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Tris(2,2′-bipyridyl-*N*,*N*′)nickel(II) thiosulfate heptahydrate

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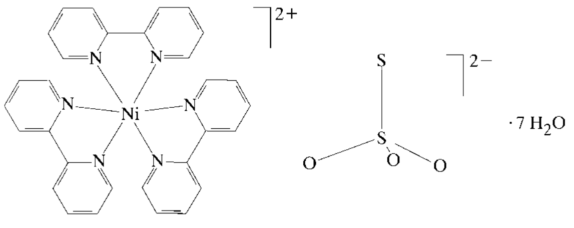
The structure of the title compound, $[Ni(C_{10}H_8N_2)_3](S_2O_3)\cdot 7H_2O$, consists of monomeric $Ni(bipy)_3^{2+}$ cations embedded in an anionic network made up of $S_2O_3^{2-}$ ions and hydration water molecules. The structure presents the unusual feature of two neighbouring thiosulfates approaching linearly head-to-head with an unusually short S···S contact distance of 3.25 Å.

Comment

The nickel thiosulfate complexes reported so far number five: in three of these complexes the anion behaves as an S,O chelator (Fava Gasparri *et al.*, 1969; Freire *et al.*, 2000), while in the remaining two (Freire *et al.*, 1999) it acts as a monodentate ligand, binding through oxygen. In all cases, the coordination scheme gives rise to monomeric species. The present structure, (I), also monomeric, displays a different scheme where the thiosulfate anion does not coordinate directly either to the distorted octahedral $Ni(bipy)_3^{2+}$ cations or to any ligand molecule. The anionic group is instead involved in a number of hydrogen bonds leading to an anionic network (Fig. 1).



(I)

The anion displays a rather regular geometry, with a slight spread on homologous parameters; range of S—O distances: 1.439 (5)–1.453 (5) Å; range of S—S—O angles: 108.1 (3)–109.2 (3)°. These values, as well as the S—S bond length of 1.969 (3) Å, are in good agreement with those reported previously in other ionic moieties (Teng *et al.*, 1984; Baggio *et al.*, 1997).

The Ni^{2+} cation, situated in a general unconstrained position, is attached to three independent bipyridine groups in a 'propeller-like' binding mode which provides a somewhat distorted octahedral coordination. This $Ni(bipy)_3$ group is rather common in the literature: of 17 entries in the Cambridge Structural Database (CSD; Allen & Kennard, 1993), nine have *R* factors below 10%. A systematic analysis of this latter selected group revealed a rather rigid structural pattern for the Ni coordination polyhedron, with bond distances and bite angles ranging in a very narrow band: Ni—N 2.066–2.138 Å and N—Ni—N 78.14–79.80°. The values in the present structure [2.086 (3)–2.101 (3) Å and 78.36 (12)–78.63 (14)°] fit into this pattern.

Interatomic bonds and angles in the bipyridine ligands are unexceptional, the six individual heterocyclic groups being basically planar and the maximum departure from the weighted least-squares planes as calculated with *PARST* (Nardelli, 1983) being for atom C9*B*, 0.019 (5) Å. However, none of the three independent bipyridine moieties is planar as a whole, as they display a variety of twist angles around the C5—C6 bond which range from 4.2 (1)° for bipy *A* to 11.3 (1)° for bipy *B*.

The structure is completed by seven hydration water molecules [thermogravimetric analysis (TGA) measurements in

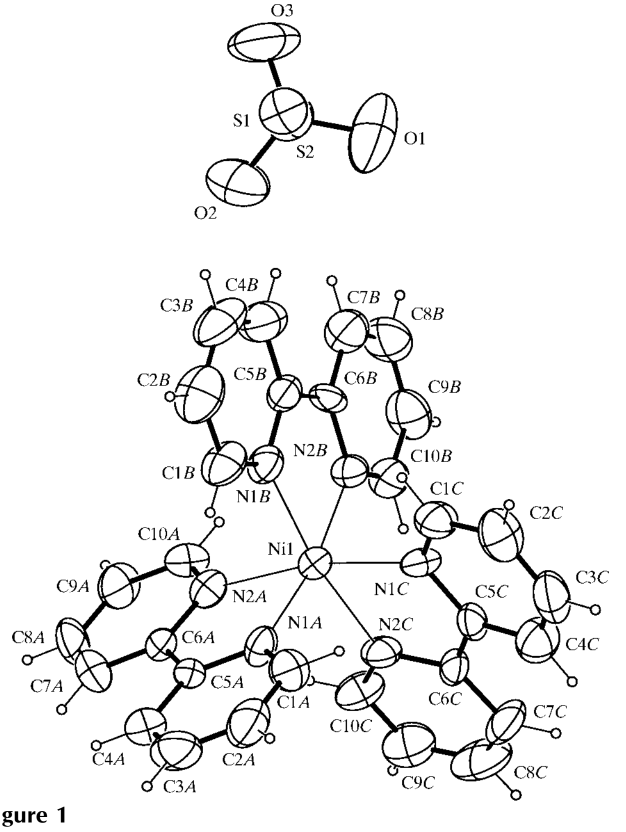


Figure 1
View of the ions making up the structure of (I) showing the numbering scheme used and with displacement ellipsoids drawn at the 50% probability level.

