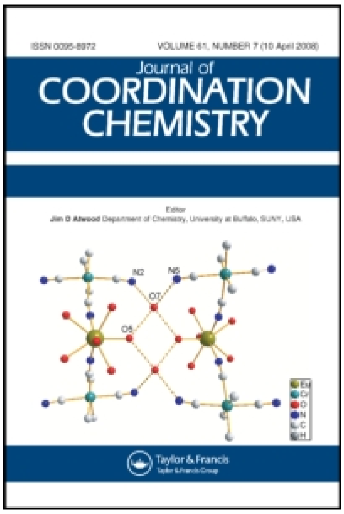

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Synthesis, crystal structure and magnetic properties of a nickel(II) complex containing a 2-pyridyl-substituted nitronyl nitroxide

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A NICKEL(II) COMPLEX CONTAINING A 2-PYRIDYL-SUBSTITUTED NITRONYL NITROXIDE

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A new complex of formula $[Ni(NIT2Py)_2Cl(H_2O)]Cl\cdot 2CH_3OH$, where NIT2Py is 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, was synthesized and characterized structurally and magnetically. The structure consists of a $[Ni(NIT2Py)_2Cl(H_2O)]^+$ ion, a chloride anion and two methanol molecules. The nickel(II) ion lies in a distorted octahedral environment; two nitrogen atoms and two oxygen atoms from NIT2Py ligands from the basal plane; one oxygen atom from a water molecule and one chloride anion occupy axial positions. Variable temperature magnetic susceptibility data show that there is strong antiferromagnetic coupling between the nickel(II) ion and nitronyl nitroxide radicals. The results suggest that the sign of the magnetic interaction depends on structural and ligand effects.

Keywords: Crystal structure; Nitronyl nitroxide; Nickel(II) complex; Magnetism; Antiferromagnetic interaction

INTRODUCTION

There has been much interest in the study of transition metal complexes containing nitroxide radicals in recent years [1]. Complexes of nitronyl or imino nitroxides substituted by *N*-heteroaromatic groups have been extensively studied because the auxiliary heteroaromatic–N donor forces the nitroxide-O atom to bind to a weakly electrophilic metal centre by the chelate effect [2–7]. As stable organic radicals, nitronyl nitroxide radicals (NITR) have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [8,9].

In particular, their magneto-structural correlation has been widely investigated. Magnetic coupling between metal ion and organic radical is either ferromagnetic or antiferromagnetic and this depends on the nature of each magnetic orbital and the coordination environment. The most typical of the *N*-heteroaromatic-substituted

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nitronyl nitroxides is 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide (NIT2Py). Herein, we report a new nickel(II) complex, $[Ni(NIT2Py)_2Cl(H_2O)]Cl\cdot 2CH_3OH$, which is different from other reported complexes, $[NiCl_2(NIT2Py)_2]\cdot 2CH_2Cl_2$ [2] and $[NiCl_2(NIT2Py)_2]\cdot CH_2Cl_2$ [10]. It is interesting to compare the crystal and molecular structures of $[Ni(NIT2Py)_2Cl(H_2O)]Cl\cdot 2CH_3OH$ and $[NiCl_2(NIT2Py)_2]\cdot nCH_2Cl_2$, ($n = 1$ or 2) from the viewpoint of the magnetic properties. A structure analysis of the title complex would be helpful in understanding magnetic properties.

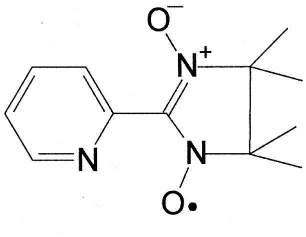
EXPERIMENTAL

General

All starting materials were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Perkin Elmer 240 instrument. Infrared spectra were recorded on a Shimadzu 408 spectrophotometer in the 4000–600 cm^{-1} region, using KBr pellets. Magnetic susceptibility measurements of a crystal sample were carried out in the temperature range 77–300 K, on an LDJ9600VSM magnetometer at a field strength of 5000 G. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and magnetic moments were calculated using the equation $\mu_{eff} = 2.828\ (\chi_M T)^{1/2}$.

Preparation of $[Ni(NIT2Py)_2Cl(H_2O)]Cl\cdot 2CH_3OH$

2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (Scheme 1) was prepared according to a literature method [11,12].



