metal-organic compounds

Aqua-2κO-μ-{N,N′-bis[2-(dimethylamino)ethyl]oxamidato(2–)}-1κ²O,O′:2κ⁴N,N′,N″,N‴-bis(4,4′-dimethyl-2,2′-bipyridine-1κ²N,N′)-copper(II)nickel(II) bis(perchlorate) methanol hemisolvate

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In the crystal structure of the title complex, [CuNi(C$_{10}$H$_{20}$N$_4$O$_2$)(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)](ClO$_4$)$_2$·0.5CH$_4$O or [CuNi(dmaeoxd)(phen)$_2$(H$_2$O)](ClO$_4$)$_2$·0.5CH$_3$OH {H$_2$dmaeoxd is N,N′-bis[2-(dimethylamino)ethyl]oxamide and phen is 1,10-phenanthroline}, the deprotonated dmaeoxd^{2-} ligand is in a *cis* conformation and bridges the Cu^{II} and Ni^{II} atoms. The Cu^{II} atom is located in a slightly distorted square-based pyramidal environment, while the Ni^{II} atom is in an irregular octahedral environment. The binuclear Cu–Ni units interact with each other *via* π–π interactions, which results in an extended chain along the *b* axis.

Comment

The study of polynuclear complexes is a fundamental requirement not only for gaining insight into the pathways of electron transfer in biological systems, but also for obtaining information about designing and synthesizing molecular-based ferromagnets and for investigating the spin-exchange mechanism between paramagnetic metal ions (Benelli & Gatteschi, 2002; Kahn *et al.*, 1999; Winpenny, 1998). Compared with the number of studies dealing with homopolynuclear complexes, relatively few studies dealing with heteropolynuclear complexes have been reported to date, owing to the relative difficulty of synthesizing new compounds. Against this background, we selected N,N′-bis[2-(dimethylamino)ethyl]-oxamide (H$_2$dmaeoxd) as a polydentate ligand to synthesize the title heterobinuclear Cu^{II}Ni^{II} complex, (I), formulated as [Cu(dmaeoxd)(H$_2$O)Ni(phen)$_2$](ClO$_4$)$_2$·0.5CH$_3$OH (phen is 1,10-phenanthroline), and report its crystal structure here.

Compound (I) consists of a [Cu(dmaeoxd)(H$_2$O)Ni-(phen)$_2$]$^{2+}$ cation, one-half of a methanol molecule and two

uncoordinated perchlorate anions. A view of the compound is depicted in Fig. 1 and selected bond lengths and angles are listed in Table 1. The deprotonated dmaeoxd^{2-} ligand exhibits a *cisoid* conformation and bridges the Cu^{II} and Ni^{II} atoms,

(I)
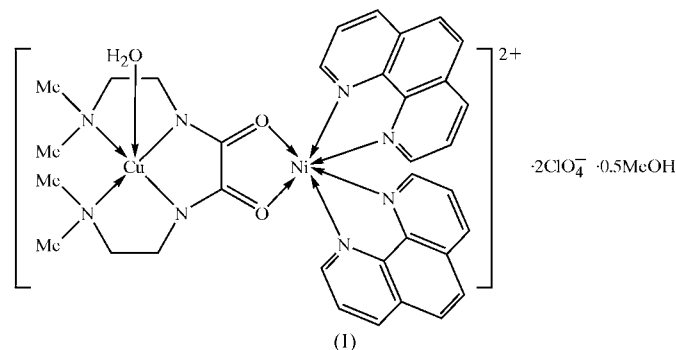
with a Cu···Ni distance of 5.3424 (13) Å. Within the bridging oxamide fragment, the C—O and C—N bonds have partial double-bond character [N2—C5 = 1.303 (6) Å and N3—C6 = 1.307 (6) Å, and C5—O2 = 1.262 (6) Å and C6—O3 = 1.268 (5) Å], while the C5—C6 bond of 1.526 (7) Å is identical to the standard value for a single bond (1.53 Å; Allen *et al.*, 1987). These bonds are similar to those in many other oxamidate complexes (Lloret *et al.*, 1989; Real *et al.*, 1993). The Cu and Ni atoms are displaced towards the same side of the planar bridge plane between them by 0.095 (5) and 0.037 (5) Å, respectively.

