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cis-Diaquabis(1,10-phenanthroline)nickel(II) 5-sulfonatosalicylate tetrahydrate

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Key indicators

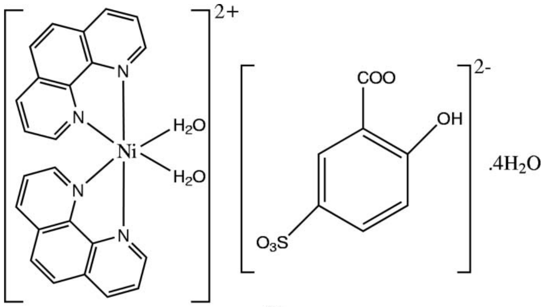
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.114
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title complex, $[Ni(C_{12}H_8N_2)_2(H_2O)_2](C_7H_4O_6S)\cdot 4H_2O$, the cation interacts with the anion and uncoordinated water molecules through hydrogen bonding with the coordinated water molecules, giving rise to a hydrogen-bonded sheet architecture. In the cation, the Ni atom exists in an octahedral geometry with two *cis*-arranged water ligands.

Comment

Recently, 5-sulfosalicylate complexes have been receiving much attention due to their structural and biological interest (Smith *et al.*, 2005; Gao *et al.*, 2005; Fan *et al.*, 2005). Only one nickel complex has been reported (Ma *et al.*, 2003) and it exists as a hexaaquanickel(II) salt in which the 5-sulfosalicylate is singly deprotonated. In the presence of the heterocyclic ligand 1,10-phenanthroline (phen), a mixed solution of $Ni(NO_3)_2$, phen, 5-sulfosalicylic acid (H_3ssal) and base (NaOH) in water and methanol yielded a doubly deprotonated 5-sulfosalicylate anion in the title complex, (I).



(I)

In the cation (Fig. 1 and Table 1), the Ni atom adopts an octahedral geometry defined by four N-atom donors from two phen ligands and two O atoms from two water molecules that are *cis* to each other. The Hssal^{2-} ligand is doubly deprotonated and exists as an anion uncoordinated to the metal atom. The uncoordinated water molecules interact with the cation and anion to produce a hydrogen-bonded sheet structure (Fig. 2) in which neighbouring phen ligands exhibit strong π–π interactions, with a separation distance of 3.39 (1) Å.

Comparison of four reported nickel complexes containing the $[Ni(phen)_2(H_2O)_2]^{2+}$ cation, *viz*. $[Ni(phen)_2(H_2O)_2]$-$[ZnCl_4]\cdot H_2O$, (II) (Ferbinteanu *et al.*, 1998), $[Ni(phen)_2$-$(H_2O)_2]$.2Hba$\cdot 6H_2O$ (Hba = 4-methylbenzenesulfonic acid), (III) (Yang *et al.*, 2003), $\{[Ni(phen)_2Cl(H_2O)]$-$[Ni(phen)_2(H_2O)_2]\}(PF_6)_3\cdot 4.5H_2O$, (IV) (Brewer *et al.*, 2003), and $[Ni_3(\text{L-Asp})(phen)_5(H_2O)_3](ClO_4)_4\cdot 4.75H_2O$ (L-Asp = L-aspartato), (V) (Ma *et al.*, 2004), with (I), shows that the Ni—

N bond distances in all five complexes are similar, while the Ni—O(water) bond distances in (I), (II) and (III) are shorter than those of (V). The coordination geometry in (IV) is more distorted than those of (I), (II), (III) and (V), and the two Ni—O(water) bond distances are of two types; one is longer and the other is shorter.

Experimental

Nickel(II) nitrate hexahydrate (0.146 g, 0.50 mmol) and 5-sulfosalicylic acid dihydrate (0.129 g, 0.51 mmol) were dissolved in water (20 ml). The solution was mixed with a solution of 1,10-phenanthroline (0.102 g, 0.51 mmol) in methanol (5 ml). NaOH (0.006 g, 0.15 mmol) was then added to the above solution. After 1 d, blue crystals of (I) were obtained. Block-shaped crystals suitable for single-crystal X-ray analysis were obtained after recrystallization from a methanol–water mixture (1:5 (*v*/*v*).

Crystal data

$[Ni(C_{12}H_8N_2)_2(H_2O)_2]$-$(C_7H_4O_6S)\cdot 4H_2O$
$M_r = 743.38$
Triclinic, $P\bar{1}$
$a = 10.016\ (1)$ Å
$b = 12.174\ (1)$ Å
$c = 13.848\ (1)$ Å
$\alpha = 96.983\ (2)^\circ$
$\beta = 101.346\ (2)^\circ$
$\gamma = 99.316\ (2)^\circ$
$V = 1613.1\ (2)$ Å^3
$Z = 2$
$D_x = 1.531$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4918 reflections
$\theta = 2.5$–25.6°
$\mu = 0.74$ mm^{-1}
$T = 295\ (2)$ K
Block, blue
0.32 × 0.29 × 0.12 mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.798$, $T_{max} = 0.917$
11738 measured reflections
5647 independent reflections
5142 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.0^\circ$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.114$
$S = 1.06$
5647 reflections
504 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 1.1955P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.068 (2)	Ni1—N2	2.088 (2)
Ni1—O2	2.061 (2)	Ni1—N3	2.080 (2)
Ni1—N1	2.094 (2)	Ni1—N4	2.082 (2)
O2—Ni1—O1	89.3 (1)	O2—Ni1—N4	94.30 (9)
O1—Ni1—N1	173.19 (9)	N2—Ni1—N1	79.3 (1)
O1—Ni1—N2	94.0 (1)	N3—Ni1—N1	92.37 (9)
O1—Ni1—N3	89.34 (9)	N3—Ni1—N2	95.86 (9)
O1—Ni1—N4	93.40 (9)	N3—Ni1—N4	79.87 (9)
O2—Ni1—N1	89.7 (1)	N4—Ni1—N1	93.40 (9)
O2—Ni1—N2	90.16 (9)	N4—Ni1—N2	171.4 (1)
O2—Ni1—N3	173.91 (9)		

