

Diaquabis(ethylenediamine)copper(II) bis[tris(ethylenediamine)nickel(II)] tris(naphthalene-2,6-disulfonate) tetrahydrate

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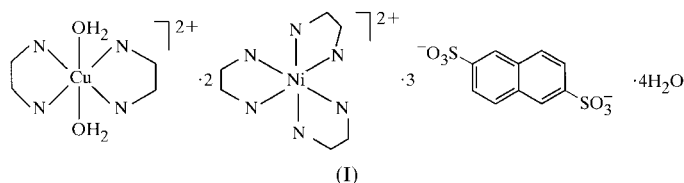
Received 18 May 2001

Accepted 9 August 2001

The title mixed-metal compound, $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot [\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)_3 \cdot 4\text{H}_2\text{O}$, was obtained during investigations of the porous frameworks constructed by amino-coordinated metal complex cations and large organic anions. All three naphthalene-2,6-disulfonate anions and the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cation are located on crystallographic inversion centers and assemble into an extended two-dimensional network through intermolecular hydrogen bonds, creating cavities in which the $[\text{Ni}(\text{en})_3]^{2+}$ cations and water molecules are included.

Comment

Promising applications of porous crystalline materials include separation, shape-selective catalysis, trapping and storage of toxic materials, off-peak energy storage and heterogeneous catalysis (Thompson, 1994; Endo *et al.*, 1997). The general approach toward the construction of porous coordination networks is the use of coordination polymerization to align inorganic complexes (Munakata *et al.*, 1996; Hunter, 1995). Recently, the ability to design and control the assembly of coordination networks through both coordination and hydrogen-bonding interactions, by employing organic ligands with hydrogen-bonding functionality combined with coordination sites for the transition metal, has been of great interest for both crystal engineering and the search for functional materials (MacDonald *et al.*, 2000). We have been exploring an approach, using amino-coordinated metal complex cations and large naphthalenedisulfonate anions as building blocks, to construct porous crystalline materials and mixed-metal systems. The amino H atoms of the metal complex can form



strong ionic hydrogen bonds with the sulfonate O atoms. If the hydrogen bonds are directive, a porous framework can be built which can accommodate guest molecules of diverse nature. Indeed, this is what was observed in the adduct $[\text{Co}(\text{trien})(\text{phen})](1,5\text{nds})_{1,5}\cdot 2\text{phen}\cdot 8\text{H}_2\text{O}$ (trien is triethylenetetramine, phen is 1,10-phenanthroline and nds is naphthalenedisulfonate; Cai, Feng & Hu, 2001). We report here the crystal

