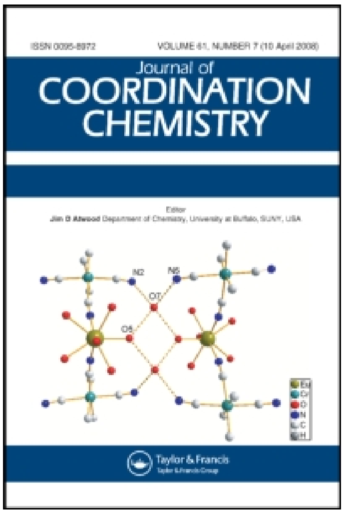

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Synthesis, crystal structure and magnetic properties of a one-dimensional chain polymer, [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$)

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Synthesis, crystal structure and magnetic properties of a one-dimensional chain polymer, $[Ni(IM2\text{-}Py)_2(NO_3)](NO_3)$

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A novel complex $[Ni(IM2\text{-}Py)_2(NO_3)](NO_3)$, where IM2-Py is 2-(2′-pyridyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl, has been synthesized and characterized structurally and magnetically. The structure consists of $[Ni(IM2\text{-}Py)_2(NO_3)]^+$ and a NO_3^- anion. The nickel(II) is in a distorted octahedral environment with four nitrogen atoms from two IM2-Py units and two oxygen atoms from a NO_3^- anion. The units of $[Ni(IM2\text{-}Py)_2(NO_3)]^+$ were connected as a one-dimensional polymer by intermolecular interactions. Variable temperature magnetic susceptibility data show antiferromagnetic interactions between the nickel(II) and imino nitroxide radicals.

Keywords: Crystal structure; Imino nitroxide radical; Magnetic properties; Nickel(II) complex

1. Introduction

The design and synthesis of molecule-based magnetic materials is one of the major goals of materials science with emphasis on the chemical design of molecular assemblies that exhibit spontaneous magnetization and hand the rationalization of magnetostructural correlation [1].

Nitronyl nitroxide radicals (NITR), stable organic radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [2, 3]. There have been many studies on the magnetic properties of imino nitroxide radicals of metal complexes [4–7]. However, studies of nitrate complexes with pyridyl-substituted imino nitroxide radicals have been lacking. In the present work, we obtained a novel one-dimensional nickel(II) complex with 2-pyridyl-substituted imino nitroxide radicals, 2-(2′-pyridyl)-4,4,5,5-teramethyl-2-imidazoline-1-oxyl (IM2-Py in scheme 1), in which nitrate is coordinated as a bidentate ligand. In this article we report the synthesis, X-ray structure and magnetic properties of the title complex.

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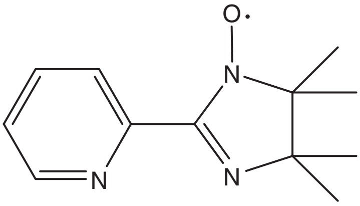

Scheme 1.

2. Experimental

2.1. *General*

All chemicals and solvents purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen atoms were carried out on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was taken on an Avatar^{TM} 360 E. S. P. IR spectrometer in the 4000–600 cm^{-1} region, using KBr pellets. Variable-temperature magnetic susceptibilities were measured on a MPMS XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$.

2.2. *Preparation of the title compound*

IM2-Py was prepared by the literature method [8, 9]. The complex [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$) was synthesized by adding IM2-Py (0.055 g, 0.25 mmol) to a 20 mL ethanol solution of Ni(NO$_3$)$_2$ · 6H$_2$O (0.036 g, 0.125 mmol). The mixture was stirred for 4 h and then filtered; the clear red filtrate was diffused with diethyl ether vapour at room temperature. Brown crystals formed and were collected by filtration and dried in air. Anal. Calcd for [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$) (%): C, 46.54; H, 5.21; N. 18.10. Found: C, 46.49; H, 5.27; N, 18.25. IR (KBr): $\nu_{N\text{–}O}$ (cm^{-1}) 1381.

