

Synthesis, Crystal Structure, and Magnetic Properties of a Mn(III)-radical Complex

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The design and synthesis of metal-radical complexes has attracted much attention in several fields of chemistry, optics, physics and material science for the purpose of exploiting new molecule-based magnetic materials.¹⁻⁷ Among these metal-radical complexes, much attraction has been paid to the research of nitronyl nitroxide radicals since they are used as spin labels or paramagnetic building blocks in the construction of multidimensional magnetic materials.⁸ Moreover, they are usually stable in the open-shell organic molecule and exhibit coordination versatility in the structure in which they can act as bridging ligands or terminal ligands.⁹⁻¹⁴ A larger number of complexes based on the nitronyl nitroxide radical and transition metal ions, such as Mn(II), Co(II), Ni(II) and Cu(II), or rare earth metals assembly have been reported.¹⁵⁻¹⁹

2-(4-Pyridyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide (pPyNN) radical as one of the most attractive radicals has been widely used to assemble metal-radical complexes such as [M(II)(acac)₂(pPyNN)]^{x-} (M = Co, Ni, Mn).²⁰ The Mn(III) ion has a large spin state ($S = 2.0$) and a strong axial magnetic anisotropy and has attracted much more interest in the design of molecular magnets especially single-molecule magnets (SMMs) and single-chain magnets (SCMs).²¹ However, to the best of our knowledge, magnetic complexes based on Mn(III) and nitronyl nitroxide radicals have not yet been reported. In the paper, we report the synthesis, crystal structure and magnetic properties of a new Mn(III)-radical complex [Mn^{III}(acacen)(pPyNN)(H₂O)]ClO₄ (**1**) (acacen²⁻ = dianion of *N,N'*-ethylenebis(acetylacetonyl)-ideneaminato).

Experimental Section

Measurements. Elemental analyses (C, H and N) were carried out on an Elemental Vario E1. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000-400 cm⁻¹ region. Variable-temperature magnetic susceptibilities of powdered samples were measured on a Quantum Design MPMS SQUID magnetometer in the applied field of 1000 Oe. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascal's constants.

Synthesis of Complex 1. The dark brown block single crystals of complex **1** were obtained by carefully mixing pPyNN (0.2 mmol) in ethanol/aqueous solution (8 mL, v:v =

3:1) and [Mn^{III}(acacen)]ClO₄ (0.2 mmol) in ethanol solution (5 mL) at room temperature for about several days. Yield: 40%. Elemental analysis calculated for: C₂₄H₃₆ClMnN₅O₉, (628.97): C, 45.59; H, 5.72; N, 11.13%. Found: C, 45.66; H, 5.68; N, 11.10%. Selected IR frequencies (KBr disk, cm⁻¹): 1084 (vs, νClO₄).

Crystal Structure Determination. Crystals data of complex **1** was selected on a Bruker APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) at 293 K using the ω -scan technique. The structure was solved by direct methods with the SHELXS-97 computer program, and refined by full-matrix least-squares methods. Detailed information about the crystal data and structure determination for complex **1** is summarized in Table 1. The selected bond distances and bond angles are given in Table 2. Copies of this information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax(int.code) 44(1223)336-033 or E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. CCDC NO.: 908099 for **1**.

Results and Discussion

Crystal Structure of Complex 1. The single crystal X-ray diffraction analysis indicates that the crystal structure of complex **1** consists of a [Mn^{III}(acacen)(pPyNN)(H₂O)]⁺ unit and an anion ClO₄⁻. In the [Mn^{III}(acacen)(pPyNN)(H₂O)]⁺ unit, the Mn(III) ion is six-coordinated by two imine nitrogen atoms and two oxygen atoms from the acacen²⁻ in the equatorial plane, one nitrogen atom (N(3)) from pyridine of pPyNN and one oxygen atom (O(1w)) from water in the two *trans* axial positions, forming a MnN₃O₃ elongated distorted octahedral geometry as shown in Figure 1.