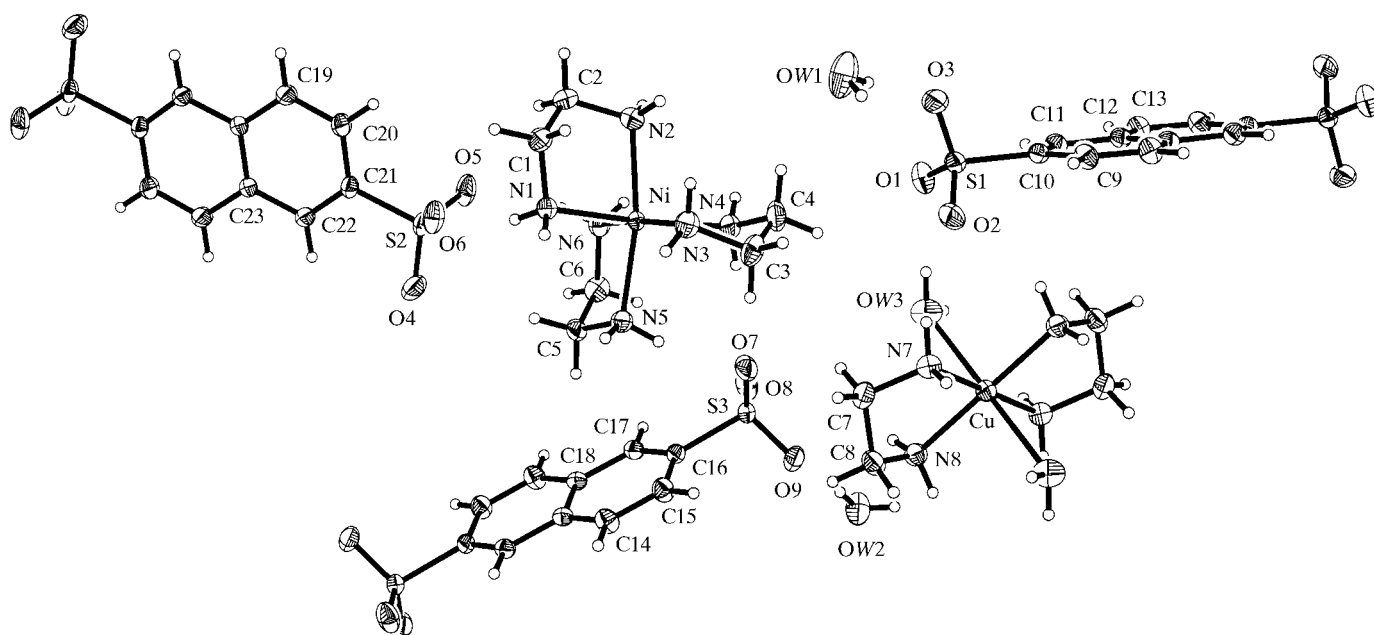


Figure 1

The structure of a portion of (I) showing 30% probability displacement ellipsoids. Only the unique portions are labeled.

structure of the title mixed-metal compound, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_3]_2(2,6\text{nds})_3 \cdot 4\text{H}_2\text{O}$, (I), where en is ethylenediamine.

Fig. 1 shows the structure of (I). The coordination geometries of the elongated octahedral $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ and octahedral $[\text{Ni}(\text{en})_3]^{2+}$ cations are regular and compatible with reported analogs (Kovbasyuk *et al.*, 1997; Emsley *et al.*, 1988, 1990; Urrutigoity *et al.*, 1996). The Cu atom and all three independent naphthalene-2,6-disulfonate anions are located on inversion centers. The OW3 water molecule is weakly coordinated to Cu^{2+} in an axial position [$\text{Cu} \cdots \text{O}$ 2.448 (2) Å]. The amino H atoms of the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragment are involved in hydrogen-bonding interactions with the sulfonate O atoms, as shown in Fig. 2 [the $\text{N} \cdots \text{O}$ distances are in the range 3.086 (3)–3.226 (3) Å and the $\text{N}-\text{H} \cdots \text{O}$ angles are in the range 136–160°], resulting in an extended porous two-dimensional network. The cavities along the *c* axis, each constructed by four $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cations and four 2,6nds anions, are filled by the $[\text{Ni}(\text{en})_3]^{2+}$ cations. The amino H atoms of the $[\text{Ni}(\text{en})_3]^{2+}$ fragments are also involved in extensive hydrogen bonding with the sulfonate O atoms. The remaining two water molecules exist as a dimer with strong intermolecular hydrogen bonds [$\text{OW} \cdots \text{OW1}$ 2.751 (4) Å and

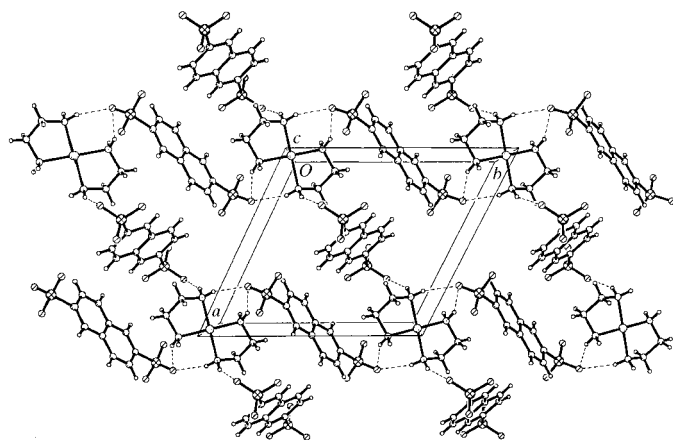


Figure 2

The packing arrangement of the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cations and 2,6nds anions along the *c* axis, showing the extended two-dimensional network formed by hydrogen bonds.

$\text{OW2}-\text{H} \cdots \text{OW1}$ 174°], and also reside in the cavities, hydrogen bonded to the sulfonate O atoms. During a previous investigation of the coordination behavior of sulfonate anions with transition metal atoms (Cai, Chen *et al.*, 2001), we demonstrated that the coordination strength of the sulfonate could be tailored chemically. In the structures of $[\text{Cu}(\text{en})_2](1,5\text{nds}) \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{N-me-en})_2](2,6\text{nds}) \cdot 2\text{H}_2\text{O}$ (N-me-en is *N*-methylethylenediamine; Cai, Chen *et al.*, 2001), the Cu atom is weakly coordinated in the axial positions by sulfonate O atoms instead of water O atoms. In the title compound, there is no direct interaction between the Cu and sulfonate O atoms. This observation further illustrates that metal sulfonates display a wide range of structural chemistry that calls for extensive investigation.

Experimental

To an aqueous solution of sodium naphthalene-2,6-disulfonate, equimolar amounts of $[\text{Cu}(\text{en})_2]\text{Cl}_2$ and $[\text{Ni}(\text{en})_3]\text{Cl}_2$ were added with stirring. After heating at 333 K for several hours in a water bath, the solution was maintained at room temperature and crystals suitable for data collection were obtained after several days.