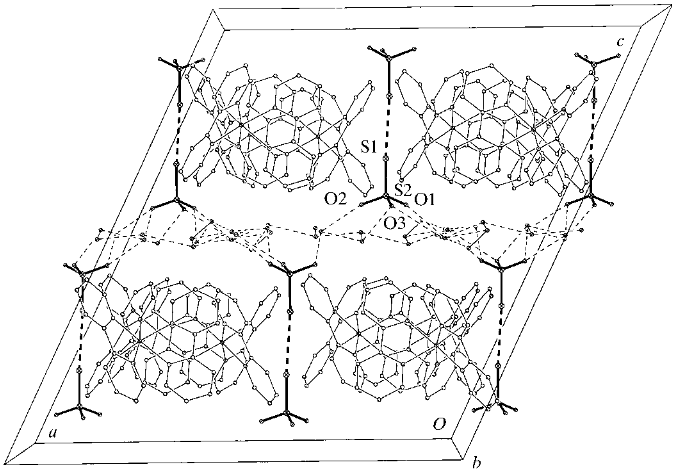


Figure 2
A simplified packing diagram showing the anionic network with the embedded cations occupying the voids. H atoms are not represented.

bulk give a slightly lower figure of 6.5], three of which appear scattered in seven different positions (O5*W* to O11*W*). This characteristic prevented the finding of all the water H atoms and hence a precise discussion of the hydrogen-bonding interactions. However, inspection of a schematic unit-cell diagram (Fig. 2) allows a simple description of the packing: the hydration water molecules form a narrow cloud normal to the *c* axis at heights of $\mathbf{c} \sim 0$ and $\mathbf{c} \sim 0.5$. Moreover, the thiosulfate groups couple into pairs through a head-to-head $(\mathrm{O_3S{-}S})\cdots(\mathrm{S{-}SO_3})(2-x, y, \frac{3}{2}-z)$ interaction where the S atoms lie 3.250 (3) Å apart, a much shorter distance than the sum of the most commonly accepted van der Waals radii [~3.60 Å according to Taylor & Kennard (1982) and ~3.70 Å according to Pauling (1960)]. A search in the CSD showed that out of some 14 330 entries with reported S···S intermolecular contacts in the range 2.51–3.75 Å, only 295 (*ca* 2%) showed values below the value of 3.25 Å reported herein. These thiosulfate linear pairs, with their centers at $c \sim 0.25$ and $c \sim 0.75$, lie normal to the water planes, and bridge them into an anionic network through a dense hydrogen-bonding interaction scheme involving two thiosulfate-O atoms and all the hydration water molecules (Table 2). The resulting 'niches' are occupied by the $\mathrm{Ni(bipy)_3}^{2+}$ cations. The interaction of the latter with the anionic network takes place mainly through weak C—H···O interactions.

A similar disposition has been found in two compounds which are very nearly isostructural with the one herein reported, namely the homologous tris(2,2′-bipyridyl)zinc(II) thiosulfate heptahydrate (Baggio *et al.*, 1997) and tris(2,2′-bipyridyl)nickel(II) sulfate hydrate (Wada *et al.*, 1976). The former structure presents a similar 'inter-thiosulfate' interaction to (I), though a bit weaker (S···S 3.36 Å), while the latter presents a slight modification, the coupling between opposed anions (too far apart for any direct interaction) involving a water molecule, which is 2.63 Å from each of the two innermost O atoms.

Experimental

Compound (I) appeared as a by-product in the synthesis of bis(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*O*,*S*)nickel(II) hydrate methanol solvate (Freire *et al.*, 2000). During the synthesis reported therein (slow diffusion of an aqueous solution of nickel nitrate and sodium thiosulfate into a methanolic solution of 1,10-phenanthroline in a 1:3:2 molar ratio), a few imperfect red crystals of some secondary phase appeared. This suggested that some other composition besides the dominant $\mathrm{NiS_2O_3(bpy)_2}.n\mathrm{H_2O}.m\mathrm{CH_3OH}$ could also be stable, and so attempts were made to obtain them starting from different reactant concentrations. The best results were obtained with a 1:3:2.5 ratio, where very stable deep-red prismatic crystals were obtained by the same diffusion method.

