

氮氧自由基-锌配合物 $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$ 的合成、结构和磁行为

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Synthesis, Crystal Structure and Magnetic Behavior of A New Zn(II) Nitronyl Nitroxide Complex $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$

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Abstract: A Zn(II) complex with nitronyl nitroxide radicals $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$ (**1**) ($\text{NIT3Py} = 2\text{-(3'-pyridinyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide}$) has been synthesized and structurally characterized by X-ray diffraction crystal structure determination method. The complex has a mononuclear-metal structure in which each Zn(II) ion adopts a distorted tetrahedral geometry and is coordinated by two Cl^- anions and two pyridyl-N atoms from two NIT3Py radical ligands. The magnetic measurements show the weak antiferromagnetic interaction between the nitroxide radicals through the diamagnetic Zn(II) ion. CCDC: 292363.

Key words: Zn(II) complex; nitronyl nitroxide radical; crystal structure; magnetic behavior

The molecular magnetic materials have attracted an increasing interest during the last several decades because of their potential application in future devices^[1-4]. In particular, the combinations of metal complexes and nitroxide radicals have been proven to be the good components for building such magnetic materials^[5,6]. The nitroxide radicals have been the subject of extensive investigation over many years, as they have a unique combination of chemical stability and versatility that makes them attractive candidates for spin labels and paramagnetic building blocks. Paramagnetic metal complexes of nitronyl nitroxides and imino nitroxides have been extensively studied^[7-11].

On the other hand, diamagnetic metal ions are believed not to mediate magnetic interactions for a long time. However, some diamagnetic metal complexes with stable organic radical ligands have shown that antiferro- or ferromagnetic interactions between the radicals were operative through the diamagnetic metal ions, such as Cu(I)^[12], Hg(II)^[13] and Cd(II)^[14]. When the paramagnetic centers are separated by the diamagnetic metal ions, the magnetic interaction depends on the nature of the diamagnetic metal ions, while the super-exchange and spin-polarization mechanisms play an important role in determining the magnetic interactions. Till now, there have been a few articles concerning Zn(II), Cd(II)

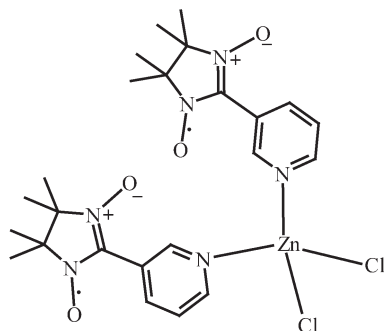
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organic radical complexes^[15–19], and most of them showed antiferromagnetic interactions. In the present paper, we report a new diamagnetic-metal nitroxide complex [Zn(NIT3Py)₂Cl₂] (**1**) (shown in Scheme 1) exhibiting the weak antiferromagnetic interactions.



Scheme 1

1 Experimental

1.1 Material required and instrumentation

All chemicals were reagent grade and used without purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was taken on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the 4 000~600 cm⁻¹ regions, using KBr pellets. The variable temperature magnetic susceptibility measurements were carried out with a SQUID MPMS XL7 magnetometer in the temperature range 2.0~300 K at a magnetic field of 2 000 G. The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants.

1.2 Preparation of NIT3Py

The radical ligand 2-(3'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT3Py), was prepared

according to the literature method^[20].

1.3 Preparation of the title complex

ZnCl₂ (0.1 mmol) and radical ligand NIT3Py (0.2 mmol) were dissolved in 20 mL methanol and the solution was stirred for 2 h. After the filtrate was allowed to stand at room temperature for 4 weeks, dark green block crystals of the title complex suitable for X-ray structure analysis were obtained by the slow evaporation. Anal. Calcd. (%) for C₂₄H₃₂Cl₂N₆O₄Zn: C, 47.58; H, 5.48; N, 13.92. Found (%): C, 47.66; H, 5.33; N, 13.89. Important IR absorptions (KBr pellet, cm⁻¹): 1 589(ν_{as}(C=C)), 1 372(ν_{as}(N-O)).

