2891 reflections
211 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ga1—O9	1.761 (4)	P2—O8	1.555 (4)
Ga1—O8	1.798 (4)	N1—C1	1.469 (5)
Ga1—O7^{i}	1.802 (3)	N1—C6	1.473 (5)
Ga1—O4^{ii}	1.812 (3)	N1—C2	1.479 (5)
P1—O5	1.489 (3)	N2—C4	1.485 (6)
P1—O1	1.521 (3)	N3—C5	1.476 (6)
P1—O4	1.559 (3)	N4—C3	1.481 (5)
P1—O6	1.578 (3)	C1—C3	1.520 (6)
P2—O2	1.506 (3)	C2—C4	1.508 (6)
P2—O3	1.513 (3)	C6—C5	1.510 (6)
P2—O7	1.543 (4)		
O9—Ga1—O8	105.5 (3)	O2—P2—O8	111.0 (2)
O9—Ga1—O7^{i}	109.0 (2)	O3—P2—O8	105.7 (2)
O8—Ga1—O7^{i}	108.4 (2)	O7—P2—O8	106.7 (2)
O9—Ga1—O4^{ii}	112.1 (2)	P1—O4—Ga1^{iii}	123.9 (2)
O8—Ga1—O4^{ii}	108.9 (2)	P2—O7—Ga1^{i}	136.7 (2)
O7^{i}—Ga1—O4^{ii}	112.6 (2)	P2—O8—Ga1	131.0 (2)
O5—P1—O1	114.0 (2)	C1—N1—C6	111.0 (3)
O5—P1—O4	111.2 (2)	C1—N1—C2	111.1 (3)
O1—P1—O4	109.1 (2)	C6—N1—C2	110.5 (3)
O5—P1—O6	110.2 (2)	N1—C1—C3	111.8 (3)
O1—P1—O6	108.3 (2)	N1—C2—C4	111.6 (3)
O4—P1—O6	103.5 (2)	N4—C3—C1	111.5 (3)
O2—P2—O3	114.6 (2)	N2—C4—C2	112.5 (4)
O2—P2—O7	110.1 (2)	N3—C5—C6	111.1 (4)
O3—P2—O7	108.4 (2)	N1—C6—C5	112.4 (3)

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

The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990): one Ga and two P atoms were first located and all the remaining atoms, except the H atoms of the HPO_4 and $HGaO_4$ groups, were revealed from the difference Fourier map. The Fourier map analysis indicates three residues around the three terminal N atoms corresponding to three ammonium groups. No residue was observed around the central N atom. All H atoms, except those of the water molecule, were refined with restraints applied to maintain C—H and N—H geometry.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1179). Services for accessing these data are described at the back of the journal.

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Tris(2,2′-bipyridyl-*N*,*N*′)zinc(II) Thiosulfate Heptahydrate

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Abstract

The structure of the title compound, $[Zn(C_{10}H_8N_2)_3]$-$S_2O_3.7H_2O$, consists of cations, $Zn(bipy)_3^{2+}$ (where bipy is bipyridine), and anions, $S_2O_3^{2-}$. There is an unusually short S···S contact of 3.361 (3) Å between the anions and a complex hydrogen-bonding scheme involving the seven molecules of water of crystallization.

Comment

The present work is part of a larger study of the preparation and structures of thiosulfates of Cd and Zn with the organic ligands phen, dmph or bipy (where phen is 1,10-phenanthroline, dmph is 2,9-dimethyl-1,10-phenanthroline and bipy is bipyridine), which have been the subject of our interest in the last few years.

The compounds $[Zn_2(phen)_3(S_2O_3)_2]$, (1) (Baggio, Baggio, Pardo & Garland, 1996), and $[Zn(S_2O_3)$-$(dmph)]_2NaHO.CH_3OH.5H_2O$, (2) (Baggio, Pardo, Baggio & Garland, 1997), show different modes of coordination of the $S_2O_3^{2-}$ ion. In (1), the structure consists of $[Zn(phen)_2]^{2+}$ cations and $[Zn(phen)(S_2O_3)_2]^{2-}$ anions, with the thiosulfate group bonded to the metal through sulfur. In (2), the thiosulfate acts as a bidentate and bridging ligand with sulfur binding to Zn^{2+} and an oxygen to Na^+, thus giving a ten-membered ring structure.

