

Ming-Tian Li, Cheng-Gang  
Wang,\* Yu Wu and Xu-Cheng FuDepartment of Chemistry, Central China Normal  
University, Wuhan, Hubei 430079, People's  
Republic of ChinaCorrespondence e-mail:  
wangcg23@yahoo.com.cn

## Key indicators

Single-crystal X-ray study  
 $T = 292\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.038  
 $wR$  factor = 0.114  
Data-to-parameter ratio = 14.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Diaquabis(ethylenediamine)nickel(II) bis(4-amino-  
naphthalene-1-sulfonate) dihydrate

In the title complex,  $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_2 \cdot 2\text{H}_2\text{O}$ , the Ni atom of the centrosymmetric cation has a distorted octahedral coordination geometry, and is bonded to four N atoms, from two diethylenediamine ligands, and to two water O atoms. Symmetry-related 4-aminonaphthalene-1-sulfonate anions are antiparallel. The crystal structure is stabilized by  $\pi$ - $\pi$  interactions and  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds.

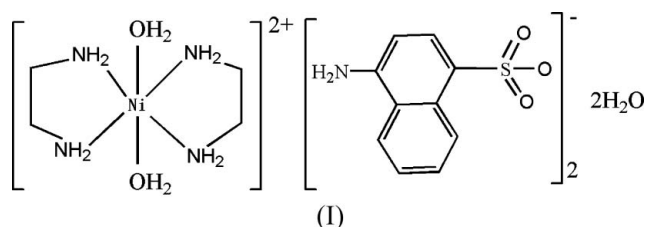
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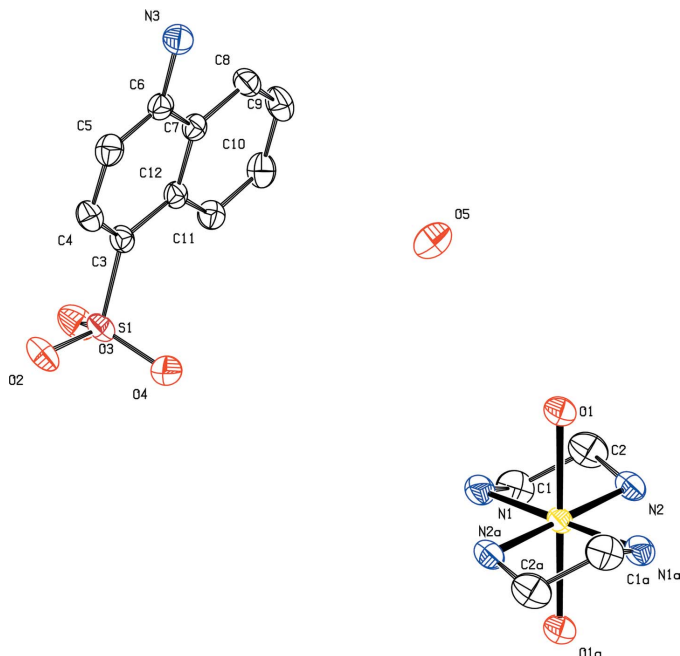
## Comment

Owing to the weak coordination ability of sulfonate anions with transition metals, sulfonates usually act as uncoordinated counter-ions (Chen *et al.*, 2002). We report the crystal structure of such a compound,  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2](\text{ans})_2 \cdot 2\text{H}_2\text{O}$ , (I) (en is diethylenediamine and ans is 4-aminonaphthalene-1-sulfonate).



The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The Ni atom of the centrosymmetric cation has a distorted octahedral geometry and is coordinated by four N atoms from two diethylenediamine ligands, which lie in the equatorial plane, and by two water O atoms occupying the axial sites. The Ni—N distances [2.081 (2) and 2.094 (2) Å] are in close agreement with the equivalent distances in the complex  $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_4)_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$  [2.0857 (17) and 2.0962 (17) Å; Sbai *et al.*, 2002]. However, they are shorter than those in the complex  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_3]_2(2,6\text{-nds})_3 \cdot 4\text{H}_2\text{O}$  [2.122 (2), 2.124 (2) and 2.132 (2) Å; 2,6-nds is naphthalene-2,6-disulfonate; Cai, Feng & Hu, 2001; Cai, Chen *et al.*, 2001]. The Ni—O distance is 2.1421 (19) Å, which is slightly longer than the corresponding distances in the complex  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2(-\text{H}_2\text{O})_2](\text{C}_6\text{H}_6\text{NO}_3\text{S})_2$  [2.1358 Å; Kim & Lee, 2002].

As shown in Fig. 2, an organic cation layer is linked to an inorganic anionic layer through a series of  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds (Table 2), and adjacent 4-aminonaphthalene-1-sulfonate anions are antiparallel, showing significant  $\pi$ - $\pi$  interactions. The plane-to-plane distances and displacement angles of  $\text{Cg}1\cdots\text{Cg}2^1$  are 3.371 and 3.359 Å, and 0.96 and 16.41°, respectively [ $\text{Cg}1$  and  $\text{Cg}2$  are


**Figure 1**

View of the molecular structure of (I), showing the labelling scheme and 50% probability displacement ellipsoids. Only one anion and one water molecule of crystallization are shown. [Symmetry code: (a)  $-x, -y, -z$ ]. H atoms have been omitted for clarity.

the C3–C7/C12 and C7–C12 ring centroids; symmetry code: (i)  $1 - x, 1 - y, -z$ ]. These interactions together with the hydrogen bonds stabilize the crystal structure.

