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(μ-Oxalato-O^1,O^2:$O^{1'}$,$O^{2'}$)bis[aqua(diethylenetriamine)nickel(II)] bis(hexafluorophosphate) dihydrate

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The title compound, $[Ni_2(C_2O_4)(C_4H_{13}N_3)_2(H_2O)_2](PF_6)_2\cdot 2H_2O$, contains a dinuclear oxalato-bridged nickel(II) complex cation. The structure determination reveals the presence of a centrosymmetric binuclear complex where the oxalate ligand is coordinated in a bis-bidentate mode to the Ni atoms. The distorted octahedral environment of each Ni atom is completed by the three N atoms of the diethylenetriamine ligand in a *fac* arrangement and by one O atom from a water molecule. PF_6^- acts as counter-anion. A two-dimensional network of hydrogen bonds links the cations and anions and stabilizes the structure.

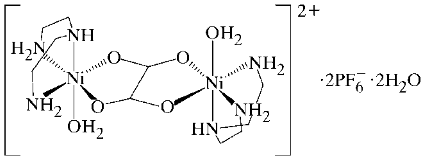
Comment

The design and synthesis of molecular magnetic compounds has attracted increased attention over the past two decades (Gatteschi *et al.*, 1991; Bruce & O'Hare, 1992). A significant amount of magneto-structural research work during the last 25 years has been devoted to analysing the remarkable ability of the oxalate bridge to mediate exchange coupling between first-row transition metal ions (Alvarez *et al.*, 1990; Cano *et al.*, 1999). The simple binuclear geometry involving symmetric in-plane bridging with a single oxalate anion binding through two O atoms to each of two metal centres has been observed in the chemistry of nickel (Alcock *et al.*, 1987; Battaglia *et al.*, 1988; Bencini *et al.*, 1990; Castro *et al.*, 1997; Travnicek *et al.*, 1997), and these *O*-bridged Ni^{II} complexes have attracted much attention due to the strong magneto-structural correlations found in these compounds (Khan, 1993).

Despite these exhaustive studies, dimeric structures are predominant in the solid-state chemistry of μ-oxalate Ni^{II} complexes and only in recent years have infinitely extended networks based on transition metal oxalate complexes been reported (Decurtins *et al.*, 1996).

Compounds containing the $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]^{2+}$ cation (dien is diethylenetriamine and ox is oxalate) are known as the dichloride, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]Cl_2$ (Román *et al.*, 1996), dibromide, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]Br_2$ (Muga, 2001), diperchlorate monohydrate, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](ClO_4)_2\cdot H_2O$ (Travnicek *et al.*, 1997), and dinitrate, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](NO_3)_2$ (Guzmán *et al.*, 2001).

We report here the synthesis and crystal structure of $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](PF_6)_2\cdot 2H_2O$, (I). This compound was obtained starting from $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]Cl_2$ by exchanging Cl^- for PF_6^-. Analogous to $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]Cl_2$, the title compound can be used as a precursor in the synthesis of other derivatives owing to the extreme lability of its water molecules (Román *et al.*, 1996; Muga *et al.*, 1997; Muga *et al.*, 2000).



(I)

The asymmetric unit of (I) consists of a non-coordinated hexafluorophosphate ion, a water molecule, and half of a $[Ni_2(dien)_2(H_2O)_2(\mu\text{-ox})]^{2+}$ dinuclear cation, which has an inversion centre at the midpoint of the C—C bond of the oxalate bridge. The oxalate ligand joins two adjacent Ni coordination polyhedra, with its O atoms occupying two *cis* equatorial positions, and the dien ligand acts as a facially coordinated tridentate ligand.

The coordination geometry around each metal ion is distorted NiN_3O_3 octahedral. The equatorial plane is built by two O atoms from opposite ends of the oxalate ligand, and the terminal N atoms, N1 and N7, from the dien ligand, whereas the axial positions are occupied by a water molecule, O3*w*, and the central N4 atom from the dien ligand.

