A novel hydrogen-bonded micro-porous framework constructed from two different metal complexes

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A hydrogen-bonded coordination supramolecule, (meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-$\kappa^4 N$)nickel(II) [N,N-o-phenylenebis(oxamato)-$\kappa^4 O,N,N',O'$]-nickelate(II) dihydrate, $[Ni(C_{16}H_{36}N_4)][Ni(C_{10}H_4N_2O_6)]\cdot 2H_2O$ or $[Ni(meso\text{-}cth)][Ni(opba)]\cdot 2H_2O$, has been prepared and characterized by X-ray crystallographic analysis. The two complex ions, i.e. $[Ni(meso\text{-}cth)]^{2+}$ and $[Ni(opba)]^{2-}$, are hydrogen bonded to each other, resulting in two-dimensional neutral supramolecular sheets. The sheets stack along the a direction to produce a three-dimensional architecture with one-dimensional channels in which hydrogen-bonded chains of water molecules are included.

Comment

One-, two- or three-dimensional supramolecular architectures assembled via intermolecular non-covalent interactions are of considerable interest for the crystal engineering of new functional solid-state materials, as well as for their fascinating structures (see, for example, MacDonald & Whitesides, 1994; Brunet et al., 1997; Munakata et al., 1997; Tadokoro et al., 1999). Hydrogen bonding, which combines directionality, selectivity and strength, has been noted as the most versatile organizing force for supramolecular assembly. Ionic interactions also play important roles in the construction of hydrogen-bonded crystals from charged subunits (Braga et al., 1998; Burrows et al., 1996).

Among various supramolecular architectures, those containing internal channels or chambers of various sizes have received much attention. A number of such materials have been recognized as zeolite analogues with interesting properties, such as selective guest inclusion and exchange, and catalytic activity (Brunet et al., 1997; Endo et al., 1997; Kepert et al., 1998).

We describe here a novel microporous hydrogen-bonded framework built from $[Ni(meso\text{-}cth)]^{2+}$ (meso-cth is meso-

5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $[Ni(opba)]^{2-}$ [opba is ortho-phenylenebis(oxamate)]. The title compound, (I), has the formula $[Ni(meso\text{-}cth)][Ni(opba)]\cdot 2H_2O$.

(I)
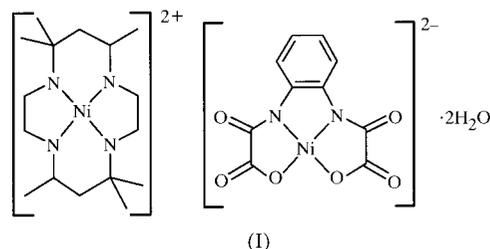
A perspective view of the above building blocks with the atom-labelling scheme is depicted in Fig. 1. Selected bond distances and angles are listed in Table 1.

In the anionic bis(oxamato)nickel(II) complex moiety, the metal atom is ligated by two deprotonated amido N atoms and two carboxylate O atoms. The NiO_2N_2 coordination chromophore exhibits nearly strict planarity; the largest deviation of the donor atoms from the O_2N_2 mean plane is only 0.0010 (11) Å, and the Ni atom is displaced out of the plane by 0.0099 (11) Å. The Ni3—N distances (average 1.817 Å) are significantly shorter than those of Ni3—O (average 1.886 Å), consistent with the greater basicity of the deprotonated amido nitrogen donors. The constrained N1—Ni3—N2 chelate angle [86.54 (9)°] is also significantly smaller than the O1—Ni3—O2 non-chelate angle [100.62 (9)°]. The above features lead to a planar trapezoidal coordination environment around Ni3, with the O···O distance being remarkably longer than the N···N one.

