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

Wei-Qin Cheng, Li-Fang Zhang, Zhong-Hai Ni, and Hui-Zhong Kou

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, P.R. China. *E-mail: zhanglfang@cumt.edu.cn

Abstract

The design and synthesis of metal-radical complexes has attracted much attention in several fields of chemistry, physics, and material science for the purpose of exploiting new molecule-based magnetic materials. 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. 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. 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. 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 [Mn(III)(acacen)(pPyNN)(H₂O)]. The Mn(III) ion has a large spin state (S = 2) 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). 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) (acacen = dianion of N,N'-ethylenbis(acetylacetonyl)-ideneaminato).

Experimental Section

Measurements. Elemental analyses (C, H and N) were carried out on an Elemental Vario El. 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: C₂₂H₂₀ClMnN₂O₅ (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, vClO₄⁻).

Crystal Structure Determination. Crystals data of complex 1 was selected on a Bruker APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) at 293 K using the o-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 MnN₂O₄ 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. 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)°.
The angle between the plane and pyridine ring plane is 9.57°. The maximum deviation is 0.087(4) Å for N(5), the dihedral angle between the radicals and coordinated water molecules is almost lay in the same plane, the five atoms N(4), N(5), O(3), O(4) and C(18) are presented in Figure 3. 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 $\theta = 1.86$ K and the Curie constant $C = 3.21$ emu K mol$^{-1}$. The relative small negative Weiss constant is consistent with the observed value.

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 ClO$_4^-$ (O(1w)−H(101)⋯O(4)# $[-x+2, -y, -z]$ and O(1w)−O(4) = 2.715 Å). These hydrogen bonds link two [Mn(acacen)$_2$(pPyNN)($H_2$O)]$^+$ cations and two ClO$_4^-$ anions into the dimeric supramolecular structure as shown in Figure 2.
constant further suggests the there exists overall weak antiferromagnetic 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 $g = 2.0$, and is obviously lower than the data of the Brillouin curve based on $S = 2 + 1/2$ spin system assuming $g = 2.0$. This feature further indicates that the existence of overall antiferromagnetic interaction between the pPyNN radical and Mn(III) ions.

If only considered the intramolecular magnetic coupling ($J$) and intermolecular magnetic interaction ($J'$), the magnetic susceptibilities of complex 1 can be fitted accordingly by the following expressions (1 and 2) derived from the Hamiltonian $H = -2JS_{\text{rad}}S_{\text{Mn}}$. The best-fit parameters obtained are $J = -1.15(2)$ cm$^{-1}$, $J' = -0.28(2)$ cm$^{-1}$, $g = 1.95(1)$, $R = \frac{(\chi_{\text{MnRad}} - \chi_{\text{MnRad}}^{\text{calcd}})^2}{\Sigma (\chi_{\text{Mn}} - \chi_{\text{Mn}}^{\text{calcd}})} = 5.6 \times 10^{-5}$. The small negative values of $J$ and $J'$ also evidence the intramolecular and intermolecular magnetic interactions are all weak antiferromagnetic.

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

$$
\chi_m = \frac{\chi_{\text{MnRad}}}{1 - 2gJ\chi_{\text{MnRad}}/Ng^2\beta^2}
$$

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 $H = -2JS_{\text{rad}}S_{\text{Mn}} + D_{\text{Mn}}S_z^2 - S_{\text{Mn}}(S_{\text{Mn}} + 1/3) + g\beta HS - zJ'(S_{\text{rad}}^2 S_z)$. The best-fit parameters obtained are $J = -1.92(1)$ cm$^{-1}$, $g = 1.95(1)$, $D_{\text{Mn}} = 0.85(3)$ cm$^{-1}$, $J' = -0.15(3)$ cm$^{-1}$, and $R = 3.6 \times 10^{-5}$. The calculated positive $D_{\text{Mn}}$ value (0.85 cm$^{-1}$) of complex 1 is normal for high-spin tetragonally elongated octahedral Mn(III) ion. The $D_{\text{Mn}}$ value also can be comparable to those of [{Fe(bpy)(CN)$_6$}]$^{3-}$/Mn(III) (H$_2$O)$_2$]·ClO$_4$ and Mn(saltn)(MeOH)][Fe(bpy)(CN)$_6$]$_2$ 3H$_2$O which have the same spin system ($S_{\text{Mn}} = 1/2$, $S_{\text{Mn}} = 2$) to the complex 1. It must be point out that $D_{\text{Mn}}$ and $zJ'$ are often correlated, and they should be treated with care.

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

$$
A = \left(\frac{25J}{4} + 4D\right)/kT
$$

$$
B = \left[\frac{25J + 5D}{2} + \frac{25J - 9J_1/2 + 9D}{4}\right]/kT
$$

$$
C = \left[\frac{25J + D}{2} + \frac{25J - 9J_1/2 + 9D}{4}\right]/kT
$$

$$
D = \left[\frac{25J + 5D}{2} - \frac{25J - 9J_1/2 + 9D}{4}\right]/kT
$$

$$
E = \left[\frac{25J + D}{2} - \frac{25J - 9J_1/2 + 9D}{4}\right]/kT
$$

$$
\chi_m = \frac{\chi_{\text{MnRad}}}{1 - 2gJ\chi_{\text{MnRad}}/Ng^2\beta^2}
$$

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 Mn$^{III}$(DCNNQI)$_2$: complex displays antiferromagnetic coupling with the coupling constant of $J = -23.0$ K (DCNNQI is $N,N'$-dicyano-1,4-naphthoquinone-diminate radical).

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 antiferromagnetic interaction can be qualitatively explained from the angle of the magnetic orbital overlap. The radical pPyNN has an unpaired electrons in the $\pi^*$ 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 ($d_{xz}/d_{yz} + \pi^*$) which is in favor of antiferromagnetic coupling. Therefore, the overall magnetic interaction depends on the sum of all possible exchange contributions of $J_{\parallel \pi^*}$, $J_{\perp \pi^*}$, $J_{\parallel \pi^*}$ and $J_{\parallel \pi^*}$. 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 [Mn$^{III}$(acacen)-(pPyNN)-(H$_2$O)]ClO$_4$ has been synthesized by the reaction of pPyNN
radical and [Mn(II)(acacen)]ClO$_4$. The single crystal structure analysis reveals that the complex is composed of a cation [Mn$^{III}$ (acacen)(pPyNN)(H$_2$O)]$^+$ unit and an anion ClO$_4^-$. 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.

Acknowledgments. This work was supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions, the Fundamental Research Funds for the Central Universities (2013QNA17). And the publication cost of this paper was supported by the Korean Chemical Society.

References

9. Caneschi, A.; Ferraro, F.; Gatteschi, D.; Rey, P.; Sassoli, R.