

(Aqua-2κO)bis(2,2'-bipyridine-1κ²N,N'){μ-N-[3-(dimethylamino)propyl]-N'-(2-oxidophenyl)oxamidato(3-)-1:2κ²O,O':κ⁴O'',N,N',N''}]copper(II)nickel(II) perchlorateXi-Teng Yue,^a Jin-Ju Nie,^b Yan-Tuan Li,^{b*} Zhi-Yong Wu^b
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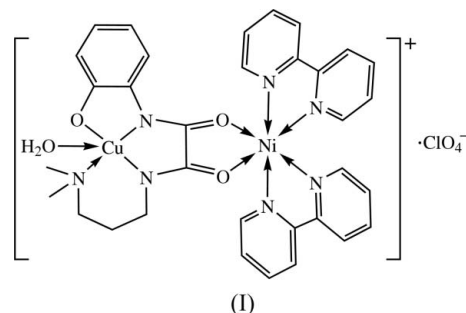
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The title complex, [CuNi(C₁₃H₁₆N₃O₃)(C₁₀H₈N₂)₂(H₂O)]·ClO₄, has a *cis*-oxamide-bridged heterobinuclear cation, with a Cu···Ni separation of 5.3297 (6) Å, counterbalanced by a disordered perchlorate anion. The Cu^{II} and Ni^{II} cations are located in square-pyramidal and octahedral coordination environments, respectively. The complex molecules are assembled into a three-dimensional supramolecular structure through hydrogen bonds and π–π stacking interactions. The influence of the two types of metal cation on the supramolecular structure is discussed.

Comment

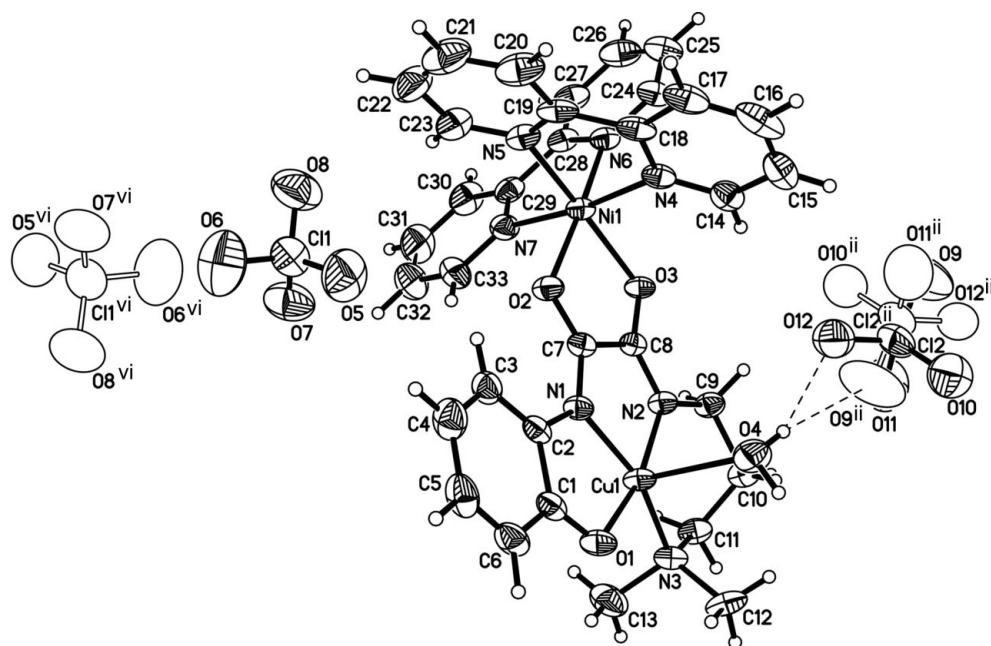
The design and synthesis of heterometallic systems with two different paramagnetic centres has been an active field of research (Li, Wu *et al.*, 2004; Tercero *et al.*, 2002; Wang *et al.*, 2004; Willett *et al.*, 1985). Interest in this field is aimed at understanding the nature of electronic exchange coupling through multi-atom bridging ligands, and mimicking the active sites and functions of biological substances, as well as designing and preparing new magnetic materials (Baron *et al.*, 1996; Li, Yan & Guan, 2004). One of the best strategies for constructing heterobinuclear species is the 'complex as ligand' approach, using a complex which contains a potential donor group capable of coordinating to another metal cation (Cronin *et al.*, 1999; Fukita *et al.*, 2001). (*N,N'*-Disubstituted oxamide)copper(II) mononuclear complexes are a very suitable type of ligand for designing heterometallic species, due to their ability to coordinate to metal cations as bidentate ligands through their carbonyl O atoms (Ruiz *et al.*, 1999). To date, several heterobinuclear complexes based on symmetric *N,N'*-disubstituted oxamide ligands with interesting magnetic

