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Synthesis, Crystal Structure, and Magnetic Properties of a New Manganese(II) Complex with Nitronyl Nitroxide[1]

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Abstract—A new manganese(II) complex $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$ (NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) has been prepared and structurally characterized by single-crystal X-ray diffraction. The complex crystallizes in monoclinic, space group $C2/c$, $Z = 4$. Crystal data: $C_{30}H_{38}Cl_2MnN_8O_8$, $M = 764.52$, $a = 17.261(3)$ Å, $b = 21.317(4)$ Å, $c = 11.744(2)$ Å, $\beta = 108.464(2)°$. The X-ray analysis reveals that Mn(II) atom is six-coordinated with a distorted octahedral geometry. The complex was linked by intermolecular hydrogen bonds, leading to a 2D network configuration. Magnetic investigation indicates the existence of interamolecular interactions is ferromagnetic with $J = 1.11$ cm^{-1}.

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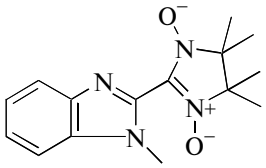
INTRODUCTION

During the past two decades, the field of molecular magnets has triggered fast-growing interest in free radicals as building blocks in the engineering of molecular based magnets. They have played a prominent role in the design and construction of molecular magnetic materials [1–4]. The major research aims in the field of molecular magnetism are the chemical design of molecular assemblies that exhibit a spontaneous magnetization and on the other hand the rationalization of magneto-structural correlation [5–8]. In many different types of organic radicals, research has focused on the nitronyl nitroxide radicals (NITR) family because of their flexibility and functionality. So far, there have been many investigations concerning paramagnetic metal complexes with the organic radicals.

The family of α-nitronyl nitroxide radicals and their complexes have been widely investigated for a long time. However, the complex concerning 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) (NIT-1'-MeBzIm) has rarely been found to be reported so far. At present, we have synthesized a new complex $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$ (**I**). In addition, we extend to report the hydrogen-bonded molecular structure of the complex which is a 2D network configuration. Magnetic investigation indicates the existence of interamolecular interactions is ferromagnetic with $J = 1.11$ cm^{-1}.

[1] The article is published in the original.



NIT-1'-MeBzIm

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. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Synthesis. The nitronyl nitroxide radical, NIT-1'-MeBzIm, was prepared according to the literature method [9, 10]. Complex **I** was synthesized by adding dropwise an orange methanol solution (5 mL) of NIT-1'-MeBzIm (0.054 g, 0.2 mmol) into 5 mL of methanol solution of $MnCl_2 \cdot 6H_2O$ (0.068 g, 0.2 mmol). The mixture was stirred for 4 h at room temperature and then filtered. The clear orange filtrate was diffused with diethyl ether vapour at room temperature and

Table 1. Crystallographic data and details of the experiment and refinement for $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$

Parameter	Value
Formula weight	764.52
Temperature, K	294(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	17.261(3)
b, Å	21.317(4)
c, Å	11.744(2)
β, deg	108.464(2)
V, Å^3	4098.9(13)
Z; ρ_{calcd}, g cm^{-3}	4; 1.239
Absorption coefficient, mm^{-1}	0.504
F(000)	1588
Crystal size, mm	0.45 × 0.33 × 0.28
θ Range for data collection, deg	2.64°–25.50°
Reflections collected	12934
Unique reflections (R_{int})	3784 (0.0437)
Reflections with ($I > 2\sigma(I)$)	2400
Parameters	215
GOOF	1.084
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0721$, $wR_2 = 0.2378$
R indices (all data)	$R_1 = 0.1068$, $wR_2 = 0.2711$
Largest diff. peak and hole, *e* Å^{-3}	0.829, −0.554

darkpurple block crystals were obtained after one week. The yield was 62.3%.

For $C_{30}H_{38}N_8O_8Cl_2Mn$

anal. calcd., %:	C, 44.07;	H, 4.87;	N, 10.82.
Found, %:	C, 43.96;	H, 4.95;	N, 10.79.

IR (KBr disc; ν, cm^{-1}): 1372 ν(N–O), 1374 ν(C–N), 1488 δ(CH_3), 1375 ω(CH_3), 1621—the framework vibration of benzimidazole.

