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Diaquabis(1,3-propanediamine-κ^2N,N')nickel(II) bis(sulfanilate)

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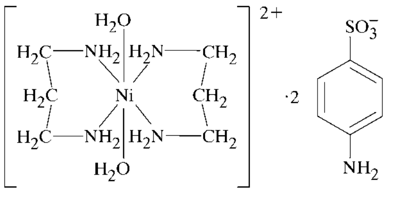
The title compound, $[Ni(C_3H_{10}N_2)_2(H_2O)_2](C_6H_6NO_3S)_2$, contains alternating layers of sulfanilate anions and diaquabis(1,3-propanediamine)nickel(II) cations. The Ni atom lies on an inversion centre and is hexacoordinated by the 1,3-propanediamine ligands, which function as *N*,*N*′-bidentate ligands, and the water molecules, which are in a *trans* arrangement. The sulfanilate anions are arranged in layers, with the sulfonate and amine groups directed towards opposite sides of the layer. The structure is stabilized by a network of hydrogen bonding between the O and N atoms of the sulfanilate anions, the water molecules, and the N atoms of the 1,3-propanediamine ligands.

Comment

Layered compounds have been of great interest in both academic research and industrial applications because of their possible use as ion exchange and intercalation materials (Clearfield, 1988). In particular, synthetic compounds such as the metal phosphates have been extensively studied as a new family of layered materials (Alberti, 1996). Most commonly, these layered compounds contain covalent metal–oxygen–non-metal (Si or P) frameworks. In recent years, metal–organosulfonate compounds have been studied as a new family of layered materials by Squattrito *et al.* (Kosnic *et al.*, 1992; Benedetto *et al.*, 1997). In our group, research has focused on the development of new layered and porous materials, using weaker metal–sulfonate interactions and the chelating behaviour of diamine ligands, such as ethylenediamine or 1,2-propanediamine (Kim & Lee, 2001). In this paper, we report the preparation and crystal structure of the nickel(II) sulfanilate complex with the 1,3-propanediamine ligand, (I).

As shown in Fig. 1, the Ni^{II} atom of the cation of (I) rests on a crystallographic inversion centre, and is hexacoordinated by the O atoms of two water molecules in a *trans* arrangement and by the amine N atoms of two 1,3-propanediamine ligands at the equatorial positions. It is suggested that the *trans* geometry is favoured when the amine ligand is more bulky. Thus, the coordination environment of Ni in (I) is slightly distorted octahedral, similar to what is observed in the previously reported nickel(II)–1,3-propanediamine–thiocyanate system (Moore & Squattrito, 1999).



(I)

The six-membered chelate rings of the 1,3-propanediamine ligands are in the stable chair conformation [Ni1—N10—C11—C12 −55.7 (2)° and Ni1—N20—C13—C12 51.9 (2)°]. As listed in Table 1, the Ni—N distances range from 2.100 (1) to 2.113 (1) Å and the Ni—O distance is 2.136 (1) Å. The intra-ligand N—Ni—N angle is 92.39 (6)°, while the inter-ligand N—Ni—N angle is 87.61 (6)°. The N—Ni—O angles are in the range 88.80 (6)–91.20 (6)°. The bond distances and angles of the sulfanilate anion are consistent with those reported previously (Shakeri & Haussuhl, 1992).

As shown in Fig. 2, the packing diagram of (I) reveals a layered structure, composed of dicationic diaquabis(1,3-propanediamine)nickel(II), $[Ni\{NH_2(CH_2)_3NH_2\}_2(H_2O)_2]^{2+}$, layers and anionic sulfanilate, $NH_2C_6H_4SO_3^-$, layers stacked along the *a* axis. Neighbouring sulfanilate anions within a layer have the amine and sulfonate groups oriented towards opposite sides of the layer. In addition, they are slightly slanted towards the *c* axis.

