

μ -{*N,N'*-Bis[2-(dimethylamino)ethyl]-oxamidato(2-)}-1 κ^2 O,*O'*:2 κ^4 *N,N',-N'',N'''*-bis(4,4'-dimethyl-2,2'-bipyridine)-1 κ^2 *N,N'*}dinickel(II) bis(perchlorate)

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Received 25 December 2006

Accepted 18 January 2007

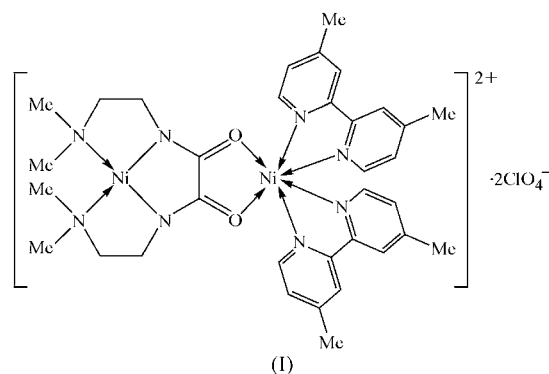
Online 17 February 2007

In the crystal structure of the title complex, [Ni₂(C₁₀H₂₀N₄O₂)(C₁₂H₁₂N₂)₂](ClO₄)₂ or [Ni(dmaeoxd)Ni(dmbp)₂](ClO₄)₂ {H₂dmaeoxd is *N,N'*-bis[2-(dimethylamino)ethyl]-oxamide and dmbp is 4,4'-dimethyl-2,2'-bipyridine}, the deprotonated dmaeoxd²⁻ ligand is in a *cis* conformation and bridges two Ni^{II} atoms, one of which is located in a slightly distorted square-planar environment, while the other is in an irregular octahedral environment. The cation is located on a twofold symmetry axis running through both Ni atoms. The dmaeoxd²⁻ ligands interact with each other *via* C—H...O hydrogen bonds and π - π interactions, which results in an extended chain along the *c* axis.

Comment

There has been great interest in the crystal engineering of self-assembled supramolecular architectures formed through relatively weak C—H...O and π - π stacking interactions (Blake *et al.*, 1999; Lin *et al.*, 2003). Considerable attention has been devoted to metal-polypyridyl complexes (Kalyanasundaram & Grätzel, 1998; Ye *et al.*, 1998), in which the hydrophilic groups are linked *via* hydrogen bonds while the hydrophobic groups are stacked *via* π - π interactions. *N,N'*-Disubstituted oxamidates are well known as versatile bridging ligands, which can afford symmetric and asymmetric oxamidate bridges by the *cis*-*trans* conformational change (Ruiz *et al.*, 1999). Four crystal structures of dinuclear oxamidate-bridged Ni^{II} complexes with the Ni atoms in different coordination geometries have been reported to date, namely [Ni(obbz)-Ni(H₂O)₄].2H₂O, (II) (Chen *et al.*, 1994), [Ni(aeox)-Ni(en)(SCN)₂], (III) (Chen *et al.*, 1994), [Ni(aeox)Ni(phen)₂](ClO₄)₂.3H₂O, (IV) (Wei *et al.*, 1995), and [Ni(apox)-

Ni(phen)₂](ClO₄)₂.CH₃OH.2H₂O, (V) (Jiu *et al.*, 2000) [obbz is deprotonated *N,N'*-bis(2-aminobenzoato)oxamide, aeox is deprotonated *N,N'*-bis(2-aminoethyl)oxamide, en is ethylenediamine, phen is 1,10-phenanthroline and apox is deprotonated *N,N'*-bis(3-aminopropyl)oxamide]. In these complexes, however, the types of hydrogen-bond interactions were not discussed in detail and the π - π stacking was not studied at all. In order to study the supramolecular architecture of this kind of complex, we chose H₂dmaeoxd as a polydentate ligand to synthesize the title binuclear Ni^{II} complex, (I), formulated as [Ni(dmaeoxd)Ni(dmbp)₂](ClO₄)₂, and report its crystal structure here.