In the cationic complex moiety, the metal atom, which resides on an inversion centre, is coordinated by the four
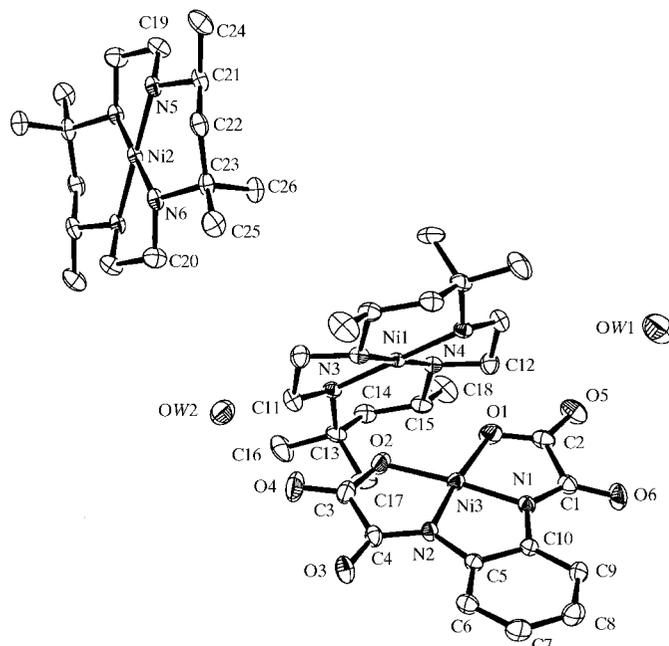
Figure 1
A view of the building blocks in $[Ni(meso\text{-}cth)][Ni(opba)]\cdot 2H_2O$ (30% probability displacement ellipsoids).
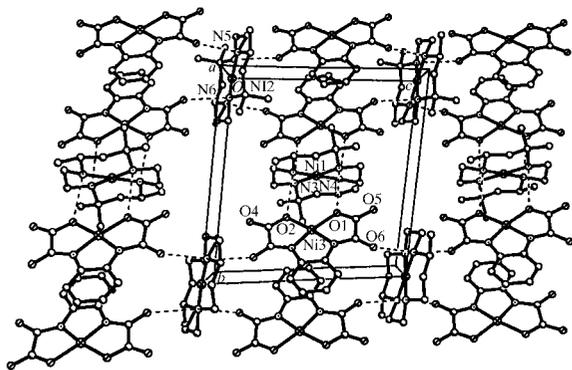
Figure 2
Projection of the heterobimetallic hydrogen-bonded sheet in the title compound down the *a* axis, showing two cavities. Water molecules have been omitted for clarity.

amino N atoms of the macrocyclic ligand. The NiN_4 chromophore exhibits strict planarity. There are two sets of crystallographically independent cationic moieties, with no significant differences in molecular structure, as shown in Table 1.