1.4 Crystal structure determination

A green block crystal of the title complex **1**, having the approximate dimensions 0.22 mm×0.18 mm×0.12 mm, was selected for structure analysis. All measurements were made on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ=0.071 073 nm). A total of 15 021 reflections were collected by using Φ-ω scan technique at room temperature including 4 970 independent reflections (R_{int}=0.023 7) and 3 870 with I≥2σ(I) were considered as observed. The empirical absorption corrections were carried out with SADABS. The structure was solved by direct methods using SHELXS-97 program^[21] and refined by full-matrix least-squares techniques on F² with SHELXL-97^[22]. All non-hydrogen atoms were refined anisotropically, while the H atoms were located geometrically and refined isotropically. The details of crystallographic data and structure refinement parameters are summarized in Table 1, and the selected bond distances and angles are listed in Table 2, respectively.

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Table 1 Crystallographic data and structure refinement parameters for complex **1**

Empirical formula	C ₂₄ H ₃₂ Cl ₂ N ₆ O ₄ Zn	F(000)	1 256
Formula weight	604.83	Crystal size / mm	0.22×0.18×0.12
Temperature / K	293(2)	θ range for data collection / (°)	1.97~25.03
Wavelength / nm	0.071 073	Limiting indices	-8 ≤ h ≤ 8, -24 ≤ k ≤ 24, -21 ≤ l ≤ 18
Crystal system	Monoclinic	Reflections collected / unique (R _{int})	15 021 / 4 970 (0.0237)
Space group	P2 ₁ /c	Completeness to θ=25.03° / %	99.9
a / nm	0.744 0(2)	Absorption correction	Semi-empirical from equivalents
b / nm	2.067 0(7)	Max. and min. transmission	1.000 000 and 0.546 290
c / nm	1.842 2(6)	Refinement method	Full-matrix least-squares on F ²

Continued Table 1

$\beta / (^{\circ})$	95.885(4)	Data / restraints / parameters	4 970 / 28 / 341
Volume / nm ³	2.818 2(16)	Goodness-of-fit on F^2	1.045
Z	4	Final R indices [$I > 2\sigma(I)$]	$R_1=0.063$ 5, $wR_2=0.182$ 5
Calculated density / (Mg·m ⁻³)	1.425	R indices (all data)	$R_1=0.0803$, $wR_2=0.1983$
Absorption coefficient / mm ⁻¹	1.101	Largest diff. peak and hole / (e·nm ⁻³)	1 213 and -822

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) for complex 1

Zn(1)-N(4)	0.206 3(4)	Zn(1)-Cl(2)	0.220 41(17)	Zn(1)-N(1)	0.208 1(4)
Zn(1)-Cl(1)	0.221 11(15)	O(1)-N(2)	0.127 7(6)	O(3)-N(5)	0.125 2(7)
O(2)-N(3)	0.128 6(6)	O(4)-N(6)	0.124 8(7)		
N(4)-Zn(1)-N(1)	100.16(16)	N(4)-Zn(1)-Cl(1)	109.45(12)	N(4)-Zn(1)-Cl(2)	109.46(13)
N(1)-Zn(1)-Cl(1)	107.91(13)	N(1)-Zn(1)-Cl(2)	108.59(13)	Cl(2)-Zn(1)-Cl(1)	119.52(7)

2 Results and discussion

2.1 Crystal structure of the title complex

The title complex $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$ (**1**) exists as discrete mononuclear molecules and the ORTEP drawing of the complex is shown in Fig.1. In the complex, each Zn(II) ion adopts a distorted tetrahedral coordination geometry and is four-coordinated by two chlorine atoms (Cl(1) and Cl(2)) and two nitrogen atoms (N(1) and N(4)) of the pyridine ring of NIT3Py. The Zn(1)-Cl(1) and Zn(1)-Cl(2) bond distances are 0.221 11(15) and 0.220 41(17) nm, respectively. The Zn(1)-N(1) and Zn(1)-N(4) bond distances are 0.208 1(4) and 0.206 3(4) nm, respectively. The bond angles of Cl(1)-Zn(1)-Cl(2) and N(1)-Zn(1)-N(4) are $119.52(7)^{\circ}$ and $100.16(16)^{\circ}$. The radicals only behave as the monodentate ligands through the pyridyl nitrogen

