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Hexaaquanickel(II) bis(*p*-tolylsulfonate)

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The monoclinic (space group $P2_1/n$) structure of $[Ni(H_2O)_6](p\text{-}H_3CC_6H_4SO_3)_2$, with the octahedral cation at an inversion centre and the anion in a general position, shows a strong pseudo-orthorhombic (‘*Pnnm*’) symmetry. The structure comprises layers of hydrophilic and hydrophobic moieties, the former connected by hydrogen bonds.

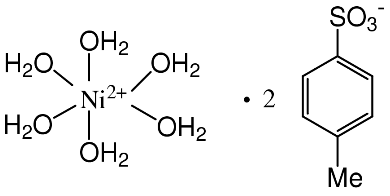
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.101
Data-to-parameter ratio = 15.5

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

Comment

For many purposes, including catalysis, transition metal complexes are required, containing anions which coordinate weakly or not at all. *p*-Toluenesulfonate (OTs) groups are commonly used, and for nickel(II), a useful starting compound is the hexaaqua complex, $[Ni(H_2O)_6](OTs)_2$, (I), where tosyl Ts is $p\text{-}MeC_6H_4SO_2$. (I) is easily prepared from the basic carbonate and the sulfonic acid. In it, the aqua ligands can be readily displaced by phosphine ligands, yielding such products as $[Ni(dppe)_2](OTs)_2$. In the course of our studies of Ni-based catalytic systems, we determined the crystal structure of (I).



(I)

The Ni atom is located at a crystallographic inversion centre and has an octahedral coordination; the OTs^- anion lies in a general position (Fig. 1). The crystal structure of (I) comprises alternate layers of hydrophilic (cations and sulfonate groups, connected by a network of hydrogen bonds) and hydrophobic (tolyl groups) moieties. Structures with such layering can have unusual thermodynamic properties, making them prospective materials for thermal energy storage (Groh *et al.*, 1990).

Structure (I) shows a strong pseudo-orthorhombic symmetry, approximating the space group *Pnnm* (No. 58) in the lattice setting $a = 6.299$, $b = 24.933$, $c = 6.914$ Å and ‘$\alpha = \beta = \gamma = 90°$’, the cation occupying a $2/m$ special position and the anion lying on the m plane, with the benzene ring disordered between two orientations, intersecting the plane at an acute angle. In fact, the structure could be solved and (poorly) refined in the space group *Pnnm*, converging at $wR(F^2) = 0.213$ for all 1644 ‘independent’ reflections, $R = 0.107$ for 1350 reflections with $F^2 > 2\sigma(F^2)$. Merging the data in the orthorhombic symmetry gives $R_{int} = 0.27$.

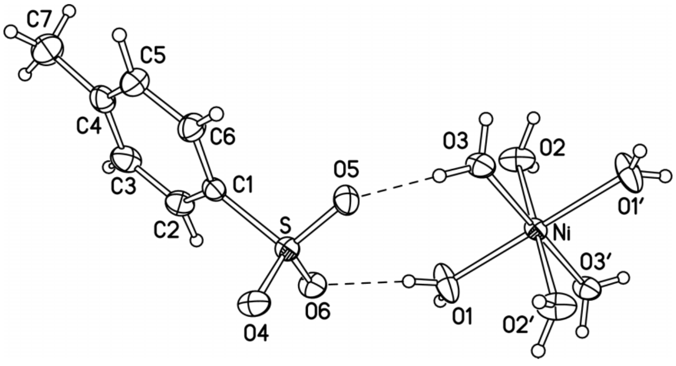


Figure 1
The cation and anion in the structure of (I). Primed atoms have been generated by the inversion centre. Displacement ellipsoids are drawn at the 50% probability level.

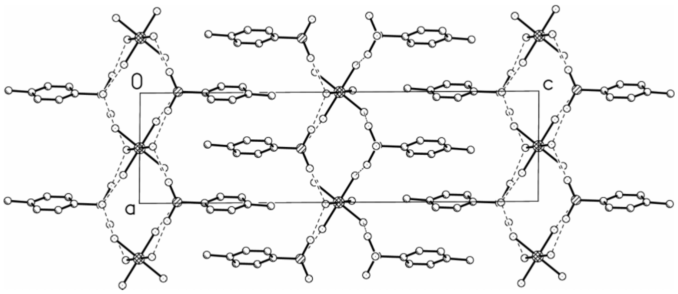


Figure 2
The crystal packing of (I). Dashed lines show the direction of the hydrogen bonds.

