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Syntheses, structures and magnetic properties of four-spin Mn-Imino nitroxide radical complexes

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ABSTRACT

Based on the nitroxide radicals, four-spin complexes $[Mn(hfac)_2(IMpPhCl)]_2 \cdot NITpPhCl$ (**1**) and $[Mn(hfac)_2(IMmPhCl)]_2 \cdot NITmPhCl$ (**2**) (IMpPhCl = 2-(4'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, IMmPhCl = 2-(3'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, hfac = hexafluoroacetylacetonate) have been synthesized and characterized by single-crystal X-ray diffraction. The X-ray crystal structure analyses show that the structures of the two compounds are similar and the imino nitroxide radical ligand acts as a bridge ligand linking two Mn(II) ions through the oxygen atom of the N–O group to form a four-spin system. Two kinds of nitroxide radicals: nitronyl nitroxide and imino nitroxide radicals coexist in the cyclic Mn(II) complexes. The magnetic studies show that there exists an antiferromagnetic interaction between Mn(II) ions and the imino nitroxide radical ligands, which is explained by spin polarization mechanism. The antiferromagnetic interaction of Mn–Rad in complex **2** ($J_1 = -9.36\ cm^{-1}$) is stronger than that in complex **1** ($J_1 = -9.19\ cm^{-1}$), which is consistent with crystal structure of complexes (The bond length of the shortest Mn-O in complex **2** (2.1625 Å) is smaller than complex **1** (2.1898 Å)).

1. Introduction

In the building of novel magnetic metal–organic framework architectures, the combination of metal ions and nitronyl nitroxides (metal radical approach) has proved to be particularly efficient for making molecular magnetic materials in the last few years [1,2].

Recently, several compounds, comprising transition metal ions [3–8] and organic radical derivatives [9,10], have been designed for understanding the mechanism of the magnetic exchange interaction occurring in complexes, especially in cyclic metal-radical complexes [11–13]. Therefore, one of the main research works is the synthesis of cyclic complexes between transition metal and organic ligand to design magnetic molecular materials. Along this line, some paramagnetic metal ions have been employed to synthesize cyclic compounds, such as Mn(II), Cu(II) [14–16]. Nitroxides radicals are the most common open-shell bridging species but very poor electron-donating groups. However, hexafluoroacetylacetonate ligands act as electron-withdrawing groups, which can enhance the radical coordination ability when bound to the metal center [17,18]. Therefore, one intriguing strategy in this respect is to combine metal hfac salts and nitroxide radicals.

In terms of cyclic metal-radical complexes, the oxygen atoms of nitronyl nitroxide groups acting as bridging ligands can also form cyclic dimer complexes with metal ions and some cyclic complexes show particularly interesting temperature-dependent spin-transition-like behavior [19,20]. In recent years, single-molecule toroics (SMTs) are defined [21–24]. By analogy with single-molecule magnets, SMTs seem to be most promising for future applications in quantum computing and information storage and to be used as multiferroic materials with magnetoelectric effect [21,25]. Toroidal moments can be influenced by the molecular symmetry, the coordination environment and/or the bridging ligands which act as superexchange pathways, which should be considered when designing new SMTs in the future [21].

To the best of our knowledge, there is no report on nitronyl nitroxide and imino nitroxide radicals appeared in one molecule. Along this line and in order to investigate magneto-structure

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correlation between the transition metal and the radical, by using two different nitroxide radicals and Mn(II) ion, two four-spin Mn(II) complexes, $[Mn(hfac)_2(IMpPhCl)]_2 \cdot NITpPhCl$ (**1**) and $[Mn(hfac)_2(IMmPhCl)]_2 \cdot NITmPhCl$ (**2**) (IMpPhCl = 2-(4'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, IMmPhCl = 2-(3'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, hfac = hexafluoroacetylacetonate), were synthesized and structures and magnetic properties were described in this paper.

2. Experimental section

2.1. Material and physical measurements

All chemicals and solvents used for the syntheses were of reagent grade and were used without further purification. All reactions were conducted in aerobic conditions. 2-(4'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl IMpPhCl and 2-(3'-chlorophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl IMmPhCl radical ligands were prepared from 4-chlorobenzaldehyde and 3-chlorobenzaldehyde by the method similar to a literature [26–28]. 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 4000–400 cm^{-1}, using KBr pellets. The complexes of the thermogravimetry-differential thermal analysis (TG-DTA) were studied by SDT-Q600 at a heating rate of 20 $°C \cdot min^{-1}$ in a nitrogen atmosphere. The X-ray powder diffraction patterns (PXRD) of complexes **1** and **2** were recorded on a Shimadzu LabX XRD-6100 diffractometer, operated at 40.0 kV and 30.0 mA, using a Cu target tube and graphite monochromator. The intensity data were recorded by continuous scan in $2\theta/\theta$ mode from 5° to 50° with a step size of 0.02° and a scan speed of 5° min^{-1}. Temperature-dependent *DC* magnetic susceptibility was measured on a Quantum Design SQUID magnetometer working in the range 2.0–300 K at a magnetic field of 1000 G.

