



Two novel cyclic dimer M_2L_2 complexes constructed from 2-[(4-carboxyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3 oxide: Crystal structure and magnetic properties

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ABSTRACT

Two novel complexes derived from 2-[(4-carboxyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPBAH), $[Mn(hfac)_2(NITPBAH)]_2$ (**1**) and $[Co(hfac)_2(NITPBAH)]_2$ (**2**) (hfac = hexafluoroacetylacetonate), have been synthesized as well as characterized structurally and magnetically. The X-ray crystal structure analyses show that the structures of the two compounds are isomorphous and both consist of cyclic dimer units bridged by NITPBAH ligands, in which metal ion Mn(II) or Co(II) is coordinated by four oxygen atoms from two hfac ligands, one oxygen atom from nitronyl nitroxide and one oxygen atom from carboxyl group of another radical ligand. The magnetic studies show that the manganese(II) or cobalt(II) ion strongly antiferromagnetically interacts with the directly coordinated nitroxide group. There exists a weak antiferromagnetic coupling between the metal ion and the nitroxide through phenyl ring and carboxyl group of the radical ligand, which is in agreement with spin polarization mechanism.

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1. Introduction

The increasing attention has been focused on the coordination complexes of paramagnetic metal ions with organic radical ligands in order to exploit new molecular magnetic materials involving practical magnetic properties and diversified topological structures [1–5]. Among the organic paramagnetic molecules, nitroxide [6], verdazyl [7], semiquinone [8] and thiazyl [9] radical ligands have been used extensively. In particular, nitronyl nitroxide derivatives are one of the most explored in this strategy [10]. So far, a large quantity of complexes based on diverse nitroxyl nitroxides with various topological structures and magnetic behaviors have been prepared and characterized [11–20]. Recently, a few interesting cyclic metal–radical complexes by the means of nitroxide radical ligands have been described [21–26]. Among these cyclic complexes, some show particularly interesting temperature-dependent spin-transition-like behavior [17,18]. Such cyclic complexes are important. They are good candidates not only for fundamental studies of magnetic-structural correlations, especially how the structural factors affect the interaction between metal and radical, but also for the development of novel molecular magnetic materials. One method for obtaining such cyclic complexes is to use nitro-

oxides substituted by a nitrogen-containing group, which can not function as a chelating ligand such as 3-pyridyl [27] and phenylpyrimidyl groups [28]. Along this line, we use 2-[(4-carboxyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPBAH) with non-chelating carboxyl group to build new cyclic metal–radical complexes. In this paper, we report on the synthesis, crystallography and magnetic characterization of two new cyclic complexes $[M(hfac)_2(NITPBAH)]_2$ ($M = Mn(II)$ **1**, $Co(II)$ **2**).

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased from commercial sources and used as received. NITPBAH radical ligand was prepared from 4-carboxybenzaldehyde by the method similar to a literature [29]. Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Perkin–Elmer elemental analyzer model 240. Infrared spectra were taken on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the region $4000\text{--}400\text{ cm}^{-1}$, using KBr pellets. Temperature dependence of magnetic susceptibilities was performed on a Quantum Design SQUID magnetometer working at 1000 G field strength in the 2–300 K temperature range. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

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2.2. Synthesis of complexes

2.2.1. Synthesis of $[Mn(hfac)_2(NITPBAH)]_2$ **1**

A solution of $Mn(hfac)_2 \cdot 2H_2O$ (20 mg, 0.04 mmol) in 20 mL dry heptane was refluxed for 3 h to azeotropically remove hydration water molecules. After that, the solution was cooled to 60 °C, and then a solution of NITPBAH (11 mg, 0.04 mmol) in 4 mL dry CH_2Cl_2 was added. The resulting dark blue solution was stirred for 10 min at this temperature, cooled to room temperature and filtered. The filtrate was allowed to stand at room temperature for slow evaporation. After one week, the dark blue crystals suitable for single crystal diffraction were collected. Yield: 63%. *Anal.* Calc. for $Mn_2C_{48}H_{38}N_4O_{16}F_{24}$: C, 38.62; N, 3.75; H, 2.57. Found: C, 38.32; N, 3.79; H, 2.72%. FT-IR (KBr, cm^{-1}): 1647(w), 1617(m), 1505(s), 1254(s), 1196(s), 1142(s), 792(m), 663(m).

