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A New Zinc(II) Complex Containing Nitronyl Nitroxide Radicals: Synthesis, Crystal Structure, and Magnetic Properties[1]

G. Liu*, B. Liu, and J. T. Cheng

Engineering Research Centre for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing, 400067 P.R. China

**e-mail: lycy9945@163.com*

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Abstract—A new one-dimensional dicyanamide bridged zinc(II) complex containing nitronyl nitroxide radicals [Zn(Hfac)$_2$(NIT-1'-MeBzIm)] (NIT-1'-MeBzIm = 2-{2'-[(1'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, Hfac = hexafluoroacetylacetonate) has been prepared and structurally characterized by single-crystal X-ray diffraction. The complex crystallizes in monoclinic, space group $P2_1/c$, $Z = 4$. Crystal data: $C_{25}H_{21}F_{12}N_4O_6Zn$, $Mr = 766.83$, $a = 12.1812(13)$ Å, $b = 16.8770(18)$ Å, $c = 15.5230(16)$ Å, $\beta = 98.009(2)°$, $V = 3160.1(6)$ Å^3, $\rho_c = 1.612$ g/cm^3, $\mu(MoK_\alpha) = 0.893$ mm^{-1}, $F(000) = 1540$, $R = 0.0925$ and $wR = 0.2652$ for 5875 observed reflections with $I > 2\sigma(I)$. The X-ray analysis reveals that the zinc(II) ion is six-coordinated with a distorted octahedral geometry. These units develop as 1D species by intermolecular hydrogen bonds. Magnetic investigation indicates the existence of weak intermolecular interactions is antiferromagnetic with $J = -1.35$ cm^{-1}, where the spin Hamitonian is defined as $H = -2\Sigma_{i,j}J_{i,j}S_iS$ within the complex.

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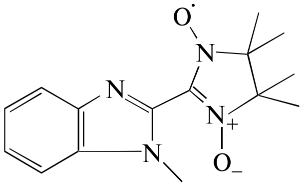
INTRODUCTION

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 [1–6]. 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. Nitronyl nitroxide radicals (NITR), stable organic radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [7–13]. Paramagnetic metal complexes of nitronyl nitroxide radicals have been extensively studied [14, 15], and large spin clusters, magnetic chains and even bulk ferromagnetism have resulted from these studies. However, the reports of the diamagnetic metal ions with radicals are much less than that of the paramagnetic metals ions with radicals. Some diamagnetic metal ions with radicals have shown antiferro or ferromagnetic interactions between the radicals through the diamagnetic metal ions [16, 17].

In the present paper, we have synthesized a new zinc(II) complex containing nitronyl nitroxide radicals [Zn(Hfac)$_2$(NIT-1'-MeBzIm)] (**I**), where NIT-1'-MeBzIm = 2-{2'-[(1'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide):



In addition, we extend to report the intermolecular hydrogen bonds to form a 1D chains configuration. Magnetic investigation indicates the existence of weak intermolecular antiferromagnetic interactions with $J = -0.27$ 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.

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

Parameter	Value
Formula weight	766.83
Temperature, K	291(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
a, Å	12.1812(13)
b, Å	16.8770(18)
c, Å	15.5230(16)
β, deg	98.009(2)
Volume, Å^3	3160.1(6)
Z; ρ_{calcd}, g cm^{-3}	4, 1.612
Absorption coefficient, mm^{-1}	0.893
F(000)	1540
Crystal size, mm	0.36 × 0.18 × 0.12
θ Range for data collection, deg	2.33–25.50
Limiting indices h, k, l	$-14 \le h \le 14$, $-18 \le k \le 18$, $-20 \le l \le 20$
Reflections collected/unique (R_{int})	10040/4962 (0.0631)
Reflections with $I > 2\sigma(I)$	2804
Data/restraints/parameters	5875/986/496
Goodness-of-fit on F^2	1.058
R_1, wR_2 ($I > 2\sigma(I)$)	0.0925, 0.2652
R_1, wR_2 (all data)	0.1656, 0.3245
Largest diff. peak and hole, e Å^{-3}	0.608 and –0.529

