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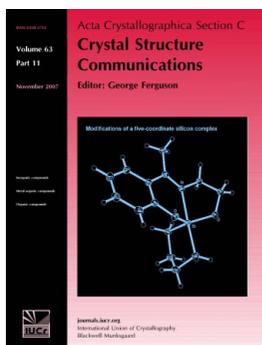
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Bis(di-2-pyridylamine- κ^2N^2, N^2')-(nitrate- κ^2O, O')nickel(II) nitrate

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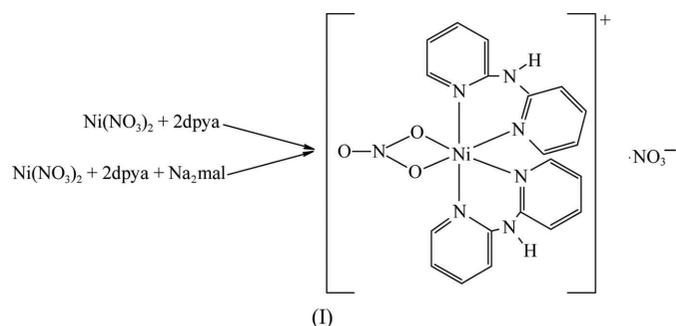
In the ionic title compound, $[\text{Ni}(\text{NO}_3)(\text{C}_{10}\text{H}_9\text{N}_3)_2]\text{NO}_3$, the central Ni^{II} atom exhibits *cis*- NiN_4O_2 octahedral coordination with three chelating ligands, *viz.* one nitrate anion and two di-2-pyridylamine (dpya) molecules. A second nitrate group acts as a counter-ion. The complex cations and the nitrate anions are also linked by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The compound was prepared in two different reproducible ways: direct synthesis from $\text{Ni}(\text{NO}_3)_2$ and dpya yielded systematically twinned crystals (the twinning law is discussed), while single crystals were obtained unexpectedly from the $\text{Ni}(\text{NO}_3)_2/\text{dpya}/\text{maleic acid}/\text{NaOH}$ system.

Comment

Complexes of Ni^{II} ($S = 1$) represent a class of model compounds suitable for studies of various physical phenomena associated with magnetism (Haldane, 1983*a,b*; Orendáč *et al.*, 1995; Boča & Titiš, 2008). Previously, we have prepared and studied several low-dimensional Ni^{II} complexes in which diamagnetic cyano complex anions were used as bridging species (Černák *et al.*, 2002, 2003; Paharová *et al.*, 2003). In order to replace them, we decided to explore the bridging ability of dicarboxylate ligands, namely maleate (mal). Literature data indicate that the maleate ligand can effectively link central atoms; examples are the maleate complexes $[\text{Ni}(\text{mal})(\text{phen})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (phen is 1,10-phenanthroline) and $[\text{Ni}(\text{mal})(\text{py})(\text{H}_2\text{O})]$ (py is pyridine) (Zheng *et al.*, 2002; Chen *et al.*, 2003). As part of our effort to prepare the above-mentioned low-dimensional maleate complex of Ni^{II} , in which di-2-pyridylamine (dpya) should act as a blocking ligand, we have isolated from an aqueous ethanol system the title compound, $[\text{Ni}(\text{NO}_3)(\text{dpya})_2]\text{NO}_3$, (I), in an unexpected but nonetheless reproducible way.

Two synthetic procedures led to the formation of the same product, $[\text{Ni}(\text{NO}_3)(\text{dpya})_2]\text{NO}_3$ (see scheme). Preliminary studies showed crystals from both batches to exhibit the same structure, but while those obtained from the maleate synthesis