It is evident that there may be a π–π interaction between the sulfanilate anions (Janiak, 2000). Such π–π interactions

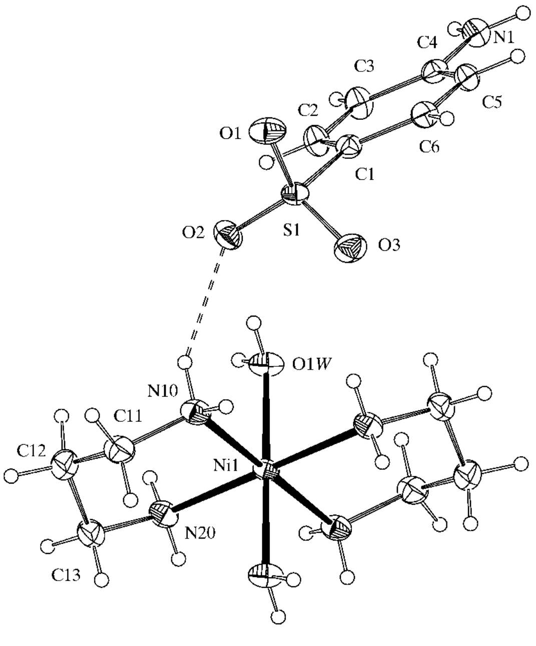


Figure 1
A view of the molecule of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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provide important non-covalent intermolecular forces similar to hydrogen bonding, because they can contribute to the formation of the crystal structure of a metal complex from building blocks with aromatic moieties. This anion packing arrangement is also observed in another metal sulfanilate complex (Bats, 1977). However, there is no direct bonding between the Ni^{II} atom and the sulfonate O or amine N atoms of the anion in (I). On the other hand, the Cu^{II} cation in $[Cu(NH_2C_6H_4SO_3)_2(H_2O)_2]\cdot 2H_2O$ and the Mn^{II} cation in $[Mn(NH_2C_6H_4SO_3)_2(H_2O)_2]$ are coordinated to the sulfonate O and amine N atoms of the sulfanilate anions (Gunderman *et al.*, 1996). The Nd^{III} cation in $[Nd(NH_2C_6H_4SO_3)_2(H_2O)_7](NH_2C_6H_4SO_3)\cdot H_2O$ is directly coordinated to the sulfonate O atoms of two sulfanilate anions and not coordinated to one sulfanilate anion (Starynowicz, 1992). Therefore, the title Ni^{II} sulfanilate compound, (I), is quite different in structure from the previously reported Cu^{II}–, Mn^{II}– and Nd^{III}–sulfanilate complexes.

As listed in Table 2, the coordinated water molecules in the Ni^{II} cations and the sulfonate O and N atoms of the sulfanilate anions are linked together by hydrogen bonds (O1*W*—H1*WB*···O2, O1*W*—H1*WA*···N1, N1—H1*A*···O1 and N1—H1*B*···O2) along the [010] axis. These hydrogen-bonded chains are crosslinked in the (110) plane by $N_{diamine}$—H···$O_{sulfonate}$ (N10—H10*A*···O1, N10—H10*B*···O2 and N20—H20*B*···O3) hydrogen-bonding interactions between the amine H atoms of the 1,3-propanediamine ligands and the sulfonate O atoms of the sulfanilate anions. Therefore, all the hydrogen bonds are formed by contacts between cations and anions, and the crystal structure is reinforced by intermolecular hydrogen bonds involving the N and O atoms of the sulfanilate anions. This layer structure, with extended hydrogen-bonding interactions between metal-ligated cations and unligated anions, is also observed in calcium naphthionate octahydrate (Brown *et al.*, 1984) and diaminobipyridine metal complexes (Janiak *et al.*, 1999).

