metal-organic papers

Diaquasulfato(2,4,6-tri-2-pyridyl-1,3,5-triazine)nickel(II) dihydrate

Maria Enriqueta Díaz de Vivar,[a]***
Sergio Baggio**[a] **and
Ricardo Baggio**[b]

[a]Universidad Nacional de la Patagonia, Sede Puerto Madryn, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, and [b]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

Correspondence e-mail: undiaz@cenpat.edu.ar

The title compound, $[Ni(SO_4)(C_{18}H_{12}N_6)(H_2O)_2]\cdot 2H_2O$, is isostructural with the zinc and cobalt analogues already reported in the literature. The compound is monomeric, with an octahedral Ni centre coordinated by a tridentate 2,4,6-tri-2-pyridyl-1,3,5-triazine ligand, two water molecules and a monodentate sulfate ligand. The presence of two additional water molecules of crystallization leads to a total of eight hydrogen-bond donors, from which a very complex hydrogen-bonding scheme is built up.

Comment

We report here a nickel(II) sulfate complex, *viz.* $[Ni(SO_4)(tpt)(H_2O)_2]\cdot 2H_2O$ (tpt is 2,4,6-tri-2-pyridyl-1,3,5-triazine), (I), which is isostructural with its Zn and Co analogues (Harvey *et al.*, 2004; Majumder *et al.*, 2005) but obtained from a radically different synthetic approach (see *Experimental*).

(I)
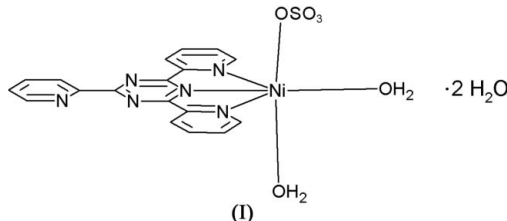
The Ni ion is surrounded by a slightly distorted octahedron, formed by three N atoms from the tridentate tpt molecule, two O atoms from water molecules and one O atom from the sulfate ion (Fig. 1). Its axial sites are occupied by O2W and O1, which subtend an angle of 175.54 (10)° at the metal. The equatorial plane is formed by atoms N1, N2, N3 and O1W.

The tpt ligand, which coordinates through N2 from the triazine ring and through N1 and N3 from two pyridine rings, has a planar core (within 0.04 Å). The terminal pyridyl group is rotated from the main least-squares plane (atoms N1/C1–C5–N2,N4,N5/C6–C8–N3/C9–C13) by 7.3 (1)°.

The two Ni—O$_{water}$ bond lengths differ by *ca* 3%, the equatorial Ni—O1W distance being shorter [2.036 (2) Å] than the axial Ni—O2W distance [2.095 (2) Å].

The S—O distances in the sulfate group are rather similar, suggesting double-bond delocalization.

The more obvious motifs in the packing are the double chains of monomers running along the *a* axis (Fig. 2). The internal linkage of a single chain involves atoms O2 and O4 from the sulfate ion as acceptors and the two water molecules in the Ni coordination polyhedron as donors. The double chains result from the O2W—H2WA$\cdots$N6[ii] hydrogen bonds
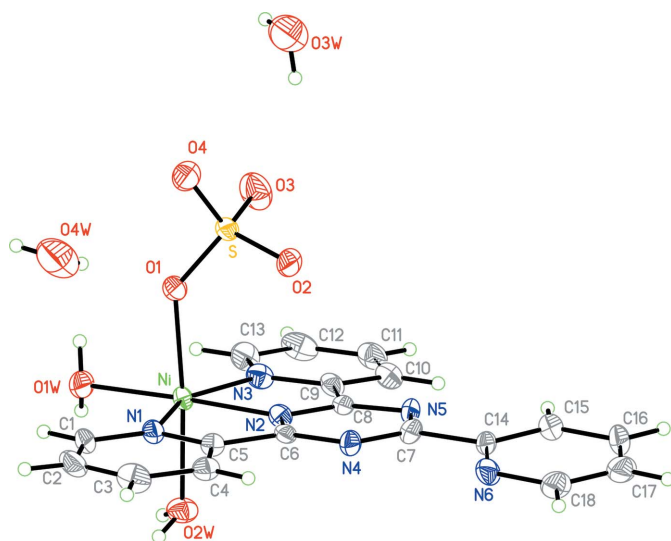
Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.
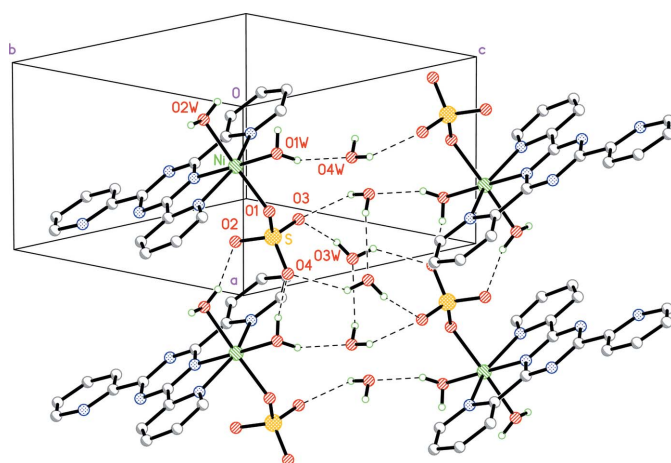