Scheme 1

The title complex, $[Ni(NIT2Py)_2Cl(H_2O)]Cl\cdot 2CH_3OH$, was synthesized as follows: 0.234 g (1 mmol) NIT2Py and 0.117 g (0.5 mmol) $NiCl_2\cdot 6H_2O$ were dissolved in 20 cm^3 absolute methanol. The solution was stirred at room temperature for 2 h and then filtered; the purple filtrate was allowed to stand at room temperature for five days. Darkblue crystals were obtained. Yield: 76%. Anal. Calcd. for $C_{26}H_{42}N_6O_7Cl_2Ni$(%): C, 45.90; H, 6.22; N, 12.35; Found: C, 45.86; H, 6.18; N, 12.54. IR (KBr): $\nu_{N\text{–}O}$ 1345 s cm^{-1}.

Crystal Structure Determination

A dark-blue single crystal of the title complex with approximate dimensions 0.26 × 0.20 × 0.16 mm was selected and mounted on a glass fibre. All measurements were

TABLE I Crystallographic data for $[Ni(NIT2Py)_2Cl(H_2O)]Cl{\cdot}2CH_3OH$

Empirical formula	$C_{26}H_{42}N_6O_7Cl_2Ni$
Formula weight	680.27
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit-cell dimensions (Å,°)	$a = 16.088(5)$ $b = 20.894(6)$ $\beta = 112.85(1)°$ $c = 10.420(3)$
Volume ($Å^3$)	3235.1(11)
Z	4
Absorption coefficient (mm^{-1})	0.817
$F(000)$	1432
Crystal size (mm^3)	$0.26 \times 0.20 \times 0.16$
θ range for data collection (°)	2.25 to 25.01
Limiting indices	$-18 \leq h \leq 19$, $-24 \leq k \leq 10$ $-12 \leq l \leq 12$
Reflections collected	7270
Independent reflections	2858 ($R_{int} = 0.0447$)
Completeness to $\theta = 25.20$	99.9%
Maximum and minimum transmission	0.7919 and 0.8671
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2858/0/199
Goodness-of-fit on F^2	1.000
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0434$, $wR2 = 0.0887$
R indices (all data)	$R1 = 0.0832$, $wR2 = 0.1037$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.439 and -0.275

made on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the ω–2φ scan technique in the range $2.25° \leq \theta \leq 25.01°$ with index ranges $-18 \leq h \leq 19$, $-24 \leq k \leq 10$, $-12 \leq l \leq 12$. A total of 7270 reflections were collected, including 2858 independent ones ($R_{int} = 0.0447$). A summary of crystallographic data is given in Table I. The structure was solved with direct methods using the SHELXS-97 program. H atoms were assigned 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 SHELXL 97. The weighting scheme used was $w = 1/[\sigma^2(F_0^2) + (0.0431P)^2 + 2.6185P]$ where $P = (F_0^2 + 2F_c^2)/3$. Positional parameters and selected bond parameters are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Crystal Structure of $[Ni(NIT2Py)_2Cl(H_2O)]Cl{\cdot}2CH_3OH$

An ORTEP drawing of $[Ni(NIT2Py)_2Cl(H_2O)]^+$ is shown in Fig. 1. The coordination geometry about the nickel(II) ion shows a distorted octahedral N_2O_3Cl environment. The equatorial plane is formed by O(1), O(1A) and N(1), N(1A) from two NIT2Py ligands. Deviations of the four donor atoms [N(1), O(1), O(1A), N(2A)] from their mean plane are -0.704 (for N), 0.704 Å (for O), respectively, and Ni(1) lies 0.105 Å out of the plane. Axial positions are occupied by an oxygen atom from a water molecule and a chlordie anion. The Ni–N (pyridyl) bond length is 2.065(3) Å and the Ni–O