Compound (I) consists of an [Ni(dmaeoxd)Ni(dmbp)₂]²⁺ cation 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 dmaeoxd²⁻ ligand exhibits a *cisoid* conformation and bridges two Ni^{II} atoms, with an Ni...Ni distance of 5.2955 (18) Å. A crystallographic twofold axis passes through this Ni...Ni vector and the middle of the C5—C5ⁱ bond [symmetry code: (i) 1 - *x*, *y*,

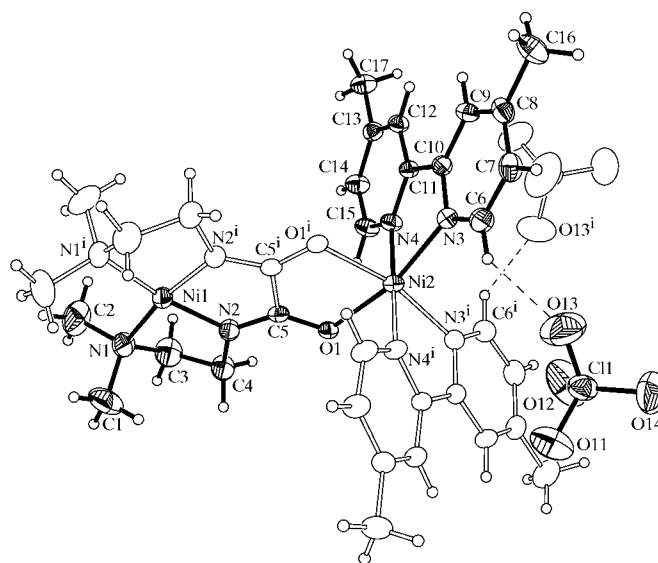
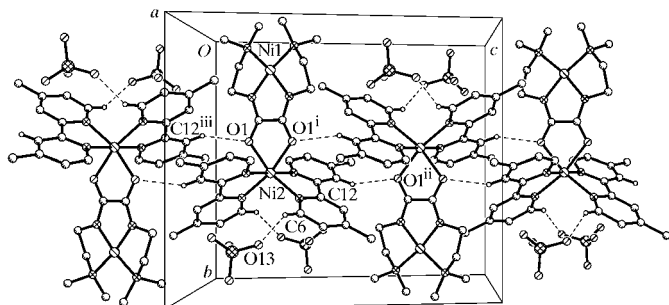


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) 1 - *x*, *y*, $\frac{1}{2}$ - *z*.]


Figure 2

A view showing the ribbon extending along [001], formed by C—H...O hydrogen bonds (dashed lines) and π - π stacking interactions. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x, 1 - y, \frac{1}{2} + z$; (iii) $x, 1 - y, z - \frac{1}{2}$].

$\frac{1}{2} - z$]. Within the bridging oxamide fragment, the C—O and C—N bonds have partial double-bond character [N2—C5 = 1.299 (4) Å and C5—O1 = 1.255 (4) Å], while the C5—C5ⁱ bond of 1.521 (6) Å is identical to the standard value of 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).

Atom Ni1 is coordinated by four N atoms of dmaeoxd²⁻, with the maximum deviation from the coordinated plane being 0.023 (3) Å for atom N2. The Ni1—N2 bond length of 1.853 (3) Å is comparable with the distances between the Ni and amide N atoms in compounds (II)–(V) (1.837–1.895 Å). The Ni1—N1 distance [1.976 (3) Å] is longer than the corresponding distance in compounds (III)–(V), which is perhaps due to the steric hindrance between the two pairs of methyl groups on atom N1. The bridging ligand coordinates atom Ni1 by forming three five-membered chelate rings. Those formed by the ethylenediamine fragment adopt a twist form, with puckering parameters (Cremer & Pople, 1975) $Q = 0.418$ (4) Å and $\varphi = 62.4$ (5)°.

Atom Ni2 is coordinated by four N-atom donors of two dmbp molecules and two O atoms of the dmaeoxd²⁻ ligand. Due to the rigidity of the three bidentate ligands, the hexacoordinated atom Ni2 has a distorted octahedral geometry. Atom N4 and its symmetry-related atom N4ⁱ are axially coordinated, with an approximately linear N—Ni—N angle. The equatorial plane is defined by the other four atoms and the mean displacement from this plane is 0.173 Å. Atom Ni2 lies exactly in the plane. The terminal dmbp ligands are present in the usual chelating bidentate mode, except for the envelope form of the chelate ring on Ni2. The torsion angles Ni2—N3—C10—C11 and Ni2—N4—C11—C10 are -11.2 (4) and 15.5 (4)°, respectively.