## Experimental

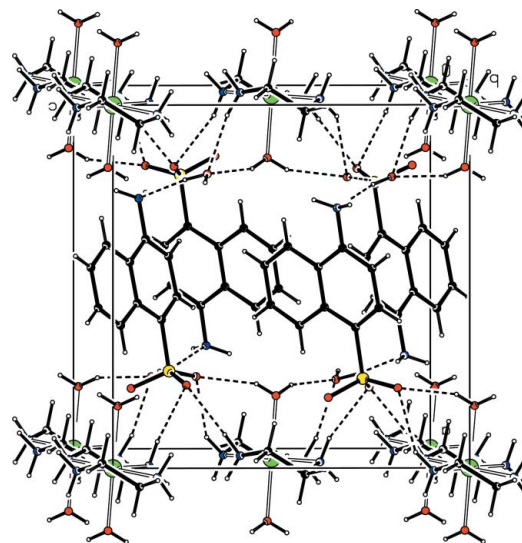
Ethylenediamine (0.06 g, 1 mmol) was added to an aqueous solution (20 ml) of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.15 g, 0.5 mmol). The mixture was stirred for 2 h at room temperature. The solution was then treated with the sodium salt of 4-aminonaphthalene-1-sulfonic acid tetrahydrate (0.32 g, 1 mmol) in ethanol (10 ml). After filtration, the pale-red solution obtained was allowed to stand at room temperature. Well shaped pale-purple block-like crystals were obtained by slow evaporation of the solvent over a period of about one week.

### Crystal data

$[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot (\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_2 \cdot 2\text{H}_2\text{O}$	$D_x = 1.573 \text{ Mg m}^{-3}$
$M_r = 695.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2427 reflections
$a = 12.406 (2) \text{ \AA}$	$\theta = 2.7\text{--}27.0^\circ$
$b = 9.6396 (17) \text{ \AA}$	$\mu = 0.87 \text{ mm}^{-1}$
$c = 12.276 (2) \text{ \AA}$	$T = 292 (2) \text{ K}$
$\beta = 90.479 (3)^\circ$	Block, pale purple
$V = 1468.0 (5) \text{ \AA}^3$	$0.30 \times 0.18 \times 0.12 \text{ mm}$
$Z = 2$	

### Data collection

Bruker SMART CCD area-detector diffractometer	3336 independent reflections
$\varphi$ and $\omega$ scans	2698 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.781, T_{\text{max}} = 0.903$	$\theta_{\text{max}} = 27.5^\circ$
8920 measured reflections	$h = -15 \rightarrow 16$
	$k = -10 \rightarrow 12$
	$l = -14 \rightarrow 15$


**Figure 2**

A view of the crystal packing of (I), showing the hydrogen bonds as dashed lines (see Table 2 for details).

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.114$   
 $S = 1.07$   
 3336 reflections  
 236 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Ni1–N2	2.081 (2)	Ni1–O1	2.1421 (19)
Ni1–N1	2.094 (2)		
N2–Ni1–N2 <sup>i</sup>	180	N2–Ni1–O1	88.26 (8)
N2–Ni1–N1	83.15 (9)	N1–Ni1–O1	89.10 (8)
N2 <sup>i</sup> –Ni1–N1	96.85 (9)	N1 <sup>i</sup> –Ni1–O1	90.90 (8)
N2–Ni1–N1 <sup>i</sup>	96.85 (9)	O1 <sup>i</sup> –Ni1–O1	180
N2–Ni1–O1 <sup>i</sup>	91.74 (8)		

Symmetry code: (i)  $-x, -y, -z$ .

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1–H1B $\cdots$ O3 <sup>ii</sup>	0.87 (2)	2.56 (2)	3.358 (3)	153 (2)
N1–H1A $\cdots$ O2 <sup>iii</sup>	0.88 (2)	2.36 (2)	3.147 (3)	148 (3)
N2–H2B $\cdots$ O5 <sup>iv</sup>	0.90 (2)	2.11 (2)	2.995 (3)	167 (3)
N2–H2A $\cdots$ O3 <sup>v</sup>	0.89 (2)	2.25 (2)	3.107 (3)	161 (3)
O1–H1F $\cdots$ O2 <sup>v</sup>	0.72 (3)	2.13 (4)	2.803 (3)	156 (3)
N3–H3B $\cdots$ O3 <sup>vi</sup>	0.81 (2)	2.64 (2)	3.449 (3)	173 (3)
N3–H3A $\cdots$ O4 <sup>vii</sup>	0.84 (2)	2.26 (2)	3.079 (3)	167 (2)
O5–H5B $\cdots$ O2 <sup>viii</sup>	0.80 (3)	2.19 (4)	2.940 (3)	157 (7)
O1–H1E $\cdots$ O5 <sup>viii</sup>	0.87 (4)	1.99 (4)	2.822 (3)	159 (3)
O5–H5A $\cdots$ N3 <sup>ix</sup>	0.86 (2)	2.03 (2)	2.879 (3)	169 (3)

Symmetry codes: (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x, -y, -z + 1$ ; (iv)  $-x, -y + 1, -z$ ; (v)  $x, y, z - 1$ ; (vi)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $-x + 1, -y, -z + 1$ ; (viii)  $x, y - 1, z$ ; (ix)  $-x + 1, -y + 1, -z + 1$ .

The water and amine H atoms were located in difference Fourier maps and refined isotropically. All the other H atoms were placed in

geometrically idealized positions and constrained to ride on their parent atoms with C–H distances of 0.93–0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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