metal-organic compounds

Bis(ethylenediaminium) bis[oxalohydroxamato(3−)]nickelate(II) dihydrate

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The title compound, $(C_2H_{10}N_2)_2[Ni(C_2HN_2O_4)_2]\cdot 2H_2O$, has an ionic structure containing a centrosymmetric complex 4− anion, charge-balancing ethylenediaminium dications and solvent water molecules. The oxalohydroxamate unit is triply deprotonated and forms five-membered chelate rings with the central Ni ion; the Ni ion lies on an inversion centre. The two hydroxamate O atoms in the complex anion are linked by short intramolecular hydrogen bonds.

Comment

Many mononuclear complexes of transition metals containing additional vacant donor sets and chelate centers are taken as ligands for the building of homo- and heteropolynuclear systems which are widely used in bioinorganic modeling, electron transfer and molecular magnetism (Kokozay & Vassilyeva, 2002; Powell *et al.*, 1995; Goodwin *et al.*, 2000; Kahn, 1993). Polydentate ligands containing hydroxamic groups attract particular attention owing to their potential for their bridging mode of coordination and mediation of very strong magnetic exchange interactions between metal ions analogous to bridging oxime-containing complexes (Colacio *et al.*, 1994). Oxalohydroxamic acid (H_2oxha) is an efficient chelating ligand for Cu^{II} and Ni^{II} ions (Świątek-Kozłowska *et al.*, 2000). Several possible coordination modes of oxha have been realized in metal complexes, as summarized by Świątek-Kozłowska *et al.* (2000) and Huang *et al.* (1991). To date, only complexes containing the doubly deprotonated ligand have been isolated, and one of them, $K_2[Ni(oxha)_2]\cdot 2H_2O$, (II), has been structurally characterized (Świątek-Kozłowska *et al.*, 2000).

The title compound, (I), has an ionic structure containing Ni^{II}-centered complex tetraanions, ethylenediaminium

dications and solvent water molecules (Fig. 1). The Ni^{II} complex anion is centrosymmetric, with a distorted square-planar coordination geometry formed by four N atoms belonging to the deprotonated hydroxamic groups. Thus, the coordinated residues of oxha are triply deprotonated (two N and one O hydroxamic atoms), resulting in non-equivalence of the two hydroxamic functions.
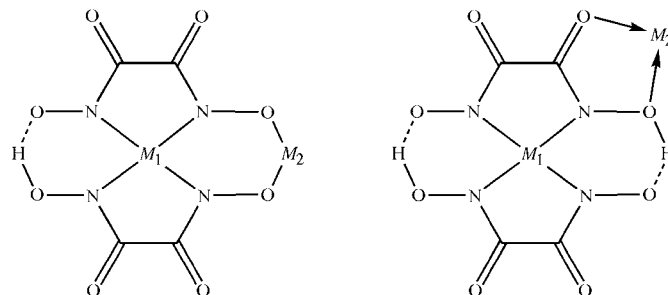
The Ni—N bond lengths (Table 1) are typical for square-planar Ni^{II} complexes with deprotonated amide ligands (Leininger *et al.*, 2000; Hlavica & Lewis, 2001). The bite angles around the central atom deviate from an ideal square-planar configuration [*e.g.* N1—Ni1—N2 = 82.17 (8)°], which is a consequence of the formation of five-membered chelate rings. The latter ring is puckered, with a deviation of the Ni atom from the plane defined by the other four atoms of 0.0376 (1) Å. The C—O, N—O and C—N bond lengths in the coordinated hydroxamate group suggest its existence in the hydroxamic form rather than in the oximic form (Brown *et al.*, 1982).

(I)
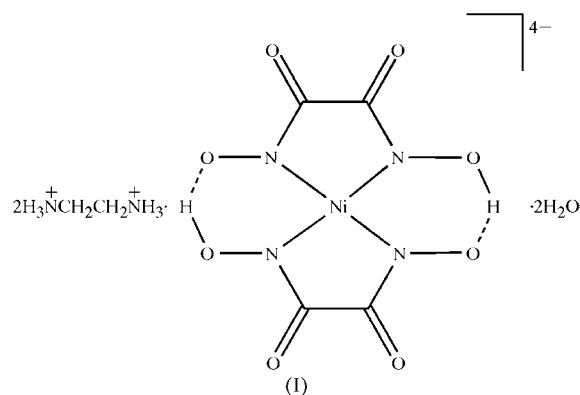
The structure of the complex anion of (I) is similar in its geometrical parameters to that of complex (II) (Świątek-Kozłowska *et al.*, 2000). The principal differences between these compounds are in the charges of the complex anions (4− and 2−, respectively) and in the parameters of the short intramolecular hydrogen bonds between the hydroxamate O atoms. The O3···O4 separations (Table 2) in (I) are significantly shorter than those in (II) [2.64 (3) Å] and close to those observed in typical *cis*-bis(oximate) complexes (Dobosz *et al.*, 1998, 1999).

