

A nitronyl nitroxide complex of nickel(II) with nitrate as a ligand

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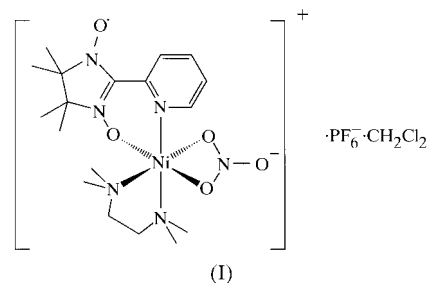
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The complex cation in [4,5-dihydro-4,4,5,5-tetramethyl-2-(2-pyridyl- κN)imidazol-1-oxyl 3-oxide- κO^3](nitrato- $\kappa^2 O, O'$)-(N, N, N', N' -tetramethyl-1,2-ethanediamine- $\kappa^2 N, N'$)nickel(II) hexafluorophosphate dichloromethane solvate, $[\text{Ni}(\text{NO}_3)(\text{C}_6\text{H}_{16}\text{N}_2)(\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_3)]\text{PF}_6 \cdot \text{CH}_2\text{Cl}_2$, is the first example of a nitronyl nitroxide complex of a transition metal ion having d electrons in which nitrate is coordinated as a bidentate ligand. Owing to the smaller steric requirement of NO_3^- , the Ni—O(nitroxide) bond length [2.014 (2) Å] is remarkably shorter than that in the corresponding β -diketonate complexes [2.052 (4)–2.056 (2) Å].

Comment

During the last two decades, there has been a large number of investigations of the magneto/structural chemistry of transition metal complexes bearing nitronyl nitroxide radicals. Initially, most of the complexes contained 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hfac) or a halide as a ligand because of the weak Lewis basicity of the nitroxide-O donor (Caneschi *et al.*, 1991). However, other types of nitronyl nitroxide complexes have recently been reported, such as those in which nitroxides are bound to carboxylate-bridged dinuclear metal centres (Handa *et al.*, 1998; Conge *et al.*, 1994) and those having oxalate (Oshio *et al.*, 2000) or *cis*-1,2-dicyano-1,2-ethylenedithiolate (Sutter *et al.*, 1996) as a ligand. The *N*-heteroaromatic derivatives of nitronyl nitroxides have also been used advantageously to construct various types of transition metal–nitroxide complexes, because the auxiliary *N*-heteroaromatic donor group can make the nitroxide-O atom bind to a poorly electrophilic metal centre through the chelate effect (Luneau *et al.*, 1993). Such nitronyl nitroxides also opened up the syntheses of transition metal complexes having various kinds of co-ligands. In fact, using the 2-pyridyl derivative 4,5-dihydro-4,4,5,5-tetramethyl-2-(2-pyridyl)imidazol-1-oxyl 3-oxide (NIT2py), we have recently succeeded in preparing and characterizing novel Ni^{II} –nitronyl nitroxide complexes containing both N, N, N', N' -tetramethyl-1,2-ethanediamine (tmen) and various kinds of β -diketonate

ligands (Yoshida *et al.*, 1999). We report here another intriguing Ni^{II} –nitronyl nitroxide complex containing nitrate instead of β -diketonate, *i.e.* $[\text{Ni}(\text{NO}_3)(\text{tmen})(\text{NIT2py})]\text{PF}_6 \cdot \text{CH}_2\text{Cl}_2$, (I). This is the first nitronyl nitroxide complex of the late transition metal ions containing nitrate as a ligand, although there has been a recent report concerning lanthanide(III)–nitronyl nitroxide complexes having three nitrate ligands, *viz.* $[\text{Ln}(\text{NO}_3)_3(\text{NITtrz})_2]$ (Ln = Y, La or Gd; NITtrz = 4,5-dihydro-4,4,5,5-tetramethyl-2-(4,5-dimethyl-1,2,4-triazol-3-yl)imidazol-1-oxyl 3-oxide) (Sutter *et al.*, 1998).