properties have been reported (Brewer *et al.*, 2001; Li, Wu *et al.*, 2004; Li, Yan & Guan, 2004; Nakatani *et al.*, 1989, 1991; Nie *et al.*, 2010; Sun *et al.*, 2007; Tang *et al.*, 2002, 2003; Wang *et al.*, 2004). In contrast, little work has been carried out on assemblies of heterobinuclear complexes containing asymmetric *N,N'*-disubstituted oxamides (Larionova *et al.*, 1997; Pei *et al.*, 1991), owing to the difficulty of their synthesis. To the best of our knowledge, no heterobinuclear copper(II)–nickel(II) complex bridged by an asymmetric *N,N'*-disubstituted oxamide containing a phenolate group has hitherto been reported.



Recently, Gao & Wang (2010) reported a binuclear copper(II) complex bridged by *N*-[3-(dimethylamino)propyl]-*N'*-(2-oxidophenyl)oxamidate (pdmapo) and end-capped with 1,10-phenanthroline (phen), namely [Cu(pdmapo)(H₂O)Cu(phen)]NO₃, (II), but in order to provide more examples of pdmapo-bridged binuclear complexes and to better understand the factors affecting the supramolecular structures of these complexes, it is necessary to synthesize a series of binuclear complexes of essentially the same structure except for the metal cations. In this paper, we have selected the mononuclear copper(II) complex, Na[Cu(pdmapo)]·1.5H₂O, as the bridging ligand and 2,2'-bipyridine (bpy) as the terminal ligand, to synthesize the title new heterobinuclear copper(II)–nickel(II) complex, formulated as [Cu(pdmapo)(H₂O)Ni(bpy)₂]ClO₄, (I), and we compare the crystal structure of (I) with that of (II).

Compound (I) consists of a heterobinuclear [Cu(pdmapo)(H₂O)Ni(bpy)₂]⁺ cation and an uncoordinated perchlorate anion (Fig. 1). The complex cation can be described as a *cis*-oxamide-bridged binuclear Cu^{II}–Ni^{II} fragment, in which the Cu^{II} and Ni^{II} cations are at the inner and *exo* sites of the oxamide bridge, respectively. The Cu···Ni separation is 5.3297 (6) Å. The Cu^{II} cation has an {N₃O₂} square-pyramidal geometry with a τ value of 0.1 (Addison *et al.*, 1984). The basal plane is defined by four coordination atoms from the oxamide ligand, with a maximum deviation from the least-squares plane of 0.1630 (15) Å (for atom N1). The apical position is occupied by a water molecule (O4), with a Cu–O bond length of 2.456 (3) Å (Table 1). The Cu^{II} cation is displaced 0.1976 (15) Å from the basal plane. The Cu1–N1 and Cu1–N2 bonds are shorter than Cu1–N3, which is consistent with the stronger donor abilities of N atoms in *sp*² hybridization than *sp*³ (Jubert *et al.*, 2002). The Ni^{II} cation is chelated by two *exo* O atoms of the oxamide group and by two bpy


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The disordered parts of the equally populated perchlorate anions have been drawn with different styles for clarity. [Symmetry codes: (ii) $-x + 1, -y + 1, -z$; (vi) $-x, -y + 2, -z + 1$.]

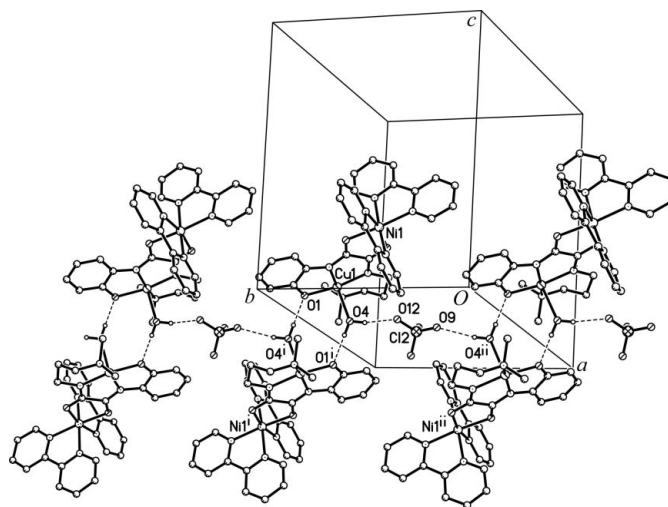
terminal ligands, *viz.* in an $\{N_4O_2\}$ octahedral environment. The equatorial plane is composed of atoms O2, N4, N6 and N7, with a maximum displacement of 0.0667 (14) Å (for atom N7); the Ni^{II} cation deviates from this plane by 0.0280 (14) Å.