2.2.2. Synthesis of $[Co(hfac)_2(NITPBAH)]_2$ **2**

Complex **2** was synthesized using the same procedure for complex **1** but with $Co(hfac)_2 \cdot 2H_2O$ instead of $Mn(hfac)_2 \cdot 2H_2O$. Yield: 50%. *Anal.* Calc. for $Co_2C_{48}H_{38}N_4O_{16}F_{24}$: C, 38.42; N, 3.73; H, 2.55. Found: C, 38.16; N, 3.69; H, 2.57%. FT-IR (KBr, cm^{-1}): 1644(w), 1616(m), 1524(s), 1256(s), 1197(s), 1143(s), 791(m), 667(m).

2.3. X-ray crystal structure determinations

Diffraction intensity data of the single crystals of complexes **1** and **2** were collected on a Rigaku Saturn CCD diffractometer at 113 K employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods by using the program SHELXS-97 [30] and refined by full matrix least-squares methods on F^2 with the use of the SHELXL-97 [31] program package. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Disorders were observed in complexes **1** and **2** for some fluorine atoms. The pertinent crystallographic data and structure refinement parameters for two complexes were listed in Table 1. Selected bond lengths and angles of the complexes **1** and **2** were presented in Table 2.

Table 1
Crystallographic and refinement data for complexes **1** and **2**.

	1	2
Formula	$Mn_2C_{48}H_{38}N_4O_{16}F_{24}$	$Co_2C_{48}H_{38}N_4O_{16}F_{24}$
Mr	1492.70	1500.68
<i>T</i> (K)	113(2)	113(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	9.441(3)	9.139(4)
<i>b</i> (Å)	12.170(4)	12.062(6)
<i>c</i> (Å)	13.425(4)	13.982(6)
α (°)	85.248(9)	83.096(11)
β (°)	87.057(7)	87.295(16)
γ (°)	89.562(10)	89.196(15)
<i>V</i> (Å ³)	1535.2(8)	1528.4(12)
<i>Z</i>	1	1
<i>D</i> _{calc} (g cm ^{−3})	1.615	1.630
μ (mm ^{−1})	0.550	0.682
θ range (°)	1.52–26.01	1.47–27.32
Limiting indices	−11 ≤ <i>h</i> ≤ 10 −15 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 16	−10 ≤ <i>h</i> ≤ 11 −15 ≤ <i>k</i> ≤ 15 −17 ≤ <i>l</i> ≤ 18
Unique reflections (<i>R</i> _{int})	5995 0.0406	6737 0.0434
Goodness-of-fit (GOF)	1.027	0.991
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0564	0.0569
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.1147	0.1496
<i>R</i> 1 (all data)	0.0816	0.0798
<i>wR</i> 2 (all data)	0.1273	0.1613