Crystal data

$[\text{Cu}(\text{C}_2\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]-$ $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3]_2(\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)_3 \cdot$ $4\text{H}_2\text{O}$	$V = 1786.9$ (4) Å ³
$M_r = 1628.69$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.514$ Mg m ⁻³
$a = 11.8728$ (17) Å	Mo $K\alpha$ radiation
$b = 12.5961$ (17) Å	Cell parameters from 856 reflections
$c = 13.903$ (2) Å	$\theta = 3.6$ – 24.3°
$\alpha = 91.553$ (2)°	$\mu = 1.07$ mm ⁻¹
$\beta = 105.950$ (2)°	$T = 293$ (2) K
$\gamma = 115.017$ (2)°	Plate, brown
	$0.24 \times 0.20 \times 0.08$ mm

Data collection

Bruker CCD area-detector diffractometer	7625 independent reflections
φ and ω scans	6452 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.78$, $T_{\text{max}} = 0.92$	$\theta_{\text{max}} = 27.0^\circ$
10 504 measured reflections	$h = -12 \rightarrow 15$
	$k = -15 \rightarrow 16$
	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.1603P]$
$R(F) = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.83$ e Å ⁻³
7625 reflections	$\Delta\rho_{\text{min}} = -0.45$ e Å ⁻³
430 parameters	
H-atom parameters constrained	

The H atoms of the en ligands and the 2,6nds anions were placed in idealized positions ($\text{N}-\text{H} = 0.90$ Å, and $\text{C}-\text{H} = 0.97$ and 0.93 Å for CH_2 and CH , respectively) and refined as riding atoms. The water H atoms were located from a difference Fourier map and were not refined.

Table 1

Hydrogen-bonding geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O6}$	0.90	2.06	2.929 (3)	162
$\text{N1}-\text{H1B} \cdots \text{O4}^i$	0.90	2.39	3.274 (3)	166
$\text{N1}-\text{H1B} \cdots \text{O6}^i$	0.90	2.56	3.262 (3)	135
$\text{N2}-\text{H2A} \cdots \text{OW2}$	0.90	2.14	3.001 (3)	161
$\text{N2}-\text{H2B} \cdots \text{O8}^{ii}$	0.90	2.35	3.130 (3)	144
$\text{N3}-\text{H3A} \cdots \text{OW2}$	0.90	2.19	3.059 (3)	161
$\text{N4}-\text{H4A} \cdots \text{O7}$	0.90	2.22	3.081 (3)	161
$\text{N4}-\text{H4B} \cdots \text{O8}^{ii}$	0.90	2.17	3.006 (3)	155
$\text{N5}-\text{H5A} \cdots \text{O7}$	0.90	2.23	3.095 (3)	161
$\text{N5}-\text{H5B} \cdots \text{O6}^i$	0.90	2.15	2.992 (3)	156
$\text{N6}-\text{H6A} \cdots \text{O5}$	0.90	2.31	3.151 (3)	156
$\text{N6}-\text{H6B} \cdots \text{O8}^{ii}$	0.90	2.46	3.246 (3)	146
$\text{N7}-\text{H7A} \cdots \text{O5}^{iii}$	0.90	2.39	3.226 (3)	155
$\text{N7}-\text{H7B} \cdots \text{O2}^{iv}$	0.90	2.23	3.094 (3)	160
$\text{N8}-\text{H8A} \cdots \text{O9}$	0.90	2.37	3.086 (3)	136
$\text{N8}-\text{H8B} \cdots \text{O2}^v$	0.90	2.44	3.268 (3)	153
$\text{OW1}-\text{HW1} \cdots \text{O3}^{iv}$	0.90	1.93	2.817 (3)	168
$\text{OW1}-\text{HW2} \cdots \text{O2}^{vi}$	0.94	1.93	2.804 (4)	154
$\text{OW2}-\text{HW3} \cdots \text{O9}^{vii}$	0.84	1.98	2.809 (3)	174
$\text{OW2}-\text{HW4} \cdots \text{OW1}$	0.85	1.90	2.748 (3)	173
$\text{OW3}-\text{HW5} \cdots \text{O1}^{iv}$	0.92	1.98	2.889 (3)	170
$\text{OW3}-\text{HW6} \cdots \text{O5}^{ii}$	0.91	1.88	2.771 (3)	169

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $x, y, 1+z$; (iv) $x, y-1, z$; (v) $-x, 1-y, 1-z$; (vi) $1-x, 1-y, 1-z$; (vii) $1+x, y, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This project is supported by Guangdong Provincial Natural Science Foundation of China (No. 990208).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1340). Services for accessing these data are described at the back of the journal.

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