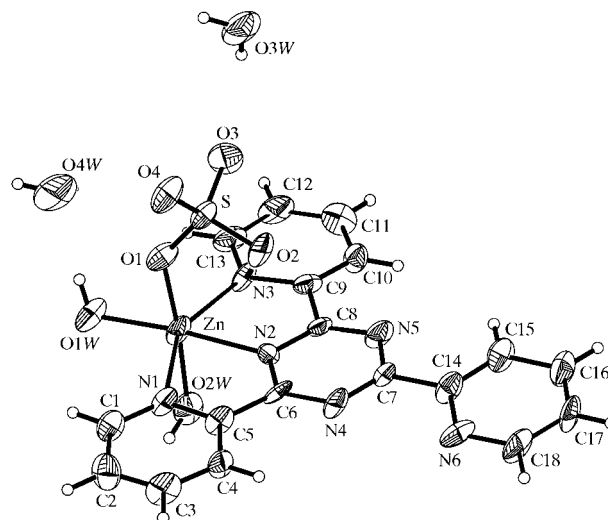

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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attributed to the short covalent radius of Zn^{II} and to the rather inflexible character of the tpt skeleton, which forces a closer approach of the central N atom. A search of the CSD revealed that 16 compounds in which Zn is complexed to tpt (or some closely related ligand) display a similar effect, with a mean $Zn-N_{central}$ distance of 2.077 (12) Å, and $Zn-N_{lateral}$ distances of 2.173 (12) (shorter) and 2.199 (17) Å (longer). These compare with values of 2.073 (4), 2.193 (4) and 2.271 (4) Å, respectively, in (I). Considering these values, it is evident that the marked asymmetry (ca 6%) of the two lateral bonds for (I) is much larger than the average. This is a rather unusual way of binding for these tridentate ligands. Also, the two aqua ligands present very different coordination lengths (Δ $Zn-O_{water}$ ca 4%), with that which is *trans* to the short $Zn-N2$ bond being shorter. Thus, the $N2-Zn-O1W$ axis is significantly shorter, giving the polyhedron a marked oblate character.

The monodentate sulfate ligand binds through atom O1, with a bond distance on the shorter side of the whole range, but there is no correlation with the corresponding S—O bond distances, the double-bond character being rather delocalized. A peculiar feature of the structure of (I) is the leaning of the sulfate anion towards the tpt group, driving one of its free O atoms to be at an almost colliding distance from one of the coordinated N atoms [$O2\cdots N2 = 2.92$ (1) Å]. As a consequence of this repulsion, the $N2-Zn-O1$ bond angle is larger than any of the remaining three (*cis*) angles involving atom O1. This binding behaviour is quite unusual: we could not trace in the literature any monocoordinated sulfate complex (irrespective of cation) in which any of its three free O atoms is less than 3.00 Å from a coordinated N or O atom, unless mediated by hydrogen bonding.
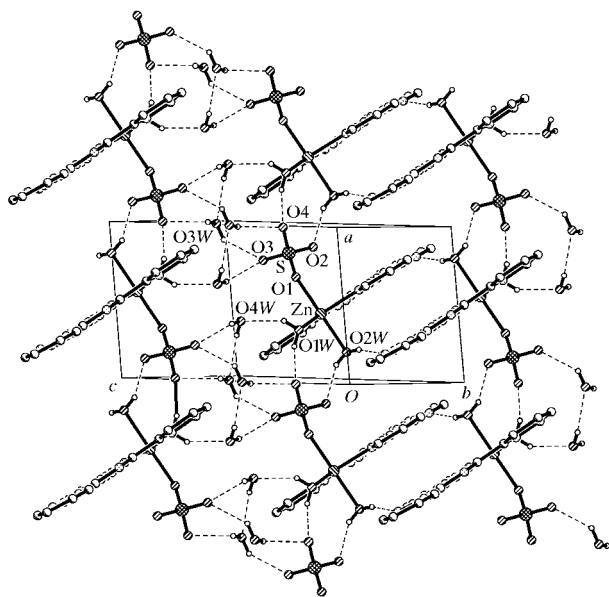
The tpt ligand in (I) presents a planar core determined by the three coordinated heterocycles (mean deviation from the least-squares plane = 0.06 Å), while the remaining terminal pyridyl group is rotated (out of this plane) by 6.9 (1)°.