Atom Cu1 is in square-based pyramidal geometry, with the equatorial plane built by an N$_2$O$_2$ donor set and the pyramidal apex occupied by a weakly coordinated water molecule [Cu1—O1 = 2.447 (5) Å]. The Cu atom is displaced by 0.207 (2) Å from the basal least-squares plane toward atom O1. The bridging ligand coordinates atom Cu1 by forming three five-membered chelate rings. Those formed by the ethylenediamine fragment adopt the twist form, with puck-
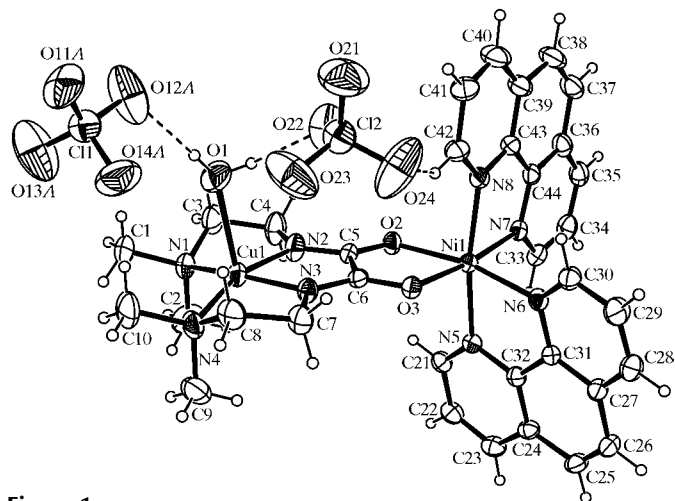

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The methanol molecule and disordered O11B–O14B atoms of the perchlorate anion have been omitted for clarity.

ering parameters (Cremer & Pople, 1975) of $Q = 0.448 (6)$ Å and $\varphi = 51.6 (7)°$ for the Cu1/N1/C3/C4/N2 chelate ring, and $Q = 0.430 (5)$ Å and $\varphi = 308.9 (7)°$ for the Cu1/N3/C7/C8/N4 chelate ring.

Atom Ni1 is coordinated by four N-donor atoms of two phen molecules and two O atoms of the dmaeoxd ligand. Due to the rigidity of the three bidentate ligands, the hexa-coordinated Ni1 atom has a distorted octahedral geometry. Atoms N5 and N8 are axially coordinated, with an approximately linear N—Ni—N angle [169.06 (15)°]. The equatorial plane is defined by the other four atoms and the mean displacement from this plane is 0.1018 Å. The terminal phen ligands are present in the usual chelating bidentate mode, with
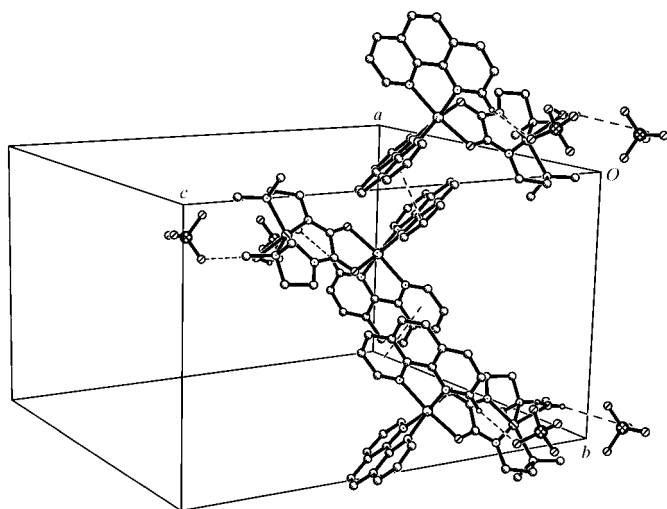

Figure 2
A view showing the ribbon extending along [010] formed by π–π stacking interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.
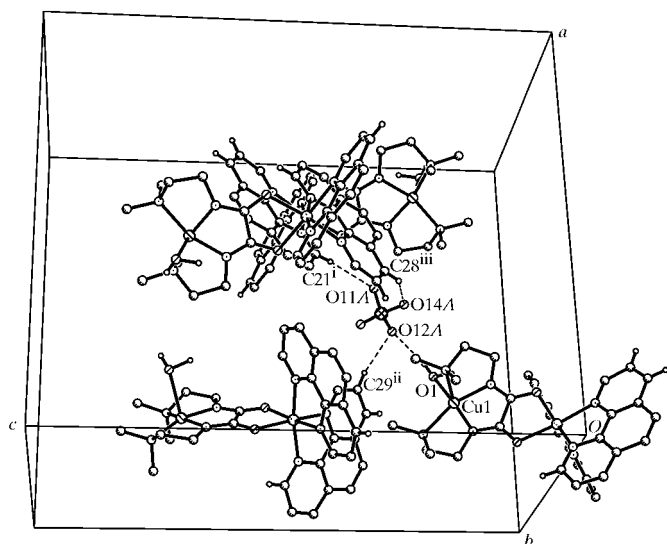

Figure 3
A packing diagram for (I), viewed approximately down [$\bar{1}$30]. Hydrogen bonds are shown as dotted lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.]

bite angles of 80.23 (15) and 79.75 (16)°. The three ligands around the Ni atom are almost perpendicular to each other. The dihedral angles between the oxalate bridge and the phen mean planes are 89.92 (11) and 81.15 (9)°, respectively, while the dihedral angle between the phen mean planes is 83.52 (7)°.