were single crystals, those obtained by direct targeted synthesis were systematically twinned. The twin domains characterized by the unit-cell vectors ($\mathbf{a}_1, \mathbf{b}_1$ and \mathbf{c}_1 for the first twin domain and $\mathbf{a}_2, \mathbf{b}_2$ and \mathbf{c}_2 for the second) in direct space are related by the symmetry operation ($\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$) = $T(\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1)$ (where as usual the elements involved are a row vector, a square matrix and a column vector, respectively, and where $T = U_1^{-1}U_2 = (-1, 0, -0.73; 0, -1, 0; 0, 0, 1)$ (expressed by rows), and U_1 and U_2 are the orientation matrices of the first and the second twin domain, respectively. In direct space the \mathbf{c}_1 and \mathbf{c}_2 axes of both domains coincide, while the \mathbf{b}_1 and \mathbf{b}_2 axes are opposite to each other, *i.e.* $\mathbf{b}_2 = -\mathbf{b}_1$. The transposed matrix T^t transforms the reciprocal base (column) vectors in the way indicated in Fig. 1. The second domain is linked to the first by a pseudo-twofold rotation axis defined by a reciprocal vector $2\mathbf{c}_1^* - 0.73\mathbf{a}_1^*$, where \mathbf{a}_1^* and \mathbf{c}_1^* are vectors of the first domain. Further discussion about the origin of the observed twinning lies outside the scope of the present report.



The ionic structure of (I) is built up of $[\text{Ni}(\text{NO}_3)(\text{dpya})_2]^+$ complex cations and nitrate counter-ions. As shown in Fig. 2, the central Ni^{II} atom exhibits a very distorted octahedral coordination. Four coordination sites are occupied by two chelating dpya ligands *via* the pyridine N atoms, while the remaining two coordination sites are occupied by a chelating nitrate ligand.

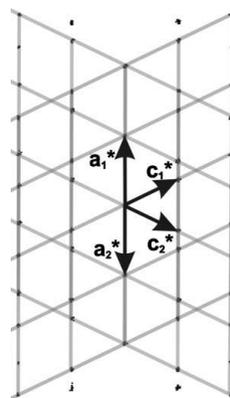


Figure 1

The relationship of the reciprocal unit cells of the two twin domains displayed on the basis of the experimental positions of the reflections (red and blue in the electronic version of the paper) found systematically in the samples of (I) prepared by targeted preparation. The view is along $\mathbf{b}_2^* = -\mathbf{b}_1^*$. The reciprocal axes \mathbf{a}_i^* and \mathbf{c}_i^* ($i = 1, 2$) are indicated by labeled arrows. The direction of \mathbf{b}_1^* (as well as that of \mathbf{b}_2^*) follows the right-hand condition.

The Ni–N coordination bond lengths are rather uniform and span the range 2.0374 (11)–2.0719 (15) Å; the dihedral angles subtended by the planes of the dpya pyridine rings are 27.85 (5)° (between the N1- and N3-containing pyridine rings) and 22.74 (4)° (between the N4- and N6-containing pyridine rings), similar to the value of 26.1 (3)° found in $[\text{Ni}(\text{C}_2\text{N}_3)_2(\text{dpya})_2]$ (Huang *et al.*, 2006).

The chelating mode of the nitrate ligand is not uncommon: for example, it was found in $[\text{Ni}(\text{NO})_3(\text{biqui})(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (biqui is 2,2'-biquinoline; Freire *et al.*, 2001). As a consequence of chelation, the O–Ni–O angle within the four-membered ring is very acute [60.56 (4)°], close to the reported mean value of 59.7 (12)° for such types of coordination (Freire *et al.*, 2001).

The nitrate ligand presents slightly shorter and more symmetrical Ni–O distances (Table 1) than the corresponding distances [2.2065 (10) and 2.1477 (10) Å] in $[\text{Ni}(\text{NO})_3(\text{biqui})(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ with the bulkier biqui ligand (Freire *et al.*, 2001). As a consequence of the binding to the metal, the coordinated N–O distances [O2–N7 = 1.2796 (16) Å and O3–N7 = 1.2789 (15) Å] appear significantly longer than the uncoordinated distance [N7–O1 = 1.2209 (19) Å]. Similar, though less marked, differences are also observed in the unbound nitrate anion, with two longer [N8–O5 = 1.2624 (19) Å and N8–O6 = 1.2646 (16) Å] and one shorter [N8–O4 = 1.228 (2) Å] N–O bond (Fig. 2). In this case, however, longer bonds correspond to O atoms strongly involved in hydrogen bonding (Table 2 and Fig. 2).

