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Note

A 3-D Polymer, $Mn(NITpPy)_2(tp)(H_2O)_2$: Crystal Structure and Magnetic Properties

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Introduction

The major research aims in the field of molecular magnetism are on one hand the chemical design of molecular assemblies that exhibit a spontaneous magnetization and on the other hand the rationalization of magnetostructural correlation.[1]

Nitronyl nitroxides, stable organic radicals, have played a prominent role in the design and construction of molecular magnetic materials.[1−3] They were used as a bridging ligand between metals with the aim of building polymeric species. However, their weakly basic character strongly limits their coordination ability. Meanwhile, the terephthalato ligand is a versatile ligand with good binding ability as manifested by the formation of polymeric structure systems.[4−8] Therefore, to combine the two synthetic approaches, namely, realizing networks and metallic centers coordinated by spin-carrying ligands, we chose the terephthalate and nitronyl nitroxide radical ligands to synthesize a 3-D network complex, $Mn(NITpPy)_2(tp)(H_2O)_2$ (NITpPy = 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide and tp = terephthalato dianion). We report here the synthesis, X-ray crystal structure, and magnetic properties of the complex $Mn(NITpPy)_2(tp)(H_2O)_2$.

Experimental Section

Preparation of a Single Crystal of the Complex $Mn(NITpPy)_2(tp)(H_2O)_2$. 2-(4′-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (NITpPy) was prepared by the literature method.[9,10]

The $Mn(NITpPy)_2(tp)(H_2O)_2$ complex was prepared by adding an aqueous solution (20 mL) of dipotassium terephthalate (0.121 g, 0.5 mmol) to a MeOH solution (30 mL) obtained by mixing $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol) and NITpPy (0.234 g, 1 mmol). The dark blue solution was allowed to stand at room temperature for one week, and dark blue crystals were obtained. Anal. Calcd for $C_{32}H_{40}N_6O_{10}Mn$: C, 53.11; H, 5.57; N, 11.61. Found C, 53.20; H, 5.50; N, 11.54. The IR spectrum displays a strong broad band at 1650 cm^{-1}, which is the characteristic ν_{COO} band. The strong band observed at 1381 cm^{-1} is the ν_{N-O} band.

Physical Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Perkin-Elmer elemental analyzer, model 240. The infrared spectrum was taken on a Shimadzu IR spectrophotometer, model 408, using KBr pellets. Variable-temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Crystal Structure Determination and Refinement. A dark blue single crystal ($0.30 \times 0.20 \times 0.15$ mm^3) of the title complex was selected and mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature to a θ_{max} of 25.03° with a total of 5656 reflections collected including 2713 independent reflections ($R_{int} = 0.0853$). A summary of the crystallographic data is given in Table 1. The structure was solved with direct methods using the SHELXS-97 program.[11] The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL 97,[12] and the goodness-of-fit on F^2 was 1.029. The final agreement factor values are $R_1 = 0.0765$ and $wR_2 = 0.1900$ ($I > 2\sigma(I)$). Maximum and minimum peaks in the final difference Fourier synthesis were 0.433 and −0.391 e $Å^{-3}$. Selected bond distances and angles are given in Table 2.

Results and Discussion

Description of the Crystal Structure. An ORTEP drawing of the title complex is shown Figure 1. Each Mn(II) ion has a distorted octahedral coordination environment with two oxygen atoms (O(1), O(1A)) from two water molecules and two carboxylato oxygen atoms (O(2), O(2A)) from two terephthalato dianions that comprise the equatorial plane, whereas the axial positions are filled by two nitrogen atoms (N(1), N(2)) from NITpPy ligands. Terephthalato dianions

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Table 1. Crystallographic Data for $Mn(NITpPy)_2(tp)(H_2O)_2$

empirical formula	$C_{32}H_{40}N_6O_{10}Mn$	V, Å^3	3485.0(13)
fw	723.64	Z	4
cryst syst	monoclinic	T, K	298(2)
space group	$C2/c$	λ(Mo Kα), Å	0.71073
a, Å	11.395(2)	μ(Mo Kα), mm^{-1}	0.443
b, Å	26.852(7)	ρ_{calcd}, g cm^{-3}	1.379
c, Å	12.688(3)	$R_1{}^a$	0.0765
β, deg	116.149(4)	$wR_2{}^b$	0.1900

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = (\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^2$. $w = 1/[\sigma^2(F_o{}^2) + (0.1163P)^2 + 1.4073P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Complex $Mn(NITpPy)_2(tp)(H_2O)_2{}^a$

