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(*meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N)nickel(II) [N,N-*o*-phenylenebis(oxamato)-κ^4O,N,N',O']-cuprate(II) dihydrate

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In the title compound, $[\mathrm{Ni(C_{16}H_{36}N_4)}][\mathrm{Cu(C_{10}H_4N_2O_6)}]\cdot 2H_2O$, the two complex ions, $[\mathrm{Ni}(meso\text{-cth})]^{2+}$ (*meso*-cth is *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $[\mathrm{Cu(opba)}]^{2-}$ [opba is *o*-phenylenebis(oxamate)] are hydrogen bonded to each other, resulting in two-dimensional neutral supramolecular sheets. The sheets stack, generating one-dimensional channels filled by water molecules. The Ni atoms lie on special positions of $\overline{1}$ site symmetry, with two half-cations in the asymmetric unit.

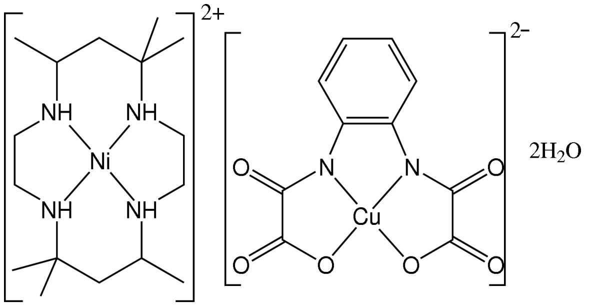
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.029
wR factor = 0.084
Data-to-parameter ratio = 12.8

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

Comment

Supramolecular architectures assembled *via* intermolecular non-covalent interactions are of considerable interest and hydrogen bonds, which combine directionality, selectivity and strength, are a powerful intermolecular force for supramolecular assembly; a large variety of hydrogen-bonded networks has been constructed from organic and metal-organic building blocks (Roesky & Andruh, 2003; Beatty, 2003; Braga *et al.*, 1998; Burrows *et al.*, 1995). In this paper, we describe a hydrogen-bonded heterobimetallic framework built from $[\mathrm{Ni}(meso\text{-cth})]^{2+}$ (*meso*-cth is *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $[\mathrm{Cu(opba)}]^{2-}$ [opba is *ortho*-phenylenebis(oxamate)]. The compound, (I), has the formula $[\mathrm{Ni}(meso\text{-cth})][\mathrm{Cu(opba)}]\cdot 2H_2O$.



(I)

In the $[\mathrm{Cu(opba)}]^{2-}$ anion, the Cu atom is ligated by two deprotonated amido N atoms and two carboxylate O atoms with a distorted square-planar geometry (Fig. 1). Consistent with the greater basicity of the deprotonated amido nitrogen donors, the Cu—N distances are shorter than the Cu—O ones. In the $[\mathrm{Ni}(meso\text{-cth})]^{2+}$ cations, each Ni atom resides on an inversion center and is tetracoordinated by the four amino N atoms of the macrocyclic ligand, with a strictly planar geometry.

All amino groups in the cation and all O atoms in the anion are involved in hydrogen bonding (Table 2). The two sets of crystallographically independent cations adopt different

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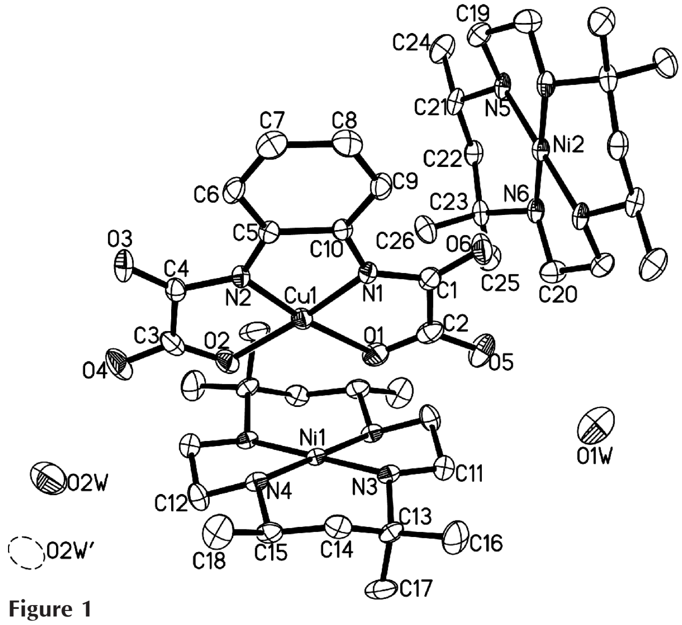

