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1D Chlorine Bridged Mercury(II) Complex Containing Nitronyl Nitroxide Radicals: Synthesis, Crystal Structures, and Magnetic Properties[1]

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Abstract—A novel 1D chlorine bridged mercury(II) complex containing nitronyl nitroxide radicals, $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)Cl_4]_n$ (NIT-1'-MeBzIm = 2-{2'-[(1'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), has been prepared and characterized by magnetic and single-crystal X-ray diffraction studies. The complex crystallizes in triclinic, space group $P\bar{1}$, $Z = 2$. Crystal data: $C_{15}H_{19}Cl_4Hg_2N_4O_2$, $M = 830.32$, $a = 7.4454(16)$, $b = 9.463(2)$, $c = 16.180(3)$ Å, $\alpha = 94.245(2)°$, $\beta = 100.747(2)°$, $\gamma = 102.523(2)°$, $V = 1085.5(4)$ Å^3, $\rho_c = 2.540$ g/cm^3, $\mu(MoK_\alpha) = 14.636$ mm^{-1}, $F(000) = 762$, $R = 0.0312$ and $wR = 0.0779$ for 3990 observed reflections with $I > 2\sigma(I)$. The X-ray analysis reveals that the Hg^{2+} ions shows two coordination geometries of five-coordinated with a distorted square pyramidal coordination geometry and quadrilateral geometry. The units of $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)Cl_4]_n$ were connected as 1D chain structure by the chlorine bridges. Magnetic investigation indicates the existence of weak intramolecular interactions is antiferromagnetic with $J = -1.23$ cm^{-1}, where the spin Hamitonian is defined as $H = -2\sum_{i,j} J_{i,j} S_i S$ within the complex.

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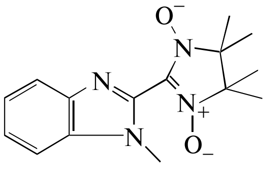
INTRODUCTION

The design and synthesis of molecule-based magnetic materials is one of the major challenges of materials science in recent years, Nitronyl nitroxide radicals (NITR), stable organic radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [1–7]. So far, there have been many investigations concerning magnetic metal complexes with the organic radicals. Paramagnetic metal complexes of nitronyl nitroxide radicals have been extensively studied [8, 9], 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 [10–12].

In the present work, we have synthesized a novel 1D chlorine bridged mercury(II) complex containing nitronyl nitroxide radicals $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)Cl_4]_n$ (**I**), where NIT-1'-MeBzIm = 2-{2'-[(1'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, Magnetic investigation indicates the existence of weak intramolecular antiferromagnetic interactions with $J = -1.23$ cm^{-1}.



(NIT-1'-MeBzIm)

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. Elemental analyses for carbon, hydrogen and nitrogen atoms were carried out on a Vario EL elemental analyzer. The infrared spectrum of a KBr pellet was recorded in the range of 4000–600 cm^{-1} on an Avatar^{TM} 360 E.S.P. IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Synthesis. The nitronyl nitroxide radical, NIT-1'-MeBzIm, was prepared according to the literature method [13, 14]. The complex was synthesized by adding dropwise an orange methanol solution (5 mL)

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Table 1. Crystal data and details of experiment for compound of $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)\,Cl_4]_n$ (**I**)

Parameter	Value
Formula weight	830.32
Temperature, K	291(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.1454(16)
b, Å	9.463(2)
c, Å	16.180(3)
α, deg	94.245(2)
β, deg	100.747(2)
γ, deg	102.523(2)
V, Å^3	1085.5(4)
Z, ρ_{calcd}, g cm^{-3}	2; 2.540
Absorption coefficient, mm^{-1}	14.636
F(000)	762
Crystal size, mm	0.47 × 0.32 × 0.18
θ Range for data collection, deg	2.43–25.50
Reflections collected/unique, R_{int}	8239/3990 (0.0294)
Parameters	249
Goodness-of-fit on F^2	1.041
R_1, wR_2 ($I > 2\sigma(I)$)	0.0312, 0.0779
R_1, wR_2 (all data)	0.0377, 0.0815
Largest diff. peak, hole, e Å^{-3}	1.070, –1.570

of NIT-1'-MeBzIm (0.056 g, 0.2 mmol) into 5 mL of a methanol solution of $HgCl_2 \cdot 0.5H_2O$ (0.286 g, 0.2 mmol). The mixture was stirred for 2 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 53.5%.