Table 2

Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

Complex 1		Complex 2	
Mn(1)–O(7)	2.118(2)	Co(1)–O(2)	2.019(2)
Mn(1)–O(4)	2.126(2)	Co(1)–O(1)	2.037(3)
Mn(1)–O(3)	2.131(2)	Co(1)–O(4)	2.040(2)
Mn(1)–O(1)	2.165(2)	Co(1)–O(3)	2.043(3)
Mn(1)–O(2)	2.189(2)	Co(1)–O(5)	2.072(2)
Mn(1)–O(5)	2.226(2)	Co(1)–O(6)	2.142(2)
O(8)–N(2)	1.273(3)	O(1)–N(2)	1.295(4)
O(7)–N(1)	1.303(3)	O(8)–N(1)	1.270(4)
N(1)–O(7)–Mn(1)	126.65(18)	N(2)–O(1)–Co(1)	124.1(2)
O(7)–Mn(1)–O(4)	89.68(8)	O(2)–Co(1)–O(1)	90.39(10)
O(7)–Mn(1)–O(3)	172.06(9)	O(2)–Co(1)–O(4)	176.82(10)
O(4)–Mn(1)–O(3)	84.62(8)	O(1)–Co(1)–O(4)	87.80(10)
O(7)–Mn(1)–O(1)	89.73(8)	O(2)–Co(1)–O(3)	90.35(10)
O(4)–Mn(1)–O(1)	173.82(10)	O(1)–Co(1)–O(3)	173.53(9)
O(3)–Mn(1)–O(1)	96.52(8)	O(4)–Co(1)–O(3)	91.74(10)
O(7)–Mn(1)–O(2)	96.14(9)	O(2)–Co(1)–O(5)	89.68(10)
O(4)–Mn(1)–O(2)	92.91(10)	O(1)–Co(1)–O(5)	98.35(10)
O(3)–Mn(1)–O(2)	89.68(9)	O(4)–Co(1)–O(5)	88.00(9)
O(1)–Mn(1)–O(2)	81.03(8)	O(3)–Co(1)–O(5)	88.09(10)
O(7)–Mn(1)–O(5)	92.07(8)	O(2)–Co(1)–O(6)	94.69(10)
O(4)–Mn(1)–O(5)	102.16(10)	O(1)–Co(1)–O(6)	90.00(10)
O(3)–Mn(1)–O(5)	83.76(9)	O(4)–Co(1)–O(6)	87.92(9)
O(1)–Mn(1)–O(5)	84.01(8)	O(3)–Co(1)–O(6)	83.53(10)
O(2)–Mn(1)–O(5)	162.88(8)	O(5)–Co(1)–O(6)	170.55(10)

3. Results and discussion

3.1. Crystal structure

3.1.1. $[Mn(hfac)_2(NITPBAH)]_2$ **1**

The X-ray crystallographic analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **1** is shown in Fig. 1. Two Mn^{II} ions are bridged by two NITPBA radicals to result in a four-spin centrosymmetric cyclic dimer. Each Mn(II) ion lies in a distorted octahedron environment, coordinated by four oxygen atoms from two hfac ligands, one oxygen atom from the nitronyl nitroxide unit and one oxygen atom from the carboxyl group of the other radical ligand. The bond lengths of Mn^{II}–O(hfac) are in the range of 2.126(2)–2.189(2) Å. The bond lengths of Mn^{II}–O(carboxyl) and Mn^{II}–O(nitroxide) are 2.226(2) and 2.118(2) Å, respectively. These bond lengths are comparable to those of the reported cyclic Mn-nitroxide dimers [21,24,26]. In NITPBAH radical ligand, the O–N–C–N–O group containing the unpaired electron makes an angle of 30.16° with the phenyl ring. In the dimer unit, two phenyl rings are parallel with a distance of 2.916 Å. The distance of two Mn^{II} ions is 9.413 Å. Intramolecular hydrogen bonding interaction exists between oxygen atom(O1) from hfac group and another oxygen atom(O6) from carboxyl group with a distance of 2.600 Å. In the packing arrangement of complex **1** (Fig. 2), the shortest distance between Mn ions in different dimer units is 9.441 Å, while the shortest contact between the uncoordinated N–O groups is 5.047 Å.

3.1.2. $[Co(hfac)_2(NITPBAH)]_2$ **2**

The labeling diagram for the crystal structure of complex **2** is depicted in Fig. 3. Complex **2** crystallizes in the triclinic $P\bar{1}$ space group, which consists of neutral dimer unit with inversion center. Two NITPBAH ligands link two Co^{II} ions to form a four-spin cyclic complex. The Co^{II} ions of the cyclic dimer exhibit a slightly distorted octahedral coordination sphere with four oxygen atoms from two hfac ligands, one oxygen from the nitronyl nitroxide unit and one oxygen atom from the carboxyl group of the other radical. The bond lengths of Co^{II}–O(hfac) are in the range of 2.019(2)–2.072(2) Å, while the bond lengths of Co(II)–O(carboxyl) and Co(II)–O(nitroxide group) are 2.142(2) and 2.037(3) Å, respec-