X-ray structure determination. Darkpurple single crystal of the complex (0.45 × 0.33 × 0.28 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. A total of 12934 reflections were collected for the complex, of which 3784 (R_{int} = 0.0437) were independent in the range of 2.64°–25.50°, 2400 observed reflections with $I > 2\sigma(I)$ were employed for structure refinements. The structure was solved by direct methods with SHELXS-97 [11]. 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 [12]. The final agreement factor val-

Table 2. Selected bond lengths (Å) and angles (deg) for $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$*

Bond	*d*, Å	Bond	*d*, Å
Mn(1)–O(1)	2.245(4)	Mn(1)–Cl(1)	2.461(2)
Mn(1)–N(1)	2.257(4)	Mn(1)–Cl(2)	2.4973(19)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Mn(1)O(1)$^{\#1}$	175.82(18)	O(1)Mn(1)Cl(2)	92.09(9)
O(1)Mn(1)N(1)	80.68(14)	N(1)Mn(1)Cl(2)	86.43(10)
O(1)$^{\#1}$Mn(1)(1)	99.58(14)	Cl(1)Mn(1)Cl(2)	180.0
N(1)Mn(1)N(1)$^{\#1}$	172.85(19)	N(3)O(1)Mn(1)	114.9(3)
O(1)Mn(1)Cl(1)	87.91(9)	C(8)N(1)C(1)	104.9(4)
N(1)Mn(1)Cl(1)	93.57(10)	C(8)N(1)Mn(1)	122.1(3)
C(1)N(1)Mn(1)	132.7(3)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 3/2$.

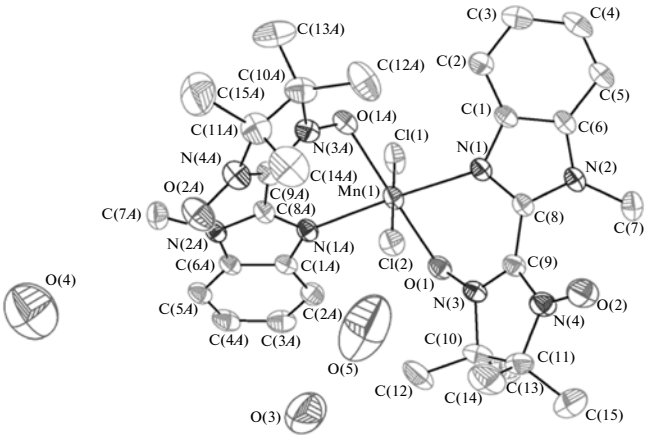


Fig. 1. ORTEP drawing of $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$ (some hydrogen atoms and methyls are deleted for clarity, the same in Fig. 2).

ues are $R = 0.0721$ and $wR = 0.2378$ ($w = 1/[\sigma^2(F_o^2) + (0.1515P)^2 + 5.4573P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.084$, $(\Delta/\sigma)_{max} = 0.089$, $(\Delta\rho)_{max} = 0.829$, $(\Delta\rho)_{min} = -0.554e/Å^3$.

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

Supplementary material for **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 694459; 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 structure **I**, Mn^{2+} ion resides in a distorted octahedron center and is coordinated by two NN and oxygen atoms O(1), O(1)#1, and two benzimidazolyl nitrogen atoms N(1) and N(1)#1 of NIT-1'-MeBzIm radicals from the equatorial position to form a *trans* configuration. The Mn^{2+} ion is highly coplanar with the basal plane with a displacement of 0.045 Å (with the bond lengths of Mn(1)–N(1) 2.257(4) Å, Mn(1)–O(1) 2.245(4) Å). The axial positions are occupied by two Cl atoms (the bond length is 2.461(2) Å for Mn(1)–Cl(1), 2.497(19) Å for Mn(1)–Cl(2)) from the dicyanamide ligand. The axial direction is slightly deviated from the normal of the equatorial plane as indicated by the average angles of 89.59°: O(1)Mn(1)Cl(1) 87.91(9)°, N(1)Mn(1)Cl(1) 93.57(10)°, O(1)Mn(1)Cl(2) 92.09(9)°, and N(1)Mn(1)Cl(2) 86.43(10)°.

The intermolecular H bonds occur between oxygen atoms of the uncoordinated NO moiety of nitronyl nitroxide and H–C from the NN O(1)–H(12)···C(12) (H···C 2.136 Å). In the unit cell, the double hydrogen bonds is alternatively arranged, resulting in a 2D network configuration (Fig. 2).