2.3. *X-ray structure determination*

A brown single crystal having approximate dimensions $0.20 \times 18 \times 0.18\,\text{mm}^3$ was put on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda=0.71073$ Å). The crystal is orthorhombic, space group $P2_12_12_1$ with unit cell dimensions $a=10.993(2)$ Å, $b=13.375(3)$ Å, $c=20.530(4)$ Å, $V=3018.5(10)$ Å^3, $Z=4$, $Dc=1.363\,\text{g cm}^{-3}$. Data were collected at room temperature by an $\omega-2\theta$ scan technique in the range of $1.82 \leq \theta \leq 25.00°$ with index ranges $-13 \leq h \leq 13$, $-15 \leq k \leq 0$, $-24 \leq l \leq 24$ with a total of 8310 reflections collected including 4827 independent ($R_{int}=0.0391$). The structure was solved with direct methods using the SHELXS-97 program. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXTL-97 [10]. The final agreement factor values are $R_1=0.0457$,

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$).

Atom	x	y	z	U_{eq}
Ni(1)	6917(1)	10,063(1)	3056(1)	37(1)
N(1)	5357(3)	10,942(2)	3013(2)	38(1)
N(2)	7293(3)	11,097(2)	3765(2)	38(1)
N(3)	6859(4)	12,576(2)	4192(2)	39(1)
N(4)	8458(3)	9151(2)	3079(2)	40(1)
N(5)	6293(3)	8897(2)	3620(2)	38(1)
N(6)	6680(3)	7414(2)	4080(2)	37(1)
N(7)	7206(4)	10,323(3)	1826(2)	59(1)
N(8)	2412(5)	9768(3)	1459(2)	66(1)
O(1)	6004(3)	13,254(2)	4440(1)	52(1)
O(2)	7533(3)	6847(2)	4441(2)	62(1)
O(3)	7645(3)	10,904(2)	2261(2)	54(1)
O(4)	6601(3)	9581(2)	2060(2)	57(1)
O(5)	7360(4)	10,444(3)	1257(2)	104(2)
O(6)	2849(3)	9145(2)	1843(2)	85(1)
O(7)	1417(3)	10,179(3)	1565(2)	100(1)
O(8)	2994(3)	9982(2)	951(2)	88(1)
C(1)	4388(4)	10,775(3)	2644(2)	50(1)
C(2)	3383(4)	11,405(3)	2641(2)	54(1)
C(3)	3428(4)	12,261(3)	3007(3)	55(1)
C(4)	4451(4)	12,451(3)	3380(2)	44(1)
C(5)	5385(4)	11,767(3)	3384(2)	37(1)
C(6)	6514(4)	11,823(3)	3787(2)	33(1)
C(7)	7816(4)	12,199(3)	4633(2)	40(1)
C(8)	8380(4)	11,397(3)	4162(2)	41(1)
C(9)	8652(4)	13,045(3)	4831(2)	59(2)
C(10)	7217(4)	11,737(3)	5232(2)	58(1)
C(11)	8911(4)	10,481(3)	4510(2)	61(1)
C(12)	9303(4)	11,848(3)	3698(2)	61(2)
C(13)	9509(4)	9312(3)	2769(2)	48(1)
C(14)	10,470(4)	8638(3)	2792(2)	59(1)
C(15)	10,313(4)	7761(3)	3131(3)	61(1)
C(16)	9227(4)	7575(3)	3441(2)	46(1)
C(17)	8309(4)	8285(3)	3412(2)	35(1)
C(18)	7096(4)	8201(3)	3712(2)	33(1)

$wR_2 = 0.0650\,(I > 2\sigma(I))$. $w = 1/[\sigma^2(F_o)^2 + (0.0256P)^2 + 0.0000P]$ where $P = (F_o^2 + F_c^2)/3$, $S = 0.961$, $(\Delta\rho)_{\max} = 0.342$ and $(\Delta\rho)_{\min} = -0.245\,\text{e}\,\text{Å}^3$. Positional parameters and selected bond distances and angles are given in tables 1 and 2, respectively.