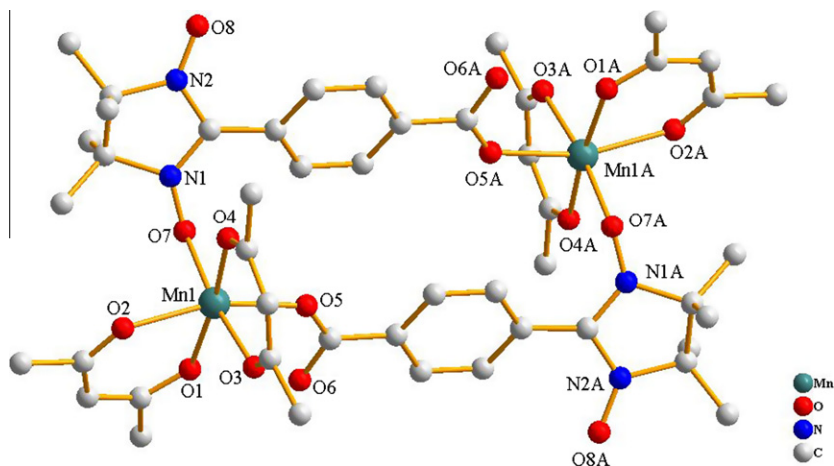


Fig. 1. The cyclic dimer structure of complex 1. Hydrogen and fluorine atoms are omitted for clarity.

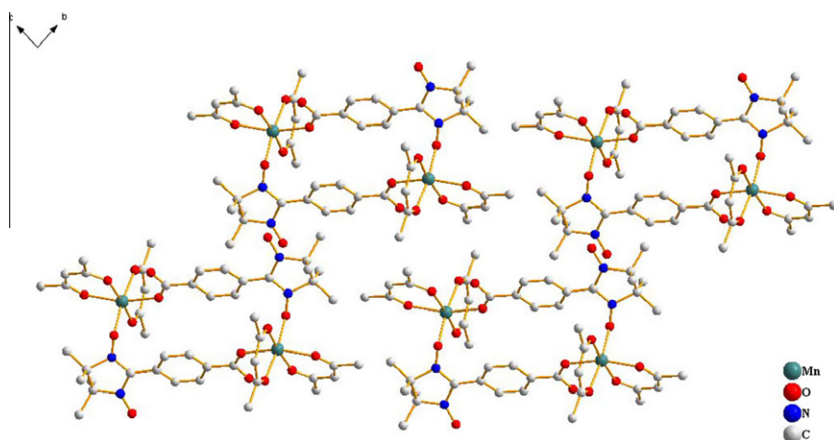


Fig. 2. The packing arrangement of complex 1.

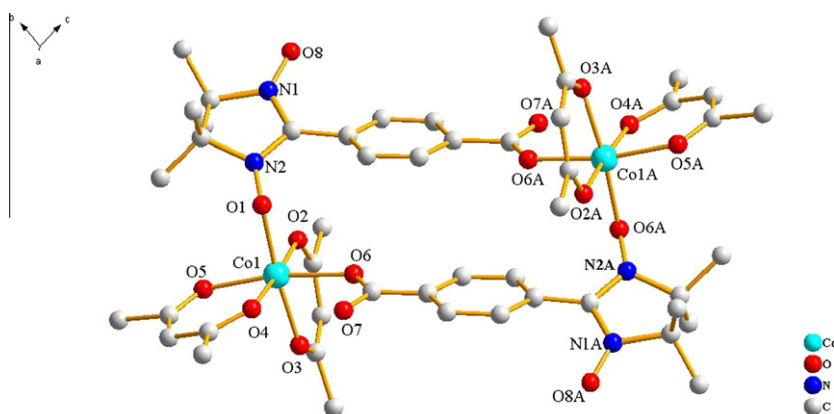


Fig. 3. The cyclic dimer structure of complex 2. Hydrogen and fluorine atoms are omitted for clarity.

tively. The dihedral angle between phenyl and the plane containing of O–N–C–N–O group is 37.04° . The distance of two metal ions is 9.305 \AA in the dimer unit, in which the two phenyl planes are parallel with an interplanar distance of 2.947 \AA . The shortest distance between Co ions in different dimer units is 8.584 \AA , while the shortest contact between uncoordinated nitroxide groups is 4.004 \AA (See Fig. 4).

