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Aquachlorobis[4,4,5,5-tetramethyl-2-(2-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide-κ^2O^1,N^2]nickel(II) nitrate methanol disolvate monohydrate

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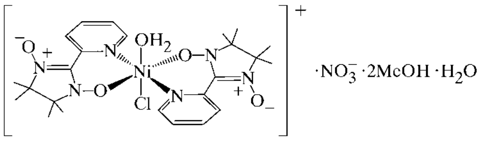
The title complex, $[NiCl(C_{12}H_{16}N_3O_2)_2(H_2O)]NO_3\cdot 2CH_4O\cdot H_2O$, was obtained from a methanolic solution of $Ni(NO_3)_2\cdot 6H_2O$, 2-pyridyl nitronyl nitroxide (2-NITpy) and $(NEt_4)_2[CoCl_4]$. The equatorial coordination sites of the octahedral Ni^{II} centre are occupied by two chelating radical ligands, with the axial positions occupied by the Cl^- and water ligands. The H_2O—Ni—Cl axis of the complex lies along a crystallographic twofold axis, so that only half the cation is present in the asymmetric unit. The Ni—Cl bond length [2.3614 (17) Å] is significantly shorter than distances typical of octahedral Ni^{II} centres [2.441 (5) Å]. However, with only one nitrate anion per formula unit, the oxidation state of the metal must be assigned as Ni^{II}. The 2-NITpy ligands bend away from the equatorial plane, forming a hydrophobic region around the Cl atoms. Conversely, the ligated water molecule forms moderately strong hydrogen bonds with the disordered methanol solvent molecules, which in turn form interactions with the water of crystallization and the disordered nitrate anion. These interactions combine to give hydrophilic regions throughout the crystal structure.

Comment

The family of stable nitronyl nitroxide radicals was first investigated by Ullman and co-workers in the late 1960s as spin-labelling compounds (Boocock *et al.*, 1968; Boocock & Ullman, 1968; Osiecki & Ullman, 1968; Ullman & Boocock, 1969; Ullman *et al.*, 1972). Subsequently, a wide range of aliphatic and aromatic molecules which incorporate nitronyl nitroxide moieties has been developed. This ready functionalization has led to the synthesis of several multidentate pyridine-based ligands which may form stable complexes with most first-row transition metals (Benelli *et al.*, 1992; Caneschi *et al.*, 1990; Huang & Wei, 1997; Ulrich *et al.*, 1994).

Of particular relevance here is 2-pyridyl nitronyl nitroxide, denoted 2-NITpy, which has been coordinated to Mn^{II} and Ni^{II} centres, giving $[M(2\text{-NITpy})_3]^{2+}$ and $[MCl_2(2\text{-NITpy})_2]$ complexes, in which there is substantial magnetic coupling between the metal and nitroxide radicals (Fegy *et al.*, 1998; Luneau *et al.*, 1993). Our research focuses on the development of three-dimensional coordination lattices containing paramagnetic metals coordinated to nitronyl nitroxide ligands. While investigating a series of nickel coordination polymers containing 2-NITpy ligands, the complex $[ClNi(OH_2)(2\text{-NITpy})_2]NO_3\cdot 2MeOH\cdot H_2O$, (I), was crystallized.



(I)

The Ni centre of (I) has octahedral geometry, with the axial sites taken by the Cl^- and water ligands, and the remaining four sites occupied by the chelating 2-NITpy radicals (Fig. 1). The O3—Ni1—Cl1 axis of (I) lies along a crystallographic twofold axis, hence only half the cation is present in the asymmetric unit. The N atoms of the pyridyl donors are mutually *trans* and consequently so are the O donor atoms of 2-NITpy.

The Ni—Cl bond length [2.3614 (17) Å] is significantly shorter than distances consistent with octahedral Ni^{II} centres [typically 2.441 (5) Å; Orpen *et al.*, 1989]. However, with only one nitrate anion per formula unit, the oxidation state of the metal must be assigned as Ni^{II}. The Ni—OH_2 bond length of 2.066 (2) Å is consistent with other octahedral complexes, irrespective of the metal oxidation state (Orpen *et al.*, 1989). There is good agreement between the Ni1—O1 [2.032 (1) Å] and Ni1—N1 [2.084 (2) Å] bond lengths and those observed in other Ni–2-NITpy structures (Table 2). In addition, the internal coordinates of the 2-NITpy ligand are comparable with those of previously determined radicals. The O—Ni—N angle of 86.1 (6)° indicates a relatively small bite angle for the bidentate ligand.