Mn(1)−O(2A)	2.073(4)	Mn(1)−O(2)	2.073(4)
Mn(1)−O(1)	2.158(4)	Mn(1)−O(1A)	2.158(4)
Mn(1)−N(1)	2.293(7)	Mn(1)−N(2)	2.340(7)
O(2)−C(15)	1.256(8)	O(3)−C(15)	1.258(7)
O(4)−N(3)	1.267(6)	O(5)−N(4)	1.281(7)
N(1)−C(8)	1.340(7)	N(2)−C(1)	1.261(8)
O(2A)−Mn(1)−O(2)	179.3(3)	O(2A)−Mn(1)−O(1)	93.05(17)
O(2)−Mn(1)−O(1)	86.95(17)	O(1)−Mn(1)−O(1A)	179.6(3)
O(2A)−Mn(1)−N(1)	90.35(13)	O(2)−Mn(1)−N(1)	90.35(13)
O(1)−Mn(1)−N(1)	89.78(13)	O(2A)−Mn(1)−N(2)	89.65(13)
O(1)−Mn(1)−N(2)	90.22(13)	N(1)−Mn(1)−N(2)	180.000(1)
C(15)−O(2)−Mn(1)	135.0(4)	C(8)−N(1)−C(8)#1	116.5(8)
O(4)−N(3)−C(4)	126.0(5)	O(5)−N(4)−C(11)	125.6(6)
O(2)−C(15)−O(3)	125.4(6)	O(3)−C(15)−C(16)	118.4(6)

[a] Symmetry transformations used to generate equivalent atoms: (I) $-x$, y, $1/2 - z$; (II) $-x - 1$, y, $1/2 - z$.

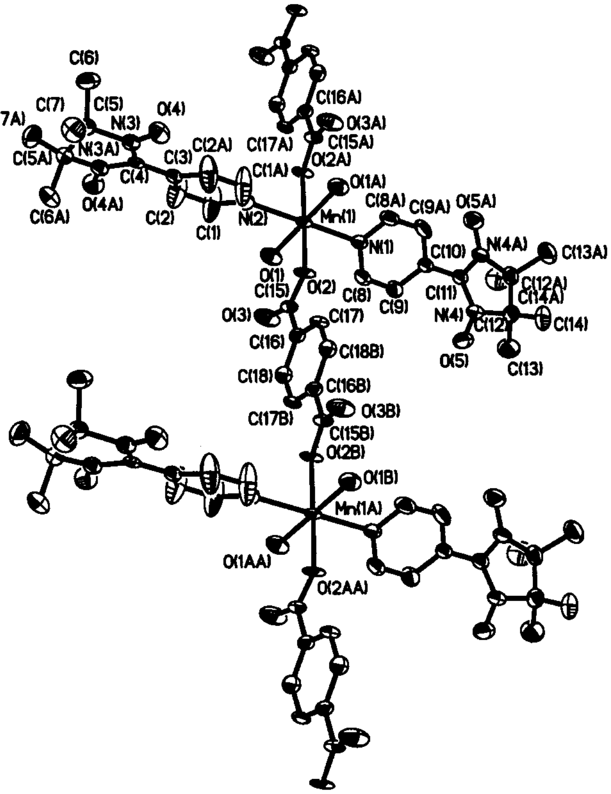

Figure 1. ORTEP drawing with 30% thermal ellipsoid probability showing atom labeling of $Mn(NITpPy)_2(tp)(H_2O)_2$.

and water molecules are in trans positions. Each terephthalato dianion binds two Mn(II) ions in a bis-monodentate mode, which results in the linear coordination chain. This 1-D coordination polymer displays C_2 symmetry, and the two halves of each NITpPy ligand are symmetrically related. The Mn−N bond lengths are 2.293(7) and 2.340(7) Å, which are close to those observed for other manganese complexes containing the NITpPy group.[13−15] The angles between the pyridyl ring and the nitroxide group for two NITpPy radicals are 39.32° and 5.13°, respectively. The Mn−O(carboxylate) bond distance is 2.073(4) Å, which is in agreement with those reported for other carboxylato-containing manganese(II) complexes.[16,17] The phenyl ring of terephthalate is coplanar to the metal basal plane (0.06°). The dihedral angle between the Mn(II) ion basal plane (O(1), O(1A), O(2), O(2A)) and the carboxylate is 5.66°. The shortest contact between nitroxide groups is 3.490 Å. Within the linear chain, the distance between successive Mn atoms is 11.395 Å, which corresponds to the cell length (a). The shortest interchain Mn(II)−Mn(II) separation is 9.097 Å. The uncoordinated carboxylate oxygen atoms form intramolecular hydrogen bonds with the coordinated water molecules (O(1)···O(3) = 2.647(9) Å). The hydrogen bond interactions exist between the 1-D chains, via the coordinated water molecules and the oxygen atoms of the NO groups of NITpPy radicals (2.775(8) Å and 173.46° for O(4)(x, $-y$, $z - 1/2$)···O(1) and O(4)···H(1C)−O(1); 3.069(6) Å and 112.04° for O(5)-($-1/2 - x$, $-1/2 - y$, $-z$)···O(1) and O(5)···H(1C)−O(1)). Thus, the whole molecular structure becomes a 3-D network (Figure 2).