Compound (I) was prepared from $[\text{Ni}(\text{NO}_3)_2(\text{tmen})]$, NIT2py and KPF_6 , and was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, affording dark-green crystals. The X-ray analysis confirmed that the nitrate acts as a bidentate ligand in the complex cation of (I) (Fig. 1). The nitronyl nitroxide, NIT2py, coordinates to the Ni^{II} ion *via* the pyridyl-N and nitroxide-O atoms to form a six-membered chelate ring. As in the other Ni^{II} –NIT2py complexes (Luneau *et al.*, 1993; Yoshida *et al.*, 1999), the coordinated N—O bond [N1—O1 = 1.296 (3) Å] is longer by *ca.* 0.02 Å than the uncoordinated N—O bond [N2—O2 = 1.276 (4) Å]. The diamine, tmen, also chelates to Ni^{II} , forming a five-membered chelate ring with a typical *gauche* conformation, and the coordination geometry around the Ni^{II} atom is a distorted octahedron. The geometrical structure of the complex cation is assigned as a *mer* (*cis, trans*) N_3O_3 configuration, similar to the corresponding pentane-2,4-dionate (acac), 1-phenylbutane-1,3-dionate (bzac) and 1,1,1-trifluoro-4-phenylbutane-2,4-dionate (tfbzac) complexes, *i.e.* $[\text{Ni}(\text{acac}/\text{bzac}/\text{tfbzac})(\text{tmen})(\text{NIT2py})]\text{PF}_6$ (Yoshida *et al.*, 1999). Also, the conformations of the NIT2py and tmen chelate rings in (I) are similar to those in the above-mentioned β -diketonate complexes; for the complex cation having a Λ absolute configuration around the Ni^{II} centre, $\delta(\text{lel})$ and $\lambda(\text{ob})$ conformations are observed for NIT2py and tmen, respectively.

The structure of the coordinated nitrate moiety is not anomalous, although the Ni—O3 and Ni—O4 bond lengths [2.129 (2) and 2.125 (2) Å, respectively] are slightly shorter than those in the related Ni^{II} – NO_3 complexes; for example, in $[\text{Ni}(\text{NO}_3)(\text{acac})(1,2\text{-dipiperidinoethane})]$ [2.168 (3) and 2.161 (3) Å; Fukuda *et al.*, 1989] and $[\text{Ni}(\text{NO}_3)(N, N'\text{-dipropyl-1,2-ethanediamine})_2]\text{NO}_3$ [2.149 (2) and 2.152 (3) Å; Laskar *et al.*, 1998]. As indicated by the small O3—Ni—O4 bite angle of 61.0 (1)°, nitrate is sterically more compact than the β -diketonates, which have bite angles in the range 90.54 (8)–92.0 (2)° (Yoshida *et al.*, 1999). Such a compactness of the NO_3^- ligand results in noticeable deviations in the structural parameters of

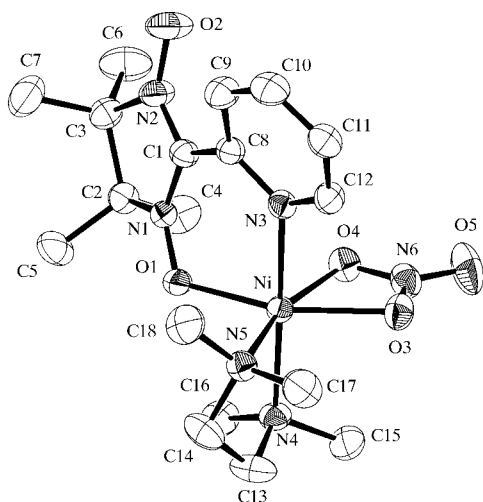


Figure 1

A perspective view of the complex cation in (I). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 40% probability level.

the nitrate complex from those of the β -diketonate complexes (Yoshida *et al.*, 1999), as mentioned below.

While the Ni–N4 bond length in (I) [2.154 (3) Å] is comparable to that of the corresponding β -diketonate complexes [2.144 (6)–2.170 (6) Å], the Ni–N5 bond [2.100 (3) Å] is much shorter than that of the β -diketonate complexes [2.168 (6)–2.171 (6) Å]. This seems to result from a reduction of the steric congestion around the Ni^{II} centre when NO₃[−] is ligated instead of β -diketonate. The wider N5–Ni–O3 bond angle of 105.2 (1)° in (I) compared with the corresponding angles in the β -diketonate complexes [91.6 (2)–93.5 (2)°] is indicative of such a reduction. The O1–Ni–O4 and O1–Ni–N5 angles of 99.3 (1) and 94.8 (1)° in (I) are also wider compared with those of the β -diketonate complexes [87.7 (2)–88.5 (1) and 87.0 (2)–88.8 (2)°, respectively]. Therefore, the reduction of steric congestion should also result in a shortening of the Ni–O1 bond length of the NIT2py coordination. Thus, while the Ni–N3 bond length of 2.134 (3) Å is almost the same as that of the β -diketonate complexes [2.123 (5)–2.144 (5) Å], the Ni–O1 bond length of 2.014 (2) Å is shorter than that of the β -diketonate complexes [2.052 (4)–2.056 (2) Å]. The Ni–O1–N1 angle in (I) [119.2 (2)°] is almost the same as that in the β -diketonate complexes [117.8 (2)–118.9 (3)°], but the dihedral angle between the nitronyl nitroxide mean plane and the plane of the pyridyl ring of (I) [32.7 (1)°] is a little larger than the corresponding angle of the β -diketonate complexes (23.2–28.7°).