The oxamide ligand (pdmap^{3-}) chelates the Cu^{II} and Ni^{II} cations with bite angles of 83.15 (10) and 81.98 (8)°, respectively. Within the bridging oxamide fragment, the C7–O2 [1.260 (4) Å], C8–O3 [1.274 (3) Å], C7–N1 [1.313 (4) Å] and C8–N2 [1.305 (4) Å] bond lengths imply partial double-bond character, similar to those in many other oxamate complexes (Lloret *et al.*, 1989; Real *et al.*, 1993). The six-membered chelate ring formed by the propylenediamine fragment adopts a screw-boat conformation, with puckering parameters (Cremer & Pople, 1975) of $Q = 0.649$ (4) Å, $\theta = 108.8$ (4)° and $\varphi = 23.4$ (3)°, while all other chelate rings around the two metal cations are almost planar. The two bpy ligands around the Ni^{II} cation are in a *cis* arrangement.

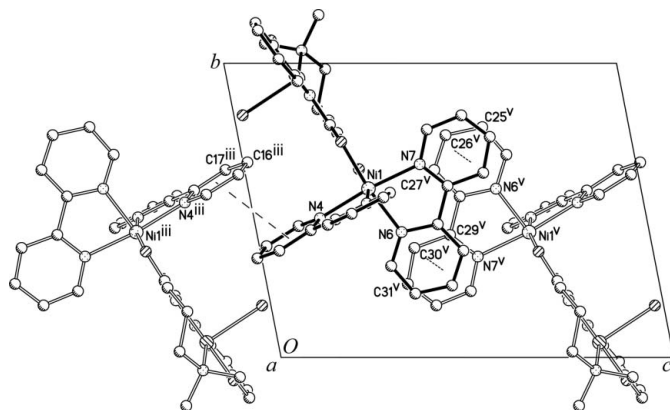
As shown in Fig. 2, complex cations related by the symmetry operation $(-x + 1, -y + 2, -z)$ [symmetry code (i)] are associated into pairs by hydrogen bonds between the coordinated water molecule and phenolic O atoms (Table 2). In this arrangement, a Cu1...Cu1ⁱ separation of 5.5492 (9) Å is observed. These pairs are, in turn, joined by the disordered Cl2 perchlorate anions, resulting in a one-dimensional hydrogen-bonded structure parallel to the *b* axis.

There are also offset aromatic stacking interactions between the bpy ligands, linking the chains together (Fig. 3). The pyridine ring containing atom N4 and that at $(-x, -y + 1, -z)$ [symmetry code (iii)] are parallel, with a centroid-centroid distance of 3.641 (2) Å and a slippage of 1.500 Å. The smallest separation is between atom C16ⁱⁱⁱ and the reference

py(N4) ring [3.315 (5) Å]. In addition, another π – π stacking interaction occurs between the bpy ligand containing atoms N6 and N7 and that at $(-x + 1, -y + 1, -z + 1)$ [symmetry code (v)]. The N6- and N7^v-containing rings have a dihedral angle of 3.9 (2)°, with a centroid-centroid distance of 3.770 (3) Å. The nearest separations are 3.345 (5) [C30^v to py(N6)] and 3.357 (5) Å [C27^v to py(N7)]. The nonclassical C–H...O hydrogen bonds given in Table 2 also play a role in the supramolecular structure. These interactions link the ions


Figure 2

A view of the one-dimensional hydrogen-bonded structure of (I), parallel to the *b* axis. Only one of the two half-occupied perchlorate anions is shown for clarity. [Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x + 1, -y + 1, -z$.]


Figure 3

The π - π stacking interactions in (I), viewed down the a axis. H atoms and perchlorate anions have been omitted for clarity. [Symmetry codes: (iii) $-x, -y + 1, -z$; (v) $-x + 1, -y + 1, -z + 1$.]

into centrosymmetric pairs. Together with the π - π stacking, a two-dimensional layer parallel to the (010) plane can be constructed. When the classical and nonclassical hydrogen bonds are considered together, a three-dimensional supramolecular structure is completed in the crystal structure.