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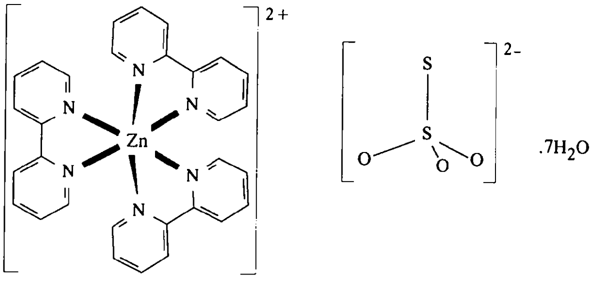
The present structure, (3), displays a completely different coordination scheme, where the thiosulfate anions do not coordinate to the cations or to any part of the ligands, but are instead involved in a number of weak hydrogen bonds contributing to the connectivity.



(3)

In the thiosulfate anions, the range of S—O distances is 1.458 (5)–1.472 (5) Å and S—S—O angles 108.4 (2)–110.2 (2)°. These values, as well as the S—S bond length of 1.990 (2) Å, are in good agreement with those previously reported in other ionic moieties (Teng, Fuess & Bats, 1984).

The Zn^{2+} cation is attached to three bipyridine groups which bind in the shape of a propeller and provide a somewhat distorted octahedral coordination. This type of environment for zinc has been previously reported: tris(2,2′-bipyridyl)zinc(II) diperchlorate (Klement, Trumbach & Yersin, 1995), tris(2,2′-bipyridyl)-zinc diperchlorate monohydrate (Krausz, Riesen & Rae, 1995), *etc.* The range of Zn—N bond lengths is small [2.134 (5)–2.183 (5) Å], the main distortions to the coordination geometry being imposed by the severely constrained N—Zn—N bite angles.

Bond lengths and angles in the bipyridine ligands are unexceptional. Each pyridine group is planar [maximum deviation 0.015 (3) Å for C4*C*]; however, none of the three independent bipyridine ligands is planar as a whole, as there is a variety of twist angles around the C5—C6 bond which range from 3.2 (3) to 10.8 (2)°.

The structure is completed by seven independent water molecules, two of which appear to be disordered and another three only partially occupied. The quality of the data prevented us from finding the H_{water} atoms and thus a detailed discussion of the hydrogen-bonding interactions is not possible. However, inspection of the packing diagram (Fig. 2, deposited) allows a simple description: the water molecules and the thiosulfate O atoms lie near the planes *c*-0 and *c*-0.5 and are connected within these planes by hydrogen bonds. There is a conspicuously short S···S contact [S2···S2($-x$, y, $\frac{1}{2}-z$) 3.361 (3) Å] across a twofold axis and between adjacent layers of water molecules; this distance is much shorter than the sum of the van der Waals radii (3.90 Å). Within the network of water molecules and thiosulfate ions there are large holes occupied by the Zn(bipy)$_3^{2+}$ cations.

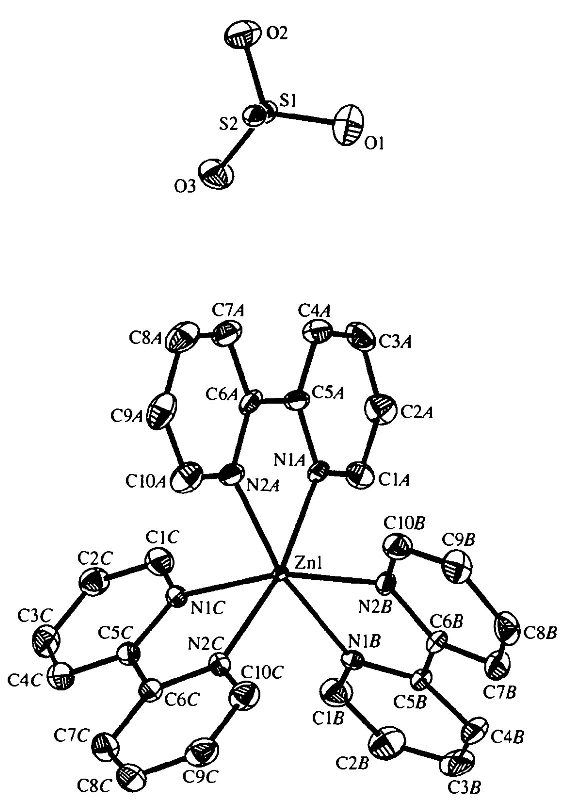


Fig. 1. A view of the ions making up the structure of the title compound, with the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was obtained by the reaction of equimolar aqueous solutions of zinc acetate and sodium thiosulfate with an excess of bipyridine dissolved in methyl alcohol. A crop of large, rather imperfect prismatic crystals was obtained by slow evaporation. In spite of the poor diffracting power of the average material, a few specimens adequate for X-ray diffraction were selected and used for data collection.