In the [Mn^{III}(acacen)(pPyNN)(H₂O)]⁺ unit, the four coordinated atoms in the equatorial plane almost lay in the same plane with the maximum deviation is 0.004 Å for N(2) and the distance of Mn(III) to the plane is 0.040 Å. The bond lengths of Mn-O_{acacen} are 1.904(3) Å for (Mn(1)-O(1)) and 1.900(3) Å for (Mn(1)-O(2)) and the Mn-N_{acacen} bond distances are 1.965(3) Å for (Mn(1)-N(1)) and 1.963(4) Å for (Mn(1)-N(2)), respectively, which accords with the corresponding bond length in the literature.²² The bond lengths of Mn(1)-N(3) and Mn(1)-O(1w) are 2.361(4) and 2.301(4) Å, and the bond angle of O(1w)-Mn(1)-N(3) is 169.72(13)°.

Table 1. Crystal Data and Structure Refinement for **1**

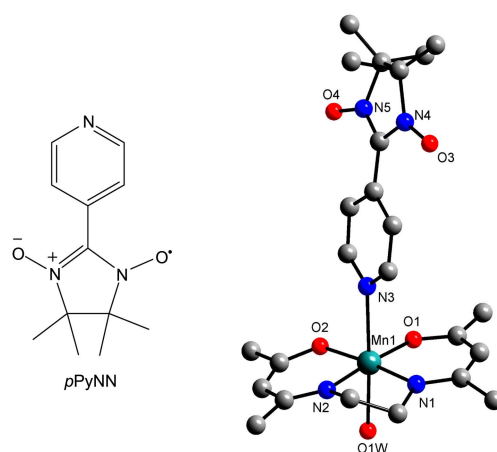
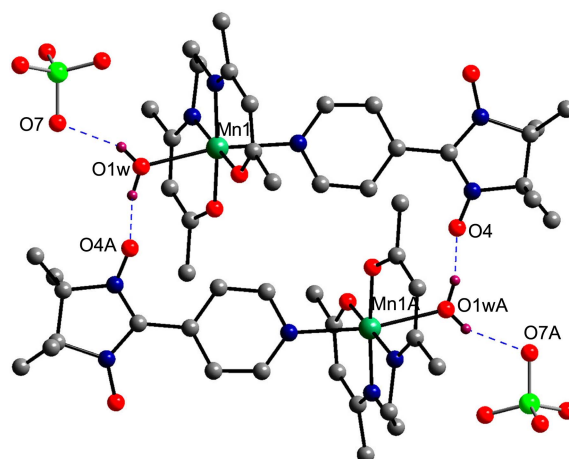
Empirical formula (<i>M</i>)	C ₂₄ H ₃₆ ClMnN ₅ O ₉ (628.97)
Wavelength (Å)	0.71075
Crystal system	Monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / <i>b</i> / <i>c</i> (Å)	8.155(5)/13.459(12)/27.18(2)
β (°)	95.88(4)
<i>V</i> (Å ³)	2968(4)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.408
μ (mm ⁻¹)	0.591
<i>F</i> (000)	1316
Crystal size (mm ³)	0.18×0.16×0.15
θ range for data collection (°)	3.01–25.00
Limiting indices	-9 ≤ <i>h</i> ≤ 9, -16 ≤ <i>k</i> ≤ 15, -32 ≤ <i>l</i> ≤ 32
Reflections collected/unique	21293/5165 [<i>R</i> (int) = 0.0273]
Reflections with <i>I</i> > 2 σ (<i>I</i>)	4157
Data Completeness (%)	99.3
Data/restraints/parameters	5165/36/364
Goodness-of-fit on <i>F</i> ²	1.031
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0645, <i>wR</i> ₂ = 0.1812
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0732, <i>wR</i> ₂ = 0.1904
Largest diff. peak and hole (e Å ⁻³)	0.662 and -0.462

