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Synthesis, Crystal Structures, and Magnetic Properties of a New Nickel(II) Complex with Nitronyl Nitroxide[1]

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Abstract—A new nickel(II) complex $[Ni(NIT\text{-}1'\text{-}MeBzIm)_2(H_2O)_2] \cdot ClO_4 \cdot H_2O$ (NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) has been prepared and structurally characterized by single-crystal X-ray diffraction. Complex I crystallizes in monoclinic, space group *C*2/*c*, $Z = 4$. Crystal data: $C_{30}H_{46}N_8O_{16}ClNi$, $Mr = 869.06$, $a = 13.958(3)$, $b = 15.904(4)$, $c = 18.514(5)$ Å, $\beta = 101.047(3)°$. The X-ray analysis reveals that Ni^{2+} ion resides in a distorted octahedron center, the complex was linked by intermolecular hydrogen bonds, resulting in a 2D network configuration. Magnetic investigation indicates the existence of interamolecular interactions is antiferromagnetic with $J = -40.76$ cm^{-1}.

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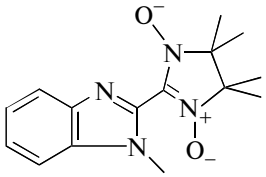
INTRODUCTION

The families of radicals and the corresponding mental-radical complexes have attracted considerable attention and have been extensively studied in the quest for new molecule based magnetic materials for several years [1–4]. The major aims in the field are on one hand the chemical design of molecular assemblies that exibit a spontaneous magnetization, and on the other hand the rationalization of magneto-structural correlation in particular the manner how structural factors affect the metal-organic radical interactions. Discrete molecular transition-metal complexes containing open shell ligands, though not themselves candidates as magnetic material, are useful as models for the magnetic exchange coupling expected in extended structures of higher lattice dimensionality.

The nitronyl nitroxides substituted with pyridyl, imidazolyl and benzimidazolyl groups (NIT-R) have the advantage of forming stable chelated complexes with the support of auxiliary substituent-groups [5–7]. Up to now, there have been a large number of investigations with regard to first-row transition metal complexes with NIT-R (R = pyridyl [8–12], imidazolyl [13, 14], benzimidazolyl, thiazolyl, triazolyl, and so on) concerning the corresponding structures and various properties especially the magnetic properties. These radicals are attractive due to their donor atoms and to assemble an extended co-ordination geometry with changing magnetic coupling, they are found to be indeed efficient in giving strongly coupled nitroxide–metal complexes with poorly acidic metal center.

In the present work, we have synthesized one metal-radical complex $[Ni(NIT\text{-}1'\text{-}MeBzIm)_2(H_2O)_2] \cdot ClO_4 \cdot H_2O$ (**I**), where NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide:



(NIT-1'-MeBzIm)

In addition, we extend to report the hydrogen-bonded molecular structure of the complex which is 2D network configuration. Magnetic investigation indicates the existence of intermolecular interactions is antiferromagnetic with $J = -40.76$ cm^{-1}.

EXPERIMENTAL

All chemicals and solvents purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellet on an Avatar^{TM} 360 E.S.P. IR spectrometer. The crystal determination was performed on a Bruker Smart APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Synthesis. The nitronyl nitroxide radical, NIT-1'-MeBzIm, was prepared according to the literature method [15, 16]. Complex **I** was synthesized by adding

[1] The article is published in the original.

dropwise an orange methanol solution (5 mL) of NIT-1'-MeBzIm (0.286 g, 1 mmol) into 5 mL methanol solution of $Ni(NO_3)_2 \cdot 5H_2O$ (0.178 g, 0.5 mmol). The mixture was stirred for 6 h at room temperature and then filtered. The clear orange filtrate was diffused with diethyl ether vapour at room temperature and darkpurple block crystals were obtained after one week. The yield was 60.5%.