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Ni(NIT2Py)_2Cl(H_2O)]Cl \cdot 2CH_3OH$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ni(1)	5000	6797(1)	7500	33(1)
Cl(1)	5000	5664(1)	7500	45(1)
O(1)	5843(2)	6882(1)	6460(2)	38(1)
O(2)	8123(2)	5549(1)	9171(3)	72(1)
O(3)	5000	7804(2)	7500	48(1)
N(1)	6149(2)	6814(1)	9308(2)	34(1)
N(2)	6480(2)	6459(1)	6831(3)	35(1)
N(3)	7545(2)	5821(2)	8113(3)	48(1)
C(1)	6104(2)	7072(2)	10448(3)	38(1)
C(2)	6846(3)	7127(2)	11692(4)	46(1)
C(3)	7662(3)	6909(2)	11764(4)	49(1)
C(4)	7723(2)	6634(2)	10603(4)	42(1)
C(5)	6954(2)	6589(1)	9402(3)	33(1)
C(6)	6987(2)	6299(2)	8130(3)	34(1)
C(7)	6734(3)	6124(2)	5763(4)	44(1)
C(8)	5880(3)	5909(2)	4568(4)	74(1)
C(9)	7238(3)	6618(2)	5262(4)	63(1)
C(10)	7345(3)	5580(2)	6658(4)	49(1)
C(11)	6854(3)	4940(2)	6544(5)	74(1)
C(12)	8237(3)	5486(2)	6498(4)	70(1)
Cl(2)	5000	7956(1)	2500	83(1)
O(4)	5235(4)	8462(2)	5441(4)	117(2)
C(13)	5313(4)	9109(3)	5519(6)	95(2)

TABLE III Selected bond lengths (Å) and angles (°) for $[Ni(NIT2Py)_2Cl(H_2O)Cl \cdot 2CH_3OH$

Ni(1)–O(1)	2.065(3)
Ni(1)–N(1)	2.045(2)
Ni(1)–O(3)	2.103(3)
Ni(1)–Cl(1)	2.3685(15)
O(1)–N(2)	1.292(3)
O(2)–N(3)	1.267(4)
O(1A)–Ni(1)–O(1)	170.15(13)
O(1)–Ni(1)–N(1A)	93.32(10)
O(1)–Ni(1)–N(1)	86.51(10)
N(1A)–Ni(1)–N(1)	178.07(15)
O(1)–Ni(1)–O(3)	85.07(6)
N(1)–Ni(1)–O(3)	89.03(8)
O(1)–Ni(1)–Cl(1)	94.93(6)
N(1)–Ni(1)–Cl(1)	90.97(8)
O(3)–Ni(1)–Cl(1)	180.0

(NIT2Py) bond distance is 2.045(2) Å. The N–O distance is 0.025 Å longer in the coordinated nitronyl group than in the uncoordinated one. Distances of the two bonds (Ni–O, Ni–N) are shorter than those reported for $[NiCl_2(NIT2Py)_2] \cdot nCH_2Cl_2$ ($n = 1$ or 2) [2,10], consistent with the bigger N–Ni–O bite angle of NIT2Py in the title complex (86.51°). The Ni–O (H_2O) bond distance is 2.103(3) Å, while the Ni–Cl bond length is 2.3685(15) Å. The structural parameters of the title complex indicate that there are two equivalent NIT2Py moieties. The dihedral angle between the NO–C–N moiety and the equatorial plane is 32.12(2)° and the dihedral angle between the NO–C–N moiety and the pyridyl ring of NIT2Py is 31.94(5)°, larger than for reported

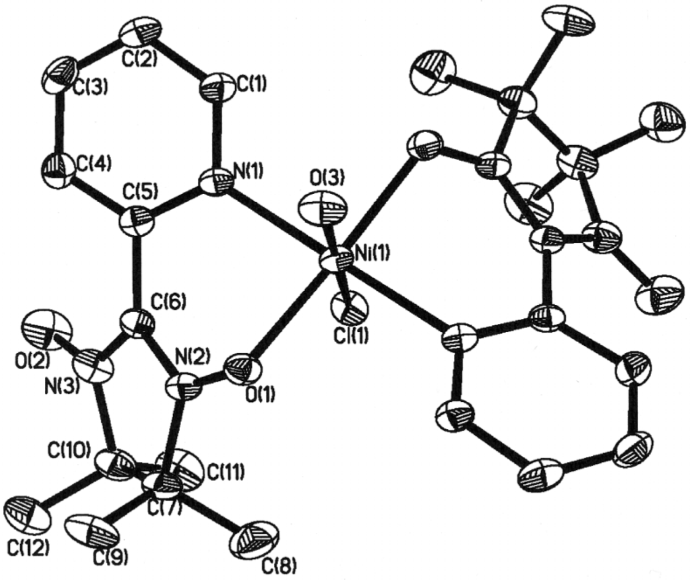


FIGURE 1 ORTEP drawing with 30% thermal ellipsoid probability showing atom labelling for $[Ni(NIT2Py)_2Cl(H_2O)]^+$.

complexes [2,10]. As is known, this structural difference can be important with respect to magnetic properties [2,13]. There are no notable short intermolecular contacts in the crystal structure of the complex, which exists as a discrete molecule.