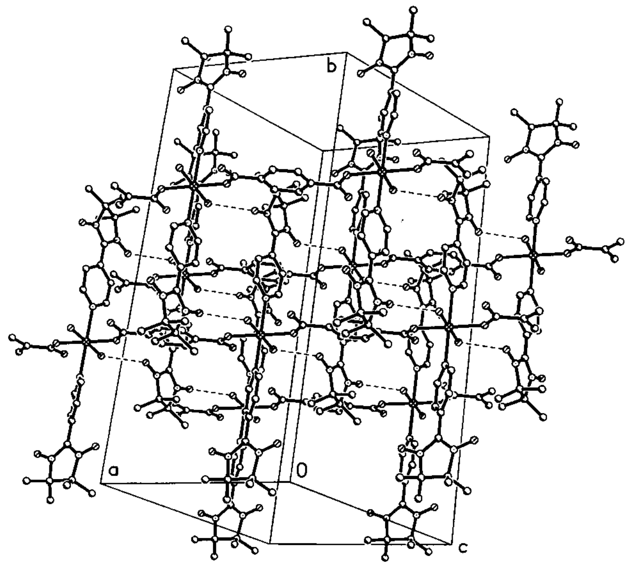

Figure 2. 3-D network of $Mn(NITpPy)_2(tp)(H_2O)_2$.

Magnetic Properties. The magnetic susceptibilities, χ_M, of the title complex were measured between 5 and 300 K at 3000 G, and Figure 3 shows the plots of χ_M and $\chi_M T$ versus T. The $\chi_M T$ value per molecule at room temperature is 5.21-

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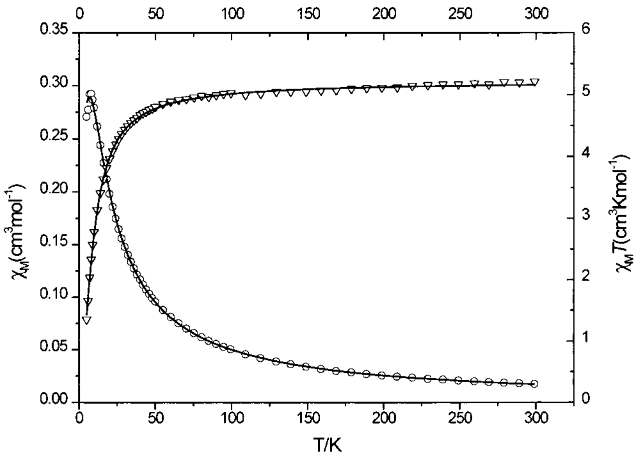
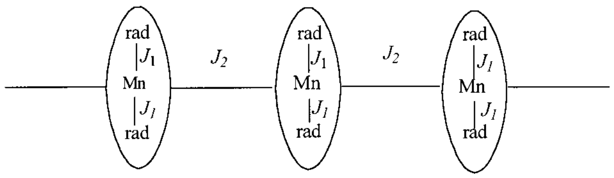


Figure 3. χ_M (○) and $\chi_M T$ (▽) for $Mn(NITpPy)_2(tp)(H_2O)_2$ as a function of temperature. The solid lines correspond to the best theoretical fits.

Chart 1



(cm^3 K mol^{-1}), close to the spin-only value expected for one $S = 5/2$ spin and two $S = 1/2$ uncorrelated spins (5.12 cm^3 K mol^{-1}). When the temperature is lowered, the $\chi_M T$ value decreases gradually down to around 25 K and then abruptly down to 5 K.