The values of the Ni—N bond lengths are in the range 2.068 (3)–2.080 (3) Å. The Ni—O(ox) bonds are also very similar (Table 1) and subtend an acute angle at Ni1 of 79.45 (9)°. The Ni—O3*w* axial bond is almost perpendicular, 87.55 (11)°, to the mean O1/O2/N1/N7 equatorial plane. The metal atom is displaced by 0.043 (1) Å from this plane in the direction of the water ligand.

The bridging oxalate anion is exactly planar, and the nickel(II) ion is 0.066 (1) Å out of this plane. The dihedral angle between the equatorial (N_2O_2) and oxalate mean planes is 4.23 (11)°. The intramolecular Ni···Ni distance is 5.4579 (11) Å, whereas the shortest intermolecular Ni···Ni separation is 5.1542 (6) Å.

One of the C atoms (C2) of the dien ligand is disordered over two unequally occupied positions, C2*A* and C2*B*. The conformations of the two chelate rings within the dien ligand can be analysed in terms of the positions of the C atoms relative to the N/Ni/N planes of each five-membered chelate ring. The two rings show an asymmetric distribution of the C atoms. Whereas one C atom is above and one below the N/Ni/N plane in the minor disordered form of the first ring and in the second ring, they are located on the same side of the plane in the major disordered form of the first ring. Consid-

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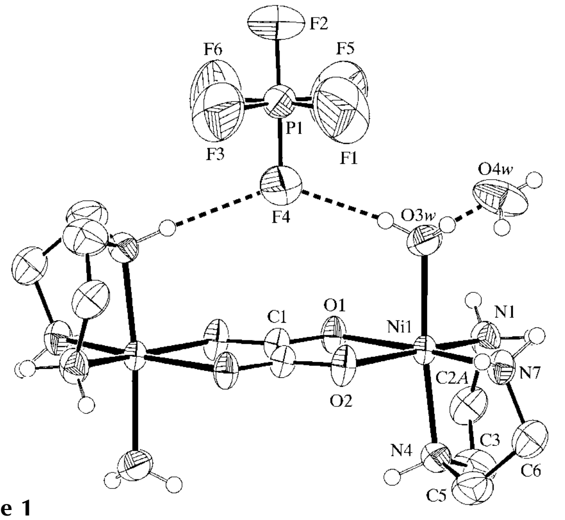

Figure 1
ORTEP-3 (Farrugia, 1997) view of the complex cation, the water molecule and the hexafluorophosphate anion, shown with 50% probability displacement ellipsoids. Ethylene H atoms have been omitted for clarity. Only the major disordered form is shown.

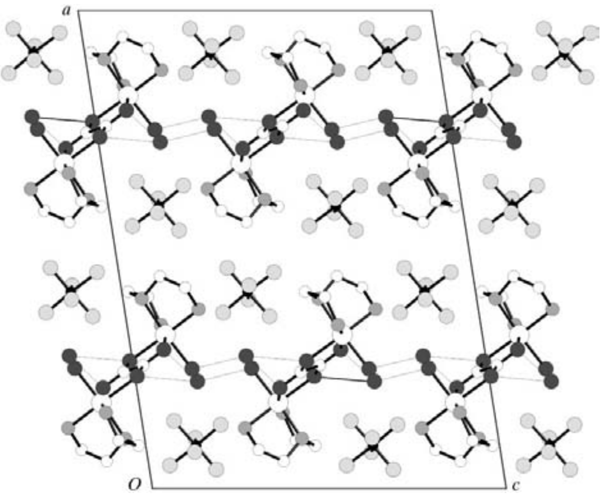

Figure 2
Packing diagram viewed down the *b* axis, showing the O—H···O hydrogen-bonding network. H atoms have been omitted for clarity.

ering only the major disordered form of the complex, the two chelate rings adopt the λ configuration, while the chelate ring spanned by atoms Ni1, N1, C2*B*, C3 and N4 adopts the δ configuration (Zelewsky, 1996).