Crystal data

$[\mathrm{Ni(C_{10}H_8N_2)_3}](\mathrm{S_2O_3})\cdot 7\mathrm{H_2O}$
$M_r = 765.49$
Monoclinic, $C2/c$
$a = 22.934$ (5) Å
$b = 13.481$ (3) Å
$c = 24.904$ (5) Å
$\beta = 115.65$ (3)°
$V = 6941$ (2) Å^3
$Z = 8$
$D_x = 1.465$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 7.5$–15.0°
$\mu = 0.743$ mm^{-1}
$T = 293$ (2) K
Polyhedral, red
0.30 × 0.28 × 0.22 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MSC/AFC Diffractometer Control Software*; Molecular Structure Corporation, 1988)
$T_{\min} = 0.80$, $T_{\max} = 0.83$
9294 measured reflections
7963 independent reflections
4723 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.031$
$\theta_{\max} = 27.50°$
$h = -29 \rightarrow 1$
$k = -17 \rightarrow 1$
$l = -29 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.209$
$S = 1.061$
7963 reflections
483 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.118P)^2 + 6.806P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.89$ e Å^{-3}

The structure appeared unusually difficult to solve by direct methods: in the (lately proved) correct space group, $C2/c$, the procedure yielded no acceptable solutions whatsoever; in $C2$, however, it gave a set of two almost complete but incorrectly positioned molecules, both in absolute as well as relative positions. In

Table 1
Selected geometric parameters (Å, °).

Ni1—N2*C*	2.086 (3)	Ni1—N1*C*	2.101 (3)
Ni1—N1*A*	2.090 (3)	S1—S2	1.969 (3)
Ni1—N2*A*	2.095 (3)	S2—O2	1.439 (5)
Ni1—N2*B*	2.096 (3)	S2—O1	1.445 (5)
Ni1—N1*B*	2.097 (3)	S2—O3	1.453 (5)
O2—S2—O1	111.5 (3)	O2—S2—S1	108.7 (3)
O2—S2—O3	109.2 (4)	O1—S2—S1	108.1 (3)
O1—S2—O3	110.2 (4)	O3—S2—S1	109.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1	0.89 (5)	1.87 (5)	2.744 (8)	166 (4)
O1*W*—H1*WB*···O1$^{\rm i}$	0.91 (9)	1.94 (9)	2.834 (11)	169 (7)
O2*W*—H2*WA*···O2	0.88 (7)	1.91 (7)	2.783 (10)	168 (5)
O2*W*—H2*WB*···O1*W*$^{\rm i}$	0.89 (9)	2.13 (8)	2.905 (9)	145 (7)
O3*W*—H3*WA*···O6*W*$^{\rm ii}$	0.90 (4)	1.95 (5)	2.821 (11)	161 (4)
O3*W*—H3*WA*···O10*W*$^{\rm ii}$	0.90 (4)	1.97 (6)	2.79 (3)	150 (4)
O3*W*—H3*WB*···O2*W*$^{\rm iii}$	0.90 (4)	1.86 (4)	2.753 (8)	170 (3)
O4*W*—H4*WA*···O1*W*	0.89 (9)	2.10 (7)	2.931 (12)	154 (7)
O4*W*—H4*WB*···O9*W*	0.90 (7)	1.87 (9)	2.72 (3)	156 (6)
O5*W*···O6*W*			2.72 (1)	
O5*W*···O9*W*			2.55 (2)	
O5*W*···O10*W*			2.13 (3)	
O6*W*···O8*W*			2.74 (1)	
O6*W*···O9*W*			2.21 (3)	
O7*W*···O9*W*			2.45 (3)	
O8*W*···O11*W*			2.67 (3)	
O9*W*···O10*W*			2.64 (4)	
O5*W*···O4*W*$^{\rm iv}$			2.82 (1)	
O7*W*···O8*W*$^{\rm v}$			2.89 (2)	

Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $2 - x, y - 1, \frac{3}{2} - z$; (iv) $\frac{5}{2} - x, \frac{1}{2} - y, 2 - z$; (v) $\frac{5}{2} - x, \frac{3}{2} - y, 2 - z$.

spite of this, the model would misleadingly refine down to a surprisingly low $R = 10\%$. The structure was finally solved through a Patterson synthesis (from where only the Ni ion was picked up) and completed by difference Fourier cycling. Refinement on F^2 was performed using the whole data set. The water content as determined from TGA measurements gave a hydration number of *ca* 6.5, in fair agreement with the refinement results. Only four water molecules (O1*W* to O4*W*) appeared well defined and refined to full occupancy. The remaining three were found to be scattered over seven different disordered sites (O5*W* to O11*W*). Due to their poor definition they were refined isotropically. H atoms bonded to carbon were added at their expected positions and allowed to ride, while those from the well behaved water molecules were found in the difference Fourier and refined without restraints and those from O5*W* to O11*W* could not be located and were accordingly ignored.

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: *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: NA1452). Services for accessing these data are described at the back of the journal.

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