(I) is isomorphous with $[Co(H_2O)_6](OTs)_2$ (Cabaleiro-Martínez *et al.*, 2000) and pseudo-isomorphous with a number of $[Ni(H_2O)_6]X_2$ salts, where *X* is $PhSO_3$ (Groh *et al.*, 1990), *p*-$ClC_6H_4SO_3$ (Bernardinelli *et al.*, 1991) and *p*-$H_2C{=}CH{-}C_6H_4SO_3$ (Leonard *et al.*, 1999). The similarity of the latter structure with the rest is somewhat obscured by the fact that it has been reported in the $P2_1/c$ setting rather than in $P2_1/n$, which corresponds to the reduced cell.

Experimental

A mixture of $Ni(CO_3)\cdot Ni(OH)_2\cdot 4H_2O$ (II) (5.81 g, 1.2 mmol), HOTs (4.74 g, 2.5 mmol) and toluene (100 ml) was stirred. Water was removed by azeotropic distillation using a Dean–Stark apparatus under nitrogen, the solvent was removed under reduced pressure and the solid was dried *in vacuo*. The IR spectrum indicated the presence of unreacted (II). The mixture was stirred, the flask heated in air to 573±50 K on a Bunsen burner, whereupon HOTs melted and the reaction was brought to completion. After cooling to room temperature the solid products were washed with degassed toluene (2 × 10 ml) and then ether, dried *in vacuo* and dissolved in methanol. The solution was filtered to remove residual (II), and the methanol was removed from the filtrate *in vacuo*, yielding a pale-green solid of (I) (2.8 g, yield 56%). IR spectrum (solid), cm^{-1}: ν(S=O) 1184 (sym. str.), 1055 (asym. str.). Recrystallization from methanol yielded crystals suitable for X-ray study.

Crystal data

$[Ni(H_2O)_6](C_7H_7O_3S)_2$
$M_r = 509.18$
Monoclinic, $P2_1/n$
$a = 6.914$ (1) Å
$b = 6.299$ (1) Å
$c = 24.933$ (4) Å
$\beta = 90.719$ (15)°
$V = 1085.8$ (3) Å^3
$Z = 2$
$D_x = 1.557$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 448 reflections
$\theta = 10$–20°
$\mu = 1.14$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.25 × 0.10 × 0.05 mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP SHELXTL*; Bruker, 1997)
$T_{\min} = 0.763$, $T_{\max} = 0.945$
8262 measured reflections
2864 independent reflections
2253 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\max} = 29.0°$
$h = -8 \rightarrow 9$
$k = -6 \rightarrow 8$
$l = -33 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.101$
$S = 1.19$
2864 reflections
185 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0083P)^2 + 2.4432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—O3	2.018 (2)	S—O4	1.465 (2)
Ni—O1	2.056 (3)	S—O6	1.467 (2)
Ni—O2	2.067 (3)	S—C1	1.775 (3)
S—O5	1.461 (2)		
O3—Ni—O1	91.39 (11)	O4—S—O6	112.23 (14)
O3—Ni—O2	90.04 (11)	O5—S—C1	106.33 (14)
O1—Ni—O2	92.06 (12)	O4—S—C1	106.27 (14)
O5—S—O4	112.11 (14)	O6—S—C1	107.01 (14)
O5—S—O6	112.38 (14)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H011···O5$^{\rm i}$	0.80 (5)	1.98 (5)	2.778 (4)	178 (5)
O1—H012···O6	0.80 (4)	2.01 (4)	2.810 (4)	175 (4)
O2—H021···O6$^{\rm ii}$	0.90 (6)	1.95 (6)	2.816 (3)	161 (5)
O2—H022···O4$^{\rm iii}$	0.85 (5)	1.92 (5)	2.767 (4)	171 (4)
O3—H031···O4$^{\rm ii}$	0.86 (5)	1.89 (5)	2.741 (3)	171 (5)
O3—H032···O5	0.85 (5)	1.91 (5)	2.756 (3)	176 (5)

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

Csp^2—H bond distances are in the range 0.91 (4)–0.97 (4) Å, and the Csp^3—H distances are 0.92 (5) and 0.98 (6) Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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