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trans-Diaqua(2,2′-biquinoline-*N*,*N*′)-(nitrato-*O*,*O*′)nickel(II) nitrate hydrate

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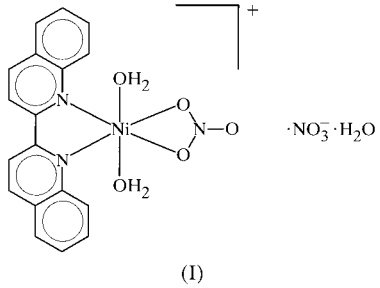
The structure of the title compound, $[Ni(NO_3)(C_{18}H_{12}N_2)(H_2O)_2]NO_3\cdot H_2O$, is composed of monomers with the nickel ion octahedrally coordinated to a bidentate biquinoline ligand, a bidentate nitrate anion and two water molecules, and is stabilized by a nitrate counter-ion and a hydrate water molecule. There is a fairly complex hydrogen-bonding scheme involving all the water H atoms and five different nitrate O atoms.

Comment

The title compound, (I), crystallizes as $[Ni(NO_3)(biqui)(H_2O)_2]$ (biqui is 2,2′-biquinoline) monomers stabilized by a nitrate counter-ion and a hydrate water molecule. The complex is octahedral, the planar base of the polyhedron being defined by the two N atoms of the bidentate biquinoline ligand and two O atoms from the bidentate NO_3^- anion. The apical sites are occupied by two water molecules. The main deformation of the polyhedron is due to the small nitrate bite angle of 59.47 (4)°; the bite angle of the biquinoline ligand is wider at 81.53 (5)°.



(I)

Nickel nitrates are common. There are 40 reported in the Cambridge Structural Database (CSD; Allen & Kennard, 1993), 28 of which are bidentate in an octahedral coordination. The mean values for the Ni—O distances and O—Ni—O angles in this group are 2.16 (4) Å and 59.7 (12)°, respectively, which compare fairly well with the values obtained in the present complex of 2.18 (3) Å and 59.47 (4)°. An examination of the geometries of the two different nitrate groups in the structure shows a clear inverse correlation of the N—O distances with the degree of involvement of the group in coordination, either directly to the cation or through hydrogen bonding to another O atom. Thus, in the bidentate nitrate anion denoted *A*, the non-coordinated O3*A* atom shows the shortest N—O distance of 1.2225 (16) Å. In the other two (coordinated) O atoms, there is a clear inverse trend, *i.e.* the longer the Ni—O bond length, the shorter the corresponding N—O bond length [Ni1—O1*A* 2.2065 (10) Å and N1*A*—O1*A* 1.2694 (15) Å; Ni1—O2*A* 2.1477 (10) Å and N1*A*—O2*A* 1.2818 (15) Å].

A similar effect seems to be present in counter-ion *B*, when hydrogen-bond interactions are considered. Thus, the O2*B* atom is an acceptor of a stronger hydrogen bond [H1*WB*···O1*B* 1.90 (2) Å] than those in which O2*B* and O3*B* are involved [H3*WA*···O2*B* 2.00 (3) Å and H3*WB*···O3*B* 2.02 (3) Å]. This correlates nicely with the nitrate N—O bond distances, *viz*. one long N1*B*—O1*B* distance of 1.2648 (17) Å, and two shorter, almost equal, N1*B*—O2*B* and N1*B*—O3*B* distances of 1.2477 (17) and 1.2467 (17) Å, respectively.

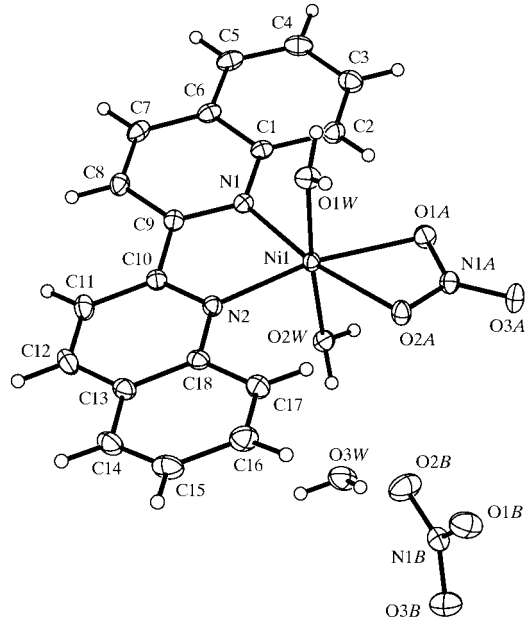


Figure 1
View of the unit-cell contents showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