Spectroscopic Properties

The infrared spectrum of $[Ni(NIT2Py)_2Cl(H_2O)Cl\cdot 2CH_3OH$ displays a strong characteristic band for the N–O group at $1345\,cm^{-1}$, at lower wave numbers than that of ν(N–O) in free NIT2Py ($1375\,cm^{-1}$). The results simply indicate coordination of the N–O group of NIT2Py. The electronic absorption spectrum of the complex was measured in methanol solution. Absorption bands around 388 nm are assigned to intraligand n–π^* transitions of NIT2Py, and bands around 348 nm correspond to π–π^* transitions of NIT2Py [13]. A broader band centred at 576 nm is attributed to d–d transitions of the nickel(II) ion.

Magnetic Properties

The variable temperature magnetic susceptibilities, χ_M, of the title complex were measured in the region 77–300 K in a magnetic field of 5000 G, and results are shown in Fig. 2. The μ_{eff} value per molecule at room temperature is $3.5\mu_B$, lower than the value expected for two non-coupled $S_{R1} = S_{R2} = 1/2$ and one $S_{Ni} = 1$ spins ($3.74\mu_B$). As the temperature is lowered, the μ_{eff} value decreases smoothly, implying the existence of antiferromagnetic spin exchange between Ni(II) and NIT2Py.

As mentioned above, the title complex exists as discrete molecules, so intermolecular interaction is negligible. The magnetic data were fitted with Eq. (1), reduced according

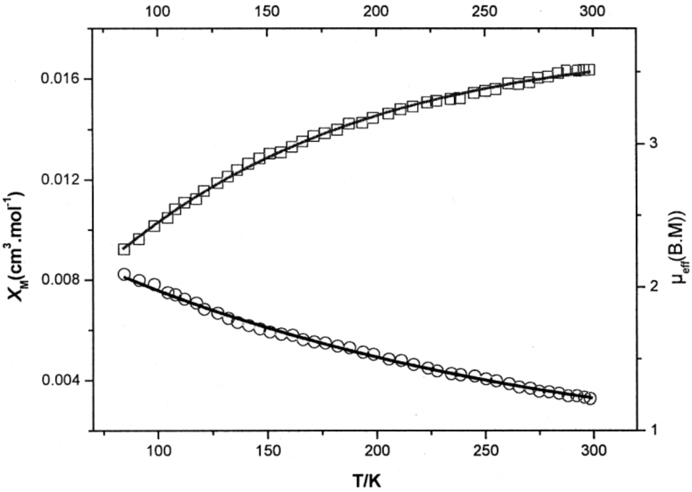


FIGURE 2 Temperature dependence on the molar susceptibility (χ_M) (o) and the magnetic moment (μ) (□) for $[Ni(NIT2Py)_2Cl(H_2O)]Cl \cdot 2CH_3OH$, and corresponding theoretical curves (solid lines).

to the Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$ ($S_1 = S_3 = 1/2$, $S_2 = 1$), where J is the interaction parameter between nickel(II) and the nitronyl nitroxide radical.

$$X_M = -\frac{2Ng^2\beta^2}{KT}\frac{A}{B} \tag{1}$$
$$A = 5\exp[4J/KT] + 1 + \exp[2J/KT]$$
$$B = 5\exp[4J/KT] + 3 + \exp[-2J/KT] + 3\exp[2J/KT]$$

The best-fit parameters are $J = -88.94\,\mathrm{cm}^{-1}$, $g = 2.09$ with $R = 1.74 \times 10^{-4}$, where R is defined as $R = \sum[(\chi_M)_{\rm obs} - (\chi_M)_{\rm calc}]^2 / \sum(\chi_M)^2_{\rm obs}$.

The result ($J = -88.94\,\mathrm{cm}^{-1}$) indicates that a strong aniferromagnetic interaction exists between Ni(II) and NIT2Py, but is smaller than for other reported complexes [2,10]. The difference may be explained on the basis structure, especially the dihedral angles between the NO–C–N moieties and pyridyl rings of the NIT2Py ligands [13].

Acknowledgments

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Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 25883. 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 www: http://www.ccdc.cam.ac.uk).

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