What interests us is the way in which the two ionic complex building blocks are linked to each other *via* hydrogen bonds to produce a supramolecular architecture. Relevant hydrogen-bond parameters are listed in Table 2. All amino groups in the complex cations and all O atoms in the complex anions are involved in extended hydrogen bonding. The two sets of crystallographically independent cations adopt different hydrogen-bonding modes. The Ni1 cation is linked to two Ni3 anions through two hydrogen bonds between amino groups and the coordinated O atoms of carboxylate groups [O1···N3[i] and O2···N4[i]; symmetry code: (i) $1 - x, 1 - y, 1 - z$], with the Ni3···Ni1 separation being 4.6080 (4) Å. The Ni2 cation is linked to four anions by single hydrogen bonds to amido O atoms [O3···N6[ii] and O6···N5[iii]; symmetry code: (ii) $1 - x, 1 - y, -z$; (iii) $x - 1, y - 1, z - 1$], with the Ni3···Ni2[iii] and
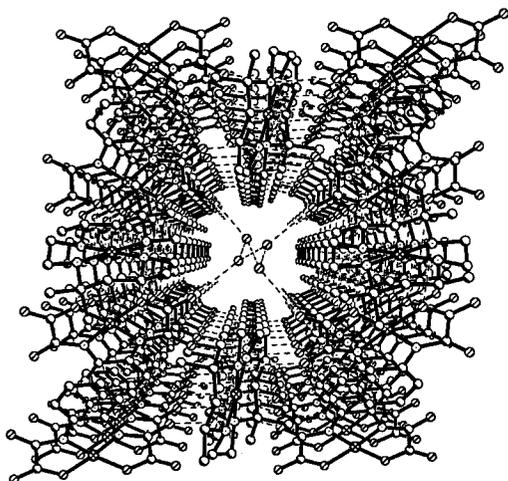
Ni3···Ni2[ii] separations being 7.6078 (6) and 6.5321 (6) Å, respectively. Therefore, each Ni3 anion is linked to three cations *via* four hydrogen bonds. These hydrogen bonds arrange the two complexes in space, giving a neutral and extended two-dimensional heterobimetallic sheet along the $(\bar{1}10)$ plane, as shown in Fig. 2. This unique sheet contains open cavities, each of which is defined by four anionic complexes and four cationic complexes connected through twelve N—H···O hydrogen bonds. Stacking the sheets in a slipped fashion results in one-dimensional channels running along the *a* axis (Fig. 3). Lined with the carbonyl O atoms (O4 and O5) that arise from the oxamate ligand, the channels are expected to be quite hydrophilic. Water molecules are enclosed in the channels and linked to the walls of the channels through hydrogen bonds to the carbonyl O atoms (O4···O*W*2 and O5···O*W*1). In addition, these water molecules are hydrogen bonded to one another to form helix-like
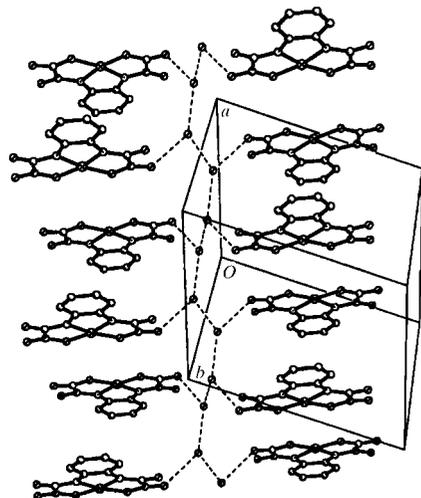
Figure 4
Side view of the hydrogen-bonded chain of water molecules included in a channel. For clarity, [Ni(*meso*-cth)]$^{2+}$ has been omitted and only one position of the disordered water molecules is shown.

chains along the channels (Fig. 4), the average O···O distance being about 2.81 Å. Taking into consideration these hydrogen bonds involving water molecules, the structure may be described as a three-dimensional hydrogen-bonded network.

In conclusion, we can describe an unusual supramolecular microporous three-dimensional architecture assembled *via* the concurrent action of hydrogen bonds and ionic interactions. The material contains two different transition metal complexes as building blocks. Recently, increasing efforts have been directed towards incorporating transition metal ions into hydrogen-bonded networks, in hopes of imparting new magnetic, electronic and optical properties to supramolecules (Burrows *et al.*, 1995; Tadokoro *et al.*, 1999; Braga *et al.*, 1998). Obviously, the introduction of two (or more) different transition metal chromophores into hydrogen-bonded networks may also lead to interesting properties. However, the diamagnetic nature of the nickel(II) ions in the present material precludes magnetic investigation in relation to magnetic interaction through hydrogen bonds.

Figure 3
Top view of the water-filled channel down the *a* axis. Only one position of the disordered water molecule is shown for clarity.

Experimental

The oxamatonickel(II) complex $Na_2[Ni(opba)]\cdot 3H_2O$ was synthesized by a modified procedure analogous to that used for the preparation of $Na_2[Cu(opba)]\cdot 3H_2O$ (Stumpf *et al.*, 1993) and the tetraazamacrocyclic Ni^{II} complex [Ni(*meso*-cth)](ClO₄)₂ was prepared according to the literature method of Tait & Bush (1978). [Ni(*meso*-cth)][Ni(opba)]·2H₂O, (I), was obtained as red–orange crystals by slow diffusion between an aqueous solution (20 ml) of $Na_2[Ni(opba)]\cdot 3H_2O$ (0.123 g, 0.3 mmol) and an acetonitrile solution (20 ml) of [Ni(*meso*-cth)](ClO₄)₂ (0.163 g, 0.3 mmol) in an H-shaped tube.

