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Tris(ethylenediamine-$\kappa^2 N,N'$)nickel(II) naphthalene-2,6-disulfonate monohydrate

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The title complex, $[Ni(C_2H_8N_2)_3](C_{10}H_6O_6S_2)\cdot H_2O$ or $[Ni(en)_3](2,6\text{-nds})\cdot H_2O$ (en = ethylenediamine and nds = naphthalene-2,6-disulfonate), contains one $[Ni(en)_3]^{2+}$ cation, one water molecule, and two separate halves of centrosymmetric 2,6-nds^{2-} dianions in the asymmetric unit. The anions lie on inversion centres. A three-dimensional open framework is assembled by means of hydrogen-bonding interactions between the anions and the cations, in which there is a channel parallel to the *c* axis, with one of the 2,6-nds dianions occupying the channel.

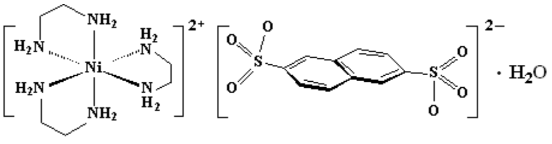
Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.159
Data-to-parameter ratio = 16.1

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

Comment

The construction of inorganic–organic hybrid architectures with zeolite-like molecular-sized channels, assembled by coordinate and hydrogen bonds, has been developed significantly in recent years (Venkataraman *et al.*, 1995). Numerous examples employing ligands containing many kinds of donor groups, especially phosphonate groups, have been reported (Kaschak *et al.*, 1998; Nakano *et al.*, 1998). Sulfonate groups have a strong structural analogy to phosphonate groups; however, hybrid systems employing sulfonates are relatively rare (Shimizu *et al.*, 1999; Côté & Shimizu, 2001).Recently, we obtained the novel hybrid complex, $[Ni(en)_3](2,6\text{-nds})\cdot H_2O$ (en = ethylenediamine and nds = naphthalene-2,6-disulfonate), (I), by the reaction of sodium naphthalene-2,6-disulfonate, ethylenediamine and nickel(II) nitrate hexahydrate. The structure of (I) is reported here.



(I)

As shown in Fig. 1, the asymmetric unit of (I) consists of an $[Ni(en)_3]^{2+}$ cation, halves of two separate centrosymmetric 2,6-nds^{2-} dianions and an uncoordinated water molecule. Selected bond distances and angles are given in Table 1. In the cation, the Ni^{II} ion is *N,N'*-chelated by three neutral ethylenediamine molecules in a distorted octahedral environment (average Ni—N = 2.114 Å, see Table 1).

The two 2,6-nds ligands are not engaged in coordination owing to their weak donor ability, and have distinct roles in the crystal structure. One of the 2,6-nds^{2-} dianions (involving atom S1) forms a three-dimensional hydrogen-bonding network with the $[Ni(en)_3]^{2+}$ units and the water molecules. These 2,6-nds^{2-} dianions and the $[Ni(en)_3]^{2+}$ cations, as well as the water molecules, form the outer walls of large channels

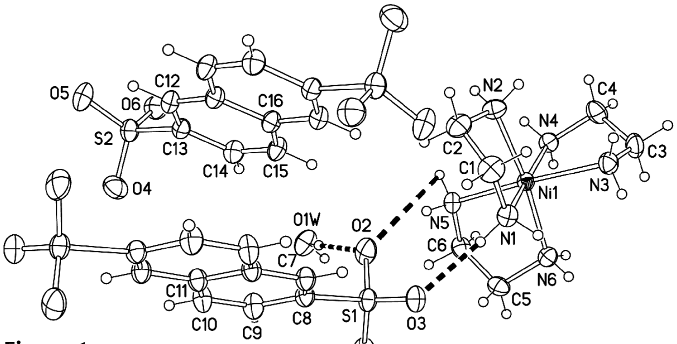


Figure 1
*ORTEP*II plot (Johnson, 1976) of the asymmetric unit of (I) and the symmetry-generated second half of each anion, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

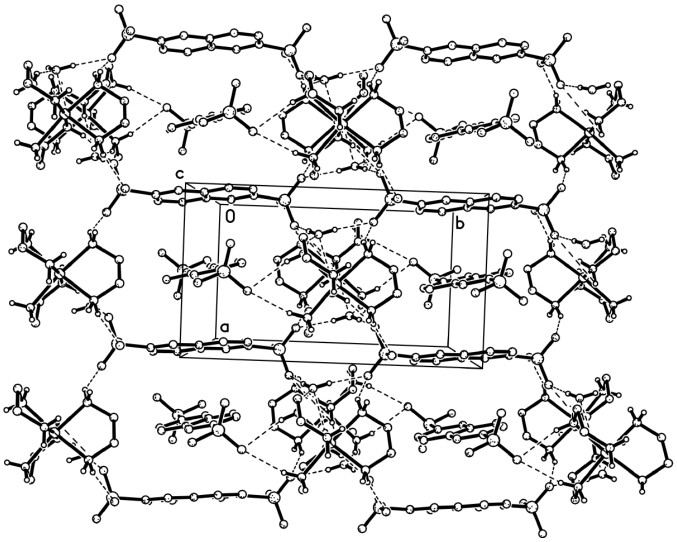


Figure 2
The crystal packing of compound (I), with the hydrogen bonds denoted by dashed lines.

parallel to the **c** direction. The other 2,6-nds^{2-} dianions (involving atom S2) fill these channels as 'guest molecules' and are linked to the 'outer walls' *via* hydrogen bonds (Fig. 2 and Table 2).

