

Diaquabis(propane-1,2-diamine-*N,N'*)-  
nickel(II) bis(*p*-toluenesulfonate)

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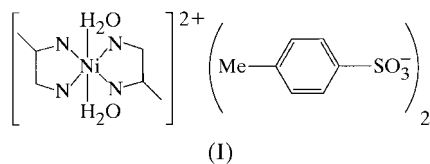
Received 6 March 2001

Accepted 1 August 2001

The crystal structure of the title compound,  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_7\text{H}_7\text{O}_3\text{S})_2$  or  $[\text{Ni}(\text{H}_2\text{O})_2[\text{NH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3]_2](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ , exhibits a layered structure in which the complex cations and the *p*-toluenesulfonate anions form alternating layers. The central  $\text{Ni}^{\text{II}}$  atom of the cation resides on a crystallographic inversion centre and has a slightly distorted octahedral coordination composed of the water ligands bonding through oxygen in a *trans* arrangement and the *N,N'*-bidentate propanediamine ligands. The *p*-toluenesulfonate anions are arranged with the sulfonate groups turned alternately towards opposite sides of the layers. The structure of the layers is stabilized by a network of hydrogen bonds between the sulfonate O atoms, water molecules and the propanediamine N atoms.

## Comment

Compounds forming layered structures have been of great interest in both academic research and industrial applications, because of their possible use as ion exchangers and intercalation materials (Clearfield, 1988; Suib, 1993). Particularly, metal phosphate and phosphonate compounds, such as zirconium and titanium phosphates and phosphonates, have been extensively studied as a new family of layered materials (Clearfield & Costantino, 1996; Alberti, 1996). Most commonly, these mixed inorganic–organic two-dimensional compounds contain covalent metal–oxygen–phosphorus frameworks. In recent years, Squattrito and co-workers have



studied metal organosulfonate compounds (Gunderman & Squattrito, 1995; Benedetto *et al.*, 1997) and have reported two-dimensional materials with layered structures analogous to the above-mentioned recently reported metal phosphonate

structures. In our group, research has been directed towards the development of new layered and porous materials (Kim & Lee, 2000), using weaker metal sulfonate interactions. This approach takes advantage of the flexible coordination behaviour of the  $\text{SO}_3^-$  group to obtain structures. In this paper, we report the preparation and crystal structure of the title nickel(II) sulfonate complex, (I), which is chelated by propanediamine ligands.

As shown in Fig. 1, the  $\text{Ni}^{\text{II}}$  cation of (I) lies on a crystallographic inversion centre and is six-coordinate, with two propanediamine ligands attached in equatorial positions and two water molecules in axial positions. Its coordination geometry can be described as a slightly distorted octahedral arrangement. The Ni–N distances range from 2.074 (2) to 2.099 (2) Å and the Ni–O distance is 2.152 (2) Å. The interligand N–Ni–N angle is 82.54 (8)° and the N–Ni–O angles are in the range 86.95 (7)–88.23 (7)°.

The S–O<sub>sulf</sub> bond lengths (where O<sub>sulf</sub> is a sulfonate O atom) in the *p*-toluenesulfonate anion range from 1.426 (2) to 1.446 (2) Å and the S–C bond length is 1.768 (2) Å. The O<sub>sulf</sub>–S–O<sub>sulf</sub> and O<sub>sulf</sub>–S–C bond angles are in the ranges 110.6 (2)–112.9 (2) and 106.6 (1)–106.8 (1)°, respectively. The geometrical data for this anion are consistent with those previously reported by Rogers *et al.* (1991).

As shown in Fig. 2, compound (I) forms a layered structure consisting of dicationic  $[\text{Ni}(\text{H}_2\text{O})_2[\text{NH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3]_2]^{2+}$  layers and anionic  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$  layers. The *p*-toluenesulfonate anions are arranged with the sulfonate groups turned alternately towards opposite sides of the layers. The water molecules coordinated to the  $\text{Ni}^{\text{II}}$  cations and most of the O atoms of the *p*-toluenesulfonate anions are linked together in hydrogen-bonded chains along [001], with strong O<sub>water</sub>–H···O<sub>sulf</sub> hydrogen bonds (O30–H30A···O2 and O30–H30B···O3; Table 1). These chains are crosslinked in the (011) plane by N<sub>diamine</sub>–H···O<sub>sulf</sub> hydrogen-bonding interactions formed between the amine H atoms of the propanediamine ligands and the sulfonate O atoms of the *p*-toluenesulfonate anions (N20–H20A···O1, N20–