Crystal data

$[Ni(C_{16}H_{36}N_4)][Ni(C_{10}H_4N_2O_6)]\cdot 2H_2O$	$Z = 2$
$M_r = 686.09$	$D_x = 1.542$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.0460 (8)$ Å	Cell parameters from 4890
$b = 12.4964 (10)$ Å	reflections
$c = 12.7901 (10)$ Å	$\theta = 2.3–25.0°$
$\alpha = 92.488 (2)°$	$\mu = 1.33$ mm^{-1}
$\beta = 110.247 (2)°$	$T = 298 (2)$ K
$\gamma = 99.408 (2)°$	Prism, orange
$V = 1477.5 (2)$ Å^3	$0.30 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	5173 independent reflections
ω scans	4408 reflections with $I > 2\sigma(I)$
Absorption correction: empirical	$R_{int} = 0.015$
(*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
$T_{min} = 0.691$, $T_{max} = 0.878$	$h = -11 \rightarrow 8$
6157 measured reflections	$k = -14 \rightarrow 14$
	$l = -10 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 0.3612P]$
$wR(F^2) = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
5173 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
411 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ni1—N3	1.947 (2)	O2—C3	1.293 (4)
Ni1—N4	1.957 (2)	O3—C4	1.237 (3)
Ni2—N6	1.951 (2)	O5—C2	1.226 (3)
Ni2—N5	1.961 (2)	O4—C3	1.219 (3)
Ni3—N2	1.8159 (19)	O6—C1	1.228 (3)
Ni3—N1	1.819 (2)	N1—C1	1.325 (3)
Ni3—O2	1.8790 (18)	N2—C4	1.325 (3)
Ni3—O1	1.8935 (18)	C1—C2	1.539 (4)
O1—C2	1.293 (4)	C3—C4	1.549 (4)
N3—Ni1—N4	93.79 (9)	C3—O2—Ni3	112.25 (17)
N6—Ni2—N5	93.68 (9)	C1—N1—Ni3	116.85 (18)
N2—Ni3—N1	86.54 (9)	C10—N1—Ni3	114.14 (15)
N2—Ni3—O2	86.58 (9)	C4—N2—Ni3	116.79 (17)
N1—Ni3—O2	173.10 (9)	C5—N2—Ni3	114.28 (15)
N2—Ni3—O1	172.77 (9)	N1—C1—C2	108.8 (2)
N1—Ni3—O1	86.25 (9)	O1—C2—C1	116.0 (2)
O2—Ni3—O1	100.62 (9)	O2—C3—C4	115.3 (2)
C2—O1—Ni3	111.56 (16)	N2—C4—C3	109.0 (2)

One of the water molecules is disordered, and two fractional oxygen sites (OW2 and OW2′), with occupancy factors of 0.5, were refined. The H atoms of all the amino groups and one H atom of one

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW1—H1W$\cdots$O5	0.89 (4)	2.13 (4)	2.917 (5)	147 (4)
N3—H3N$\cdots$O1^i	0.91 (2)	2.09 (2)	2.955 (3)	159 (2)
N4—H4N$\cdots$O2^i	0.91 (2)	2.01 (2)	2.918 (3)	175 (3)
N5—H5N$\cdots$O6^{ii}	0.90 (2)	2.11 (2)	2.944 (3)	153 (2)
N6—H6N$\cdots$O3^{iii}	0.90 (2)	2.11 (2)	2.897 (3)	145 (2)
OW2$\cdots$O4			2.855 (5)	
OW2′$\cdots$O4^{iii}			2.881 (8)	
OW1$\cdots$OW1^{iv}			2.778 (6)	
OW1$\cdots$OW2^v			2.836 (7)	
OW1$\cdots$OW2′^{v}			2.904 (9)	
OW2$\cdots$OW2^{iii}			2.79	
OW2′$\cdots$OW2′^{iii}			2.74	

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

water molecule (OW1) were located in the difference Fourier map. The other water H atoms were not added, and H atoms bound to carbon were located geometrically. H atoms were refined isotropically. The C1—C2 and C3—C4 distances are consistent with the Csp^2—Csp^2 bond distance in other oxamate complexes in the literature (see, for example, Cervera *et al.*, 1998).

Data collection: *SMART*1000 *Software* (Bruker, 1998); cell refinement: *SMART*1000 *Software*; data reduction: *SAINT* (Bruker, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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