Although the crystal structure of (I) is essentially ionic, there are a number of weak interactions exhibiting directional character and which contribute to packing stabilization, the most relevant being conventional N–H···O hydrogen bonds, nonconventional C–H···O contacts and π – π interactions.

Regarding the hydrogen bonds, the aforementioned N–H···O interactions link complex cations and nitrate anions in

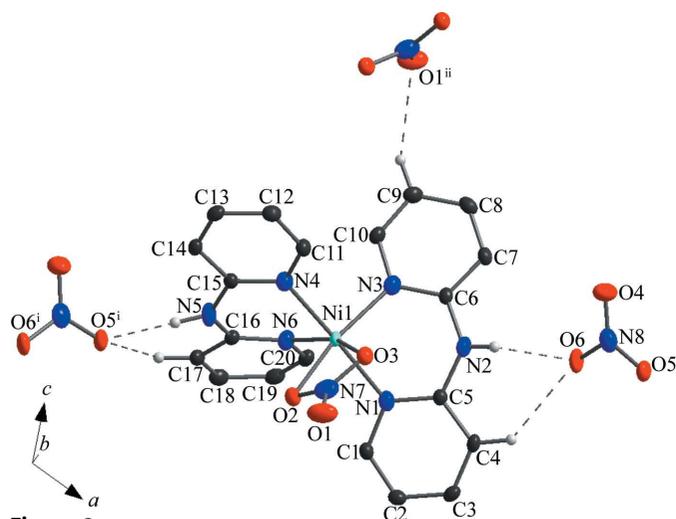


Figure 2

The one-dimensional arrangement of ions in $[\text{Ni}(\text{NO})_3(\text{dpaa})_2]\text{NO}_3$ connected by N–H···O and C–H···O hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-1 + x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$]

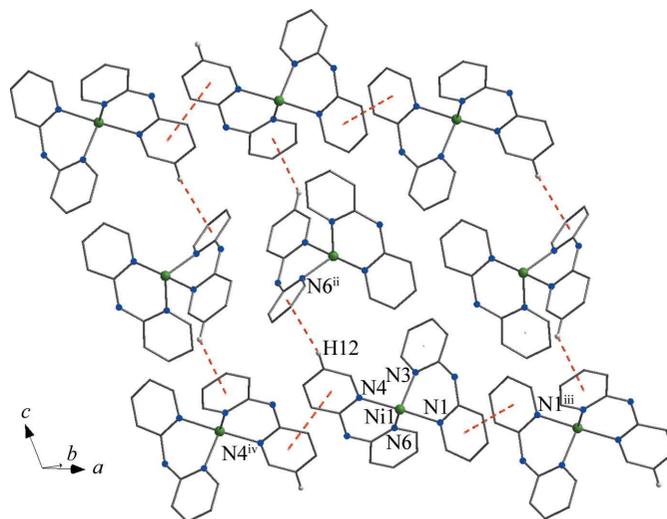


Figure 3

The packing in $[\text{Ni}(\text{NO})_3(\text{dpaa})_2]\text{NO}_3$. Dashed lines represent face-to-face π – π and C–H··· π interactions. [Symmetry codes: (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x, -y, -z$]

a chain-like arrangement parallel to the [201] direction. Furthermore, there are a number of aromatic H atoms exhibiting short C–H···O_{nitrate} contacts, many within the geometry limits commonly accepted hydrogen bonds (the most relevant are reported in Table 2).

The structure presents, in addition, face-to-face π – π interactions between pairs of centrosymmetrically related pyridine rings, *viz.* those containing N1 and N1ⁱⁱⁱ [symmetry code: (iii) $-x + 1, -y + 1, -z$], and those containing N4 and N4^{iv} [symmetry code: (iv) $-x, -y, -z$]. The corresponding rings are coplanar, with intercentroid (Cg) distances of 3.7103 (9) [Cg(N1)···Cg(N1ⁱⁱⁱ)] and 3.9998 (9) Å [Cg(N4)···Cg(N4^{iv})], and interplanar separations of 3.479 and 3.307 Å, respectively (Fig. 3). These π – π interactions, as well as the C12–H12··· π interaction reported in Table 2, serve to link the hydrogen-bonded cation–anion chains into a weakly bound three-dimensional structure.