Figure 2
The packing of (I). Dashed lines indicate hydrogen bonds.

between neighbouring chains (entry 4 in Table 2), as well as from the π–π interaction between triazine rings, with the pyridyl rings related by the $(\frac{1}{2}, \frac{1}{2}, 0)$ symmetry centre [interplanar spacing = 3.28 (1) Å, distance between centres = 3.60 (1) Å and slippage angle (Janiak, 2000) = 24.4°].

The broad two-chain 'strips' thus generated connect with each other *via* hydrogen bonds involving the remaining water molecules O3W and O4W (entries 5–8 in Table 2) to define two-dimensional structures parallel to (011). Weaker hydrogen bonds, mainly those involving aromatic H atoms (entries 9–10 in Table 2), connect these structures with each other into a final three-dimensional assembly.

Experimental

The title compound was obtained through the decomposition of pyrosulfite as an intermediary agent; while the use of mixtures of dithionite and pyrosulfite in a 1:2 molar ratio frequently results in

thiosulfate or sulfite complexes (Díaz de Vivar *et al.*, 2004; Díaz de Vivar, Baggio, Muñoz & Baggio, 2005), pure pyrosulfite solutions tend to produce sulfur oxoanions of higher oxidation states, such as trithionate (Díaz de Vivar, Baggio, Garland & Baggio, 2005) and sulfate (Díaz de Vivar *et al.*, 2006). In the present case, the synthesis was carried out by allowing a 96% ethanol solution of 2,4,6-tri-2-pyridyl-1,3,5-triazine and NiCl$_2$·6H$_2$O to diffuse into an aqueous solution containing potassium pyrosulfite. The tpt:Ni:K$_2$S$_2$O$_5$ molar ratio was 1:1.2. After five months, green prisms suitable for X-ray analysis were obtained.

Crystal data

[Ni(SO$_4$)(C$_{18}$H$_{12}$N$_6$)(H$_2$O)$_2$]·2H$_2$O	$V = 1040.9$ (3) Å^3
$M_r = 539.17$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.720$ Mg m^{-3}
$a = 7.6338$ (15) Å	Mo $K\alpha$ radiation
$b = 11.681$ (2) Å	$\mu = 1.10$ mm^{-1}
$c = 12.420$ (2) Å	$T = 295$ (2) K
$\alpha = 85.513$ (3)°	Prism, green
$\beta = 75.529$ (3)°	$0.28 \times 0.14 \times 0.10$ mm
$\gamma = 76.129$ (3)°	

Data collection

Rigaku AFC-6S diffractometer	3405 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.063$
Absorption correction: ψ scan	$\theta_{max} = 28.0°$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.75$, $T_{max} = 0.90$	every 150 reflections
4980 measured reflections	intensity decay: <2%
4438 independent reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.053$	independent and constrained
$wR(F^2) = 0.119$	refinement
$S = 0.97$	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2]$
4438 reflections	where $P = (F_o^2 + 2F_c^2)/3$
331 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.53$ e Å^{-3}
	$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni—N2	1.979 (3)	Ni—N1	2.170 (3)
Ni—O1W	2.036 (2)	S—O3	1.455 (3)
Ni—O1	2.055 (2)	S—O2	1.465 (2)
Ni—O2W	2.095 (2)	S—O4	1.471 (3)
Ni—N3	2.123 (3)	S—O1	1.475 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O4W	0.82 (3)	1.97 (2)	2.746 (4)	158 (2)
O1W—H1WB···O4^i	0.82 (2)	1.97 (1)	2.702 (3)	148 (2)
O2W—H2WA···O2^i	0.82 (2)	1.89 (2)	2.686 (3)	162 (2)
O2W—H2WB···N6^{ii}	0.82 (2)	2.05 (2)	2.846 (4)	164 (3)
O3W—H3WA···O3	0.82 (3)	2.19 (3)	2.905 (5)	146 (4)
O3W—H3WB···O4^{iii}	0.82 (3)	2.21 (3)	2.878 (4)	139 (3)
O4W—H4WA···O3^{iv}	0.82 (2)	2.07 (4)	2.774 (4)	145 (3)
O4W—H4WB···O3W^i	0.83 (5)	2.43 (5)	3.220 (7)	161 (5)
C11—H11···O2^v	0.93	2.39	3.241 (5)	153
C13—H13···O3W^i	0.93	2.41	3.178 (5)	140

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

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H atoms attached to carbon were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) values set at $1.2U_{eq}$(C). The water H atoms were found in a difference Fourier synthesis and refined with restrained distances of O—H = 0.82 (1) Å and H···H = 1.30 (2) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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