For $C_{15}H_{19}N_4O_2Cl_4Hg_2$

anal. calcd., %:	C, 21.70;	H, 2.31;	N, 6.75.
Found, %	C, 21.92;	H, 2.28;	N, 8.25.

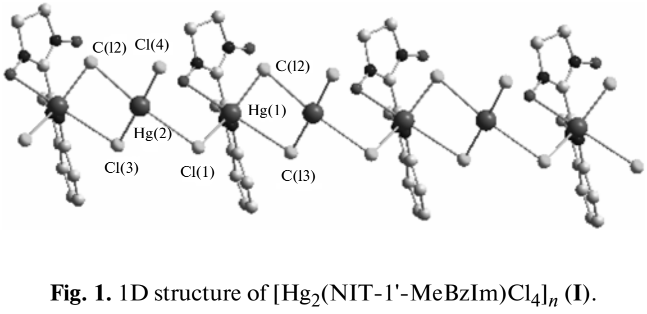

Fig. 1. 1D structure of $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)Cl_4]_n$ (**I**).

IR for **I** (KBr; ν, cm^{-1}): 1368.45 ν(N–O), 1377.98 ν(C–N), 1484.78 δ(CH_3), 1377.94 ω(CH_3), 1616.86—the framework vibration of benzimidazole.

X-ray structure determination. Darkpurple single crystal of the complex (0.47 × 0.32 × 0.18 mm) was 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. The structure was solved by direct methods with SHELXS-97 [15]. 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 [16]. The final agreement factor values are $R = 0.0312$ and $wR = 0.0779$ (($w = 1/[\sigma^2(F_o)^2 + (0.0371P)^2 + 2.1835P]$, where $P = (F_o^2 - 2F_c^2)/3$), $S = 1.039$, $(\Delta/\sigma)_{max} = 0.148$, $(\Delta\rho)_{max} = 1.070$, $(\Delta\rho)_{min} = -1.570$ e/Å^3.

A summary of the crystallographic data is given in Table 1, the selected bond lengths and bond angles in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 664576; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The ORTEP graphics of **I** is depicted in Fig. 1, in which the Hg^{2+} ions shows two coordination geometries of five-coordinated with a distorted square pyramidal coordination geometry Hg(1) and quadrilateral geometry Hg(2). Hg(1) ion combines with two atoms O(1), N(1) from the NIT-1'-MeBzIm radical and three chlorine atoms (Cl(1), Cl(2), Cl(3)). Both of Hg(1) and Hg(2) were bridged by three chlorine atoms (Cl(1), Cl(2), Cl(3)) to form 1D chain structure. From the bond lengths (Hg(1)–N(1) 2.313(5), Hg(1)–O(1) 2.728, Hg(1)–Cl(1) 2.325(2), Hg(1)–Cl(2) 2.3752(19), Hg(l)–Cl(3) 3.092 Å) and the bond angles N(1)Hg(1)Cl(1) 111.49(14)°, N(1)Hg(1)Cl(2) 107.06(13)°, Hg(1) ion shows a distorted square pyramidal coordination geometry, and Hg(2) ion shows a quadrilateral geometry, combines with four chlorine atoms. The selected bond lengths and bond angles show Hg(2) in the center of the quadrilateral geometry.

Figure 2 displays a plot $f\chi_M T$ and χ_M versus T of **I**. The magnetic susceptibilities of the title complex were measured in the range 5–300 K at a magnetic field of 10.000 G. At room temperature, the $\chi_M T$ value is 0.392 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}).