The crystal structure consists of corrugated layers of complex cations hydrogen bonded by the water molecules, which lie parallel to the (100) plane. Inside the layer, the hydration and coordinated water molecules give rise to ···O3*w*···O4*w*···O3*w*($\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$)··· hydrogen-bonded chains, in which they act alternatively as donor and acceptor atoms. Besides these, longer hydrogen bonds are formed between the O4*w* water molecules and both O atoms of an adjacent oxalate moiety [O1(x, $y - 1$, z) and O2($\frac{1}{2} - x$, $-\frac{1}{2} - y$, $1 - z$)] in a direction perpendicular to the above-mentioned chains.

The PF_6^- anions are located above and below each dinuclear complex, forming two hydrogen bonds that connect N4($\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$) and O3*w* with the F4 atom. They also contribute to the crystal packing by forming three additional N—H···F hydrogen bonds that bridge between neighbouring complex cations [N···F 3.106 (6)–3.256 (7) Å] (Fig. 2).

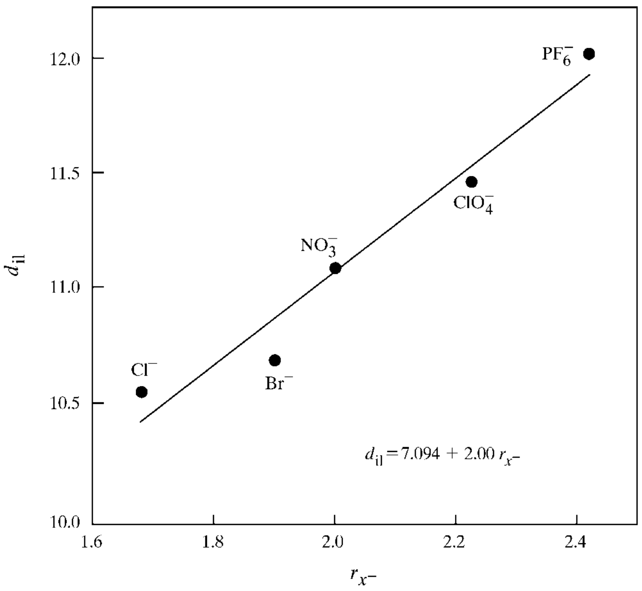

Figure 3
Correlation diagram between the interlamellar distances (Å) and the anionic radii (Å).

A remarkable aspect of the salts containing this binuclear complex cation is the different degree of hydration which gets higher as the anion becomes larger. All salts present a two-dimensional hydrogen-bonded arrangement, but the details of the hydrogen-bonding network inside these layers are strongly dependent on the anion and the number of water molecules. As can be seen in Fig. 3, the interlamellar distance, d_{il}, is strongly dependent on the anionic radius (Jenkins *et al.*, 1999), with a correlation factor of 0.975 for the five compounds.

Experimental

To an aqueous solution (50 ml) of $[\{Ni(dien)H_2O\}_2(\mu\text{-ox})]Cl_2$ (Román *et al.*, 1996; 0.5 g, 1.0 mmol), an aqueous solution (20 ml) of $AgPF_6$ (0.5 g, 2 mmol) was added slowly with continuous stirring. The mixture was stirred for 10 min. A highly insoluble grey residue precipitated during the reaction. After filtration, the resulting blue solution was allowed to stand at room temperature for several days, resulting in blue prismatic crystals of the complex. The crystals were collected, washed with cool water, and air dried. Single crystals were obtained by recrystallization from an aqueous solution (yield >95%).

Crystal data

$[Ni_2(C_2O_4)(C_4H_{13}N_3)_2(H_2O)_2](PF_6)_2 \cdot 2H_2O$
$M_r = 773.79$
Monoclinic, *C*2/*c*
$a = 22.994$ (3) Å
$b = 7.1850$ (10) Å
$c = 16.806$ (3) Å
$\beta = 98.860$ (10)°
$V = 2743.4$ (7) Å^3
$Z = 4$
$D_x = 1.873$ Mg m^{-3}

$D_m = 1.86$ (1) Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.8$–12.1°
$\mu = 1.62$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.3 × 0.3 × 0.2 mm

Table 1
Selected geometric parameters (Å, °).