Table 2. Selected Bond Distances (Å) and Angles (°) for **1**

Mn(1)–O(2)	1.900(3)	N(1)–C(9)	1.331(6)
Mn(1)–O(1)	1.904(3)	N(1)–C(7)	1.470(6)
Mn(1)–N(2)	1.963(4)	N(2)–C(4)	1.297(6)
Mn(1)–N(1)	1.965(3)	N(2)–C(6)	1.483(6)
Mn(1)–O(1w)	2.301(4)	N(3)–C(17)	1.326(5)
Mn(1)–N(3)	2.361(4)	N(3)–C(13)	1.338(5)
O(1)–C(11)	1.295(5)	N(4)–C(18)	1.354(6)
O(2)–C(2)	1.284(5)	N(4)–C(19)	1.502(8)
O(3)–N(4)	1.291(7)	N(5)–C(18)	1.279(6)
O(4)–N(5)	1.192(6)	N(5)–C(20)	1.476(6)
O(2)–Mn(1)–O(1)	92.05(13)	O(1)–Mn(1)–N(3)	85.99(13)
O(2)–Mn(1)–N(2)	91.77(15)	N(2)–Mn(1)–N(3)	96.30(13)
O(1)–Mn(1)–N(1)	92.35(15)	N(1)–Mn(1)–N(3)	94.44(15)
N(2)–Mn(1)–N(1)	83.74(16)	O(1w)–Mn(1)–N(3)	169.72(13)
O(2)–Mn(1)–O(1w)	83.11(15)	O(4)–N(5)–C(18)	126.7(4)
O(1)–Mn(1)–O(1w)	88.29(15)	O(4)–N(5)–C(20)	119.1(5)
N(2)–Mn(1)–O(1w)	89.99(15)	O(3)–N(4)–C(18)	126.9(5)
N(1)–Mn(1)–O(1w)	94.32(15)	O(3)–N(4)–C(19)	122.5(5)
O(2)–Mn(1)–N(3)	88.56(14)		

Meanwhile, the five atoms N(4), N(5), O(3), O(4) and C(18) from radical pPyNN also almost lay in the same plane, the maximum deviation is 0.087(4) Å for N(5), the dihedral angle between the plane and pyridine ring plane is 9.57°.

There exist O–H⋯O hydrogen bonds between coordinated water molecules and free anion ClO₄⁻ (O(1w)–H(101)⋯O(7)# [-*x*+2, *y*-1/2, -*z*+1/2] and O(1w)⋯O(7)# = 2.808 Å) as well as between the radicals and coordinated water molecules

**Figure 1.** Molecular structure of complex **1** shows the six-coordinated geometry of the Mn(III) ion. All hydrogen atoms and the ClO₄⁻ anion were omitted for clarity.**Figure 2.** Cell packing diagram of complex **1** along the *a* axis showing the dimeric structure.

(O(1w)–H(100)⋯O(4)# [-*x*+2, -*y*, -*z*] and O(1w)⋯O(4) = 2.715 Å). These hydrogen bonds link two [Mn(acacen)-(pPyNN)(H₂O)]⁺ cations and two ClO₄⁻ anions into the dimeric supramolecular structure as shown in Figure 2.

Magnetic Properties. The magnetic susceptibility data of complex **1** were measured between 5 and 300 K under an applied field of 1000 Oe. The $\chi_m T$ versus *T* and $1/\chi_m$ versus *T* are presented in Figure 3. The $\chi_m T$ value is close to 3.20 emu K mol⁻¹ at room temperature, which is almost equal to the spin-only value 3.375 emu K mol⁻¹ expected for the pPyNN radical (*S* = 1/2) and high-spin Mn(III) (*S* = 2) system based on *g* = 2.00. As the temperature decreasing, the $\chi_m T$ value decreases slowly until 50 K. The $\chi_m T$ value decreases rapidly below 50 K and reaches a value of 2.33 emu K mol⁻¹ at 5 K. The magnetic behavior indicates that the magnetic interaction between the two spin carriers of Mn(III) ion and radical is antiferromagnetic. The magnetic susceptibility in the whole temperature range obeys the Curie-Weiss law with the negative Weiss constant θ = 1.86 K and the Curie constant *C* = 3.21 emu K mol⁻¹. The relative small negative Weiss

