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μ-Oxalato-bis[aqua(diethylenetriamine)nickel(II)] dinitrate

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The crystal structure of the title compound, $[Ni_2(C_2O_4)(C_4H_{13}N_3)_2(H_2O)_2](NO_3)_2$, consists of uncoordinated nitrate anions and dimeric cations, where the oxalate ligand is coordinated in a bis-bidentate fashion to centrosymmetrically related Ni^{II} atoms. The distorted octahedral environment of each Ni^{II} atom is completed by the three N atoms of the diethylenetriamine ligand in a *fac* arrangement and one water O atom. Variable-temperature magnetic susceptibility measurements reveal a moderate intramolecular antiferromagnetic coupling.

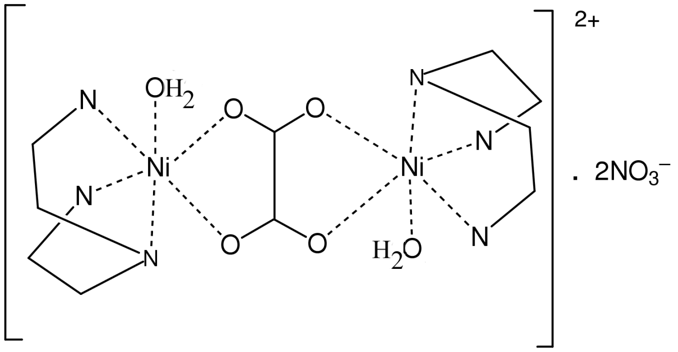
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.089
Data-to-parameter ratio = 25.7

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

Comment

The design and synthesis of oxalato-bridged nickel(II) complexes have attracted much attention during the last few years due to the strong magneto-structural correlations found in this kind of complex (Román *et al.*, 1996; Escuer *et al.*, 1994). In the framework of our current research of polynuclear oxalato-containing first-row transition metal complexes (Castillo *et al.*, 2000, 2001) we have obtained the compound μ-oxalato-bis[aqua(diethylenetriamine)nickel(II)] dinitrate, (I).



(I)

The crystal structure of (I) comprises NO_3^- anions and $[Ni_2(C_2O_4)(C_4H_{13}N_3)_2(H_2O)_2]^{2+}$ binuclear cations (Fig. 1) having a centre of symmetry at the midpoint of the C—C bond of the oxalate bridge. As observed in related compounds (Travnicek *et al.*, 1997; Román *et al.*, 1996; Escuer *et al.*, 1994), the oxalate ion joins two adjacent coordination polyhedra with its O atoms occupying two *cis* positions in both polyhedra, and the diethylenetriamine group acts as a facially coordinated tridentate ligand. The coordination geometry around each metal atom is NiN_3O_3 distorted octahedral, with the O1, O2, N1 and N7 atoms in the equatorial plane [maximum deviation 0.010 (2) Å for N7]; N4 and O3W are on the axial sites. The

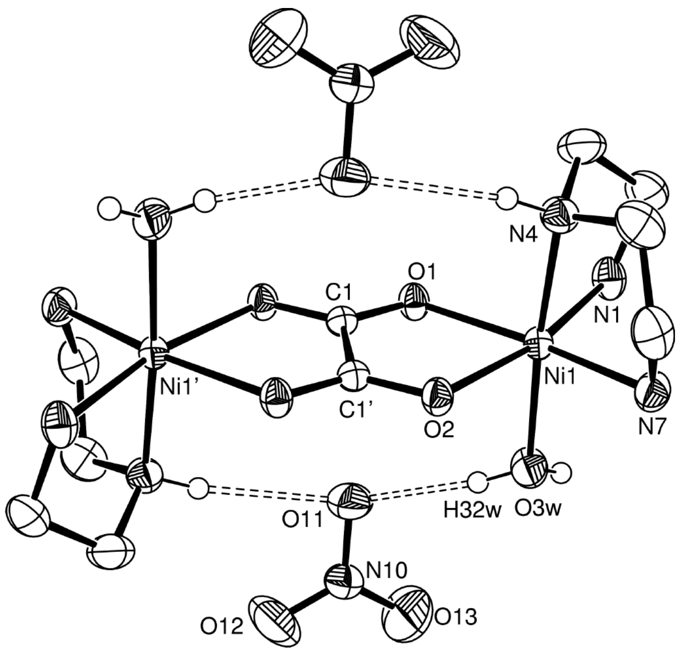


Figure 1
The molecular structure of (I) showing the hydrogen bonds between the anions and cations. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