For $C_{30}H_{46}N_8O_{16}ClNi$			
anal. calcd., %:	C, 39.85;	H, 5.13;	N, 12.39.
Found, %:	C, 39.78;	H, 5.28;	N, 12.45.

IR (KBr; ν, cm^{-1}): 1375.23 ν(N–O), 1378.13 ν(C–N), 1480.95 δ(CH_3), 1376.9 ω(CH_3), 1617.79—the framework vibration of benzimidazole; 2193 ν_s(C≡N), 2266 ν_{as}(C≡N), 1355 ν_{as}(C≡N)—the present of $[N(CN)_2]^{-1}$ ligand

X-ray structure determination. Darkpurple single crystal of complex **I** were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using a ϕ/ω scan technique at room temperature. A total of 14206 (R_{int} = 0.0249), of which 3747 observed reflections with $I > 2\sigma(I)$ were employed for structure refinements. The structure was solved by direct methods with SHELXS-97 [17]. Corrections for absorption were carried using SADABS. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [18]. The final agreement factor values are $R = 0.0502$ and $wR = 0.1433$ ($w = 1/[\sigma^2(F_o^2) + (0.1043P)^2 + 0.1165P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.054$, $(\Delta/\sigma)_{max} = 0.005$, $(\Delta\rho)_{max} = 0.618$, $(\Delta\rho)_{min} = -0.451$ $e/Å^3$.

The crystal data and experimental parameters for **I** is given in Table 1. The selected bond lengths and angles of **I** is given in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 652301; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and details of the experiment and refinement for **I**

Parameter	Value
Formula weight	869.06
T, K	291(2)
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	13.958(3)
b, Å	15.904(4)
c, Å	18.514(5)
β, deg	101.047(3)
V, $Å^3$	4033.5(17)
Z	4
ρ_{calcd}, g cm^{-3}	1.489
$F(000)$	1972
μ, mm^{-1}	0.692
Max and min transmission	0.0502 and 0.1433
θ Range for data collection, deg	2.40–25.49
Limiting indices h, k, l	$-16 \le h \le 16$, $-19 \le k \le 19$, $-22 \le l \le 22$
Collected reflections	14206
Independent reflections (R_{int})	6978 (0.0588)
Reflections with $I > 2\sigma(I)$	4572
Data/restraints/parameters	3747/343/277
GOOF	1.054
$R(F_o)$, $I > 2\sigma(I)$	0.1433
$Rw(F_o)$, $I > 2\sigma(I)$	0.1535
Largest diff. peak and hole (e $Å^{-3}$)	0.930 and –0.644

RESULTS AND DISCUSSION

The ORTEP drawing of complex **I** is shown in Fig. 1. In which Ni^{2+} ion resides in a distorted octahedron center and is coordinated by two NN oxygen atoms O(1), O(1)$^{\#1}$ and two benzimidazolyl nitrogen atoms N(1), N(1)$^{\#1}$ of NIT-1'-MeBzIm radicals from the equatorial position to form a *trans* configuration. The Ni^{2+} ion is highly coplanar with the basal plane with a displacement of 0.065 Å (with the bond lengths of 2.089(5) Å Ni(1)–O(1), Ni(1)–N(1) 2.0914(15) Å). The axial positions are occupied by two water molecular oxygen atoms O(3) and O(4) (the bond length is 2.0382(19) Å for Ni(1)–O(3) and 2.0706(19) Å for Ni(1)–O(4)). The axial direction is slightly deviated from the normal of the equatorial plane as indicated by the average angles of 91.47°, O(1)Ni(1)O(4) 89.92(4)°, N(1)Ni(1)O(4) 93.02(4)°.