3. Results and discussion

3.1. *Description of crystal structure of [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$)*

An ORTEP drawing of [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$) is shown in figure 1. The crystal structure consists of [Ni(IM2-Py)$_2$(NO$_3$)]$^+$ and an uncoordinated NO$_3^-$. In the complex, the coordination geometry about the nickel(II) ion is a distorted octahedral with chelation by two IM2-Py ligands through the pyridyl nitrogen and imino nitroxide nitrogen leading to two five-membered rings, together with one chelated nitrate anion ligand. The two oxygen atoms (O3, O4) from nitrate ligand and two nitrogen atoms (N2, N5) from two different IM2-Py radicals comprise the equatorial plane,

Table 2. Selected bond lengths (Å) and angles (°) for [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$).

Ni(1)–N(2)	2.049(3)	N(3)–O(1)	1.402(4)
Ni(1)–N(5)	2.060(3)	N(6)–O(2)	1.415(4)
Ni(1)–N(1)	2.080(3)	Ni(1)–O(3)	2.138(3)
Ni(1)–N(4)	2.089(3)	Ni(1)–O(4)	2.173(3)
N(2)–Ni(1)–N(5)	100.29(13)	C(8)–N(2)–Ni(1)	136.6(3)
N(2)–Ni(1)–N(1)	79.36(13)	C(1)–N(1)–Ni(1)	126.2(3)
N(5)–Ni(1)–N(1)	100.20(13)	C(5)–N(1)–Ni(1)	115.0(3)
N(2)–Ni(1)–N(4)	102.38(14)	C(6)–N(2)–Ni(1)	113.4(3)
N(5)–Ni(1)–N(4)	79.33(13)	C(20)–N(5)–Ni(1)	139.2(3)
N(1)–Ni(1)–N(4)	178.24(13)	C(13)–N(4)–Ni(1)	126.6(3)
N(2)–Ni(1)–O(3)	96.43(12)	C(17)–N(4)–Ni(1)	114.4(3)
N(5)–Ni(1)–O(3)	162.19(11)	C(18)–N(5)–C(20)	107.1(3)
N(1)–Ni(1)–O(3)	88.81(12)	C(18)–N(5)–Ni(1)	113.6(3)
N(4)–Ni(1)–O(3)	91.20(12)	O(5)–N(7)–O(3)	123.2(5)
N(2)–Ni(1)–O(4)	154.29(12)	O(5)–N(7)–O(4)	122.9(4)
N(5)–Ni(1)–O(4)	104.56(12)	O(3)–N(7)–O(4)	113.9(4)
N(1)–Ni(1)–O(4)	89.79(12)	O(6)–N(8)–O(7)	121.7(5)
N(4)–Ni(1)–O(4)	88.69(13)	O(6)–N(8)–O(8)	118.8(5)
O(3)–Ni(1)–O(4)	59.79(11)	O(7)–N(8)–O(8)	119.5(5)
N(7)–O(4)–Ni(1)	92.2(2)	N(7)–O(3)–Ni(1)	94.1(2)

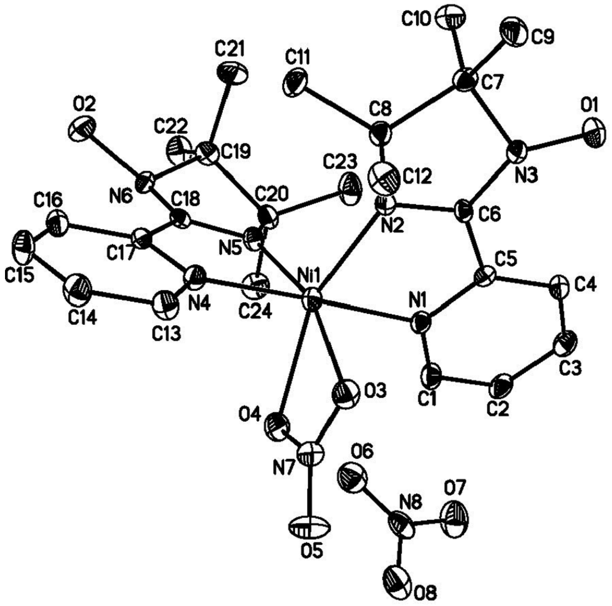

Figure 1. The structure of the title compound.