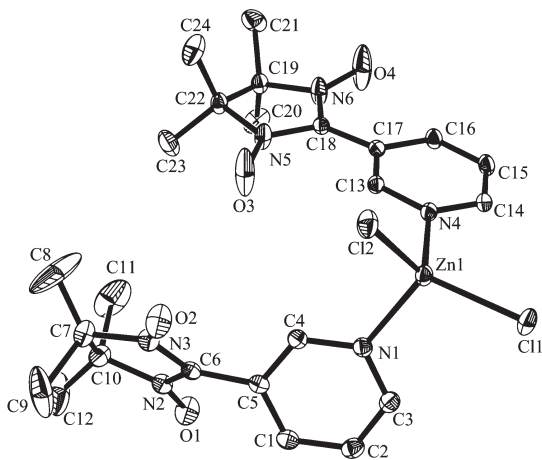


Fig.1 ORTEP drawing of the title complex with ellipsoids at 30% probability level and H atoms are omitted for clarity

atoms (N(1) and N(4)) while the oxygen atoms (O(1), O(2), O(3) and O(4)) of nitroxide moieties remain uncoordinated. The nitroxide O-N-C-N-O moieties of two radicals are almost coplanar as expected indicating the easy delocalization of the free electron within this moiety and the nitroxide moieties form the dihedral angles of 38.5° and 8.9° with the pyridyl ring planes, respectively. In the intermolecular arrangement, the shortest N-O \cdots O-N contact distance between the uncoordinated N-O groups is 0.322 8 nm. The packing diagram of the complex **1** in a unit cell is depicted in Fig.2.

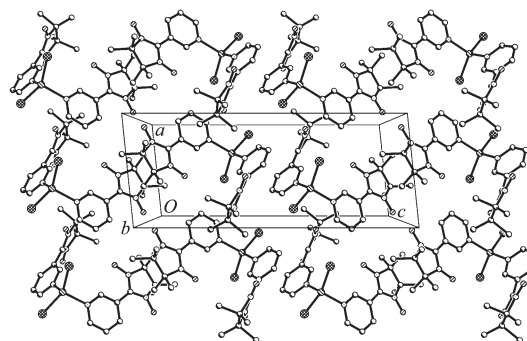
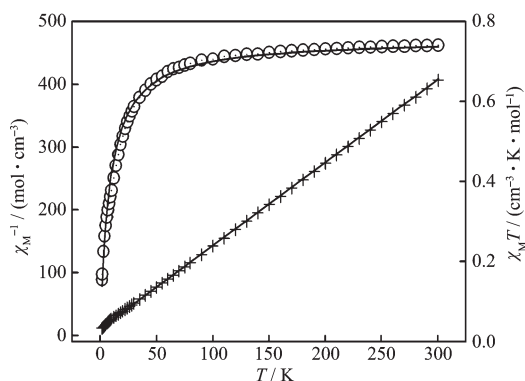


Fig.2 Packing arrangement in a unit cell of the title complex

2.2 Magnetic properties

The $\chi_M T$ and χ_M^{-1} versus T plots of the title complex are shown in Fig.3. where χ_M is the magnetic susceptibility per $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$ unit. The $\chi_M T$ value at room temperature is $0.74 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is slightly lower than that expected for two independent spins ($0.75 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for two $S_R=1/2$). As the temperature is lowered, the $\chi_M T$ value decreases slowly down to around 40 K and then decreases rapidly on

further lowering of temperature, reaching $0.15 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K.



Solid lines correspond to the best theoretical fits

Fig.3 Plots of $\chi_M T$ (○) and χ_M^{-1} (+) vs T for the title complex

Based on the structural results, it has two major magnetic interactions in the present system, (1) the exchange interaction of NIT3Py radicals through Zn(II) ion; (2) the close contacts between N-O groups of radicals through space. Both of them are expected to be weak^[5,6]. To evaluate the exchange coupling constants, it was treated as a biradical system (two spin $S=1/2$), while the average magnetic interactions of the nearest radicals through space were treated as a molecular field approximation. The Hamiltonian for the biradical system can be written as $\hat{H} = -2J\hat{S}_{R1}\hat{S}_{R2}$, and the magnetic susceptibility can be expressed as $\chi_D = [2Ng^2\beta^2/(kT)]\{3 + \exp[-2J/(kT)]\}^{-1}$, where J is the exchange interaction between two radicals. The total magnetic susceptibility is $\chi_M = \chi_D / \{1 - \chi_D[2zj'/(Ng^2\beta^2)]\}$. The least-squares analysis of the magnetic susceptibility led to $J = -5.52 \text{ cm}^{-1}$, $g = 2.01$, $zj' = -0.13 \text{ cm}^{-1}$. The agreement factor R defined as $\sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \sum[(\chi_M)_{\text{obs}}]^2$ is equal to 6.62×10^{-3} . The fitted magnetic data provide evidence for a weak antiferromagnetic interaction between two radicals through the Zn(II) ion in the complex.

