Crystal Structure of a Novel One-dimensional Chain Compound Formed by Zinc(II) and Imino Nitroxide Radicals

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The structure of novel complex formed by zinc(II) and imino nitroxides of formula $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)] \cdot (\text{NO}_3)$ (IM2-Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl) was determined by the X-ray diffraction method. The compound crystallizes in orthorhombic, space group $P2_12_12_1$ with $a = 11.026(2)$, $b = 13.575(3)$, $c = 20.435(4)$ Å, $V = 3058.6(11)$ Å³, $Z = 4$. The final R value is 0.0565 for 2637 reflections ($I > 2\sigma(I)$). X-ray analysis reveals that the crystal structure consists of $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$ moiety and a NO_3^- anion. The zinc(II) ion is six-coordinated with a distorted octahedral geometry. The units of $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$ and NO_3^- anions were connected as a one-dimensional chain compound by the intermolecular interaction.

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The design and synthesis of molecule-based magnetic materials is one of the major subjects of materials science. Nitronyl nitroxide radicals (NITR), stable organic radicals, have played a prominent role in the design and construction of molecular magnetic materials.^{1,2} The "metal-organic" strategy of combining organic radicals with paramagnetic transition metal has been particularly successful, and a wide variety of species utilizing nitronyl nitroxides as ligands have been described.³ However, the reports of the diamagnetic metal ions with radicals are much fewer than those of the paramagnetic metal

ions with radicals. In the present work, we have obtained a novel one-dimensional chain structure complex $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)] \cdot (\text{NO}_3)$ (IM2-Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl). We report herein on the synthesis and crystal structure of this new complex.

IM2-Py was prepared by a literature method.⁴ The complex $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)] \cdot (\text{NO}_3)$ was synthesized by the addition of IM2-Py (0.055 g, 0.25 mmol) to a 20 mL ethanol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.037 g, 0.125 mmol). The mixture was stirred for 4 h and then filtered; the clear red filtrate was diffused with diethyl ether vapor at room temperature. Red crystals formed and were collected by filtration and dried in air.

The X-ray data were collected on a diffractometer equipped with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at 291(2)K. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with the program SHELXTL-97. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and were included in the final refinement by using geometrical restraints. The final agreement factor value was $R = 0.0565$. The results of an X-ray structure determination are given in Tables 1 – 3.

A chemical diagram is shown in Fig. 1 and the structure is shown in Figs. 2 – 3. The crystal structure consists of unit of $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$ moiety and an uncoordinated NO_3^- anion. In the complex, the coordination geometry about the zinc(II) ion is an distorted octahedral characterized by the chelation of two IM2-Py ligands through the pyridyl nitrogen and imino

Fig. 1 Chemical diagram of $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$.

Table 1 Crystal and experimental data

Formula: $\text{C}_{24}\text{H}_{32}\text{ZnN}_8\text{O}_8$
Formula weight = 625.95
Crystal system: orthorhombic
Space group: $P2_12_12_1$ $Z = 4$
$a = 11.026(2)$ Å
$b = 13.575(3)$ Å
$c = 20.435(4)$ Å
$V = 3058.6(11)$ Å ³
$D_{\text{calc}} = 1.359$ g/cm ³
$F(000) = 1304$
$T = 291(2)$ K
$R_1 = 0.0565$
$wR_2 = 0.0882$
$(\Delta\rho)_{\text{max}} = 0.234$ eÅ ⁻³
$(\Delta\rho)_{\text{min}} = -0.354$ eÅ ⁻³
No. of reflections used = 2637
Goodness-of-fit = 1.110
θ range for data collection: 1.80 to 27.51°
Measurement: R-Axis IV
Program system: SHELXL-97
Structure determination: direct method
Refinement: full-matrix least-squares on F^2

CCDC 272493 contains the supplementary Crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2 Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the non-hydrogen atoms