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

Bond	d, Å	Bond	d, Å
Zn(1)–N(1)	2.043(6)	Zn(1)–O(3)	2.080(6)
Zn(1)–O(4)	2.060(6)	Zn(1)–O(1)	2.138(5)
Zn(1)–O(2)	2.066(6)	Zn(1)–O(5)	2.174(5)
Angle	ω, deg	Angle	ω, deg
N(1)Zn(1)O(4)	100.4(2)	O(2)Zn(1)O(5)	85.1(2)
N(1)Zn(1)O(2)	166.9(3)	O(3)Zn(1)O(5)	176.5(2)
O(4)Zn(1)O(2)	85.8(2)	O(1)Zn(1)O(5)	93.0(2)
N(1)Zn(1)O(3)	98.4(2)	C(2)O(1)Zn(1)	123.2(6)
O(4)Zn(1)O(3)	86.1(2)	C(4)O(2)Zn(1)	126.4(7)
O(2)Zn(1)O(3)	93.5(2)	C(7)O(3)Zn(1)	123.4(7)
N(1)Zn(1)O(1)	90.6(2)	C(9)O(4)Zn(1)	124.1(7)
O(4)Zn(1)O(1)	165.9(2)	N(4)O(5)Zn(1)	113.3(5)
O(2)Zn(1)O(1)	85.2(2)	C(18)N(1)C(11)	106.2(6)
O(3)Zn(1)O(1)	83.6(3)	C(18)N(1)Zn(1)	123.8(5)
N(1)Zn(1)O(5)	82.8(2)	C(11)N(1)Zn(1)	129.9(5)
O(4)Zn(1)O(5)	97.0(2)		

Synthesis. The nitroxide radical, NIT-1'-MeBzIm, was prepared according to the literature method [18, 19]. The complex was synthesized by adding dropwise a purple methanol solution (5 mL) of NIT-1'-MeBzIm (0.058 g, 0.2 mmol) into 5 mL methanol solution of Zn(Hfac)$_2$ (0.076 g, 0.2 mmol). The mixture was stirred for 2 h at room temperature and then filtered. The clear purple filtrate was diffused with diethyl ether vapour at room temperature and dark purple block crystals were obtained after one week. The yield was 60.2%.

For $C_{25}H_{21}F_{12}N_4O_6Zn$

anal. calcd., %:	C, 39.15;	H, 2.76;	N, 7.31.
Found, %:	C, 40.04;	H, 2.98;	N, 7.36.

IR (KBr; ν, cm^{-1}): 1372.65 ν(N–O), 1378.25 ν(C–N), 1483.37 δ(CH$_3$), 1376.8 ω(CH$_3$), 1620.14—the framework vibration of benzimidazole, the present of $[N(CN)_2]^{-1}$ ligand—2191.08 ν_s(C≡N); 2261.96 ν_{as}(C≡N); 1350.65 ν_{as}(C≡N).

X-ray structure determination. Dark purple single crystal of complex **I** (0.36 × 0.18 × 0.12 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a ϕ/ω scan technique at room temperature. A total of 20350 reflections were collected for complex **I**, 5875 of which ($R_{\text{int}} = 0.0344$) were independent in the range of 2.33°–25.50°, 2204 observed reflections with $I > 2\sigma(I)$ were employed for structure refinements. The structure was solved by direct methods with SHELXS-97 [20]. 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 [21]. The final agreement factor values are $R = 0.0623$ and $wR = 0.1819$ (($w = 1/[\sigma^2(F_o)^2 + (0.1659P)^2 + 3.2128P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S =$

1.063, $(\Delta/\sigma)_{\max} = 0.089$, $(\Delta\rho)_{\max} = 0.608$, $(\Delta\rho)_{\min} = -0.529\ e/Å^3$).

The crystal data and experimental parameters for **I** is given in Table 1. The selected bond lengths and angles are given in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 650789; deposit@ccdc.cam.ac.uk or http://www. ccdc cam.ac.uk).

RESULTS AND DISCUSSION

The unit of the structure of compound is displayed in Fig. 1, in which Zn^{2+} ion resides in a distorted octahedron center and is coordinated by three oxygen atoms O(1), O(2), and O(4) of Hfac molecules, one benzimidazolyl nitrogen atoms N(1) of NIT-1'-MeBzIm radicals from the equatorial position to form a *trans* configuration. The Zn^{2+} ion is highly coplanar with the basal plane with a displacement of 0.079 Å with the bond lengths of 2.138(5) Zn(1)–O(1), 2.066(2) Zn(1)–O(2), 2.060(6) Zn(1)–O(4), 2.043(6) Å Zn(1)–N(1). The axial positions are occupied by NN oxygen atoms O(3) and O(5) of Hfac molecules (the bond length is 2.080(6) for Zn(1)–O(3), 2.174(5) for Zn(1)–O(5)). The axial direction is slightly deviated from the normal of the equatorial plane as indicated by the average angles of 88.96°: O(1)Zn(1)O(2) 85.2(2)°, O(1)Zn(1)O(3) 83.6(3)°, O(1)Zn(1)O(5) 93.0(2)°, O(1)Zn(1)N(1) 90.6(2)°. A sketch of the intermolecular hydrogen bonds of the complex is shown in Fig. 2. The H-bonds interactions exist between one fluorine atom from one Hfac molecule and H–C of methyl of benzimidazole rings (F(5C)···H(17H)–C(17H) 2.459 Å, 135°). Thus the units of $[Zn(Hfac)_2(NIT\text{-}1'\text{-}MeBzIm)]$ were connected as 1D chain structure by the intermolecular hydrogen bonds.