It is noted that the structural difference between the title complex $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$ and the similar one $[\text{Zn}(\text{NIT4Py})_2\text{Cl}_2]$ ^[23] induces the opposite magnetic behavior. In $[\text{Zn}(\text{NIT4Py})_2\text{Cl}_2]$, the ferromagnetic behavior comes from the weak intermolecular contact with 0.247 7 nm based on the spin-polarization mechanism suggested by McConnell^[24]. However, in the title complex $[\text{Zn}(\text{NIT3Py})_2\text{Cl}_2]$, the contact between N-O groups of radicals through space is so long with 0.322 8 nm that

induces the antiferromagnetic interaction.

References:

- [1] Kahn O. *Molecular Magnetism*. VCH: Weinheim, **1993**, 4~58
- [2] Dougherty D A. *Acc. Chem. Res.*, **1991**, **24**: 88~97
- [3] Broderick W E, Thompson J A, Day E P, et al. *Science*, **1990**, **249**: 401~404
- [4] Miller J S, Epstein A J, Reiff W M. *Chem. Rev.*, **1988**, **88**: 201~212
- [5] Caneschi A, Gatteschi D, Sessoli R, et al. *Acc. Chem. Res.*, **1989**, **22**: 392~398
- [6] Caneschi A, Gatteschi D, Rey P. *Prog. Inorg. Chem.*, **1991**, **39**: 331~429
- [7] Vostrikova K E, Luneau D, Wernsdorfer W, et al. *J. Am. Chem. Soc.*, **2000**, **122**: 718~719
- [8] Li L C, Liao D Z, Jiang Z H, et al. *Inorg. Chem.*, **2002**, **41**: 421~424
- [9] Wang L Y, Zhao B, Zhang C X, et al. *Inorg. Chem.*, **2003**, **42**: 5804~5806
- [10] Li L C, Liao D Z, Jiang Z H, et al. *Inorg. Chem.*, **2006**, **45**: 7665~7670
- [11] Zhang J Y, Liu C M, Zhang D Q, et al. *Cryst. Eng. Comm.*, **2007**, **9**: 799~805
- [12] Oshio H, Watanabe T, Ohto A, et al. *Angew. Chem. Int. Ed. Engl.*, **1994**, **33**: 670~671
- [13] Lee C J, Wei H H, Liu Y H, et al. *J. Chem. Soc., Dalton Trans.*, **1998**: 171~176
- [14] Haung C F, Wei H H, Lee G H, et al. *Inorg. Chim. Acta*, **1998**, **279**: 233~237
- [15] Yamamoto Y, Suzuki T, Kaizaki S. *J. Chem. Soc., Dalton Trans.*, **2001**: 1566~1572
- [16] Francese G, Romero F M, Neels A, et al. *Inorg. Chem.*, **2000**, **39**: 2087~2095
- [17] Wang L Y, Ma L F, Wang Y F, et al. *Inorg. Chem. Commun.*, **2007**, **10**: 212~215
- [18] Zhang C X, Sheng J, Zhang Y Y. *Transit. Metal Chem.*, **2006**, **31**: 93~96
- [19] Wang S P, Gao D Z, Liao D Z, et al. *Chinese J. Struct. Chem.*, **2007**, **26**: 472~476
- [20] Davis M S, Morokuma K, Kreilick R W. *J. Am. Chem. Soc.*, **1972**, **94**: 5588~5592
- [21] Sheldrick G M. *SHELXS-97: Program for the Solution of Crystal Structures*, University of Gottingen, Germany, **1997**.
- [22] Sheldrick G M. *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Gottingen, Germany, **1997**.
- [23] Lee C J, Wei H H, Lee G H, et al. *J. Chin. Chem. Soc.*, **2001**, **48**: 717~722
- [24] McConnell H M. *J. Chem. Phys.*, **1963**, **39**: 1910~1915