As already stated, the same bridging ligand, *cis*-pdmapo³⁻, has also been used in complex (II) with a binuclear copper(II) cation (Gao & Wang, 2010), in which the Cu^{II} cations at the inner and *exo* sites of the pdmapo³⁻ anion are in square-planar and square-pyramidal environments, respectively. The *exo* Cu^{II} cation coordinates to a phen ligand and a water molecule. However, in complex (I), the coordinated water molecule is transferred to the inner Cu^{II} cation. In addition, the *exo* metal cation in (I), nickel(II), has two terminal bpy ligands because Ni^{II} cations usually prefer six coordination to five, in contrast to the five-coordinate *exo* Cu^{II} cation in (II). These differences lead to distinct supramolecular structures. Complex (I) has a three-dimensional supramolecular structure of classical hydrogen bonding and π - π stacking interactions depicted as above. In complex (II), instead (according to our own analysis of the freely available crystallographic data), there is just a one-dimensional hydrogen-bonded chain parallel to [101]; the cations give rise to dimers through classical hydrogen bonds. The dimers and nitrate anions further build up a two-dimensional structure extending along the (010) plane by C-H...O hydrogen bonds and π - π stacking interactions. This is a clear example of how metal cations may play an important role in the way supramolecular structures are built up.

Experimental

All chemicals were of analytical reagent grade. Na[Cu(pdmapo)]·1.5H₂O was prepared according to the method of Pei *et al.* (1991). The title complex was obtained as follows. A methanol (5 ml) solution of Ni(ClO₄)₂·6H₂O (0.0183 g, 0.05 mmol) was added dropwise to an aqueous solution (5 ml) of Na[Cu(pdmapo)]·1.5H₂O (0.0192 g, 0.05 mmol) with continuous stirring. The mixture was stirred quickly for 0.5 h and then bpy (0.0156 g, 0.1 mmol) in methanol (5 ml) was

Table 1
Selected bond lengths (Å).

Cu1—N1	1.924 (3)	Ni1—O3	2.071 (2)
Cu1—O1	1.975 (2)	Ni1—N7	2.077 (3)
Cu1—N2	1.980 (3)	Ni1—N6	2.077 (3)
Cu1—N3	2.030 (3)	Ni1—N4	2.079 (3)
Cu1—O4	2.456 (3)	Ni1—N5	2.083 (3)
Ni1—O2	2.051 (2)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4A...O1 ⁱ	0.85 (3)	1.92 (2)	2.763 (4)	176 (4)
O4—H4B...O9 ⁱⁱ	0.84 (3)	2.23 (2)	3.087 (18)	167 (4)
O4—H4B...O12	0.84 (3)	2.07 (2)	2.871 (10)	160 (4)
C15—H15...O11 ⁱⁱⁱ	0.93	2.36	3.176 (12)	146
C21—H21...O10 ⁱⁱⁱ	0.93	2.47	3.226 (10)	139
C26—H26...O7 ^{iv}	0.93	2.46	3.322 (8)	154
C27—H27...O3 ^v	0.93	2.49	3.233 (4)	138

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

added dropwise. The solution obtained was stirred at 333 K for 6 h and filtered. Green block-shaped crystals of (I) suitable for X-ray analysis were obtained from the filtrate by slow evaporation at room temperature for 17 d (yield 65%). Elemental analysis calculated for C₃₃H₃₄ClCuN₇NiO₈: C 48.67, H 4.21, N 12.04%; found: C 48.93, H 4.27, N 11.51%.

Crystal data

[CuNi(C ₁₃ H ₁₆ N ₃ O ₃)(C ₁₀ H ₈ N ₂) ₂ ·(H ₂ O)]ClO ₄	$\beta = 109.043 (3)^\circ$
$M_r = 814.37$	$\gamma = 112.911 (3)^\circ$
Triclinic, $P\bar{1}$	$V = 1770.51 (15) \text{ \AA}^3$
$a = 11.4692 (5) \text{ \AA}$	$Z = 2$
$b = 11.8976 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 15.1818 (7) \text{ \AA}$	$\mu = 1.27 \text{ mm}^{-1}$
$\alpha = 92.261 (3)^\circ$	$T = 296 \text{ K}$
	$0.24 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer	15761 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	8178 independent reflections
$T_{\min} = 0.751, T_{\max} = 0.833$	4749 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.131$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
$S = 0.96$	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
8178 reflections	
515 parameters	
45 restraints	

Both perchlorate anions (Cl1 and Cl2) are disordered around inversion centres at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, 1, \frac{1}{2})$, respectively, and correspondingly their occupancies were constrained to 0.5. The Cl—O and O...O distances were restrained by similarity conditions (SADI 0.02 in SHELXL97; Sheldrick, 2008). Water H atoms were found in a difference Fourier map and further refined with restrained distances of O—H = 0.85 (1) Å and H...H = 1.35 (1) Å; their isotropic displacement parameters were refined freely. Other H atoms were

placed in calculated positions, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The methyl groups were allowed to rotate freely around the C—N bond.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3135). Services for accessing these data are described at the back of the journal.

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