Figure 3 displays a plot of $\chi_M T$ and χ_M versus T of **I**. The magnetic susceptibilities of complex **I** were measured in the range 5–300 K at a magnetic field of 10000 G. At room temperature, the $\chi_M T$ value is 0.354 cm^3 K mol^{-1} and is lower than the value expected for non-coupling one $S_{rad} = 1/2$ spin (0.375 cm^3 K mol^{-1}). At lower temperature, a continuous slow decrease value to a minimum 0.275 cm^3 K mol^{-1} (at 3 K) of $\chi_M T$ is observed indicating the presence of intermolecular weak antiferromagnetic interactions within the complex. Clearly, the magnetic interaction does not derive from the diamagnetic Zn^{2+} ion. According to the structural analysis, the weak antiferromagnetic couplings are caused by the intramolecules between the NIT-1'-MeBzIm radicals. According to the spin Hamiltonian $H = -2\Sigma_{i,j}J_{i,j}S_iS_j$ [22]. The magnetic data can be fitted as the following:

$$\chi_M = \frac{Ng^2\mu_B^2}{\kappa_B T}\frac{1}{3+\exp(-2J/k_BT)},$$

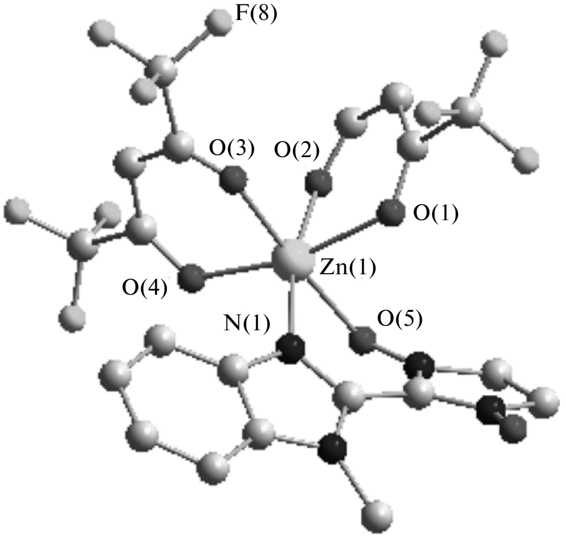

Fig. 1. The unit of molecular structure of complex **I**.

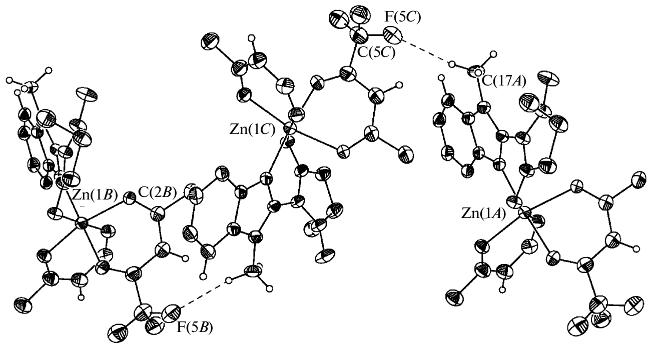

Fig. 2. 1D structure of complex **I**.

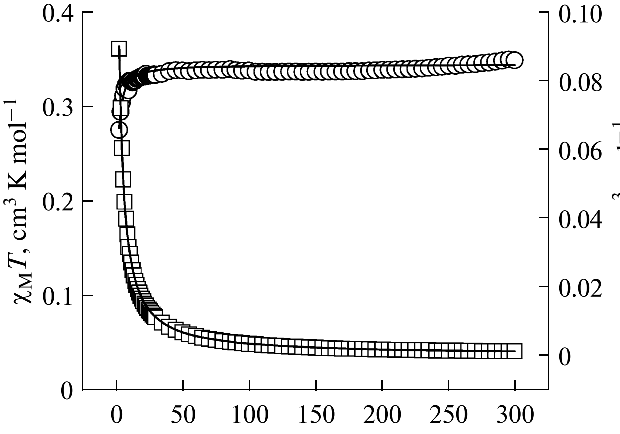

Fig. 3. Temperature dependence of $\chi_M T$ (○) and χ_M (□) versus T for complex **I** and their corresponding theoretical curves (solid lines).

the best fitting for the data gives $J = -1.35$ cm^{-1}, $g = 2.0$, $R = 2.5 \times 10^{-4}$ (the agreement factor defined as $R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2)$, where J corresponds to the existence of weak intermolecular antiferromagnetic interactions. The fitting result is in agreement with the above analysis.

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