nickel–nickel separation across the bridging oxalate is 5.487 (1) Å and the Ni–oxalato–Ni fragment is nearly planar. In the crystal structure of (I), complex cations and nitrate anions are held together by means of an extensive three-dimensional network of O*W*—H···O, N—H···O/O*W* hydrogen bonds. Magnetic susceptibility data of (I) in the temperature range 1.8–300.0 K show the occurrence of an intramolecular antiferromagnetic interaction with $J = -27.2$ cm^{-1} and $g = 2.20$. The magnitude of the exchange coupling constant is within the range found for oxalate-bridged nickel(II) complexes with a NiN_3O_3 chromophore.

Experimental

$Ni(NO_3)_2 \cdot 6H_2O$ (2.670 g, 9.20 mmol) dissolved in water (20 ml) was added dropwise to a mixture of diethylenetriamine (1.0 ml, 9.20 mmol) and $K_2C_2O_4 \cdot H_2O$ (0.850 g, 4.60 mmol) in water (30 ml) to give an immediate blue polycrystalline powder. Blue crystals of (I) suitable for X-ray analysis were obtained by recrystallization in hot water.

Crystal data

$[Ni_2(C_2O_4)(C_4H_{13}N_3)_2(H_2O)_2](NO_3)_2$
$M_r = 571.80$
Monoclinic, $P2_1/n$
$a = 12.560$ (2) Å
$b = 7.243$ (2) Å
$c = 13.387$ (2) Å
$\beta = 117.96$ (2)°
$V = 1075.7$ (4) Å^3
$Z = 2$
$D_x = 1.765$ Mg m^{-3}
$D_m = 1.75$ (1) Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–13.2°
$\mu = 1.83$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.40 × 0.40 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{min} = 0.494$, $T_{max} = 0.633$
5512 measured reflections
4732 independent reflections
3495 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 35.0°$
$h = -20 \rightarrow 17$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 21$
2 standard reflections every 98 reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.089$
$S = 1.03$
4732 reflections
184 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.5287P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.1081 (11)	Ni1—N1	2.0822 (14)
Ni1—O2	2.1125 (12)	Ni1—N4	2.0758 (18)
Ni1—O3*W*	2.0935 (17)	Ni1—N7	2.0641 (15)
O1—Ni1—O2	78.89 (4)	O2—Ni1—N7	90.55 (5)
O1—Ni1—O3*W*	90.02 (6)	O3*W*—Ni1—N1	94.82 (7)
O1—Ni1—N1	90.23 (5)	O3*W*—Ni1—N4	175.41 (6)
O1—Ni1—N4	94.34 (6)	O3*W*—Ni1—N7	92.32 (7)
O1—Ni1—N7	169.13 (5)	N1—Ni1—N4	83.75 (7)
O2—Ni1—O3*W*	88.74 (6)	N1—Ni1—N7	100.13 (6)
O2—Ni1—N1	168.57 (5)	N4—Ni1—N7	83.66 (7)
O2—Ni1—N4	93.50 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O3*W*^{i}	0.87 (2)	2.53 (2)	3.343 (2)	157 (2)
N1—H12···O11^{ii}	0.88 (2)	2.26 (2)	3.069 (2)	152 (2)
O3*W*—H31*W*···O1^{ii}	0.83 (2)	1.98 (3)	2.767 (2)	157 (3)
O3*W*—H32*W*···O11	0.83 (4)	1.96 (3)	2.764 (2)	165 (4)
O3*W*—H32*W*···O13	0.83 (4)	2.57 (4)	3.227 (3)	138 (3)
N4—H41···O11^{iii}	0.85 (2)	2.39 (2)	3.231 (2)	170 (3)
N4—H41···O12^{iii}	0.85 (2)	2.49 (3)	3.164 (3)	137 (2)
N7—H71···O13^{ii}	0.888 (19)	2.45 (2)	3.301 (3)	161 (2)
N7—H72···O2^{iv}	0.86 (3)	2.25 (3)	3.087 (2)	164 (3)

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

The diethylenetriamine ligand shows a disordered arrangement of the C6 atom over two positions. Refinement of the site-occupation factors revealed a partial occupation close to 0.9 and 0.1, which were kept fixed to these values in the final refinement.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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