3.2. Magnetic properties

The temperature dependence of magnetic susceptibility of complex 1 is plotted in Fig. 5. At room temperature the value of $\chi_M T$ is $6.63 \text{ emu K mol}^{-1}$, which is much lower than spin-only value ($9.50 \text{ emu K mol}^{-1}$) anticipated for the magnetically isolated two $S = 1/2$ and two $S = 5/2$ spins, but close to spin-only value

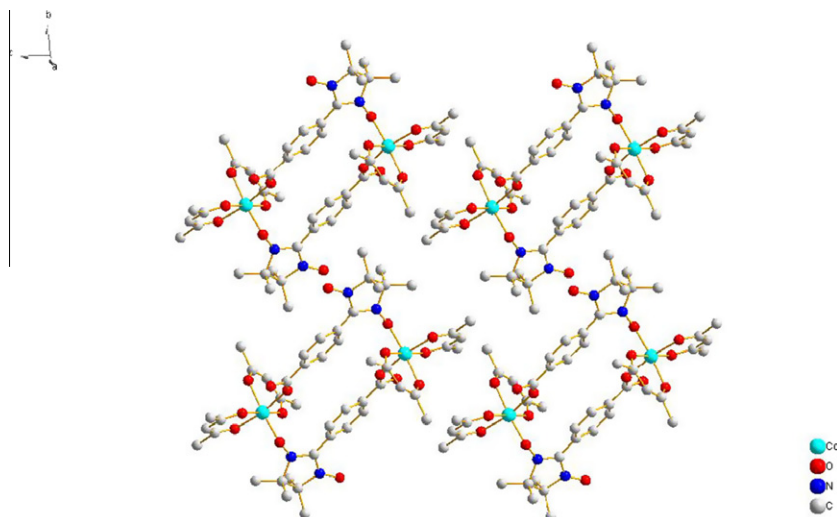


Fig. 4. The packing arrangement of complex 2.

(6.00 cm³ K mol^{−1}) expected for two isolated $S = 2$ spins. As shown in Fig. 5, the reciprocal susceptibility varied as the temperature follows the Curie–Weiss law, with a negative Weiss constant $\theta = -2.64$ K and Curie constant $C = 6.48$ cm³ K mol^{−1}. Upon cooling, the value of $\chi_M T$ gradually decreases to reach a value of 6.09 cm³ K mol^{−1} at 50 K, and then decreases rapidly to 4.44 cm³ K mol^{−1} at 2.0 K. These results show there exists strong antiferromagnetic coupling between the Mn(II) ion and the directly coordinated nitroxide group.

Based on the analysis of crystal structure, there are mainly two kinds of magnetic interactions for the present four-spin magnetic system, i.e. the magnetic interaction between Mn(II) ion and the directly coordinated nitroxide group (J_1), and the magnetic coupling between Mn(II) ion and nitroxide group through phenyl ring and carboxyl group (J_2). The magnetic interaction transmitted by phenyl ring and carboxyl group should be weak, so the magnetic behavior of complex 1 can be treated as two Mn–Rad magnetic units, and the magnetic data were analyzed by a theoretical expression (1) deduced from the spin Hamiltonian

$$\hat{H} = -J_1 \hat{S}_{\text{Rad}} \hat{S}_{\text{Mn}}.$$

$$\chi_M = \frac{Ng^2 \beta^2}{kT} \frac{10 \exp(-3J_1/kT) + 28}{5 \exp(-3J_1/kT) + 7} \quad (1)$$

