Polish J. Chem., **77**, 1229–1234 (2003)

Synthesis, Crystal Structure and Magnetic Properties of a Zinc(II) Complex with Nitronyl Nitroxide Radical

by Q.-H. Zhao[1], X.-F. Wang[1,2], D.-Y. Tang[1,2] and R.-B. Fang[2*]

[1]*Department of Chemistry, Yunnan University, Kunming 650091, P. R. China*
[2]*School of Pharmacy, Yunnan University, Kunming 650091, P. R. China*

(Received June 16th, 2003)

A new mononuclear diamagnetic metal zinc compound [Zn(NITpPy)$_4$(N$_3$)$_2$] (NITpPy = 2-(p-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) has been synthesized and characterized. The crystal structure of this compound was determined by X-ray diffraction analysis. It crystallizes in the triclinic space group $P\bar{1}$ with the Zn^{II} ion octahedrally coordinated and bound to four radical ligands through the nitrogen atoms of the pyridine rings, and the azido groups occupy the apical positions. The compound exhibits weak intermolecular antiferromagnetic interaction between the radicals, in which the diamagnetic zinc(II) plays the role of bridge.

Key words: zinc(II) compound, nitronyl nitroxide radical, azide, crystal structure, magnetic properties

In the field of molecular-based magnets, nitronyl nitroxide [1,2], a stable organic radical, has played a prominent role in design and construction of molecular magnetic materials [3]. The strength of inter-radical magnetic exchange interactions is dependent on metal ions and coordination geometry. The magnetic properties of a great number of purely organic radicals and metal-radical complexes have been synthesized and studied [4–7]. Diamagnetic metal ions are believed not to mediate magnetic interactions, but they can transmit exchange interaction by playing a bridge role (superexchange pathways). Several diamagnetic metal compounds with stable organic radical ligands have shown that antiferro- or ferromagnetic interactions were operative through the diamagnetic metal ions; such as copper(I) [8], cadmium(II) [9], mercury(II) [10] and zinc(II) [11]. These radicals are especially attractive, due to their donor atom and to assemble an extended coordination geometry with changing magnetic coupling.

On the other hand, the azido anion is a versatile and efficient magnetic coupler; it may transmit either antiferromagnetic or ferromagnetic interactions. Some complexes containing azido groups exhibit spontaneous magnetization at 16 and 40 K [12].

Taking advantage of the abilities of both nitroxide radicals and azido anion, we report herein the synthesis, structural characterization and magnetic property of zinc complex [Zn(NITpPy)$_4$(N$_3$)$_2$] (NITpPy = 2-(p-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). To the best of our knowledge, zinc(II)-radical complexes containing azido groups and studies of their magnetic properties are scarce.

---

[*] Author for correspondence.

EXPERIMENTAL

Materials and physical measurements: Elemental analysis for carbon, hydrogen and nitrogen were carried out on Elementar Carlo EL elemental analyzer. The IR spectrum was taken on a Thermo-Nicolet AVATAR FT-IR360 spectrophotometer. Variable temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Syntheses of the complex: 2-(p-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITpPy) was prepared and purified by the literature methods [13].

$[Zn(NITpPy)_4(N_3)_2]$: An aqueous solution (10 ml) of NaN_3 (130 mg, 2 mmol) was added to a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (297 mg, 1 mmol) and NITpPy (234 mg, 1 mmol) in 20 ml of methanol. The mixture was stirred for 0.5 h and filtered off. The filtrate was kept in dark at room temperature for one week to get deep blue prism crystals of $[Zn(NITpPy)_4(N_3)_2]$. Yield: 75%. Anal. Calcd. for $C_{48}H_{64}N_{18}O_8Zn$: C, 53.07, H, 5.94, N, 23.21; Found C, 53.25; H, 5.58; N, 23.78%. IR (KBr): $\nu_{as}(N_3^-)$ 2052 vs cm^{-1}; $\nu_{N\text{-}O}$ 1372s cm^{-1}.