These results agree with the fact that both nitrate groups modify their N—O bond lengths in order to maintain the valence over nitrogen. A simple calculation following Brown & Altermatt (1985) gave this value as 4.82 in the case of the coordinated moiety and 4.87 in the ionic case, quite close to the expected value of 5 for nitrogen.

The organic ligand presents no anomalies in its bond distances or angles, but departs somewhat from the expected planarity; the normals of the two lateral wings deviate from the normal of the coordination plane in opposite directions by 3.9 and 6.5°, and as a result, the group appears slightly twisted around the C9—C10 bond [N1—C9—C10—N2 6.11 (19)°]. Due to the lack of steric hindrance, the ligand binds to the cation almost parallel to the basal plane (slanting angle *ca* 3.1°).

The only other known complex with a biquinoline group coordinated to nickel is [Ni(acet)(biqui)(H_2O)$_2$] (acet is acetate; Freire *et al.*, 2001), which displays a very similar type of coordination, with the bidentate nitrate ligand being replaced by acetate and where the stabilizing counter-ion is the unusual pentathionate ion.

The profusion of donors and acceptors for hydrogen bonding is responsible for a very complex hydrogen-bonding scheme, with all six water H atoms and five out of six nitrate O atoms taking part. Table 2 displays the most important bonds, separating them into two groups. Through the interactions in the first group, the structure organizes itself into 'dimers' (Fig. 2) around the center of symmetry at $(1-x, 1-y, 1-z)$. These are the 'elemental units' of the packing. Each 'dimer' in turn interacts with four neighboring 'dimers' (represented in Fig. 2 by sites *A*, *A*′, *B* and *B*′) through the hydrogen bonds listed in the second group, resulting in a robust three-dimensional structure. Finally, there are a couple of short C—H···O contacts which also make a contribution to the stabilization of the structure.

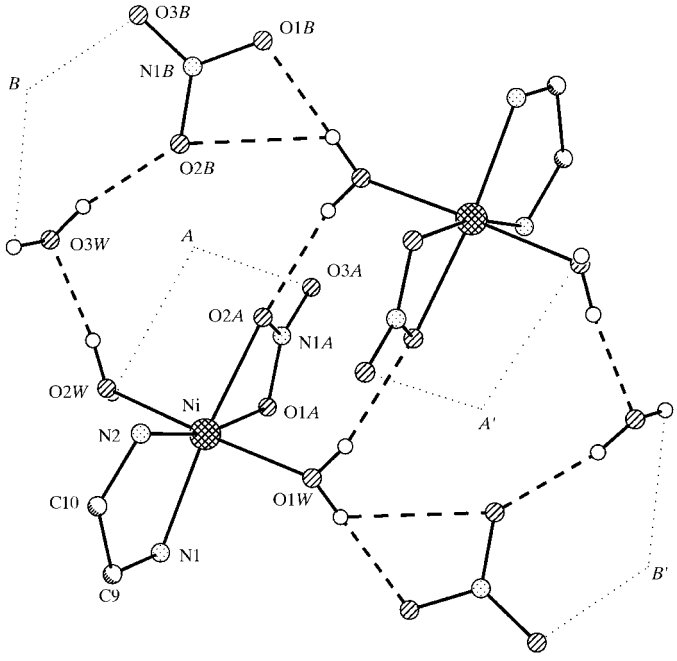


Figure 2
Schematic view of the packing showing the elemental 'dimeric unit' formed around the center of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the way in which it interacts with symmetry-related neighboring 'dimers' (*A*, *B*, *A*′ and *B*′). For clarity, the bulky biquinoline group has been idealized by the N—C—C—N loop. Heavy broken lines represent hydrogen bonds of the first group in Table 2 which define the 'dimers', while dotted lines represent hydrogen bonds of the second group which link symmetry-related neighboring 'dimers'. [Symmetry codes: (*A*) $x-1, y, z$; (*B*) $x-\frac{1}{2}, -y-\frac{3}{2}, z-\frac{1}{2}$; (*A*′) $-x+2, -y+1, -z+1$; (*B*′) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.]