The profuse availability of donors and acceptors for hydrogen bonding, as well as of aromatic groups with potential to enter into π–π interactions, gives rise to a very complex system of second-order interactions, defining the packing characteristics of the structure. Monomers connected to each other form double chains (or strips) embracing the symmetry centres at $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, while running along the *a* axis (Fig. 2). The internal single-chain linkage is achieved through two strong hydrogen bonds, which involve the two aqua ligands as donors and atoms O2 and O4 from the sulfate anion as acceptors (Table 2).

The 'dimerization' of chains into strips is achieved through the hydrogen bond involving atom O2W as donor and atom N6 from a neighbouring chain as acceptor. This chain-to-chain linkage is reinforced by the π–π parallel-displacive interaction (Fig. 3) resulting from tpt groups related by the $(\frac{1}{2}, \frac{1}{2}, 0)$ symmetry centre and characterized by an interplanar spacing of 3.28 (1) Å, with a distance between centres of 3.60 (1) Å and a slippage angle (Janiak, 2000) of 24.4°. The broad 'strips' thus generated, which are the real structural units in (I), connect with each other through hydrogen bonds involving the remaining water molecules O3W and O4W. Through these bonds evolving around the line containing the symmetry centres at $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, the solvate water molecules are attached laterally to the outermost sulfate O atom (O3), serving as strip connectors to define some sort of two-dimensional structures parallel to the (011) plane. Weaker C—H$\cdots$O interactions, mainly those involving aromatic H atoms, connect these structures with each other into the final three-dimensional assembly.

Figure 2
A packing view of (I) down the [011] direction, showing a schematic representation of the two-dimensional array. The way in which strips build up and their interactions mediated by solvate water molecules are indicated by dashed lines.
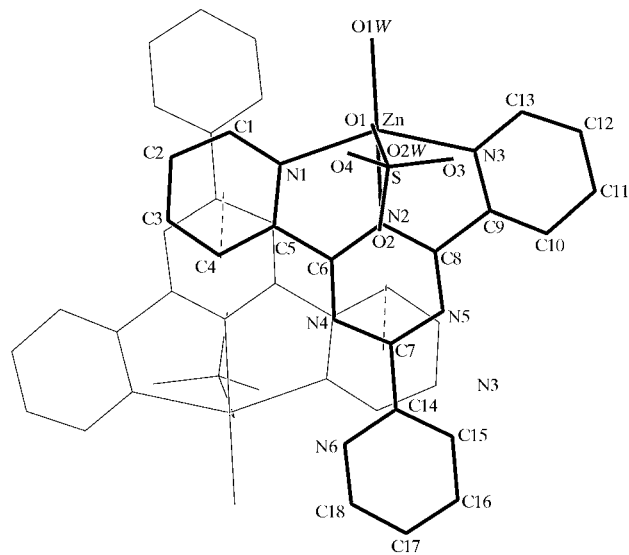

Figure 3
The overlap of two neighbouring tpt groups related by the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$, leading to a π–π interaction of the parallel-displacive type.

metal-organic compounds

Experimental

The title compound was obtained by direct mixing of equimolar (0.025 M) aqueous $ZnSO_4 \cdot 7H_2O$ and methanolic 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) solutions. After a few days, some crystalline material had precipitated, but it was found to be unsuitable for X-ray diffraction. This material was therefore dissolved in water and heated at 378 K for 2 h in a pressurized reactor. Slow evaporation of this solution resulted in the formation of some colourless prismatic crystals of (I), which were suitable for X-ray analysis.