whereas the axial positions are filled by two nitrogen atoms (N1, N4) from different pyridyl rings. The bond lengths of Ni–O(3) and Ni–O(4) are 2.138(3) and 2.173(3) Å, respectively. The bond lengths of the axial Ni–N ((Ni–N(1) = 2.080(3) Å and Ni–N(4) = 2.089(3) Å) are longer than those of the equatorial Ni–N (Ni–N(2) = 2.049(3) Å and Ni–N(5) = 2.060(3) Å), which are in the normal range [11]. Distortion along the axial direction is demonstrated by the N1–Ni–N4

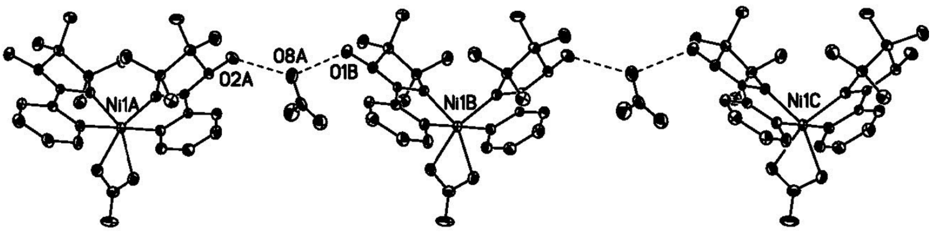

Figure 2. A sketch of the intermolecular interaction of the title compound.

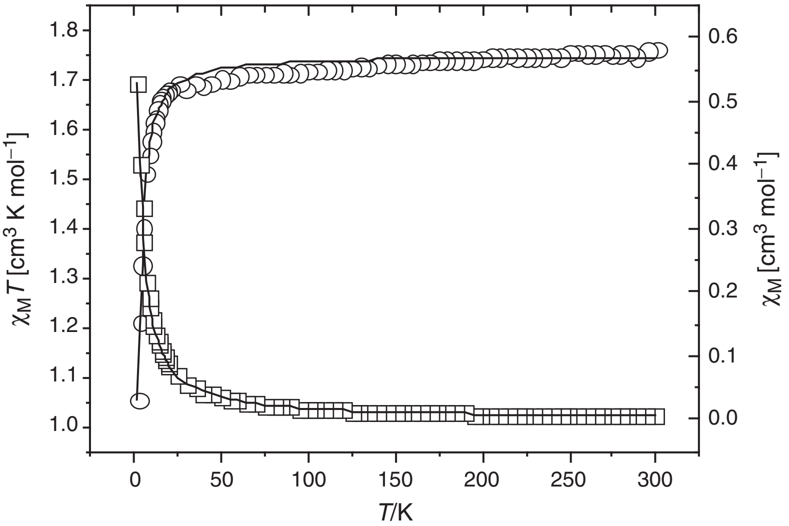

Figure 3. Temperature dependence of $\chi_M T$ (○) and χ_M (□) for [Ni(IM2-Py)$_2$(NO$_3$)](NO$_3$) and their corresponding theoretical curves (solid lines).

angle of 178.24°. The dihedral angles between the imino nitroxide fragments (N2–C6–N3–O1 and N5–C18–N6–O2) and the pyridyl rings for the two different IM2-Py ligands are 4.8 and 15.7°.