The magnetic susceptibilities of complex were measured in a range 5–300 K at a magnetic field of 10.000 G. The plots of $\chi_M T$ and χ_M versus T are shown in Fig. 3. The $\chi_M T$ value at room temperature is 5.15 cm^3 K mol^{-1}, which is nearly the same as that expected for one $S = 5/2$ and two $S_{rad} = 1/2$ uncoupled spin systems (5.12 cm^3 K mol^{-1}). The $\chi_M T$ increases gradually with decreasing temperature. This suggests the existence of ferromagnetic interaction between Mn^{2+} ion and the nitronyl nitroxide radicals. The magnetic susceptibility data were analyzed on the basis of Eq. (1) for a symmetric three-spin system derived from a spin-Hamiltonian, $H = -2J(S_{Mn}S_{rad1} + S_{Mn}S_{rad2})$ [13], where J corresponds to the coupling between the Mn^{2+} ion and the nitroxide radicals. For the sharp decrease of the $\chi_M T$ value at low temperature, a molecular field approximation was included with the three-spin model.

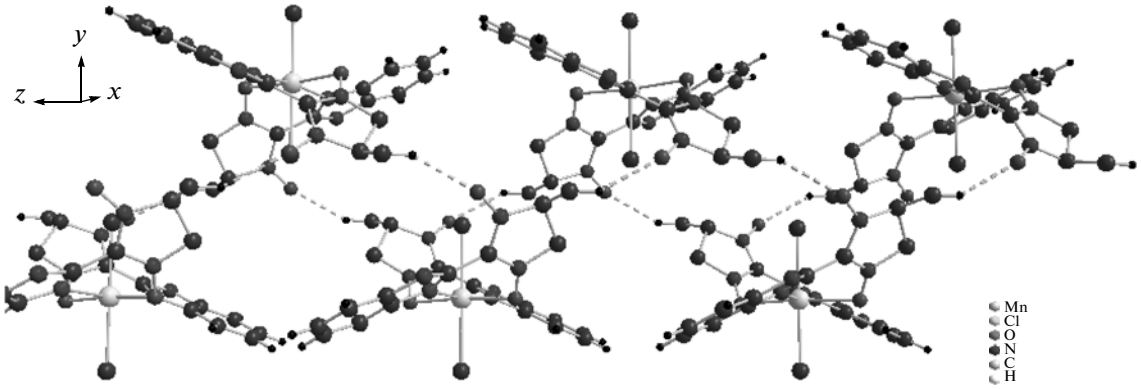


Fig. 2. 2D structure of $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$.

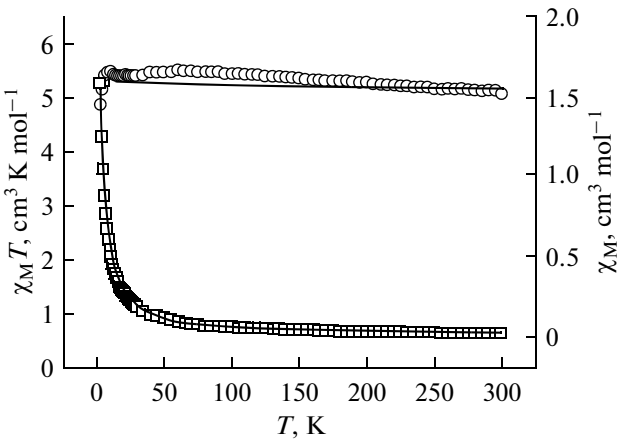


Fig. 3. Temperature dependence of $\chi_M T$ (○) and χ_M (□) for $[MnCl_2(NIT\text{-}1'\text{-}MeBzIm)_2] \cdot 3H_2O$.

$$\chi_t = \frac{Ng^2\beta^2}{4KT}\frac{A}{B},$$
$$\chi_M = \frac{\chi_t}{1-\left(2zJ'/N\beta^2g^2\right)\chi_t},$$
$$A = 10\exp(-7J/KT) + 35\exp(-2J/KT) + 35 + 84\exp(5J/KT), \quad (1)$$
$$B = 2\exp(-7J/KT) + 3\exp(-2J/KT) + 3 + 4\exp(5J/KT).$$

The best fitting for the data gives $J = 1.15$ cm^{-1}, $zJ' = -0.051$ cm^{-1}, $g = 2.02$, with an agreement factor (defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum(\chi_M)^2_{obs}$) of 5.95×10^{-5}. The positive J value confirms the intramolecular ferromagnetic couplings with participation of Mn^{2+} ion and NIT-1'-MeBzIm, and the negative θ value shows the weak intermolecular antiferromagnetic exchange interactions at lower temperature. Meantime, a remarkable decrease of the $\chi_M T$ product below 60 K seems to result from the zero-field splitting of the ground quintet state of **I** in view of no close contacts between the neighbouring nitroxide nitroxide moieties in the crystal structure.

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