In the crystal packing, the ethylenediaminium cations are connected to the complex anions through ordinary and bifurcated hydrogen bonds, where NH_3^+ groups act as donors, and the amide O, hydroxamic O, water O and hydroxamic N atoms act as acceptors. In addition, the complex anions are

connected to each other by hydrogen bonds to the water molecules (Table 2). An extensive three-dimensional system of hydrogen bonds results, as shown in Fig. 2.
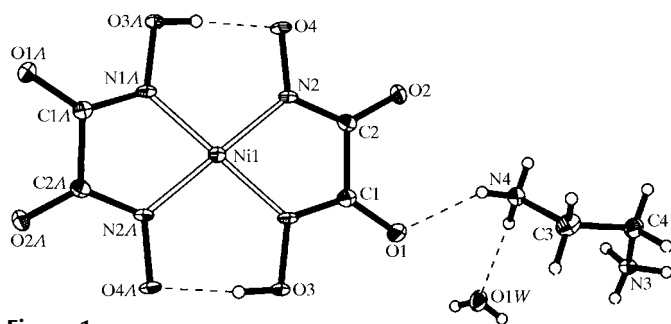

Figure 1
A view of (I), with displacement ellipsoids shown at the 50% probability level. Hydrogen bonds are indicated by dashed lines. Atoms labeled with the suffix A are related to their counterparts by the symmetry operation $(2 - x, 1 - y, 1 - z)$.
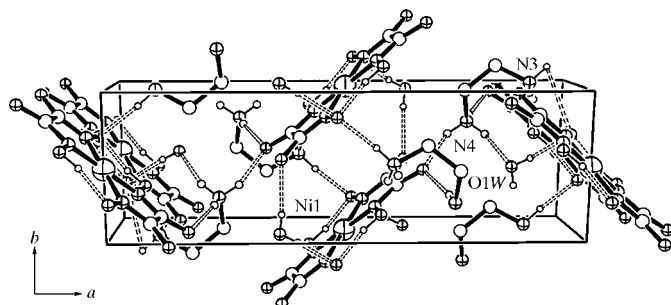

Figure 2
A packing diagram for (I) (projection along the c direction). Hydrogen bonds are indicated by dashed lines. Representative atom labels are shown (see Table 2).

Experimental

$Ni(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1 mmol) was dissolved in water (15 ml) and added to an aqueous solution (15 ml) of H_2oxha (0.240 g, 2 mmol); a solution of ethylenediamine (0.342 ml) in water (15 ml) was added to the resulting blue suspension. The mixture was stirred for 30 min at ambient temperature. The resulting clear solution was left at room temperature for crystallization in air. Bright-red crystals were separated by filtration after 72 h, washed with cold water (10 ml) and dried.

Crystal data

$(C_2H_{10}N_2)_2[Ni(C_2HN_2O_4)_2] \cdot 2H_2O$	$Z = 2$
$M_r = 453.06$	$D_x = 1.694$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.961$ (1) Å	$\mu = 1.16$ mm^{-1}
$b = 17.604$ (4) Å	$T = 100$ K
$c = 8.917$ (2) Å	Needle, red
$\beta = 108.38$ (3)°	$0.25 \times 0.15 \times 0.1$ mm
$V = 888.0$ (4) Å^3	

Data collection

Kuma KM-4 CCD area-detector diffractometer	6046 measured reflections
ω scans	2052 independent reflections
Absorption correction: ψ scan (North *et al.*, 1968)	1936 reflections with $I > 2\sigma(I)$
$T_{min} = 0.74$, $T_{max} = 0.89$	$R_{int} = 0.045$
	$\theta_{max} = 28.4°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 1.6718P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
2052 reflections	$\Delta\rho_{min} = -0.85$ e Å^{-3}
130 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.8621 (17)	O3—N1	1.410 (2)
Ni1—N2	1.8694 (18)	O3—O4^i	2.520 (2)
O1—C1	1.267 (3)	O4—N2	1.402 (2)
O2—C2	1.275 (2)	N1—C1	1.309 (3)
N1—Ni1—N2^i	97.83 (8)	N1—Ni1—N2	82.17 (8)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H13$\cdots$O4^{ii}	0.89	1.84	2.729 (2)	174
N3—H14$\cdots$O3^{iii}	0.89	2.01	2.891 (2)	172
N3—H15$\cdots$O2^{iv}	0.89	1.97	2.799 (2)	154
N4—H24$\cdots$O1^{iii}	0.89	1.98	2.831 (2)	159
N4—H23$\cdots$O1W	0.89	2.01	2.834 (2)	154
N4—H25$\cdots$O1	0.89	1.97	2.744 (2)	145
O1W—H1$W\cdots$O2^v	0.73	2.05	2.769 (2)	175
O1W—H2$W\cdots$O4^{iv}	0.82	1.89	2.712 (2)	175
O3—H1$\cdots$O4^i	0.88 (3)	1.65 (3)	2.520 (2)	167 (3)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

All H atoms were observed in a difference Fourier map, but the methylene and ammonium H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.97 (C—H) and 0.89 Å (N—H), and U_{iso}(H) values at $1.2U_{eq}$(C) and $1.5U_{eq}$(N). The H atoms of the water molecule were located in a difference Fourier map and their coordinates were allowed to ride on the coordinates of the parent atom, with U_{iso}(H) = $1.5U_{eq}$(O). For atom H1 (on O3), both the coordinates and the isotropic displacement parameter were refined without constraints.

Data collection: *KM-4-CCD Software* (Kuma, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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