Intermolecular H-bonds are found in the crystal of **I**, the corresponding stacking structure is displayed in Fig. 2. The noncoordinated clorate anions, water and methanol molecules are inserted into the crystal spacing and participate in H-bond packing as the bridges to link the molecules. Every molecule is connected with three neighboring molecules by H-bonds to form a 2D plane. There are three kinds of H-bonds, they occurred: (i) between coordinated H_2O and uncoordinated ClO_4^- (O(4)–H(2*w*)···O(8)$^{\#4}$) 2.792(3) Å;

Table 2. Selected bond lengths (Å) and angles (deg) for **I**

Bond	*d*, Å	Bond	*d*, Å
Ni(1)–O(3)	2.0382(19)	Ni(1)–O(4)	2.0706(19)
Ni(1)–O(1)	2.0579(14)	Ni(1)–N(1)	2.0915(15)
Angle	ω, deg	Angle	ω, deg
O(3)Ni(1)O(1)	90.18(4)	N(3)O(1)Ni(1)	117.84(11)
O(1)Ni(1)O(1)$^{\#1}$	179.64(7)	Ni(1)O(3)H(1*w*)	123
O(1)Ni(1)O(4)	89.82(4)	Ni(1)O(4)H(2*w*)	126
O(1)$^{\#1}$Ni(1)N(1)$^{\#1}$	87.58(6)	H(4*w*)O(9)H(3*w*)	109
O(3)Ni(1)N(1)	86.98(4)	C(7)N(1)C(1)	104.81(15)
O(1)Ni(1)N(1)	87.58(6)	C(7)N(1)Ni(1)	122.88(12)
O(4)Ni(1)N(1)	93.02(4)	C(1)N(1)Ni(1)	127.96(12)
N(1)$^{\#1}$Ni(1)N(1)	173.97(8)		

(ii) between uncoordinated oxygen atom of NN and uncoordinated H_2O (O(9)–H(3*w*)···O(2)$^{\#2}$ 2.795(3) Å); (iii) between uncoordinated H_2O and uncoordinated ClO_4^- (O(9)–H(4*w*)···O(7)$^{\#3}$ 2.951(4) Å).

The plots of $\chi_M T$ and χ_M versus T for **I** are shown in Fig. 3. The $\chi_M T$ value at room temperature is 1.73 cm^3 K mol^{-1}, close to the value expected for noncoupling one $S_{Ni} = 2/2$ spin and two $S_{rad} = 1/2$ spins (1.75 cm^3 K mol^{-1}). As the temperature decreases from 300 K down to 27 K, $\chi_M T$ value gradually decreases from 1.73 cm^3 K mol^{-1} to a minimum value of 0.029 cm^3 K mol^{-1}, indicating the existence of antiferromagnetic couplings in the complex.

There are two ways of magnetic interactions for the system: (i) intramolecular couplings of Ni(II)-coordinated NIT-1'-MeBzIm radicals and (ii) intermolecular interactions of neighboring NIT-1'-MeBzIm radicals by H-bonds. For quantitatively evaluate these magnetic interactions in the system, on the basis of spin Hamiltonian $\hat{H} = -2J(\hat{S}_{rad1}\hat{S}_{Ni} + \hat{S}_{Ni}\hat{S}_{rad2})$ ($S_{rad1} = S_{rad2} = 1/2$, $S_{Ni} = 1$), the magnetic susceptibility of the R(S_{rad1})-Ni(II)(S_{Ni})-R(S_{rad2}) (R = NIT-1'-MeBzIm) unit can be deduced as follows [19–21]:

$$\chi_M = 2\frac{Ng^2\beta^2}{KT}\frac{A}{B}$$

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

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

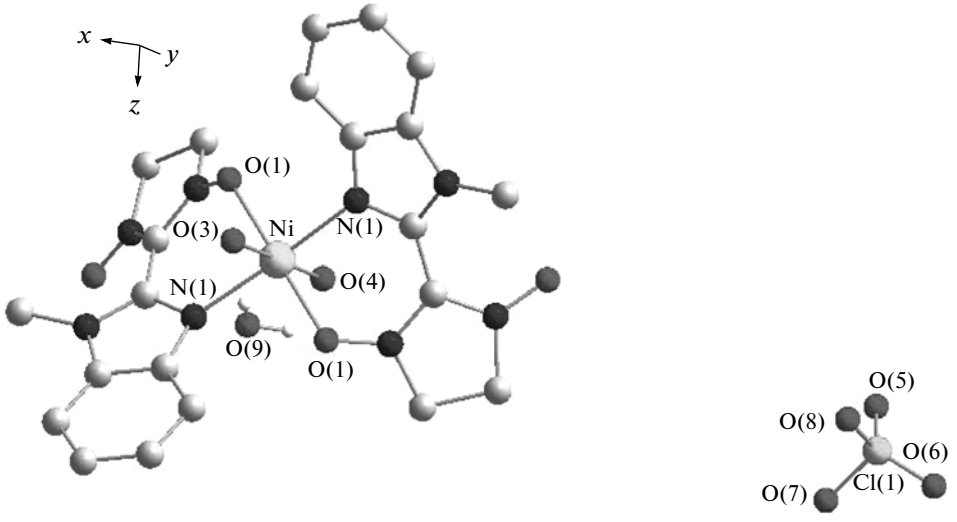


Fig. 1. Molecular structure of **I**.

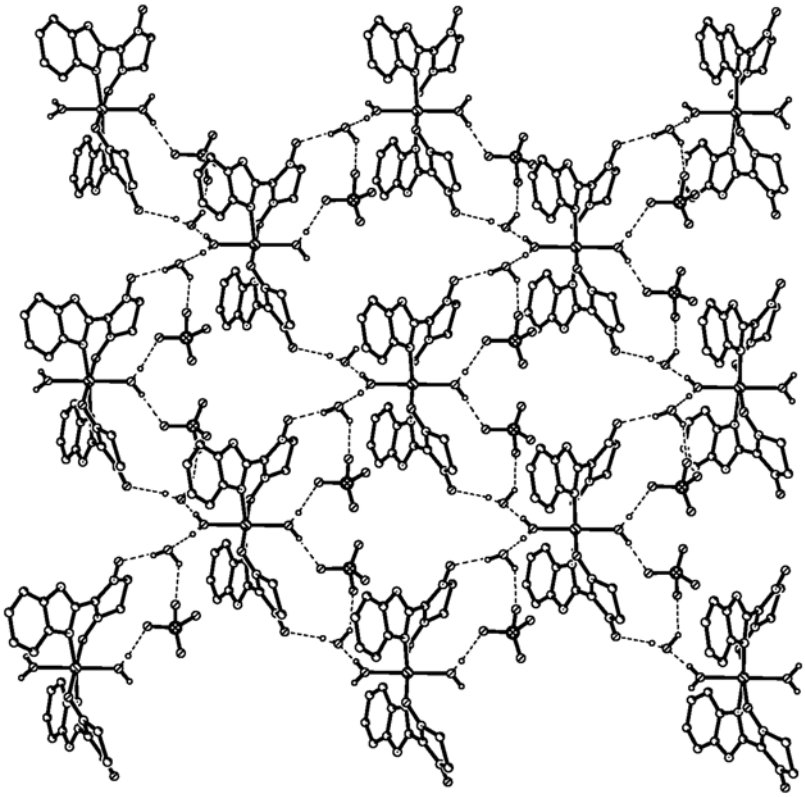


Fig. 2. A sketch of the intermolecular hydrogen bond of **I** (part of hydrogen atoms and methyls are deleted for clarity).