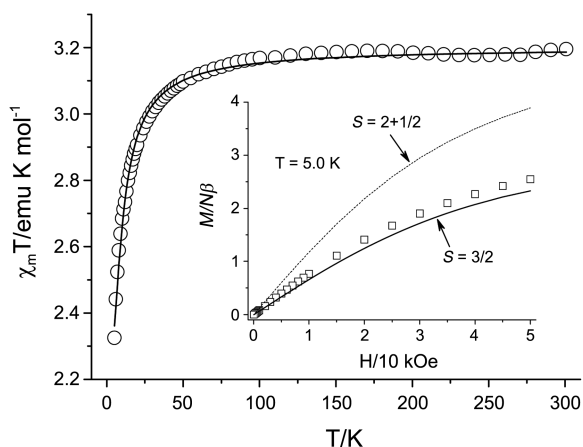


Figure 3. Temperature dependence of $\chi_m T$ for complex **1**, the solid line represents the best fit based on the parameter discussed in the text (Inset: Field dependences of magnetization, the line and the broken line represent the Brillouin function that correspond to $S = 3/2$ and $S = 2 + 1/2$, respectively, based on $g = 2.0$).

constant further suggests the there exists overall weak anti-ferromagnetic coupling in the title complex.

The field dependence of magnetization of **1** measured in the field range of 0-50 Oe at 5 K (Inset in Figure 3) is nearly close to the Brillouin function curve based on the $S = 3/2$ spin ground state with $g = 2.00$, and is obviously lower than the data of the Brillouin curve based on $S = 2 + 1/2$ spin system assuming $g = 2.00$. This feature further indicates that the existence of overall antiferromagnetic coupling between the pPyNN radical and Mn(III) ions.

If only considered the intramolecular magnetic coupling (J) and intermolecular magnetic interaction (zJ'), the magnetic susceptibilities of complex **1** can be fitted accordingly by the following expressions (1 and 2) derived from the Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}}\hat{S}_{\text{rad}}$. The best-fit parameters obtained are $J = -1.15(2) \text{ cm}^{-1}$, $zJ' = -0.28(2) \text{ cm}^{-1}$, $g = 1.95(1)$, $R = \Sigma[(\chi_m T)_{\text{obsd.}} - (\chi_m T)_{\text{calcd.}}]^2 / \Sigma[(\chi_m T)_{\text{obsd.}}]^2 = 5.6 \times 10^{-5}$. The small negative values of J and zJ' also evidence the intramolecular and intermolecular magnetic interactions are all weak antiferromagnetic.

$$\chi_{\text{MnRad}} = \frac{Ng^2\beta^2 35\exp(2J/kT) + 10\exp(-3J/kT)}{2kT \quad 6\exp(2J/kT) + 4\exp(-3J/kT)} \quad (1)$$

$$\chi_m = \frac{\chi_{\text{MnRad}}}{1 - 2zJ'\chi_{\text{MnRad}}/Ng^2\beta^2} \quad (2)$$

In order to comprehensively evaluate the strength of intramolecular magnetic coupling and intermolecular magnetic interaction and the zero-field-splitting (ZFS) parameter (D) of Mn(III) ion, the magnetic susceptibilities of complex **1** can be fitted in the whole temperature accordingly by the following expressions (3 and 4) derived from the Hamiltonian $\hat{H} = -2J\hat{S}_{\text{rad}}\hat{S}_{\text{Mn}} + D_{\text{Mn}}(\hat{S}_z^2 - S_{\text{Mn}}(S_{\text{Mn}} + 1)/3) + g\beta H\hat{S}_z - zJ'\langle\hat{S}_z^T\rangle\hat{S}_z^T$. The best-fit parameters obtained are $J = -1.92(1) \text{ cm}^{-1}$, $g = 1.95(1)$, $D_{\text{Mn}} = 0.85(3) \text{ cm}^{-1}$, $zJ' = -0.15(3) \text{ cm}^{-1}$, and $R = 3.6 \times 10^{-5}$. The calculated positive D_{Mn} value (0.85 cm^{-1}) of complex **1** is normal for high-spin tetragonally

elongated octahedral Mn(III) ion. The D_{Mn} value also can be comparable to those of $\{[\text{Fe}(\text{bpy})(\text{CN})_4][\text{Mn}(\text{TPP})(\text{CH}_3\text{OH})]\} \cdot \text{CH}_3\text{OH}^{23}$ and $[\text{Mn}(\text{saltn})(\text{MeOH})][\text{Fe}(\text{bpb})(\text{CN})_2] \cdot 3\text{H}_2\text{O}^{24}$ which have the same spin system ($S_{\text{Fe}} = 1/2$, $S_{\text{Mn}} = 2$) to the complex **1**. It must be point out that D_{Mn} and zJ' are often correlated, and they should be treated with care.