There are no remarkable intermolecular contacts between the nitronyl nitroxide moieties, the shortest intermolecular distance between them being 4.267 (5) Å for O2...N2ⁱ [symmetry code: (i) 1 − x, 1 − y, 2 − z].

The temperature dependence of the magnetic susceptibility of compound (I) was analysed by a similar method to that used for the analysis of the β -diketonate complexes, and the best-fit parameters obtained are $g = 2.24$, $J = -111.1 \text{ cm}^{-1}$ and $\theta =$

−0.649 K. Although the Ni–O(nitroxide) bond is shorter, as mentioned above, the magnetic interaction parameter is nearly equal to those found in the β -diketonate complexes, *viz.* −149.0 cm^{−1} for the acac, −110.1 cm^{−1} for the bzac and −99.8 cm^{−1} for the tfbzac complex (Yoshida *et al.*, 1999).

Experimental

A mixture of [Ni(NO₃)₂(tmen)] (0.47 mmol) and NIT2py (0.51 mmol) in CH₂Cl₂ (30 ml) was stirred at room temperature for 30 min and then evaporated to dryness under reduced pressure. The residue was dissolved in CH₃OH (50 ml) and solid KPF₆ (0.49 mmol) was added to the solution, giving a dark-green precipitate. The precipitate was filtered off and extracted with CH₂Cl₂. The extract was evaporated, again, to dryness, and the residue was recrystallized from CH₂Cl₂/Et₂O giving dark-green crystals of compound (I) (yield: 64%). Analysis found: C 32.62, H 4.80, N 12.04%; calculated for C₁₉H₃₄Cl₂F₆N₆NiO₅P: C 32.55, H 4.89, N 11.99%.

Crystal data

[Ni(NO₃)(C₆H₁₆N₂)(C₁₂H₁₆N₃O₂)]PF₆·CH₂Cl₂
 $M_r = 701.08$
 Monoclinic, $P2_1/c$
 $a = 8.6307$ (18) Å
 $b = 26.690$ (6) Å
 $c = 13.119$ (2) Å
 $\beta = 102.305$ (15)°
 $V = 2952.6$ (10) Å³
 $Z = 4$

$D_x = 1.577 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 14.7$ – 15.0°
 $\mu = 0.97 \text{ mm}^{-1}$
 $T = 296$ (2) K
 Prism, dark green
 $0.26 \times 0.22 \times 0.10 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: by integration (Coppens *et al.*, 1965)
 $T_{\min} = 0.802$, $T_{\max} = 0.881$
 9114 measured reflections
 8605 independent reflections
 3922 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = 0 \rightarrow 12$
 $k = -37 \rightarrow 0$
 $l = -18 \rightarrow 18$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.154$
 $S = 1.00$
 8605 reflections
 369 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.017$
 $\Delta\rho_{\text{max}} = 0.75 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni–O1	2.014 (2)	O1–N1	1.296 (3)
Ni–O3	2.129 (2)	O2–N2	1.276 (4)
Ni–O4	2.125 (2)	O3–N6	1.283 (4)
Ni–N3	2.134 (3)	O4–N6	1.265 (4)
Ni–N4	2.154 (3)	O5–N6	1.211 (4)
Ni–N5	2.100 (3)		
O1–Ni–O3	159.76 (10)	N5–Ni–N4	84.97 (11)
O1–Ni–O4	99.29 (10)	N1–O1–Ni	119.20 (18)
O1–Ni–N3	87.55 (9)	N6–O3–Ni	91.28 (19)
O1–Ni–N5	94.79 (10)	N6–O4–Ni	92.0 (2)
O3–Ni–O4	60.96 (10)	O5–N6–O4	122.8 (4)
N3–Ni–N4	178.03 (11)	O5–N6–O3	121.5 (3)
N5–Ni–O3	105.19 (11)	O4–N6–O3	115.7 (3)
N1–C1–C8–N3	30.1 (5)	N4–C13–C14–N5	−57.5 (5)

H-atom parameters were constrained; C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1985); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1122). Services for accessing these data are described at the back of the journal.

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