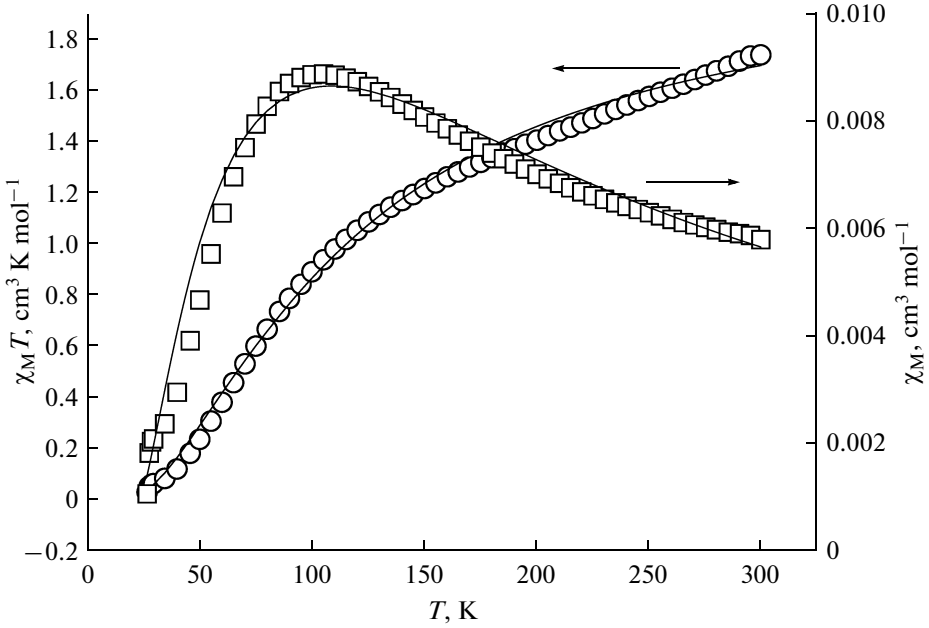


Fig. 3. The plots of $\chi_M T$ and χ_M versus T for **I**, the solid lines correspond to the best theoretical fits.

where J corresponds to the magnetic exchange coupling between Ni(II) ion and NIT-1'-MeBzIm radical. Considering the magnetic coupling between molecules, an additional coupling parameter zJ', was added in the equation at low temperature as a molecular field approximation [22]. The total magnetic susceptibility is

$$\chi_T = \frac{\chi_M}{1 - \frac{2zJ'}{N\beta^2 g^2}\chi_M}.$$

The least-squares analysis of magnetic susceptibilities data led to $J = -40.76$ cm^{-1}, $g = 2.0$, $zJ' = -0.53$ cm^{-1} and $R = 3.68 \times 10^{-3}$ (the agreement factor defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum[(\chi_M)_{obs}]^2$). The $J < 0$ indicates antiferromagnetic coupling interactions between Ni(II) ion and NIT-1'-MeBzIm radical units, as is usually observed [23, 24]. The small negative zJ' value implies very weak antiferromagnetic coupling interactions between neighboring radicals through space. In the complex, two adjacent NIT-1'-MeBzIm groups stack to form a 2D network configuration with the close inter-radical O···O distances of 4.98 Å, though a little longer, the overlap of the radical π* orbitals can occur and consistent with metrical result. The fitting for the magnetic susceptibility data below 27 K was unsuccessful, which may be attributed to the zero-field splitting of Ni^{2+} ion ($S = 1$) or to spin-orbital coupling. 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 [25], the extent of overlap between metal and radical magnetic orbitals is responsible for the antiferromagnetic couplings. From the structural and magnetic analysis: two radicals coordinate to Ni^{2+} ion in equatorial positions, the dihedral angles between the Ni^{2+} ion equatorial planes and the imidazoline rings are 64.033°. The geometry is favorable for overlap of orbitals but not to orthogonality, leading to the antiferromagnetic interactions between Ni(II) magnetic $d_{x^2-y^2}$ orbitals and the radical π* orbitals ($J = -40.76$ cm^{-1}).

In summary, a new nickel(II) complex **I** containing nitronyl nitroxide radicals has been prepared and structurally characterized. The X-ray analysis reveals that Ni(II) ion resides in a distorted octahedron center, the complex was linked by intermolecular hydrogen bonds, resulting in a 2D network configuration. Magnetic investigation indicates the existence of interamolecular interactions is antiferromagnetic with $J = -40.76$ cm^{-1}.

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