X-ray measurements and structure determination: A deep blue crystal ($0.4 \times 0.34 \times 0.28$ mm^3) was selected and mounted on a glass fiber. All measurements were made on a CCD area detector equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The data were collected at room temperature including a total of 7725 reflections in the $1.47° < \theta < 26.43°$ range including 5460 independent reflections ($R_{int} = 0.0269$). A summary of the crystallographic data is given in Table 1. The structure was solved by direct methods using the SHELXS-97 program [14]. All the non-hydrogen atoms were refined anisotropically. The H atoms were located from molecular geometry and included in the final refinement. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [15] and the goodness-of-fit on F^2 was 1.041. Maximum and minimum peaks in the final difference Fourier synthesis were 0.334 and –0.298 e $Å^{-3}$.

Table 1. Summary of the crystallographic data for $[Zn(NITpPy)_4(N_3)_2]$.

Empirical formula	$C_{48}H_{64}N_{18}O_8Zn$
Formula weight	1086.54
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.179(7)
b (Å)	13.821(6)
c (6)	13.979(6)
α (°)	90.179(7)
β (°)	103.112(7)
γ (°)	91.868(8)
Z	1
Density (g/cm^3)	1.336
$F(000)$	572
θ range for data collection	1.47–26.43°
Ranges of indices h, k, l	–5/8, –17/14, –17/17
μ (mm^{-1})	0.523
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0471$, $wR_2 = 0.0951$
R indices (all data)	$R_1 = 0.0839$, $wR_2 = 0.1166$

RESULTS AND DISCUSSION

Crystal structure: An ORTEP [16] plot of the complex is shown in Fig. 1. The selected bond lengths and angles for complex are presented in Table 2. The structure consists of a centrosymmetric mononuclear molecule Zn(NITpPy)$_4$(N$_3$)$_2$. The zinc(II) atom lies on an inversion center bound to four radicals through the nitrogen atom of the pyridine ring. The two azido groups are ligated to the zinc(II) ion as terminal ligands in the *trans* form. The coordination geometry is a compressed distorted octahedron with the Zn–N(azido) axial bond distances (2.087(2) Å) being obviously shorter than the Zn(II)–N (radical) equatorial bond distances (2.255(2) and 2.268(2) Å pyridine rings, respectively); this is in accord with other similar transition metal compound [17]. The lengths of the N–O bonds of the radicals group are about 1.27 Å. The N8–N7–Zn1 angle is 127.8(2)° and the N9–N8–N7 angle is 178.0(3)°. The dihedral angles defined by the pyridine rings and the ONCNO planes are 27.24(8)° and 35.05(4)°, respectively. The nitronyl nitroxide fragment ONCNO in the NITpPy is almost coplanar. The crystal cell of the complex is shown in Fig. 2. The shortest intermolecular contact between the oxygen atoms of N–O groups is 3.875 Å.

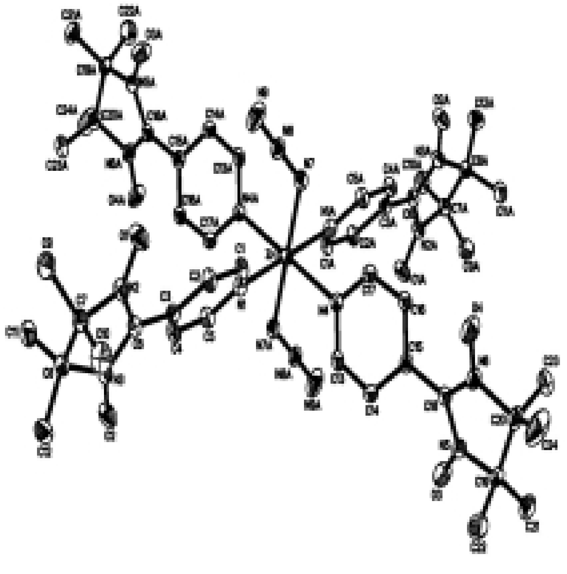

Figure 1. ORTEP drawing with 30% thermal ellipsoid probability showing atom labeling of [Zn(NITpPy)$_4$(N$_3$)$_2$].