2.2. Synthesis

2.2.1. Synthesis of the complex $[Mn(hfac)_2(IMpPhCl)]_2 \cdot NITpPhCl$ (1)

A solution of $Mn(hfac)_2 \cdot 2H_2O$(0.10 mmol) in 15 mL dry n-heptane was refluxed for 2 h to azeotropically remove hydration water molecules. Then the solution was cooled to 70 °C, and a solution of IMpPhCl (0.10 mmol) in 5 mL CH_2Cl_2 was added. The mixture was stirred for 30 min, and 0.05 mmol of NITpPhCl was added to this solution. The resulting green solution was stirred for 30 min and cooled down to room temperature. The filtrate was stored in a refrigerator at 4 °C for 3 d to give dark green crystals, which were suitable for X-ray analysis. Anal. Calc. for $Mn_2C_{59}H_{64}N_6O_{12}Cl_3F_{24}$ (Mr: 1719.20): C, 41.17; N, 4.88; H, 3.75. Found: C, 41.32; N, 4.96; H, 3.82%. FTIR (KBr, cm^{-1}): 1649(m), 1533(s), 1350(w), 1258(s), 1147(s), 780(w), 664(w).

2.2.2. Synthesis of the complex $[Mn(hfac)_2(IMmPhCl)]_2 \cdot NITmPhCl$ (2)

Complex **2** was synthesized by using the same procedure as for complex **1** but with NITmPhCl instead of NITpPhCl, IMmPhCl instead of IMpPhCl. Anal. Calc. for $Mn_2C_{59}H_{64}N_6O_{12}Cl_3F_{24}$ (1719.20): C, 41.17; N, 4.88; H, 3.75. Found: C, 41.56; N, 4.75; H, 3.66%. FTIR (KBr, cm^{-1}): 1656(m), 1547(s), 1348(w), 1240(s), 1155(s), 750(w), 654(w).

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_α radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the φ-ω scan technique in the range $2.27° \leq h \leq 25.02°$. The structure was solved by direct methods by using the program *SHELXS-97* [29] and refined by full matrix leastsquares methods on F^2 with the use of the *SHELXL-97* [30] program package. 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 S1.

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

Complex	$[Mn(hfac)_2(IMpPhCl)]_2 \cdot NITpPhCl$	$[Mn(hfac)_2(IMmPhCl)]_2 \cdot NITmPhCl$
Empirical formula	$Mn_2C_{59}H_{54}N_6O_{12}Cl_3F_{24}$	$Mn_2C_{62.50}H_{62}N_6O_{12}Cl_{13}F_{24}$
Formula weight	1711.31	1761.41
Temperature(K)	113	113
Wavelength(Å)	1.54187	0.71073
Crystal system	Monoclinic	Triclinic
Space group	C2/c	$P\bar{1}$
Unit cell dimensions		
a (Å)	24.255(7)	12.743(4)
b (Å)	12.371(3)	14.789(4)
c (Å)	23.630(6)	20.789(6)
α (°)	90.00	91.364(6)
β (°)	92.066(8)	97.388(5)
γ (°)	90.00	97.978(5)
Volume ($Å^3$)	7086(3)	3844.2(18)
Z	4	2
Calculated density(Mg/m^3)	1.604	1.522
Absorption coefficient(mm^{-1})	5.075	0.550
F(0 0 0)	3765	1784
Crystal size(mm^3)	0.16 × 0.14 × 0.12	0.20 × 0.18 × 0.10
θ range for data collection(°)	3.65–72.52	1.63–25.02
Reflections collected/unique	6894/5067	32321/13527
$R_{(int)}$	0.0848	0.0368
Data/restraints/parameters	6894/9/531	13527/241/1067
Goodness-of-fit on F^2	1.142	1.049
R_1 [$I > 2\delta(I)$]	0.1037	0.0698
wR_2 [$I > 2\delta(I)$]	0.2913	0.1948
R_1 (all data)	0.1209	0.0837
wR2 (all data)	0.3209	0.2066