As shown in Fig. 2, the binuclear cation complexes and perchlorate anions are connected through a non-classical hydrogen bond, C6—H6...O13 (Table 2), which gives rise to an ion triplet, [Ni(dmaeoxd)Ni(dmbp)₂]²⁺·2ClO₄⁻. These triplets are linked into a one-dimensional ribbon along the *c* axis by a combination of a C12—H12...O1ⁱⁱ [symmetry code:

(ii) $x, 1 - y, \frac{1}{2} + z$] interaction and a π - π stacking interaction between the dmbp ligand and that generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$, with separations of 3.505 (4) [atom C9 at $(1 - x, 1 - y, 1 - z)$] and 3.526 (4) Å [atom C13 at $(1 - x, 1 - y, 1 - z)$].

Experimental

All reagents were of AR grade and were used without further purification. The H₂dmaeoxd ligand was synthesized according to the method of Ojima & Yamada (1970). To a solution of H₂dmaeoxd (0.0230 g, 0.1 mmol) in methanol (10 ml) were added successively piperidine (0.2 mmol) and a solution of Ni(ClO₄)₂·6H₂O (0.0731 g, 0.2 mmol) in methanol (5 ml). After stirring for 20 min, dmbp (0.0368 g, 0.2 mmol) in methanol (5 ml) was added. The reaction mixture was stirred at 333 K for a further 2 h. Orange crystals of the title compound suitable for X-ray analysis were obtained from the solution by slow evaporation at room temperature on the second day (yield 67%). IR (KBr pellet, γ , cm⁻¹): 1649 (*vs*), 1615 (*vs*), 1487 (*m*), 1471 (*s*), 1088 (*vs*), 833 (*m*), 623 (*s*).

Crystal data

[Ni ₂ (C ₁₀ H ₂₀ N ₄ O ₂)(C ₁₂ H ₁₂ N ₂) ₂](ClO ₄) ₂	$Z = 4$
$M_r = 913.05$	$D_x = 1.538 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 19.068$ (6) Å	$\mu = 1.16 \text{ mm}^{-1}$
$b = 13.431$ (4) Å	$T = 298$ (2) K
$c = 15.920$ (5) Å	Block, orange
$\beta = 104.744$ (4)°	$0.45 \times 0.38 \times 0.29 \text{ mm}$
$V = 3943$ (2) Å ³	

Data collection

Bruker APEX CCD area-detector diffractometer	10149 measured reflections
φ and ω scans	3470 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2338 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.612, T_{\max} = 0.716$	$R_{\text{int}} = 0.036$
	$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 5.2848P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.02$	$\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$
3470 reflections	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
256 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	1.976 (3)	Ni2—O1	2.114 (2)
Ni1—N2	1.853 (3)	N2—C5	1.299 (4)
Ni2—N3	2.060 (3)	C5—O1	1.255 (4)
Ni2—N4	2.048 (3)	C5—C5 ⁱ	1.521 (6)
N1—Ni1—N1 ⁱ	106.7 (2)	N3—Ni2—O1 ⁱ	89.60 (10)
N1—Ni1—N2	84.78 (14)	N4—Ni2—O1	90.20 (10)
N2 ⁱ —Ni1—N1	168.43 (14)	N4—Ni2—O1 ⁱ	89.63 (11)
N2 ⁱ —Ni1—N2	83.74 (18)	N4—Ni2—N3	79.31 (11)
O1—Ni2—O1 ⁱ	80.74 (13)	N4—Ni2—N3 ⁱ	100.83 (12)
N3—Ni2—O1	165.81 (10)	N4 ⁱ —Ni2—N4	179.78 (17)
Ni2—N3—C10—C11	-11.2 (4)	Ni2—N4—C11—C10	15.5 (4)

 Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C6—H6...O13	0.93	2.57	3.379 (6)	146
C12—H12...O1 ⁱⁱ	0.93	2.43	3.267 (4)	150

Symmetry code: (ii) $x, -y + 1, z + \frac{1}{2}$.

All 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The CH₃ groups bound to the pyridine rings were allowed to rotate freely around the C—C bond.

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

This project was supported by the National Natural Science Foundation of China (grant No. 20471056).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3088). Services for accessing these data are described at the back of the journal.

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