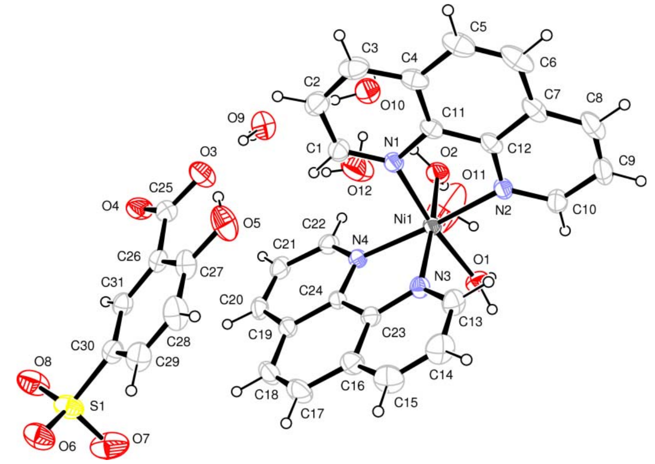


Figure 1
View of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor disorder component of the sulfonate group has been omitted for clarity.

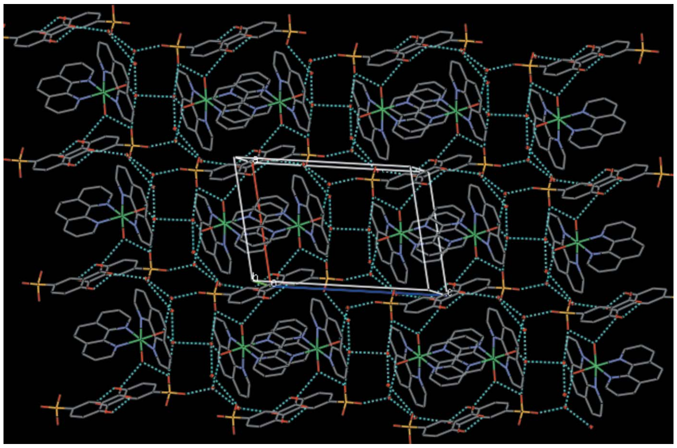


Figure 2
View of the two-dimensional layered hydrogen-bonding network. H atoms have been omitted for clarity and hydrogen bonds are shown as dashed lines.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O7^{i}	0.84 (3)	1.97 (1)	2.810 (5)	174 (4)
O1—H1$A\cdots$O7'^{i}	0.84 (3)	2.07 (2)	2.803 (7)	146 (3)
O1—H1$B\cdots$O4^{ii}	0.85 (1)	1.79 (3)	2.630 (3)	172 (4)
O2—H2$A\cdots$O11	0.85 (1)	1.81 (1)	2.656 (5)	172 (4)
O2—H2$B\cdots$O10	0.85 (1)	1.86 (1)	2.701 (4)	172 (4)
O5—H5$C\cdots$O3	0.85 (3)	1.71 (2)	2.499 (4)	153 (4)
O9—H9$A\cdots$O3	0.85 (2)	1.93 (2)	2.777 (4)	174 (4)
O9—H9$B\cdots$O7'^{iii}	0.84 (2)	2.04 (3)	2.812 (9)	153 (4)
O9—H9$B\cdots$O8^{iii}	0.84 (2)	2.06 (2)	2.874 (6)	162 (4)
O10—H10$A\cdots$O6^{iv}	0.85 (3)	1.94 (1)	2.787 (4)	178 (4)
O10—H10$A\cdots$O6'^{iv}	0.85 (3)	2.12 (2)	2.921 (11)	157 (4)
O10—H10$B\cdots$O9	0.85 (4)	1.89 (4)	2.739 (4)	174 (4)
O11—H11$A\cdots$O12	0.877 (5)	2.292 (4)	2.647 (6)	104.2 (3)
O11—H11$B\cdots$O7^{i}	0.868 (4)	1.898 (6)	2.706 (7)	154.1 (3)
O12—H12$A\cdots$O6'^{iv}	0.86 (3)	2.04 (2)	2.839 (15)	156 (3)
O12—H12$A\cdots$O6^{iv}	0.86 (3)	2.19 (2)	3.033 (6)	167 (4)
O12—H12$B\cdots$O8'^{iii}	0.85 (3)	1.77 (1)	2.619 (9)	179 (5)
O12—H12$B\cdots$O8^{iii}	0.85 (3)	2.19 (3)	2.958 (7)	150 (4)

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

Acta Cryst. (2005). E**61**, m1724–m1726 Chen *et al.* • $[Ni(C_{12}H_8N_2)_2(H_2O)_2](C_7H_4O_6S)\cdot 4H_2O$ **m1725**

The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The water and hydroxyl H atoms were located in a difference Fourier map and were refined with a distance restraint O—H = 0.85 (1) Å and a fixed isotropic displacement parameter $U_{\rm iso}$(H) = 0.08 Å^2. The sulfonate group was disordered over two positions; the occupancies refined to a 0.715 (9):0.285 (9) ratio.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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m1726 Chen *et al.* • [Ni($C_{12}H_8N_2$)$_2$(H_2O)$_2$]($C_7H_4O_6S$)·4H_2O *Acta Cryst.* (2005). E**61**, m1724–m1726