In the crystal structure of (I), the binuclear cation complexes and perchlorate anions are connected through two classical hydrogen bonds, viz. O1—H1W···O12A and O1—H2W···O22, and a nonclassical hydrogen bond, C42—H42···O24, which give rise to an ion triplet. As shown in Fig. 2, these triplets are linked into a one-dimensional ribbon along the b axis by π–π stacking interactions between the phen ligands and those generated by symmetry operations ($-x, -y, -z$) and ($-x, 1 - y, -z$), with shortest separations of 3.266 (6) [atom C22 at ($-x, -y, -z$)] and 3.391 (6) Å [atom C34 at ($-x, 1 - y, -z$)]. Atoms O11–O14 of the perchlorate ion appeared to be disordered and were refined as two groups. If atoms O11–O14 adopt the A position, as shown in Fig. 3, each perchlorate anion will interact with four [Cu(dmaeoxd)-(H₂O)Ni(phen)₂]²⁺ dications via four hydrogen bonds to form a three-dimensional supramolecular hydrogen-bonded network.

Experimental

Crystal data

[CuNi(C₁₀H₂₀N₄O₂)(C₁₂H₈N₂)₂-(H₂O)](ClO₄)₂·0.5CH₄O	$V = 7954 (3)$ Å³
	$Z = 8$
$M_r = 943.90$	Mo $K\alpha$ radiation
Orthorhombic, $Pbca$	$\mu = 1.21$ mm⁻¹
$a = 21.347 (4)$ Å	$T = 298 (2)$ K
$b = 14.852 (3)$ Å	$0.45 \times 0.15 \times 0.08$ mm
$c = 25.087 (5)$ Å	

Data collection

Bruker APEX area-detector diffractometer	40560 measured reflections
	7190 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4662 reflections with $I > 2\sigma(I)$
$T_{min} = 0.611$, $T_{max} = 0.909$	$R_{int} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	58 restraints
$wR(F^2) = 0.186$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 0.57$ e Å⁻³
7190 reflections	$\Delta\rho_{min} = -0.72$ e Å⁻³
567 parameters	

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Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.924 (4)	Ni1—O2	2.069 (3)
Cu1—N2	1.932 (4)	Ni1—N5	2.074 (4)
Cu1—N1	2.058 (5)	Ni1—N6	2.080 (4)
Cu1—N4	2.088 (5)	Ni1—O3	2.086 (3)
Cu1—O1	2.447 (5)	Ni1—N7	2.109 (4)
Ni1—N8	2.062 (4)		
N3—Cu1—N2	82.16 (17)	N8—Ni1—N6	96.40 (15)
N3—Cu1—N1	160.76 (18)	O2—Ni1—N6	167.31 (15)
N2—Cu1—N1	81.99 (19)	N5—Ni1—N6	80.23 (15)
N3—Cu1—N4	83.01 (18)	N8—Ni1—O3	94.51 (14)
N2—Cu1—N4	162.18 (19)	O2—Ni1—O3	81.66 (12)
N1—Cu1—N4	110.3 (2)	N5—Ni1—O3	95.76 (14)
N3—Cu1—O1	94.96 (18)	N6—Ni1—O3	88.09 (14)
N2—Cu1—O1	96.55 (19)	N8—Ni1—N7	79.75 (16)
N1—Cu1—O1	97.61 (19)	O2—Ni1—N7	95.05 (14)
N4—Cu1—O1	94.51 (18)	N5—Ni1—N7	90.20 (15)
N8—Ni1—O2	91.88 (15)	N6—Ni1—N7	95.88 (15)
N8—Ni1—N5	169.06 (15)	O3—Ni1—N7	173.33 (14)
O2—Ni1—N5	93.31 (14)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$W\cdots$O12A	0.86	2.22	3.081 (17)	173
O1—H2$W\cdots$O22	0.85	2.28	3.060 (8)	153
C21—H21$\cdots$O11A^{i}	0.93	2.45	3.280 (10)	148
C28—H28$\cdots$O14A^{ii}	0.93	2.59	3.346 (11)	138
C29—H29$\cdots$O12A^{iii}	0.93	2.43	3.266 (14)	150
C42—H42$\cdots$O24	0.93	2.58	3.340 (9)	139

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

The methanol solvent molecule was treated with a constrained site occupancy of 0.5. The positions of the H atoms of the methanol molecule were not located. Water H atoms were found in a difference Fourier map and were treated as riding, with a fixed U_{iso}(H) value of 0.08 Å^2. The remaining H atoms were placed in calculated positions, with C—H distances of 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and refined in riding mode, with U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C). The methyl groups were allowed to rotate freely around the C—N bond. Atoms O11–O14 of the perchlorate ion appeared to be disordered and were refined as two groups sharing the same Cl1 atom (occupancy factors = 0.7 and 0.3).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXL97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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