There are four kinds of magnetic interactions for the present system, namely, (i) Mn(II)-coordinated NITpPy radical (J_1), (ii) Mn(II)−Mn(II) through the terephthalate bridge (J_2), (iii) neighboring NITpPy radicals through space (3.490 Å), and (iv) Mn(II)−NITpPy radicals through Mn(II)−OH$_2$···ON linkages. The first two kinds of exchange coupling exist in the 1-D chain. The last two kinds of exchange coupling should be weak.[14,15] To evaluate the exchange coupling constants in such a magnetic system, it was treated as a 1-D chain of a radical−Mn(II)−radical species (Chart 1), with the exchange coupling (J') representing the magnetic interactions of Mn(II)−radical through the Mn(II)−OH$_2$···ON pathway and radical−radical through space as a molecular field approximation.[18]

The modified Fisher model for the classic spin chain system[19] was applied for the 1-D chain. The Hamiltonian for the 1-D system can be written as $H_{chain} = -J\sum S_{T_i} \cdot S_{T_{i+1}}$, where S_T represents temperature-dependent spin of the radical−Mn(II)−radical species. The magnetic susceptibility for the 1-D system can be expressed as

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}[S_T(S_T+1)]\frac{1+u}{1+u} \qquad (1)$$

$$u = \coth[J_2S_T(S_T+1)/kT] - kT/[J_2S_T(S_T+1)]$$

Table 3. Selected Structural and Magnetic Data of Terephthalato-Bridged Manganese(II) Complexes[a]

complex	bridging mode	J (cm^{-1})	γ (deg)	d_{intra} (Å)	ref
$[Mn_2(phen)_4(H_2O)_2(tp)](ClO_4)_2$	bis-monodentate	−0.065	24.8	11.5	17
$[Mn_2(phen)_4(tp)](ClO_4)_2$		−1.6			17
$Mn(NITpPy)_2(tp)(H_2O)_2$	bis-monodentate	−0.68	5.66	11.395	this work

[a] Phen = 1,10-phenanthroline. γ is the dihedral angle between the metal basal plane and the carboxylate.

$$S_T(S_T+1) = 3k\chi_T T/Ng^2\beta^2$$

$$\chi_T = \frac{Ng^2\beta^2}{4kT}\,\frac{10x^7+35x^2+35+84x^{-5}}{2x^7+3x^2+3+4x^{-5}} \qquad x = \exp(-J_1/kT)$$

The total magnetic susceptibility is

$$\chi_M = \frac{\chi_{chain}}{[1-\chi_{chain}(2zJ'/Ng^2\beta^2)]}$$

The least-squares analysis of magnetic susceptibility data led to $J_1 = 1.71$ cm^{-1}, $J_2 = -0.68$ cm^{-1}, $zJ' = -0.13$ cm^{-1}, $g = 2.02$, and $R = 5.76 \times 10^{-5}$ (R is the agreement factor defined as $R = \sum[(\chi_M)_{obsd} - (\chi_M)_{calcd}]^2/\sum[(\chi_M)_{obsd}]^2$). The small positive J_1 value implies the magnetic interaction between Mn(II)−radical is weakly ferromagnetic. This is mainly because of the orbital orthogonality between the π^* molecular orbital of the NITpPy and the metal orbitals d_{xy}, d_{yz}, and d_{xz}.[13,20] The weak antiferromagnetic interaction parameter, zJ', shows that the magnetic interactions of Mn(II)−radical through Mn(II)−OH$_2$···ON and radical−radical through space are weak.

The terephthalato ligand has been actively studied to elucidate the limiting distance of magnetic exchange between paramagnetic metal centers. Long tp bridges typically produce M···M separations of about 11 Å, which generally leads to weak antiferromagnetic interactions between metal centers for M = Mn(II), Co(II), Ni(II), and Cu(II).[17] It is interesting to make a comparison between the title complex and two related complexes, and the relevant magnetostructural information is listed in Table 3.

For both complexes $Mn(NITpPy)_2(tp)(H_2O)_2$ and $[Mn_2(phen)_4(H_2O)_2(tp)](ClO_4)_2$, the coordination modes of terephthalate bridging ligands are the same and the intramolecular metal−metal separations are almost identical. But the antiferromagnetic interactions are very different, the J value of −0.68 cm^{-1} for the former is much greater than the J value for the latter (−0.065 cm^{-1}). The magnitudes of magnetic interactions of the terethphalato-bridged complexes depend on whether the tp ligand and the metal basal plane are coplanar. When both the tp bridging ligand and the metal basal plane are coplanar, a much stronger antiferromagnetic interaction is observed.[21,22] For the title complex, the dihedral

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angle between the Mn(II) ion basal plane and the carboxylate is 5.66° [24.8° for the complex $[Mn_2(phen)_4(H_2O)_2(tp)](ClO_4)_2$]; therefore, a stronger magnetic coupling should be expected. Because of the lack of structural data, we cannot compare the magnetostructural relation with $[Mn_2(phen)_4(tp)](ClO_4)_2$. The synthesis and structural and magnetic characterization of new terephthalate-bridged manganese(II) complexes will be the subject of further work to explore the magnetostructural correlation of this kind of complex.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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