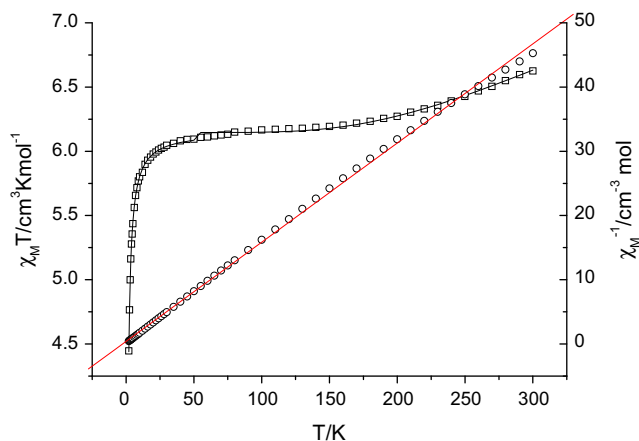


Fig. 5. $\chi_M T$ and $1/\chi_M$ vs. T plots for complex 1 and the solid line represents the best fit.

The magnetic data (300–50 K) were analyzed and a good fit of the experimental data was obtained with $g = 2.03$, $J_1 = -196.25$ cm^{−1} with $R = 1.55 \times 10^{-5}$. The strong antiferromagnetic interaction is probably due to the smaller angle of Mn–O–N (126.60(16)°), which results in the effective overlap of the magnetic orbitals. The determined J value is comparable to the reported analogous literature values [24,32,33].

Consider that the strong antiferromagnetic interaction between the directly coordinated nitroxide group and the Mn(II) ion results in one net spin with $S = 2$ below 50 K, so the magnetic data (2–50 K) were fitted to Eq. (2) for pairing of $S = 2$ and the best fitness to the magnetic data (2–50 K) produces $g = 2.03$, $J_2 = -0.20$ cm^{−1} and $R = 1.10 \times 10^{-5}$, indicating that the magnetic coupling between two Mn(II)–nitroxide units is very weak. The observed weak magnetic coupling is due to the small spin density on the oxygen atom of the carboxyl group (Chart 1).

$$\chi_M = \frac{Ng^2 \beta^2}{kT} \frac{60 + 28 \exp(-4J_2/kT) + 10 \exp(-7J_2/kT) + 2 \exp(-9J_2/kT)}{9 + 7 \exp(-4J_2/kT) + 5 \exp(-7J_2/kT) + 3 \exp(-9J_2/kT) + \exp(-10J_2/kT)} \quad (2)$$

Recently, two isostructural complexes Mn(NITPBA)₂(H₂O)₂ [29] and Co(NITPBA)₂(H₂O)₂ [34] have been obtained by the reaction of the NITPBAH radical with Mn^{II} or Co^{II} ion without hfac coligand. It is interesting to compare complex 1 with complex Mn(NITPBA)₂(H₂O)₂: complex 1 is cyclic dimer, while Mn(NIT-

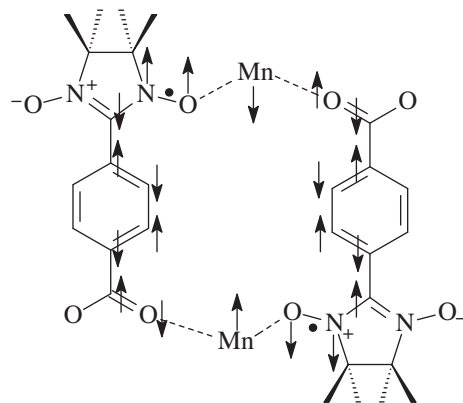


Chart 1. Spin polarization mechanism for intramolecular magnetic coupling in cyclic dimer derived from complex 1.

PBA)₂(H₂O)₂ shows one-dimensional ladder structure. But their magnetic behaviors are similar: the strong antiferromagnetic coupling was observed between the directly coordinated NO group and Mn(II) ion (-196 cm^{-1} for complex **1** and -193 cm^{-1} for Mn(NITPBA)₂(H₂O)₂) for both complexes and the magnetic interaction mediated by NITPBA or NITBAH ligand through the phenyl ring and carboxyl group is weak. These can be attributed to the same coordination mode of NITPBA and NITPBAH radical ligands in both complexes in which the NO groups of two radical ligands are directly coordinated to metal ions, resulting in strong antiferromagnetic interaction.