Crystal data

$[Zn(C_{10}H_8N_2)_3]S_2O_3.7H_2O$
$M_r = 772.16$
Monoclinic
$C2/c$
$a = 22.940\ (7)$ Å
$b = 13.611\ (5)$ Å
$c = 25.178\ (7)$ Å
$\beta = 116.00\ (1)°$
$V = 7066\ (4)$ Å^3
$Z = 8$
$D_x = 1.452$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5°$
$\mu = 0.876$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.45 × 0.24 × 0.16 mm
Colourless

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans

5158 reflections with $I > 2\sigma(I)$

Absorption correction:
 ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
 T_{min} = 0.70, T_{max} = 0.84
7932 measured reflections
6211 independent reflections

R_{int} = 0.088
θ_{max} = 25°
$h = -27 \rightarrow 24$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 29$
2 standard reflections
 every 98 reflections
 intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.204$
$S = 1.328$
6041 reflections
486 parameters
H atoms: C—H riding
$w = 1/[\sigma^2(F_o^2) + 115.5136P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.487$ e Å^{-3}
$\Delta\rho_{min} = -0.563$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

Zn1—N1*C*	2.134 (5)	Zn1—N2*C*	2.183 (5)
Zn1—N2*A*	2.141 (5)	S1—O2	1.458 (5)
Zn1—N1*B*	2.161 (5)	S1—O3	1.469 (5)
Zn1—N2*B*	2.164 (5)	S1—O1	1.472 (5)
Zn1—N1*A*	2.166 (5)	S1—S2	1.990 (2)

Refinement was performed with *SHELXL*93 (Sheldrick, 1993) on F^2, using the whole data set. H atoms bonded to C atoms were added at their expected positions and not refined, but allowed to ride. Those from water molecules could not be found in the final ΔF synthesis and were accordingly ignored. Two water molecules out of the seven independent ones in the structure appeared slightly disordered, though fully occupied. Refinement of the site-occupation factor for the other five, lying on single crystallographic sites, led to three of them being only partially occupied. This was taken as an explanation for some decay taking place in the appearance of the crystal after the diffractometric measurement had been performed. No effect on the diffracting power could be detected, however, as estimated by the regular check of two standard reflections.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program.* Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93, *PARST* (Nardelli, 1983) and *CSD* (Allen, Kennard & Taylor, 1983).

The authors would like to thank Fundación Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile.

Supplementary data and a packing diagram for this paper are available from the IUCr electronic archives (Reference: HA1190). Services for accessing these data are described at the back of the journal.

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A Nickel Complex with an Asymmetric N_2OS Schiff Base Ligand

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Abstract

In the structure of the title complex, {methyl 2-{2-[(2-hydroxyphenyl)methyleneamino]ethylamino}-1-cyclopentenedithiocarboxylato-*O*,*N*,*N′*,*S*}nickel(II), $[Ni(C_{16}H_{18}N_2OS_2)]$, the Ni^{II} atom is coordinated by S, O and two N atoms in a nearly planar environment. The two inequivalent N atoms, coordinated in a *cis* manner, show virtually identical bond lengths and angles indicating that the NS ligand fragment coordinates as a Schiff base ligand, with the N atom behaving as an imine and the S atom having a strong thiolate character.

Comment

The present compound, (I), was obtained as part of a systematic study on the effect of the ligand characteristics (coordination sphere and substituents) on the physical and chemical properties of nickel complexes, especially on the factors that influence the accessibility of several oxidation states for nickel (de Castro, Gomes & Pereira, 1997; Azevedo *et al.*, 1994). Details of synthetic procedures and physicochemical characterization will be published elsewhere (de Castro, Gomes & Pereira, 1997).

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