$$\chi_{\text{MnRad}} = \frac{Ng^2\beta^2 25\exp(A) + 9\exp(B) + \exp(C) + 9\exp(D) + \exp(E)}{4kT \quad \exp(A) + \exp(B) + \exp(C) + \exp(D) + \exp(E)} \quad (3)$$

$$A = \left(\frac{35J}{4} + 4D\right)/kT$$

$$B = \left[\frac{25J}{4} + \frac{5D}{2} + \left(\frac{25J^2}{4} - \frac{9}{2}DJ + \frac{9}{4}D^2\right)^{1/2}\right]/kT$$

$$C = \left[\frac{25J}{4} + \frac{D}{2} + \left(\frac{25J^2}{4} - \frac{1}{2}DJ + \frac{1}{4}D^2\right)^{1/2}\right]/kT$$

$$D = \left[\frac{25J}{4} + \frac{5D}{2} - \left(\frac{25J^2}{4} - \frac{9}{2}DJ + \frac{9}{4}D^2\right)^{1/2}\right]/kT$$

$$E = \left[\frac{25J}{4} + \frac{D}{2} - \left(\frac{25J^2}{4} - \frac{1}{2}DJ + \frac{1}{4}D^2\right)^{1/2}\right]/kT$$

$$\chi_m = \frac{\chi_{\text{MnRad}}}{1 - 2zJ'\chi_{\text{MnRad}}/(Ng^2\beta^2)} \quad (4)$$

The best-fit results indicate that the two kinds of models provided the similar magnetic coupling constant value between the Mn(III) ion and pPyNN radical. It is worth mentioning that a $\text{Mn}^{\text{III}}_2(\text{DCNNQI})_2$ complex displays anti-ferromagnetic coupling with the coupling constant of $J = -23.0 \text{ K}$ (DCNNQI is N,N' -dicyano-1,4-naphthoquinone-diimine radical).²⁵

The magnetic studies of complex **1** show that the pyridine ring of pPyNN radical transfers antiferromagnetic interaction between Mn(III) ion and the pPyNN radical, and the anti-ferromagnetic interaction can be qualitatively explained from the angle of the magnetic orbital overlap. The π radical pPyNN has an unpaired electrons in the π^* SOMO orbital, while the four unpaired electrons of high-spin Mn(III) ions occupy the d_{xy} , d_{xz} , d_{yz} and d_{z^2} orbitals (the x axis is taken along the Mn-N_{rad} bond). The pyridine ring acts as diamagnetic ligand in between two paramagnetic centers. According to the molecular orbital (MO) analysis in the literature, there are two modes of magnetic interaction between the magnetic orbitals: ($d_{xy}/d_{xz} + \pi^*$) which is in favor of ferromagnetic coupling and ($d_{yz}/d_{z^2} + \pi^*$) which is in favor of antiferromagnetic coupling.⁹ Therefore, the overall magnetic interaction depends on the sum of all possible exchange contributions of J_{xy,π^*} , J_{xz,π^*} , J_{yz,π^*} and J_{z^2,π^*} . In the present case, the antiferromagnetic coupling is dominating, resulting in the overall antiferromagnetic interaction in complex **1**.

Concluding Remarks

A new Mn(III)-radical complex $[\text{Mn}^{\text{III}}(\text{acacen})-(\text{pPyNN})-(\text{H}_2\text{O})]\text{ClO}_4$ has been synthesized by the reaction of pPyNN

radical and [Mn(acacen)]ClO₄. The single crystal structure analysis reveals that the complex is composed of a cation [Mn^{III}(acacen)(pPyNN)(H₂O)]⁺ unit and an anion ClO₄⁻. The magnetic studies of complex **1** show that there exists weak antiferromagnetic interaction between the Mn(III) ion and the pPyNN radical through the pyridine ring in pPyNN radical.

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