Intermolecular short contacts occur between one oxygen atom from the uncoordinated NO_3^- and two oxygen atoms of the NO groups of neighboring [Ni(IM2-Py)$_2$(NO$_3$)]$^+$ units (2.682 Å for O1A···O8A, 2.684 Å for O8A···O2B). The units of [Ni(IM2-Py)$_2$(NO$_3$)]$^+$ and uncoordinated NO_3^- anions were connected as a one-dimensional chain by the intermolecular (O···O···O) contacts (figure 2). To the best of our knowledge, this is the only nickel(II) example of a one-dimensional chain by NO_3^- anions directly contacting the oxygen atoms of radicals.

3.2. *Magnetic properties*

The variable temperature magnetic susceptibilities of the title complex were measured in the 2–300 K region at a magnetic field of 10,000 G. The plot of $\chi_M T$ and χ_M versus T is shown in figure 3. The $\chi_M T$ value at room temperature is 1.76 cm^3 K mol^{-1}, which is close to the spin-only value expected for one $S_{\mathrm{Ni}} = 2/2$ spin and two $S_{\mathrm{rad}} = 1/2$ uncorrelated spins ($1.75\,\mathrm{cm^3\,K\,mol^{-1}}$). When the temperature is lowered, the $\chi_M T$ value decreases slowly, and below approximately 20 K, the $\chi_M T$ decreases rapidly reaching a value of $1.05\,\mathrm{cm^3\,K\,mol^{-1}}$, implying the existence of a weak antiferromagnetic spin exchange interaction between Ni(II) ion and the IM2-Py units within the complex.

In order to quantitatively evaluate the magnetic interaction in the system, on the basis of spin Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$ ($S_1 = S_3 = 1/2$, $S_2 = 1$), the magnetic susceptibility of the R(S_1)–Ni(II)(S_2)–R(S_3) (R = IM2-Py) unit can be deduced as follows [12–14]:

$$\chi_M = 2\frac{Ng^2\beta^2}{K(T-\theta)}\frac{A}{B}$$

$$A = 5\exp[4J/KT] + 1 + \exp[2J/KT]$$

$$B = 5\exp[4J/KT] + 3 + \exp[-2J/KT] + 3\exp[2J/KT]$$

where J corresponds to the coupling between the nickel(II) ion and radical and θ is the resultant intermolecular interaction parameter [11]. The least-squares analysis of magnetic susceptibility data led to $J = -1.10\,\mathrm{cm^{-1}}$, $\theta = 0.9\,\mathrm{K}$, $g = 2.01$ with $R = 2.12 \times 10^{-3}$, where R is defined as $R = \sum[(\chi_M)_{\mathrm{obs}} - (\chi_M)_{\mathrm{calc}}]^2 / \sum(\chi_M)^2_{\mathrm{obs}}$. The results indicate that the antiferromagnetic interaction exits between the Ni(II) ion and the radical, as is usually observed [14, 15]. Moreover, there is a weak intermolecular ferromagnetic interaction ($\theta = 0.9\,\mathrm{K}$) in the complex.

The geometrical parameters of the binding of the radical to the metal are of great importance for understanding magnetic properties of the complex. Following the Kahn–Briat rules [16], the extent of overlap between metal and radical magnetic orbitals is responsible for the appearance of antiferromagnetic interactions, whereas orthogonality of the same orbitals induces ferromagnetic contributions. The structural analysis of the title compound shows that two radical groups coordinate in equatorial positions. The geometry is favorable for overlap of orbitals but not to orthogonality, leading to decreasing the ferromagnetic interaction and then increasing the antiferromagnetic interaction [17] between nickel(II) magnetic $d_{x^2-y^2}$ orbitals and the radical π^* orbitals. In this complex, the dihedral angles between the Ni(II) ion basal plane and two imidazoline planes are 44.5 and 51.8° respectively, which greatly deviate from 90°, leading to poor magnetic coupling ($J = -1.12\,\mathrm{cm^{-1}}$). Furthermore, a remarkable decrease of $\chi_M T$ below 20 K may be due either to the zero-field splitting or to spin-orbit coupling.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 240142. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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