Offset face-to-face interactions have also been found between the 'guest molecules' and the 2,6-nds^{2-} dianions in the hydrogen-bonding framework, with a centroid–centroid distance of 3.891 (3) Å. This further stabilizes the position of the guest 2,6-nds^{2-} dianions in the channels.

The naphthalene ring systems of the dianions are planar, with a small mean deviation of 0.003 Å. The structure of the complex can be described as the alternation of inorganic layers of $[Ni(en)_3]^{2+}$ cations with organic layers of 2,6-nds dianions along the **b** direction.

Experimental

The title complex was prepared by the addition of $Ni(NO_3)_2 \cdot 6H_2O$ (20 mmol) and ethylenediamine (20 mmol) to an aqueous solution of sodium naphthalene-2,6-disulfonate (40 mmol) at room temperature. The solution was then filtered and from the filtrate red crystals were obtained after about one month. Elemental analysis calculated for $C_{16}H_{32}N_6NiO_7S_2$: C 35.37, H 5.94, N 15.47%; found: C 35.09, H 6.03, N 15.31%.

Crystal data

$[Ni(C_2H_8N_2)_3](C_{10}H_6O_6S_2) \cdot H_2O$
$M_r = 543.30$
Monoclinic, $P2_1/n$
$a = 7.5989$ (17) Å
$b = 13.185$ (4) Å
$c = 23.380$ (5) Å
$\beta = 91.527$ (12)°
$V = 2341.7$ (10) Å^3
$Z = 4$

$D_x = 1.541$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 18755 reflections
$\theta = 3.0$–27.4°
$\mu = 1.06$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.37 × 0.26 × 0.22 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.696$, $T_{max} = 0.801$
19154 measured reflections

5320 independent reflections
4195 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.159$
$S = 1.06$
5320 reflections
331 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2 + 1.0885P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N5	2.101 (3)	Ni1—N6	2.119 (3)
Ni1—N4	2.109 (3)	Ni1—N2	2.118 (3)
Ni1—N1	2.117 (3)	Ni1—N3	2.122 (3)
N1—Ni1—N6	92.44 (11)	N5—Ni1—N2	93.71 (12)
N1—Ni1—N2	81.80 (12)	N5—Ni1—N6	81.68 (11)
N1—Ni1—N3	92.13 (12)	N5—Ni1—N4	91.83 (11)
N2—Ni1—N3	93.01 (13)	N5—Ni1—N1	94.76 (11)
N4—Ni1—N1	172.15 (11)	N5—Ni1—N3	170.99 (12)
N4—Ni1—N6	92.74 (12)	N6—Ni1—N2	172.33 (12)
N4—Ni1—N2	93.53 (13)	N6—Ni1—N3	92.26 (12)
N4—Ni1—N3	81.77 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O1^{i}	0.85 (3)	1.95 (3)	2.790 (4)	168 (4)
O1W—H1W2···O2	0.85 (3)	1.94 (3)	2.781 (4)	169 (4)
N1—H1N1···O6^{ii}	0.89 (3)	2.38 (2)	3.206 (4)	153 (4)
N1—H1N1···O5^{ii}	0.89 (3)	2.53 (3)	3.326 (4)	148 (4)
N1—H1N2···O3	0.89 (3)	2.11 (3)	2.977 (4)	161 (4)
N2—H2N1···O1^{iii}	0.89 (3)	2.37 (3)	3.175 (4)	150 (4)
N3—H3N1···O5^{ii}	0.90 (3)	2.50 (2)	3.339 (5)	155 (4)
N3—H3N2···O4^{iv}	0.90 (3)	2.24 (3)	3.058 (4)	151 (3)
N4—H4N1···O1W^{v}	0.90 (3)	2.23 (2)	3.049 (4)	151 (4)
N4—H4N2···O6^{v}	0.90 (3)	2.35 (3)	3.219 (4)	161 (3)
N5—H5N1···O1W^{v}	0.90 (3)	2.23 (3)	3.071 (5)	156 (3)
N5—H5N2···O2	0.90 (3)	2.10 (3)	2.977 (4)	165 (3)
N6—H6N1···O5^{ii}	0.89 (3)	2.22 (3)	3.054 (4)	155 (4)
N6—H6N2···O6^{v}	0.89 (3)	2.33 (3)	3.163 (4)	155 (3)

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

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The H atoms of the NH_2 groups and the water molecule were located in a difference Fourier map and refined isotropically [N—H = 0.89–0.90 (3) Å, O—H = 0.85 (3) Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N,O)]. The other H atoms were placed in calculated positions and were allowed to ride on their parent C atoms [C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)].

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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