While the four atoms of the radical ligand coordinated to the Ni atom all lie in the equatorial plane, the rest of the

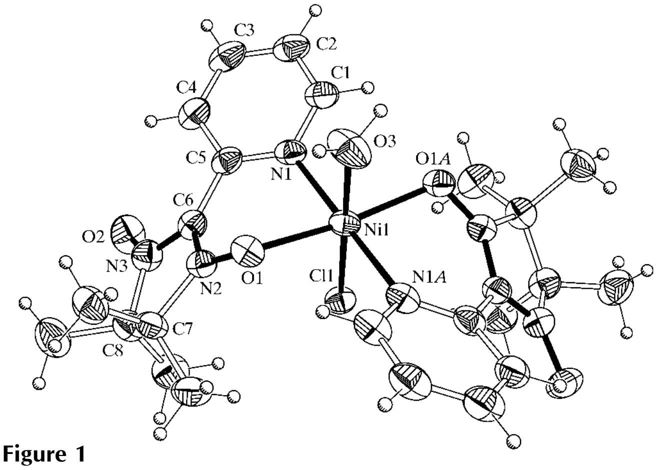


Figure 1
Displacement ellipsoid plot of the cation of (I), with atoms represented at the 50% probability level. H atoms have been omitted for clarity.

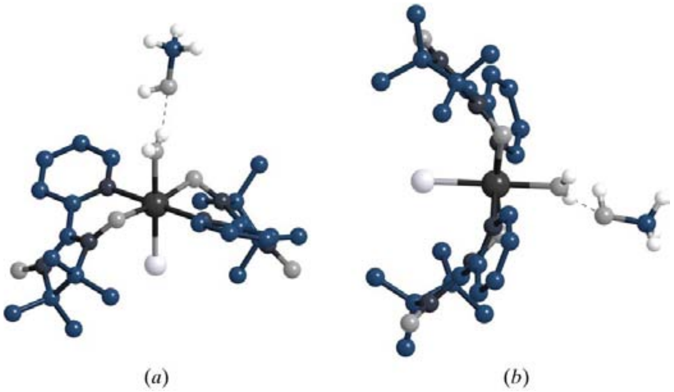


Figure 2
Two views of (I), illustrating (*a*) the distortion of the chelating 2-NITpy ligands, and (*b*) the hydrogen bonds formed between the water ligand and the methanol solvent molecules.

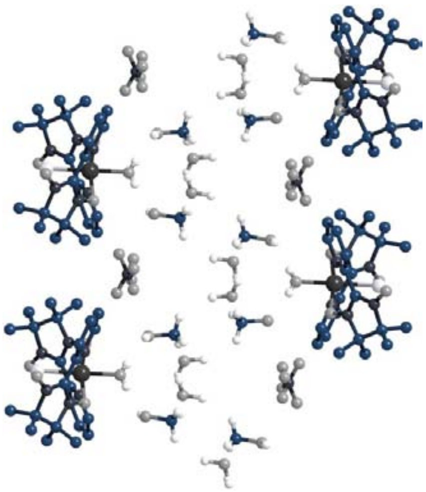


Figure 3
The crystal structure of (I), illustrating the hydrophilic regions, in which methanol molecules form moderate hydrogen bonds with bound and lattice water molecules and also with disordered nitrate anions.

ligands are bent away from the same plane (Fig. 2*a*). This is quantified by three angles: (i) the 25.2 (2)° twist of the pyridyl ring (mean plane defined by N1/C1–C5) with respect to the equatorial plane (defined by Ni1/N1/O1), (ii) the 45.5 (2)° twist of the tetramethylimidazolyl ring (defined by O1/N2/C6/N3/O2), and (iii) the 30.1 (2)° angle formed between the pyridyl and tetramethylimidazolyl rings. As a result of this deformation, the two ligands form a 'bowl' around the Cl atom, with the tetramethylimidazolyl rings giving an apparently hydrophobic region to the molecule, which is distorted away from the coordinated water molecule.

The coordinated water molecule forms moderate hydrogen bonds (Jeffrey, 1997) with both positions of the disordered methanol molecule (O3—H3*A*···O4 and O3—H3*A*···O5; Table 3). The second orientation of the methanol molecule also forms C—H···O contacts with the disordered nitrate anions (C14—H14*A*···O7*A* and C14—H14*A*···O7*E*; Table 3). The combination of these interactions results in hydrophilic channels throughout the crystal structure (Fig. 3).

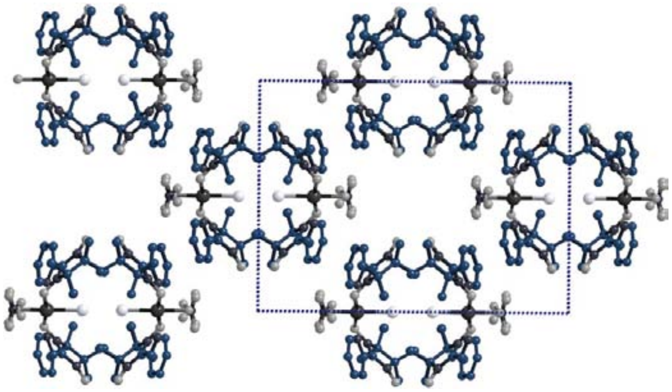


Figure 4
The face-centred array of cations in (I).

The crystal structure of (I) comprises a face-centred arrangement of Ni complexes, separated by the hydrophilic regions of nitrate anions and methanol molecules described above. Consequently, the hydrophobic sides of neighbouring molecules also face each other. There are no significant intermolecular interactions between the tetramethylimidazolyl rings and/or the Cl$^-$ ligands (Fig. 4). There is no residual solvent-accessible volume in the lattice, with the volume occupied by the methanol molecules being 565.2 Å^3 per formula unit, or 16.5% of the unit-cell volume.