Figure 1
Perspective view of the building blocks in the title compound (30% probability displacement ellipsoids). The minor component of the disordered water molecule is shown as a dashed ellipse. H atoms have been omitted.

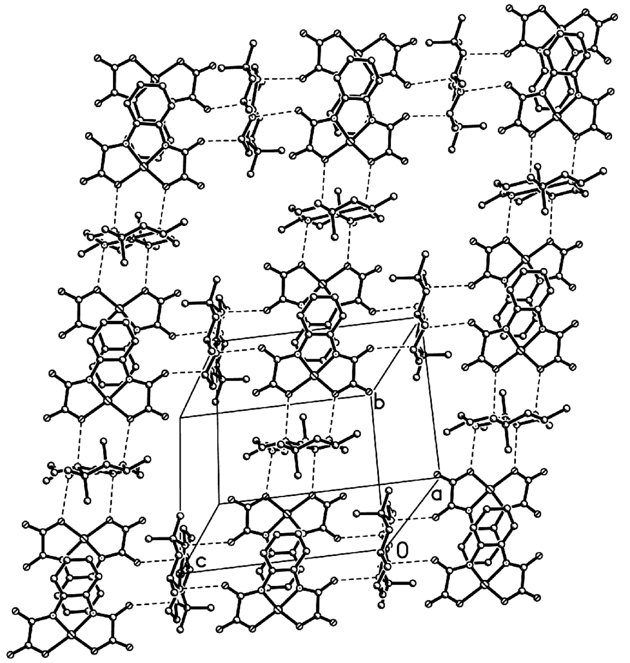

Figure 2
Perspective view of the hydrogen-bonded sheet. Hydrogen bonds are shown as dashed lines.

hydrogen bonding modes. The Ni1 cation is linked to two $[Cu(opba)]^{2-}$ anions through two *DD–AA* double hydrogen bonds between amino groups (*D*) and the coordinated O atoms (*A*) of carboxylate groups (N3···O1 and N4···O2); the Ni2 cation is linked to four anions by four single hydrogen bonds to amido O atoms (N6···O3^{i} and N5···O6^{ii}, Table 2). Therefore, each anion is linked to three cations *via* four hydrogen bonds. These hydrogen bonds arrange the two different complex ions in space to result in a neutral extended two-dimensional heterobimetallic sheet parallel to the $(\bar{1}10)$ plane (Fig. 2). The sheet contains open cavities, each of which is defined by four complex anions and four complex cations connected through 12 N—H···O hydrogen bonds. The sheets are stacked along the *a* axis, resulting in one-dimensional channels. Enclosed within the channels are water molecules, half of which are disordered. The water molecules interact with the channel walls by forming hydrogen bonds [O4···O2*w* (or O2*w*′) and O5···O1*w*] with the carbonyl O atoms of the $[Cu(opba)]^{2-}$ anions.

Incorporating transition metal ions into hydrogen-bonded networks has attracted much attention due to the promise of introducing new magnetic, electronic and optical properties into supramolecules (Burrows *et al.*, 1995; Tadokoro *et al.*, 1999; Braga *et al.*, 1998). This study shows that one can incorporate two (or more) different transition metal chromophores into a hydrogen-bonded network.