Magnetic properties: The temperature dependence of the magnetic susceptibility was measured between 2–300 K, with an applied field of 1 T. The magnetic behavior of the compound is presented in Fig. 2 in the form of plot of $\chi_M T$ *versus T.* The $\chi_M T$ value at room temperature is 1.46 cm^3 K mol^{-1}, which is lower than the spin-only value expected for a non-coupled four S = 1/2 spin system (1.5 cm^3 K mol^{-1}). When the temperature is lowered, the magnetic moments decrease slowly. This is characteristic of a weak antiferromagnetic spin exchange interaction in the complex. Clearly, the magnetic interaction does not arise from the diamagnetic zinc(II) ions. Accordingly, the structural analysis of complex shows that four radicals are coordinated with a zinc ion and have the closest contact between two molecules. Consequently, the magnetic susceptibility data were analyzed by a four spins arranged prism model. The spin Hamiltonian $H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) - 2J_2S_2S_4$ is adopted [18], where J_1 and J_2 are the spin coupling constants between radical-Zn-radical and radical-radical, respectively. The magnetic susceptibility of the compound can be expressed as

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

$$A = 1 + 5\exp(-2J_1/KT) + \exp(-2J_2/KT) + 2\exp(2J_1/KT)$$
$$B = 3 + 5\exp(-2J_1/KT) + 3\exp(-2J_2/KT) + 3\exp(2J_1/KT) + \exp(4J_1/KT)$$

Table 2. Selected bond lengths (Å) and angles (°).

Zn–N7	2.087(2)	N7–N8	1.189(3)
Zn–N7A	2.087(2)	N8–N9	1.147(3)
N1–C1	1.341(3)	N2–O1	1.349(3)
N4–C17	1.336(3)	N5–O3	1.274(3)
Zn–N1	1.255(2)	Zn–N4	2.268(2)
Zn–N1A	2.255(2)	Zn–N4A	2.268(2)
N1---Zn---N7	92.56(9)	N7A–Zn–N7	180.0
N1---Zn---N4	88.42(8)	N7A–Zn–N1	87.44(9)
N1---Zn---N4A	91.58(8)	N7A–Zn–N4	92.12(9)
N7---N8---N9	178.0(3)	N7–Zn–N4	87.88(9)
N8---N7---Zn	127.8(2)	O3–N5–C18	125.9(2)
O1---N2---C6	126.5(3)	N5–C18–C15	125.3(2)

Symmetry transformations used to generate equivalent atoms: A: –x + 1, –y + 1, –z + 1.

The best fit parameters are $J_1 = -1.12$ cm^{-1}, $J_2 = -0.84$ cm^{-1}, $g = 1.98$ and $R = 5.8\times10^{-3}$ (R is the agreement factor defined as $R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$). The fitting results indicate that a weak antiferromagnetic interaction exists between the radicals, in which the diamagnetic zinc(II) plays the role of bridge.

Supporting information. Crystallographic data for structure reported in this paper have been deposited at Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-211825. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

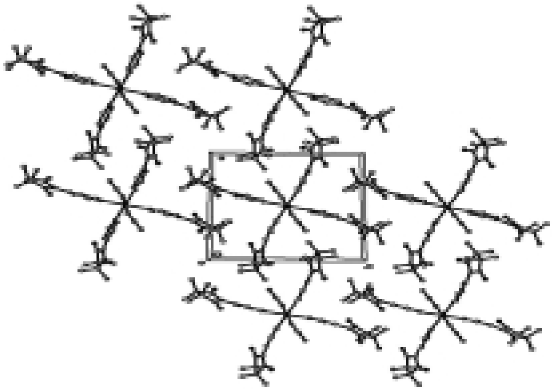

Figure 2. The unit cell of [Zn(NITpPy)$_4$(N$_3$)$_2$].