Experimental

The title compound was obtained by chance as a by-product in one of the many unsuccessful attempts to obtain single crystals of Ni(biqui) thiosulfate, a synthesis problem which is still unsolved. The procedure used was as follows: the biquinoline was dissolved in hot acetone and in order to facilitate the dissolution of the inorganic salts to be added later, water was incorporated into the solution, taking care to avoid ligand precipitation. To this solution, nickel nitrate was first added, followed by sodium thiosulfate (which partially decomposed). Crystals of the product appeared after evaporation in the form of nicely shaped pale-blue prisms. The starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N, S) were performed on a Carlo Erba EA 1108 instrument. Nickel was determined on a Shimadzu AA6501 spectrophotometer.

Crystal data

[Ni(NO_3)($C_{18}H_{12}N_2$)(H_2O)$_2$]-NO_3·H_2O
M_r = 493.07
Monoclinic, $P2_1/n$
a = 8.4250 (7) Å
b = 11.2156 (7) Å
c = 20.8889 (14) Å
β = 94.499 (3)°
V = 1967.7 (2) Å^3
Z = 4
D_x = 1.664 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 971 reflections
θ = 12.1–23.5°
μ = 1.05 mm^{-1}
T = 110 (2) K
Elongated prism, pale blue
0.64 × 0.14 × 0.08 mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL-NT*; Bruker, 1999)
T_{min} = 0.691, T_{max} = 0.921
24 538 measured reflections
4880 independent reflections
4290 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.3°
$h = -11 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -27 \rightarrow 27$

Table 1
Selected bond lengths (Å).

Ni1—O1*W*	2.0441 (11)	N1*A*—O1*A*	1.2694 (15)
Ni1—O2*W*	2.0507 (11)	N1*A*—O2*A*	1.2818 (15)
Ni1—N1	2.0476 (12)	N1*A*—O3*A*	1.2225 (16)
Ni1—N2	2.0622 (12)	N1*B*—O1*B*	1.2648 (17)
Ni1—O1*A*	2.2065 (10)	N1*B*—O2*B*	1.2477 (17)
Ni1—O2*A*	2.1477 (10)	N1*B*—O3*B*	1.2467 (17)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O2*A*^{i}	0.79 (2)	2.09 (2)	2.858 (2)	165 (2)
O1*W*—H1*WB*···O1*B*^{i}	0.84 (2)	1.90 (2)	2.733 (1)	168 (2)
O1*W*—H1*WB*···O2*B*^{i}	0.84 (2)	2.49 (2)	2.987 (2)	119 (2)
O2*W*—H2*WA*···O3*A*^{ii}	0.82 (2)	2.08 (2)	2.878 (2)	165 (2)
O2*W*—H2*WB*···O3*W*	0.83 (2)	1.81 (2)	2.634 (2)	173 (2)
O3*W*—H3*WA*···O2*B*	0.82 (3)	2.00 (3)	2.811 (2)	169 (3)
O3*W*—H3*WB*···O3*B*^{iii}	0.83 (3)	2.02 (3)	2.814 (2)	162 (3)
C2—H2···O1*A*	0.90 (2)	2.27 (2)	3.131 (2)	161 (2)
C17—H17···O2*A*	0.91 (2)	2.30 (2)	3.156 (2)	156 (2)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 1.308P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.064$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
4880 reflections	
361 parameters	
All H-atom parameters refined	

Refinement was performed with isotropic displacement parameters for H atoms and C—H distances were in the range 0.899 (18)–0.973 (19) Å.

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1991); software used to prepare material for publication: *PARST* (Nardelli, 1983) and CSD (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1615). Services for accessing these data are described at the back of the journal.

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