Table 2. Selected bond lengths and bond angles for compound of **I**

Bond	d, Å	Bond	d, Å
Hg(1)–N(1)	2.313(5)	Hg(1)–O(1)	2.728(3)
Hg(1)–Cl(1)	2.325(2)	O(1)–N(3)	1.291(6)
Hg(1)–Cl(2)	2.3752(19)	O(2)–N(4)	1.285(6)
Hg(2)–Cl(4)	2.280(2)	N(1)–C(7)	1.321(8)
Hg(2)–Cl(3)	2.3026(19)	C(7)–C(8)	1.471(8)
Hg(2)–Cl(1)	3.051(2)	N(3)–C(8)	1.338(7)
Angle	ω, deg	Angle	ω, deg
N(1)Hg(1)Cl(1)	111.49(14)	Hg(1)Cl(1)Hg(2)	97.65(7)
N(1)Hg(1)Cl(2)	107.06(13)	C(7)N(1)Hg(1)	125.6(4)
Cl(1)Hg(1)Cl(2)	141.45(10)	O(1)N(3)C(8)	125.1(5)
Cl(4)Hg(2)Cl(3)	176.61(8)	N(1)C(7)C(8)	122.8(5)
Cl(4)Hg(2)Cl(1)	96.40(8)	N(3)C(8)C(7)	123.7(5)
Cl(3)Hg(2)Cl(1)	85.54(8)	N(3)C(8)N(4)	109.4(5)

At lower temperature, a continuous slow decrease value to a minimum 0.306 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. According to the spin Hamiltonian $H = -2\sum_{i,j} J_{i,j}S_iS_j$ [16], the magnetic data can be fitted as the following [17]:

$$\chi = [Ng^2\mu_B/4k(T-\theta)](N/D)^{2/3},$$

$$\chi = J/2kT,$$

$$N = 1.0 + 5.7979916\chi + 16.902653\chi^2 + 29.376885\chi^3 + 29.832959\chi^4 + 14.036918\chi^5,$$

$$D = 1.0 + 2.7979916\chi + 7.008678\chi^2 + 8.6538644\chi^3 + 4.5743114\chi^4.$$

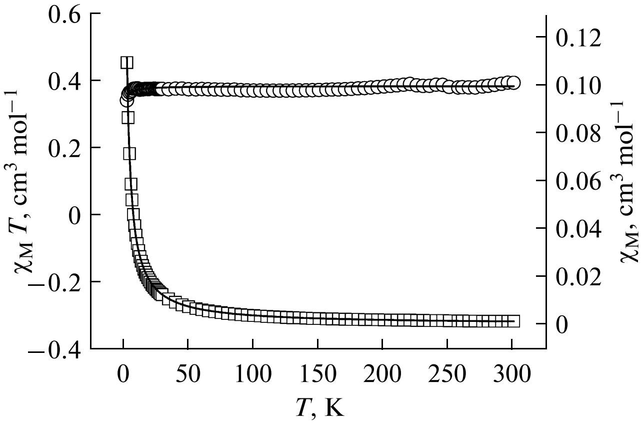

Fig. 2. Temperature dependence of $\chi_M T$ (○) and χ_M (□) for **I** and their corresponding theoretical curves (solid lines).

The best fitting for the data gives $J = -1.23$ cm^{-1}, $g = 1.98$, $R = 2.10 \times 10^{-4}$ (the agreement factor defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$), where J corresponds to the existence of weak intramolecular antiferromagnetic interactions. The fitting result is in agreement with the above analysis.

In summary, a novel 1D chlorine bridged mercury(II) complex containing nitronyl nitroxide radicals, $[Hg_2(NIT\text{-}1'\text{-}MeBzIm)Cl_4]_n$, was obtained and characterized structurally and magnetically. Magnetic investigation indicates the existence of weak intramolecular antiferromagnetic interactions.

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