Experimental

The starting materials, $Na_2[Cu(opba)]\cdot 3H_2O$ and [Ni(*meso*-cth)]$(ClO_4)_2$, were synthesized according to literature methods (Stumpf *et al.*, 1993; Tait & Bush, 1978). [Ni(*meso*-cth)][Cu(opba)]$\cdot 2H_2O$ was obtained as red crystals by slow diffusion between an aqueous solution (20 ml) of $Na_2[Cu(opba)]\cdot 3H_2O$ (0.124 g, 0.3 mmol) and an acetonitrile solution (20 ml) of [Ni(*meso*-cth)]$(ClO_4)_2$ (0.163 g, 0.3 mmol) in an H-shaped tube.

Crystal data

$[Ni(C_{16}H_{36}N_4)][Cu(C_{10}H_4N_2O_6)]\cdot 2H_2O$
$M_r = 690.92$
Triclinic, $P\bar{1}$
$a = 10.0629\ (8)$ Å
$b = 12.4020\ (8)$ Å
$c = 12.8630\ (8)$ Å
$\alpha = 92.241\ (5)^\circ$
$\beta = 110.245\ (5)^\circ$
$\gamma = 99.343\ (7)^\circ$
$V = 1478.26\ (18)$ Å^3

$Z = 2$
$D_x = 1.552$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 52 reflections
$\theta = 4.8$–13.1°
$\mu = 1.41$ mm^{-1}
$T = 293\ (2)$ K
Prism, red
0.32 × 0.25 × 0.20 mm

Data collection

Siemens *P*4 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.660$, $T_{max} = 0.755$
6239 measured reflections
5202 independent reflections
3616 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$
$\theta_{max} = 25.0^\circ$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.084$
$S = 1.02$
5202 reflections
407 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 3.4692P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.895 (3)	Ni1—N3	1.941 (3)
Cu1—N2	1.887 (3)	Ni1—N4	1.959 (3)
Cu1—O1	1.959 (3)	Ni2—N5	1.959 (3)
Cu1—O2	1.936 (2)	Ni2—N6	1.949 (3)
N1—Cu1—N2	83.86 (12)	O1—Cu1—O2	105.14 (12)
N1—Cu1—O1	84.83 (12)	N3—Ni1—N4	93.72 (12)
N1—Cu1—O2	169.13 (12)	N3—Ni1—N4^{i}	86.28 (12)
N2—Cu1—O1	168.43 (12)	N5—Ni2—N6	93.62 (12)
N2—Cu1—O2	85.96 (11)	N5—Ni2—N6^{ii}	86.38 (12)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*n*···O1	0.91	2.05	2.923 (4)	161
N4—H4*n*···O2	0.91	2.02	2.924 (4)	176
N6—H6*n*···O3^{iii}	0.91	2.09	2.894 (4)	148
N5—H5*n*···O6^{ii}	0.91	2.11	2.962 (4)	156
O1*w*—H1*w*···O5	0.841 (10)	2.25 (5)	2.891 (5)	134 (6)
O2*w*—H3*w*···O4	0.838 (10)	2.01 (2)	2.838 (7)	168 (10)
O2*w*′—H4*w*···O4^{iv}	0.848 (10)	2.14 (2)	2.884 (10)	146 (4)

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

One of the water molecules is disordered over two sites, with refined occupancies of 0.592 (5) (O2*w*) and 0.408 (5) (O2*w*′). The H atoms bound to carbon were positioned geometrically and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å and $U_{\rm iso}$(H) values equal to $1.5U_{\rm eq}$(C) (methyl) or $1.2U_{\rm eq}$(C) (others). The methyl groups were allowed to rotate freely about the C—C bond. The amino H atoms were initially located in a difference Fourier map and allowed to ride on their parent atoms, with an N—H distance of 0.91 Å and $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(N). The water H atoms were initially located in a difference map and refined with the O—H distance restrained to 0.85 (1) Å. Only one H atom was located and refined for O1*w*. The C1—C2 and C3—C4 distances (1.56 Å) are comparable to the bond distances in related oxamate complexes in the literature [see, for example, Gao *et al.* (2001) and Cervera *et al.* (1998)].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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