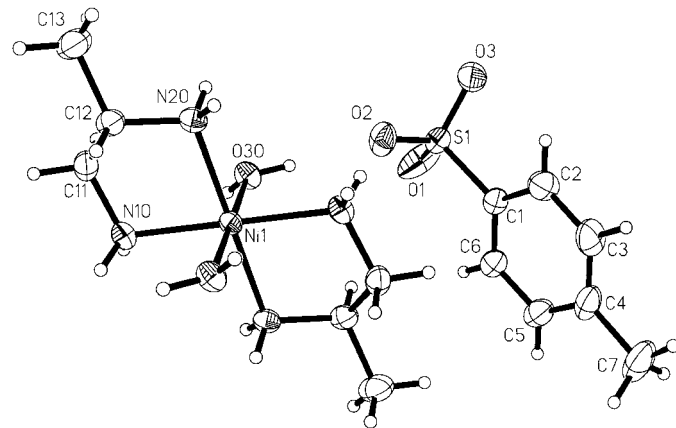
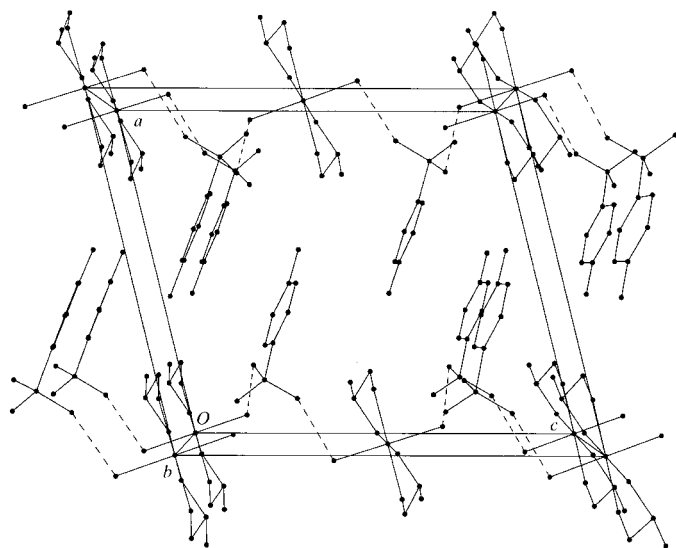


Figure 1

The molecular structure of (I), with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

H20B···O1, N10—H10B···O2 and N10—H10A···O3; Table 1). Thus, all hydrogen bonds are formed by contacts between cations and anions, and so all contribute to the stabilization of the crystal structure.

In conclusion, the crystal structure of (I) consists of a highly layered two-dimensional network, with hydrophilic and hydrophobic sections alternating along [100]. The crystal



**Figure 2**

A perspective view of the unit cell of (I) along the *b* axis; hydrogen bonds are shown by broken lines and H atoms have been omitted for clarity.

structure is stabilized through hydrogen bonding. There is no direct bonding between the Ni<sup>II</sup> cation and the sulfonate O atoms of the anion. Therefore, this Ni<sup>II</sup> sulfonate compound is quite different in structure from the reported metal phosphonates (Clearfield & Costantino, 1996; Alberti, 1996).

## Experimental

To an aqueous solution (50 ml) of NiCl<sub>2</sub>·6H<sub>2</sub>O (2.38 g, 10 mmol) was added *p*-toluenesulfonic acid (1.90 g, 10 mmol) with stirring at room temperature, followed by dropwise addition of neat propanediamine (0.74 g, 10 mmol). The resulting solution was kept in a refrigerator at 278 K. Blue block crystals of (I) suitable for X-ray analysis were obtained after a few weeks. Analysis calculated for C<sub>20</sub>H<sub>38</sub>N<sub>4</sub>NiO<sub>8</sub>S<sub>2</sub>: C 41.04, H 6.54, N 9.57, O 21.86, S 10.96, Ni 10.03%; found: C 41.35, H 6.69, N 9.64, O 21.08, S 10.93, Ni 10.18%.

### Crystal data

[Ni(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S)<sub>2</sub>  
*M<sub>r</sub>* = 585.37

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 13.060 (2) Å

*b* = 7.3266 (11) Å

*c* = 15.0029 (18) Å

β = 103.842 (10)°

*V* = 1393.9 (3) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.395 Mg m<sup>-3</sup>

*D<sub>m</sub>* = 1.40 Mg m<sup>-3</sup>

*D<sub>m</sub>* measured by flotation in  
 mesitylene–bromoform

Mo *K*α radiation

Cell parameters from 42

reflections

θ = 5.4–12.5°

μ = 0.89 mm<sup>-1</sup>

*T* = 295 (2) K

Block, blue

0.40 × 0.32 × 0.23 mm

### Data collection

Siemens *P4* diffractometer

ω/2θ scans

Absorption correction: empirical  
 (North *et al.*, 1968)

*T<sub>min</sub>* = 0.280, *T<sub>max</sub>* = 0.339

4187 measured reflections

3216 independent reflections

2697 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.028

θ<sub>max</sub> = 27.5°

*h* = −16 → 1

*k* = −9 → 1

*l* = −19 → 19

3 standard reflections

every 97 reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039

*wR* (*F*<sup>2</sup>) = 0.112

*S* = 1.06

3216 reflections

168 parameters

H atoms treated by a mixture of  
 independent and constrained  
 refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0577*P*)<sup>2</sup>  
 + 0.4802*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.73 e Å<sup>-3</sup>

Δρ<sub>min</sub> = −0.53 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N10—H10A···O3 <sup>i</sup>	0.90	2.34	3.154 (3)	151
N10—H10B···O2 <sup>ii</sup>	0.90	2.16	2.989 (3)	153
N20—H20A···O1 <sup>iii</sup>	0.90	2.08	2.984 (3)	178
N20—H20B···O1 <sup>iv</sup>	0.90	2.32	3.195 (3)	164
O30—H30A···O2	0.902 (18)	1.93 (2)	2.755 (3)	151 (3)
O30—H30B···O3 <sup>i</sup>	0.893 (18)	1.93 (2)	2.772 (3)	156 (4)

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

The H atoms of the water molecules were freely refined. All other H atoms were treated as riding, with C—H = 0.93–0.98 Å and N—H = 0.90 Å, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub> of the parent atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1030). Services for accessing these data are described at the back of the journal.

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