Crystal data

$[Zn(SO_4)(C_{18}H_{12}N_6)(H_2O)_2] \cdot 2H_2O$	$Z = 2$
$M_r = 545.83$	$D_x = 1.700$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.7120\,(15)$ Å	Cell parameters from 25
$b = 11.771\,(2)$ Å	reflections
$c = 12.523\,(3)$ Å	$\theta = 7.5\text{--}12.5°$
$\alpha = 85.27\,(3)°$	$\mu = 1.31$ mm^{-1}
$\beta = 75.38\,(3)°$	$T = 293\,(2)$ K
$\gamma = 75.82\,(3)°$	Prism, colourless
$V = 1066.2\,(4)$ Å^3	$0.32 \times 0.12 \times 0.12$ mm

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.076$
$\omega/2\theta$ scans	$\theta_{max} = 27.1°$
Absorption correction: ψ scan	$h = -9 \rightarrow 9$
(North $et\ al.$, 1968)	$k = -14 \rightarrow 15$
$T_{min} = 0.78$, $T_{max} = 0.85$	$l = 0 \rightarrow 15$
5725 measured reflections	3 standard reflections
4670 independent reflections	every 150 reflections
2117 reflections with $I > 2\sigma(I)$	intensity decay: <2%

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.058$	independent and constrained
$wR(F^2) = 0.140$	refinement
$S = 0.92$	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2]$
4670 reflections	where $P = (F_o^2 + 2F_c^2)/3$
336 parameters	$(\Delta/\sigma)_{max} = 0.014$
	$\Delta\rho_{max} = 0.90$ e Å^{-3}
	$\Delta\rho_{min} = -1.00$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—O1W	2.019 (4)	Zn—N1	2.271 (4)
Zn—O1	2.068 (4)	S—O2	1.474 (4)
Zn—N2	2.073 (4)	S—O4	1.479 (4)
Zn—O2W	2.154 (5)	S—O1	1.480 (4)
Zn—N3	2.193 (4)	S—O3	1.498 (4)
O1W—Zn—O1	87.93 (17)	N2—Zn—N3	75.17 (15)
O1W—Zn—N2	174.68 (19)	O2W—Zn—N3	88.19 (16)
O1—Zn—N2	97.22 (16)	O1W—Zn—N1	105.48 (16)
O1W—Zn—O2W	88.71 (17)	O1—Zn—N1	90.39 (16)
O1—Zn—O2W	175.89 (15)	N2—Zn—N1	73.25 (15)
N2—Zn—O2W	86.09 (16)	O2W—Zn—N1	88.23 (17)
O1W—Zn—N3	105.84 (16)	N3—Zn—N1	148.38 (15)
O1—Zn—N3	94.99 (16)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1WA$\cdots$O4W	0.82 (2)	2.01 (2)	2.741 (8)	148 (3)
O1W—H1WB$\cdots$O4^i	0.82 (2)	2.04 (2)	2.684 (6)	135 (3)
O2W—H2WA$\cdots$O2^i	0.82 (3)	1.93 (2)	2.705 (6)	156.1 (14)
O2W—H2WB$\cdots$N6^{ii}	0.82 (3)	2.05 (2)	2.849 (6)	165 (4)
O3W—H3WA$\cdots$O3	0.82 (3)	2.23 (2)	2.898 (8)	139 (3)
O3W—H3WB$\cdots$O4^{iii}	0.82 (2)	2.21 (3)	2.868 (7)	137 (4)
O4W—H4WA$\cdots$O3^{iv}	0.82 (3)	2.09 (6)	2.778 (7)	141 (8)
O4W—H4WB$\cdots$O3W^i	0.82 (5)	2.45 (6)	3.263 (14)	171 (12)
C11—H11$\cdots$O2^v	0.93	2.38	3.250 (7)	156
C13—H13$\cdots$O3W^i	0.93	2.41	3.228 (8)	147

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

H atoms attached to C atoms were included in their calculated positions, with C—H distances of 0.93 Å, and allowed to ride, with $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were located from difference Fourier syntheses and refined with restrained O—H and H$\cdots$H distances of 0.82 (1) and 1.30 (2) Å, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *SHELXTL/PC* (Sheldrick, 1994); 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*; software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1195). Services for accessing these data are described at the back of the journal.

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