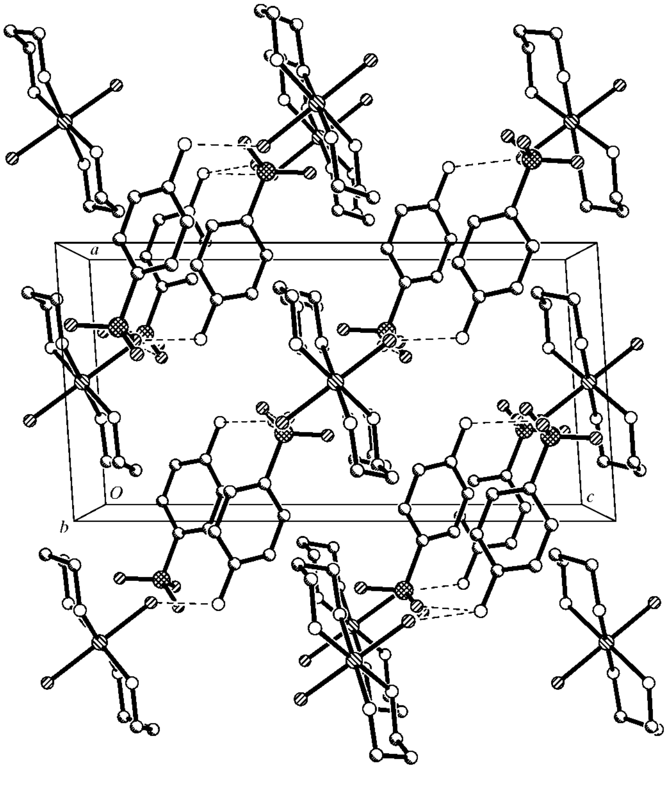

Figure 2
A perspective view of the unit cell of (I) along the *b* axis. Hydrogen bonds are shown by broken lines.

Experimental

$NiCl_2\cdot 6H_2O$ (2.38 g) was mixed with sulfanilic acid (1.90 g) in water (50 ml). To this solution, 1,3-propanediamine (1.5 ml) was added dropwise. The resulting solution was filtered and the filtrate was kept in a refrigerator at 278 K. Blue block-shaped crystals of (I) suitable for X-ray analysis were obtained after a few weeks (yield 70%). Analysis calculated for $C_{18}H_{36}N_6NiO_8S_2$: C 36.81, H 6.18, N 14.31, O 21.79, S 10.92, Ni 9.99%; found: C 36.77, H 6.22, N 14.32, O 21.03, S 10.85, Ni 10.18%.

Crystal data

$[Ni(C_3H_{10}N_2)_2(H_2O)_2]$-$(C_6H_6NO_3S)_2$
$M_r = 587.36$
Monoclinic, $P2_1/c$
$a = 8.6079\ (12)$ Å
$b = 8.9177\ (11)$ Å
$c = 16.717\ (3)$ Å
$\beta = 93.841\ (13)^\circ$
$V = 1280.3\ (3)$ Å^3
$Z = 2$
$D_x = 1.524$ Mg m^{-3}
$D_m = 1.52$ Mg m^{-3}
D_m measured by flotation in mesitylene–bromoform
Mo $K\alpha$ radiation
Cell parameters from 54 reflections
$\theta = 3.5$–12.5°
$\mu = 0.98$ mm^{-1}
$T = 293\ (2)$ K
Block, blue
0.50 × 0.41 × 0.32 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.604$, $T_{max} = 0.732$
3949 measured reflections
2932 independent reflections
2766 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5^\circ$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 11$
$l = -21 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.084$
$S = 1.06$
2932 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.5564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.080 (3)

Table 1
Selected geometric parameters (Å, °).

Ni1—N10	2.1002 (14)	S1—O1	1.4512 (13)
Ni1—N20	2.1125 (14)	S1—O2	1.4656 (13)
Ni1—O1*W*	2.1358 (13)	S1—C1	1.7706 (17)
S1—O3	1.4454 (13)		
N10—Ni1—N20	92.39 (6)	O1—S1—O2	111.80 (9)
N10—Ni1—O1*W*	90.69 (6)	O3—S1—C1	106.70 (8)
N20—Ni1—O1*W*	91.20 (6)	O1—S1—C1	106.95 (8)
O3—S1—O1	112.63 (9)	O2—S1—C1	105.44 (8)
O3—S1—O2	112.73 (9)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···N1^{i}	0.83 (3)	2.06 (3)	2.880 (2)	172 (3)
O1*W*—H1*WB*···O2	0.81 (3)	1.96 (3)	2.760 (2)	168 (3)
N10—H10*A*···O1^{ii}	0.90	2.21	3.098 (2)	168
N10—H10*B*···O2	0.90	2.37	3.189 (2)	151
N20—H20*B*···O3^{iii}	0.90	2.23	3.055 (2)	152
N1—H1*A*···O1^{i}	0.86	2.14	2.958 (2)	159
N1—H1*B*···O2^{iv}	0.86	2.32	3.011 (2)	138

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

Water H atoms were refined freely. All other H atoms were treated as riding, with N—H = 0.86–0.90 Å and C—H = 0.93–0.97 Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002) and *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1184). Services for accessing these data are described at the back of the journal.

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