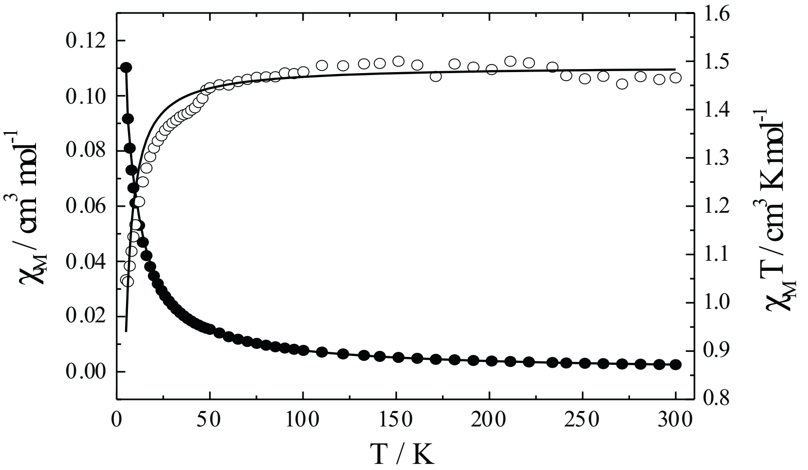

Figure 3. Plot of $\chi_M T$ and χ_M *versus* T for [Zn(NITpPy)$_4$(N$_3$)$_2$].

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No: 29961002), National Natural Science Foundation of Yunnan Province (No: 2002FXX05), National Natural Science Foundation of Yunnan University under the Grant (No: 2002Z001GC) and National Natural Science Foundation of Educational Committee of Yunnan Province (No: 0111158).

REFERENCES

1. Osiecki J.H. and Ullman E.F., *J. Am. Chem. Soc.*, **90**, 1078 (1968).
2. Ullman E.F., Osiecki J.H., Boocock D.G.B. and Darcy R., *J. Am. Chem. Soc.*, **94**, 7049 (1972).
3. Kahn O., Molecular Magnetism, VCH, Weinheim, 1993.
4. Inoue K. and Iwamura H., *J. Am. Chem. Soc.*, **116**, 3173 (1994).
5. Hayami S. and Inoue K., *Chem. Lett.*, 545 (1999).
6. Stumpf H.O., Pei Y. and Sessoli R., *J. Am. Chem. Soc.*, **115**, 6738 (1993).
7. Villamena F.A., Dickman M.H. and Crist D.R., *Inorg. Chem.*, **37**, 1454 (1998).
8. Oshio H., Watanabe T., Ohto A., Ito T. and Masuda H., *Inorg. Chem.*, **35**, 472 (1996).
9. Haung C.F., Wei H.H., Lee G.H. and Wang Yu, *Inorg. Chim. Acta*, **279**, 233 (1998).
10. Lee C.J., Wei H.H., Liu Y.H., Lee G.H. and Wang Yu, *J. Chem. Soc. Dalton Trans.*, 171 (1998).
11. Francese G., Romero F.M., Neels A., Stoeckli-Evans H. and Decurtins S., *Inorg. Chem.*, **39**, 2087 (2000).
12. Escuer A., Vicente R., Goher M.A.S. and Mautner F.A., *Inorg. Chem.*, **36**, 3440 (1997).
13. Ullman E.F., Call L. and Osiecki J.H., *J. Org. Chem.*, **35**, 3623 (1970).
14. Sheldrick G.M., SHELXS-97, *Program for the Solution of Crystal Structure*, University of Göttingen, 1997.
15. Sheldrick G.M., SHELXS-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, 1997.
16. Johonson C.K., ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
17. Fettouhi M., Khaled M., Waheed A., Golhen S., Ouahab L., Sutter J.P. and Kahn O., *Inorg. Chem.*, **38**, 3967 (1999).
18. Flood M.T., Barraclough C.G., Gray H.B., *et al.*, *Inorg. Chem.*, **8**, 193 (1969).