Ni1—N7	2.068 (3)	Ni1—O1	2.100 (2)
Ni1—N1	2.074 (3)	Ni1—O3*w*	2.102 (3)
Ni1—N4	2.080 (3)	Ni1—O2	2.111 (2)
N7—Ni1—N1	101.84 (13)	N7—Ni1—O2	90.42 (11)
N7—Ni1—N4	83.67 (13)	N1—Ni1—O2	166.94 (12)
N1—Ni1—N4	83.52 (13)	N4—Ni1—O2	93.51 (12)
N7—Ni1—O1	169.86 (11)	O1—Ni1—O2	79.45 (9)
N1—Ni1—O1	88.27 (11)	O3*w*—Ni1—O2	91.13 (13)
N4—Ni1—O1	96.98 (11)	O1—C1—O2^{i}	125.5 (3)
N7—Ni1—O3*w*	92.40 (12)	O1—C1—C1^{i}	116.9 (3)
N1—Ni1—O3*w*	92.81 (14)	O2^{i}—C1—C1^{i}	117.6 (3)
N4—Ni1—O3*w*	173.94 (12)	C1—O1—Ni1	113.35 (19)
O1—Ni1—O3*w*	87.70 (11)	C1^{i}—O2—Ni1	112.63 (19)

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

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.605$, $T_{\max} = 0.799$
4099 measured reflections
3969 independent reflections
3370 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 30°$
$h = -32 \rightarrow 32$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 23$
2 standard reflections every 98 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.061$
$wR(F^2) = 0.191$
$S = 1.08$
3969 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1249P)^2 + 5.9096P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -1.40$ e Å^{-3}

The dien ligand has a disordered arrangement of the C2 atom over two positions. During the refinement, soft restraints were imposed on atoms N1, C2*A*, C2*B* and N3 so that equivalent distances and angles between them, and the components of the anisotropic displacement parameters of C2*A* and C2*B*, were similar. Refinement of the site-occupation factors revealed partial occupancies of 0.692 (14) and 0.308 (14) for C2*A* and C2*B*, respectively. The water H atoms were found from difference Fourier maps and their positions were refined with their $U_{\rm iso}$ values fixed at 1.5 times the $U_{\rm eq}$ values of their parent atoms. The positions of all remaining H atoms were calculated geometrically and were treated as riding, with their $U_{\rm iso}$ values fixed at 1.2 (C or N) times the $U_{\rm eq}$ values of their parent atoms. The maximum peak of residual density is 1.08 Å from F2, while the minimum is 0.88 Å from Ni1.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *DIRDIF*96 (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*w*—H31*w*···F4	0.82 (4)	2.11 (3)	2.926 (6)	168.9 (17)
O3*w*—H32*w*···O4*w*	0.84 (4)	1.79 (4)	2.628 (5)	175.5 (18)
O4*w*—H41*w*···O3*w*^{i}	0.72 (4)	2.14 (5)	2.840 (5)	165 (4)
O4*w*—H42*w*···O1^{ii}	0.76 (4)	2.47 (3)	3.131 (5)	147 (4)
O4*w*—H42*w*···O2^{iii}	0.76 (4)	2.30 (5)	3.019 (4)	158 (3)
N1—H11*A*···O4*w*^{iv}	0.90	2.42	3.163 (5)	140
N1—H12*A*···F6^{i}	0.90	2.45	3.256 (7)	150
N1—H12*B*···F6^{i}	0.90	2.49	3.256 (7)	143
N4—H4···F4^{v}	0.90	2.28	3.187 (7)	174
N7—H71···F5^{i}	0.90	2.25	3.106 (6)	158
N7—H72···O2^{iii}	0.90	2.43	3.285 (4)	159

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1124). Services for accessing these data are described at the back of the journal.

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