Experimental

The radical ligand 2-NITpy (Fegy *et al.*, 1998) and $(NEt_4)_2[CoCl_4]$ (Gill & Taylor, 1967) were prepared according to published methods. $Ni(NO_3)_2·6H_2O$ was purchased from Aldrich and used as received. A deep-purple solution of 2-NITpy (7 mg, 0.084 mmol) in MeOH (5 ml) was added to a green solution of $Ni(NO_3)_2·6H_2O$ (12 mg, 0.042 mmol) in MeOH (5 ml), giving no immediate change in appearance. A pale-blue solution of $(NEt_4)_2[CoCl_4]$ (20 mg, 0.042 mmol) in MeOH (5 ml) was then added, and the mixture was left to stand for a period of six weeks, during which time a small crop of dark-red crystals suitable for X-ray analysis formed.

Crystal data

$[NiCl(C_{12}H_{16}N_3O_2)_2(H_2O)]$-
  $NO_3·2CH_4O·H_2O$
M_r = 724.82
Monoclinic, $C2/c$
a = 16.892 (5) Å
b = 20.624 (6) Å
c = 10.854 (3) Å
β = 115.267 (5)°
V = 3419.6 (17) Å^3
Z = 4

D_x = 1.408 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 436
  reflections
θ = 1.6–27.4°
μ = 0.71 mm^{-1}
T = 150 (2) K
Cube, dark red
0.17 × 0.16 × 0.16 mm

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.032 (3)	N2—O1	1.292 (5)
Ni1—O3	2.067 (5)	N2—C6	1.335 (6)
Ni1—N1	2.083 (4)	N3—O2	1.282 (5)
Ni1—Cl1	2.3614 (17)	N3—C6	1.349 (6)
O1—Ni1—O3	84.59 (8)	O1—Ni1—Cl1	95.41 (8)
O1—Ni1—N1	86.05 (14)	N1—Ni1—Cl1	90.39 (9)
O3—Ni1—N1	89.61 (9)	N2—O1—Ni1	114.5 (2)

Table 2
Ni—O and Ni—N bond lengths (Å) in Ni–2-NITpy structures.

Refcode†	Ni—O	Ni—N
BEBMOK	2.053	2.143
BEBMUQ	2.055	2.123
BEBNUR	2.056	2.139
FEFROX	2.013—2.059	2.059—2.107
LIZTOD	2.021—2.038	2.066 (× 2), 2.065 (× 2)
PIFROL	2.063	2.088
PIFSAY	2.029	2.072
POPMIQ	2.022, 1.979	2.029, 2.022
POPQAM	1.993, 1.986	2.016, 2.017

† Cambridge Structural Database refcode references (October 2001 Release; Allen *et al.*, 1991; Allen & Kennard, 1993; Allen, 2000): BEBMOK, BEBMUQ and BEBNUR: Yoshida *et al.* (1999); FEFROX: Fegy *et al.* (1998); LIZTOD: Francese *et al.* (2000); PIFROL and PIFSAY: Luneau *et al.* (1993); POPMIQ and POPQAM: Romero *et al.* (1998).

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O4	0.89 (7)	1.773 (7)	2.603 (3)	164 (3)
O3—H3*A*···O5	0.89 (7)	1.838 (7)	2.726 (3)	173 (2)
O5—H5*A*···O7A^{i}	0.84	1.85	2.646 (4)	159
O5—H5*A*···O7E^{i}	0.84	1.91	2.749 (4)	173

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

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SAINT*; Bruker, 2001)
$T_{\min} = 0.889$, $T_{\max} = 0.895$
21 522 measured reflections
3014 independent reflections
2467 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 25°$
$h = -20 \rightarrow 17$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.198$
$S = 1.07$
3014 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1259P)^2 + 7.0626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.070$
$\Delta\rho_{\max} = 1.92$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

The H atoms of the cation were located in difference maps and constrained to idealized geometries. The nitrate anion and methanol solvent molecules were both disordered. The O atoms of the nitrate anion were modelled as occupying two positions each (O7*A*, O7*B* and O7*C*, and O7*D*, O7*E* and O7*F*) in the asymmetric unit, sharing atom N4, which sits on a crystallographic twofold axis. The relative occupancies of the two positions was assigned as 0.25:0.25 after refinement. All of these atom sites were refined as isotropic, with the N—O bond lengths restrained to 1.23 (1) Å and the molecules constrained to lie in the same plane. The methanol molecule was also modelled as occupying two positions (C13 and O4, and C14 and O5), each of occupancy 0.5. Likewise, these atoms were refined isotropically, with the hydroxy H atoms located in the difference map and the methyl H atoms assigned idealized geometries. The O atom of the water of crystallization was also refined isotropically, with H atoms located in the difference map and constrained to idealized geometries.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1109). Services for accessing these data are described at the back of the journal.

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