Atom	x	y	z	U_{eq}
Zn1	0.31144(5)	0.99664(4)	0.81318(3)	0.0431(2)
N1	0.1510(4)	1.0894(3)	0.8103(2)	0.0440(12)
N2	0.3266(4)	1.2645(3)	0.9097(2)	0.0410(16)
N3	0.3687(4)	1.1188(3)	0.8647(2)	0.0417(14)
N4	0.4703(4)	0.9043(3)	0.8069(2)	0.0447(14)
N5	0.3120(4)	0.7395(3)	0.9195(2)	0.0417(16)
N6	0.2708(4)	0.8863(3)	0.8784(2)	0.0400(14)
N7	0.2830(5)	0.9676(4)	0.6841(3)	0.0683(19)
N8	0.7561(5)	1.0246(4)	0.6488(3)	0.065(2)
O1	0.2403(3)	1.3215(3)	0.94364(19)	0.0587(14)
O2	0.3971(3)	0.6723(2)	0.94492(18)	0.0520(14)
O3	0.2330(4)	0.9114(3)	0.7242(2)	0.0730(17)
O4	0.2716(6)	0.9585(4)	0.6259(2)	0.129(3)
O5	0.3463(4)	1.0360(3)	0.7089(2)	0.0707(16)
O6	0.7107(4)	1.0868(3)	0.6862(2)	0.0830(17)
O7	0.7037(4)	1.0037(3)	0.5955(2)	0.0821(15)
O8	0.8519(4)	0.9806(4)	0.6630(3)	0.101(2)
C1	0.0469(5)	1.0724(4)	0.7790(3)	0.0540(19)
C2	-0.0486(5)	1.1402(4)	0.7793(3)	0.061(2)
C3	-0.0316(5)	1.2285(4)	0.8105(3)	0.062(2)
C4	0.0766(5)	1.2484(4)	0.8423(3)	0.0473(17)
C5	0.1661(4)	1.1774(3)	0.8420(2)	0.0360(16)
C6	0.2875(5)	1.1861(3)	0.8729(2)	0.0360(16)
C7	0.4325(5)	1.2302(4)	0.9487(3)	0.0500(19)
C8	0.4824(5)	1.1521(4)	0.8988(3)	0.0487(19)
C9	0.3851(6)	1.1806(5)	1.0111(3)	0.070(3)
C10	0.5148(5)	1.3153(4)	0.9658(3)	0.066(3)
C11	0.5632(6)	1.1995(5)	0.8460(3)	0.070(3)
C12	0.5491(6)	1.0659(5)	0.9299(3)	0.079(3)
C13	0.5688(5)	0.9201(4)	0.7713(3)	0.056(2)
C14	0.6648(5)	0.8540(4)	0.7684(3)	0.061(2)
C15	0.6522(5)	0.7662(4)	0.8010(3)	0.059(2)
C16	0.5487(5)	0.7480(4)	0.8373(3)	0.0463(17)
C17	0.4608(4)	0.8197(4)	0.8407(3)	0.0400(17)
C18	0.3477(5)	0.8151(4)	0.8806(3)	0.0373(17)
C19	0.2170(5)	0.7774(4)	0.9650(3)	0.0447(17)
C20	0.1624(4)	0.8581(4)	0.9183(3)	0.0443(17)
C21	0.1326(5)	0.6941(4)	0.9839(3)	0.065(2)
C22	0.2781(5)	0.8206(5)	1.0250(3)	0.064(2)
C23	0.0688(5)	0.8156(5)	0.8706(3)	0.068(3)
C24	0.1109(6)	0.9468(4)	0.9535(3)	0.066(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

Zn(1)-N(6)	2.055(3)	Zn(1)-O(3)	2.318(3)
Zn(1)-N(3)	2.065(3)	N(2)-O(1)	1.411(4)
Zn(1)-N(4)	2.158(3)	N(5)-O(2)	1.409(4)
Zn(1)-N(1)	2.171(3)	N(7)-O(3)	1.242(5)
Zn(1)-O(5)	2.234(3)	N(7)-O(5)	86.75(13)
N(6)-Zn(1)-N(3)	108.91(13)	N(4)-Zn(1)-O(5)	88.57(13)
N(6)-Zn(1)-N(4)	77.92(13)	N(1)-Zn(1)-O(5)	93.53(13)
N(3)-Zn(1)-N(4)	104.46(13)	N(6)-Zn(1)-O(3)	156.03(13)
N(6)-Zn(1)-N(1)	105.21(13)	N(3)-Zn(1)-O(3)	88.03(12)
N(3)-Zn(1)-N(1)	78.37(12)	N(4)-Zn(1)-O(3)	87.89(12)
N(4)-Zn(1)-N(1)	175.01(13)	N(1)-Zn(1)-O(3)	55.63(12)
N(6)-Zn(1)-O(5)	146.23(12)	O(5)-Zn(1)-O(3)	115.6(4)
N(3)-Zn(1)-O(5)	103.97(12)	O(4)-N(7)-O(3)	123.4(5)

nitroxide nitrogen, leading to two five-membered rings together with one chelated nitrate anion ligand. The two oxygen atoms (O3, O5) from the nitrate ligand and two nitrogen atoms (N3, N6) from two different IM2-Py radicals that comprise the equatorial plane, whereas the axial positions are filled by two nitrogen atoms (N1, N4) from different pyridyl rings. The bond

Fig. 2 Molecular structure of the Zn(II) complex.

Fig. 3 A sketch of the intermolecular interaction of the Zn(II) complex.

lengths of Zn(1)-O(3) and Zn(1)-O(5) are 2.318(3) and 2.234(3) $\text{\AA}$, respectively. The bond lengths of the axial Zn-N (Zn(1)-N(1) = 2.171(3) $\text{\AA}$ and Zn(1)-N(4) = 2.158(3) $\text{\AA}$) are longer than those of the equatorial Zn-N (Zn(1)-N(3) = 2.065(3) $\text{\AA}$ and Zn(1)-N(6) = 2.055(3) $\text{\AA}$), which are in the normal range.⁵ The bond lengths of uncoordinated N-O are 1.411(4) $\text{\AA}$ and 1.409(4) $\text{\AA}$ for N(2)-O(1) and N(5)-O(2), respectively. The distortion along the axial direction is demonstrated by the N1-Co1-N4 angle of 176.64(14) $^\circ$.

There are significant intermolecular contacts in the structure of the complex. The intermolecular short contacts occur between one oxygen atom from the uncoordinated NO_3^- anion and two oxygen atoms of the NO groups of neighbor $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$ units (2.682 $\text{\AA}$ for O1A...O8A, 2.684 $\text{\AA}$ for O8A...O2B). The units of $[\text{Zn}(\text{IM2-Py})_2(\text{NO}_3)]^+$ and uncoordinated NO_3^- anions were connected as a one-dimensional chain by the intermolecular (O...O...O) contacts (Fig. 3). To the best of our knowledge, this is the only zinc(II) complex example of the one-dimensional chain by NO_3^- anions directly contact the oxygen atoms of radicals.

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