The magnetic susceptibility of complex **2** in form of $\chi_M T$ and $1/\chi_M$ versus T plots are given in Fig. 6. Above 40 K, The reciprocal susceptibility varied as the temperature obeys the Curie–Weiss law with negative Weiss constant $\theta = -32.1\text{ K}$ and Curie constant $C = 5.78\text{ cm}^3\text{ K mol}^{-1}$, indicating the global antiferromagnetic interaction in complex **2**. Using Eq. (3) with $g_{\text{rad}} = 2.0$, this leads to $g_{\text{Co}} = 2.32$, which is a reasonable value for octahedral high-spin cobalt(II) complexes [35].

$$C = \frac{N\beta^2}{3k} [2g_{\text{rad}}^2 S_{\text{rad}}(S_{\text{rad}} + 1) + 2g_{\text{Co}}^2 S_{\text{Co}}(S_{\text{Co}} + 1)] \quad (3)$$

At room temperature, the value of $\chi_M T$ is $5.30\text{ cm}^3\text{ K mol}^{-1}$. Upon cooling, $\chi_M T$ value decreases smoothly, reaching a value of $1.75\text{ cm}^3\text{ K mol}^{-1}$ at 2.0 K. For octahedral high-spin Co(II) ion, a typical value of $\chi_M T$ is about $3.2\text{ cm}^3\text{ K mol}^{-1}$ [35], so the value of $\chi_M T$ for the dimer containing two Co(II) ions and two radical ligands should be about $7\text{ cm}^3\text{ K mol}^{-1}$, much higher than that observed. This indicates that there is a strong antiferromagnetic coupling between the Co(II) ion and the directly bonding nitroxide group. Although the strict quantitative analysis of magnetic data for complex **2** is difficult and the magnetic coupling constant between Co(II) ion and the radical ligand can not precisely be evaluated, it is obvious that the strong antiferromagnetic interaction exists between Co(II) ion and the directly coordinated oxygen atom of nitronyl nitroxide from the previous analyses.

4. Conclusion

We have successfully obtained two new cyclic complexes by using the carboxyl substituted nitronyl nitroxide radical ligand with $M(\text{hfac})_2$ ($M = \text{Mn(II)}, \text{Co(II)}$). The nitronyl nitroxide radical acts as bridge ligand linking two metal ions through the oxygen atoms of the N–O and carboxyl groups. In complexes **1** and **2**, the magnetic coupling between the metal ion and the directly coordinated nitroxide group is strong antiferromagnetic. There is a weak antiferromagnetic interaction between metal ion and nitroxide

unit through the phenyl ring and carboxyl group. A spin polarization mechanism can be used to explain the magnetic coupling in the complex.

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Appendix A. Supplementary material

CCDC 870396 and 870397 contains the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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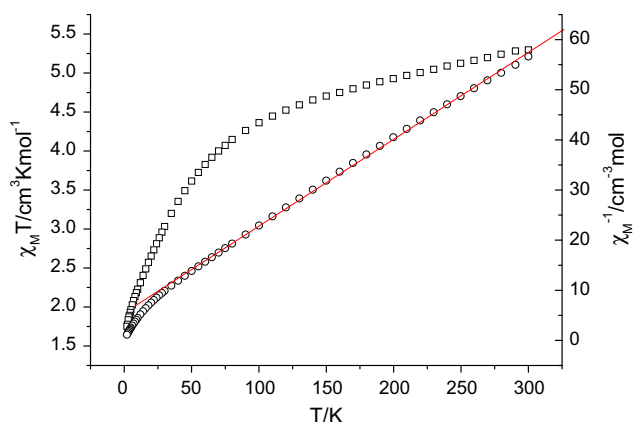


Fig. 6. $\chi_M T$ and $1/\chi_M$ vs. T plots for complex **2**.

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