Experimental

Single crystals of the title compound were prepared fortuitously. An aqueous solution (7.5 ml) of Na₂mal (0.8 g, 5 mmol) was added slowly to an aqueous solution (20 ml) containing Ni(NO₃)₃·6H₂O (1.454 g, 5 mmol). To the resulting green solution, an ethanol solution (2 ml) of dpaa (0.856 g, 5 mmol) was added with stirring. The resulting violet solution was filtered and left aside for crystallization at room temperature. Violet single crystals in the form of parallelepipeds of the unexpected complex $[\text{Ni}(\text{NO})_3(\text{dpaa})_2]\text{NO}_3$ were obtained by crystallization at laboratory temperature for two weeks (yield 1.16 g, 80%).

For the targeted preparation (twins), Ni(NO₃)₃·6H₂O (1.454 g, 5 mmol) and dpaa (0.856 g, 5 mmol) were successively dissolved in 10 ml of an ethanol/water mixture (1:1 v/v). The resulting violet solution was filtered and left for crystallization at room temperature. After two weeks, violet irregular cubes of the title compound were collected (yield 0.957 g, 54%). Analysis calculated for C₂₀H₁₈N₈NiO₆: C 45.74, H 3.45, N 21.33, Ni 11.17%; found: C 45.46, H 3.47, N 21.30, Ni 10.35%.

Crystal data

[Ni(NO ₃)(C ₁₀ H ₉ N ₃) ₂]NO ₃	$V = 2118.95 (7) \text{ \AA}^3$
$M_r = 525.1$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.5928 (2) \text{ \AA}$	$\mu = 0.98 \text{ mm}^{-1}$
$b = 9.8699 (2) \text{ \AA}$	$T = 120 \text{ K}$
$c = 16.0846 (3) \text{ \AA}$	$0.42 \times 0.22 \times 0.16 \text{ mm}$
$\beta = 113.843 (2)^\circ$	

Data collection

Oxford Diffraction Xcalibur 2 diffractometer with a Sapphire 2 CCD detector	25248 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	4401 independent reflections
$T_{\min} = 0.740$, $T_{\max} = 0.900$	3553 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
4401 reflections	
322 parameters	
2 restraints	

Table 1

Selected bond lengths (\AA).

Ni1—O2	2.1621 (11)	Ni1—N3	2.0374 (11)
Ni1—O3	2.1342 (11)	Ni1—N4	2.0595 (15)
Ni1—N1	2.0719 (15)	Ni1—N6	2.0384 (12)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$C_g(N6)$ is the centroid of the C16–C20/N6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 <i>n</i> ···O6	0.856 (13)	1.959 (13)	2.8046 (19)	169.4 (14)
N5—H5 <i>n</i> ···O5 ⁱ	0.863 (14)	1.898 (14)	2.7442 (18)	166.3 (14)
C4—H4 <i>c</i> ···O6	0.96	2.53	3.2550 (19)	133
C9—H9 <i>c</i> ···O1 ⁱⁱ	0.96	2.48	3.325 (2)	147
C17—H17 <i>c</i> ···O5 ⁱ	0.96	2.50	3.228 (2)	133
C12—H12 <i>c</i> ··· $C_g(N6)$ ⁱⁱ	0.96	2.99	3.7871 (17)	141

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

All H atoms could be located in a difference Fourier map, but according to the commonly used practice, those bonded to C atoms were constrained to ideal positions and allowed to ride with C—H =

0.96 \AA . The positions of the H atoms bonded to N2 and N5 were refined freely, with restrained N—H distances of 0.87 \AA . The U_{iso} values of all H atoms were calculated as $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2007); geometric calculations: *PLATON* (Spek, 2009); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3101). Services for accessing these data are described at the back of the journal.

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