A four-spin ring with alternating magnetic interactions formed by pyridine-substituted nitronyl nitroxide radicals and Gd(III) ions: Crystal structure and magnetic properties

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ABSTRACT

A novel complex, [Gd(hfac)$_3$(NIT-5-Br-3py)]$_2$ (hfac = hexafluoroacetylacetonat, NIT-5-Br-3py = 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-5-bromo-3-pyridine) has been synthesized and characterized structurally and magnetically, in which a NIT-5-Br-3py molecular acts as a bridge ligand linking two Gd(III) ions through the oxygen atom of the N–O group and nitrogen atom from the pyridine ring to form a four-spin system. The fitting result of the magnetic susceptibility shows two different magnetic interactions between Gd(III) ion and NIT-5-Br-3py in one complex: a weak ferromagnetic interaction (J_1 = +2.60 cm^{-1}) through the N–O group, and a much weaker antiferromagnetic (J_2 = −0.24 cm^{-1}) interaction through pyridine ring.

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In recent years, the approach based on paramagnetic metal coordination of organic radicals has attracted much interest for the design of molecular magnetic materials [1–9]. Compared with transition metal complexes, there are less numerous investigations on rare earth metal complexes because their large orbital contribution makes their magnetic behavior difficult to be treated. However, gadolinium(III) with f^7 electron configuration and quenched orbital angular momentum makes it easier to be studied, and many researches are focused on Gd(III) complexes with the paramagnetic centers like nitroxide free radicals, copper(II) or vanadyl(II). The earlier studies showed that the magnetic coupling between Gd(III) and radicals were usually ferromagnetic [10–14] (Table 1), which could be generally explained by the spin polarization mechanism [16]. The antiferromagnetic interaction has also been found recently in the Gd(III)-radical complexes [9,14,15] (Table 1) as well. However, the coexistence of two kinds of interactions in same complex has never been reported to the best of our knowledge. Recently we get a Gd(III)-radical complex with both ferromagnetic and antiferromagnetic interactions in one complex because of the different bridging mode of radical and Gd(III). In this paper we report the crystal structure and the magnetic property of [Gd(hfac)$_3$-(NIT-5-Br-3py)]$_2$ complex.

Single crystals suitable for X-ray analysis for the complex were obtained by the method described as follows: A solution of Gd(hfac)$_3$ · 2H2O [17] (82 mg, 0.1 mmol) in 15 mL of dry *n*-heptane was heated under reflux for 1 h. After that, the solution was cooled to about 65 °C, and a solution of NIT-5-Br-3py [18] (31 mg, 0.1 mmol) in 5 mL of CH$_2$Cl$_2$ was added. The resulting mixture was stirred for 30 min and then cooled to room temperature. After filtration, the resulting solution was left at 4 °C for several days to give light violet elongated crystals suitable for X-ray analysis [19] (the selected bond lengths and angles have been placed in supporting information). Elemental analysis calculated for C$_{54}$H$_{36}$Br$_2$F$_{36}$Gd$_2$N$_6$O$_{16}$: C, 29.71; H, 1.66; N, 3.85. Found: C, 29.65; H, 1.58; N, 3.89%. IR(cm^{-1}): 1370(v(NO)), 1650(v(C=O)).

The molecular structure with partial atom label is shown in Fig. 1. The cluster is a centrosymmetric cyclic dimer comprising two asymmetric units of Gd(hfac)$_3$(NIT-5-Br-3py) (Fig. 2). To gadolinium(III) ion (Gd1), there are eight coordination sites which are occupied by six oxygen atoms (O3, O4, O5, O6, O7,O8) from the hfac ligand,one oxygen atoms (O1) from the nitronyl nitroxide unit, and one nitrogen atom (N1A) from the pyridine ring, respectively. The oxygen atoms (O1) and the nitrogen atom (N1A) are coordinated to Gd(III) in a *cis*-configuration with the O1–Gd1–N1A angle of 74.2°. The bond lengths of Gd1–N1A and Gd1–O1 are 2.626 and 2.337 Å. The lengths of the six Gd1–O3–8 bonds from hfac are in the range of 2.322–2.415 Å. The nitronyl nitroxide moiety acts as a bridge ligand linking two gadolinium ions by the oxygen atom of the N–O group and the nitrogen atom of the pyridine ring. The dihedral angle between the pyridine plane and the nitronyl nitroxide N–C–N plane in the ligand moiety is about 49.6°.

The temperature dependence of the magnetic susceptibility for the complex is displayed in Fig. 3. The observed room-temperature

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Table 1
Compounds reported in the literature

Compounds	Types of structure	J_{Gd-rad} (cm^{-1})	Ref.
1. [Gd(hfac)$_3$(NITiPr)(H$_2$O)]	Polymeric chain	+0.30	[11]
2. [Gd(hfac)$_3$(NITPh)$_2$]	Polymeric chain	+1.0	[12]
3. [Gd(hfac)$_3$(NITEt)$_2$]	Polymeric chain	+0.25	[10]
4. [Gd(hfac)$_3$(NIToPy)]	Molecular	+1.51	[13]
5. [Gd(hfac)$_3$(NITpPy)]	Dimer	J_1 = +0.89 J_2 = +0.085	[13]
6. [Gd(NITtrz)$_2$(NO$_3$)$_3$]	Molecular	+6.1	[14]
7. [Gd(hfac)$_3$(NITBzImH)]	Molecular	+1.7	[14]
8. [Gd(NITMeBzImH)$_4$] · (ClO$_4$)$_3$ · 2THF · 1H$_2$O	Molecular	−3.8	[14]
9. [Gd(NITBzImH)$_4$] · (ClO$_4$)$_3$ · 2THF · 2H$_2$O	Molecular	−1.8	[14]
10. [Gd(NITBzImH)$_2$(NO$_3$)$_3$]	Molecular	J_1 = −4.05 J_2 = −0.80	[14]
11. [Gd(hfac)$_3$(IMBzImH)]	Molecular	−2.6	[14]
12. [Gd(IMPy)(hfac)$_3$]	Molecular	−1.9	[14]
13. [Gd(hfac)$_3$(IMoPy)]	Molecular	−2.59	[15]
14. [Gd(hfac)$_3$(NIT-5-Br-3py)]$_2$	Dimer	J_1 = +2.60 J_2 = −0.24	This work
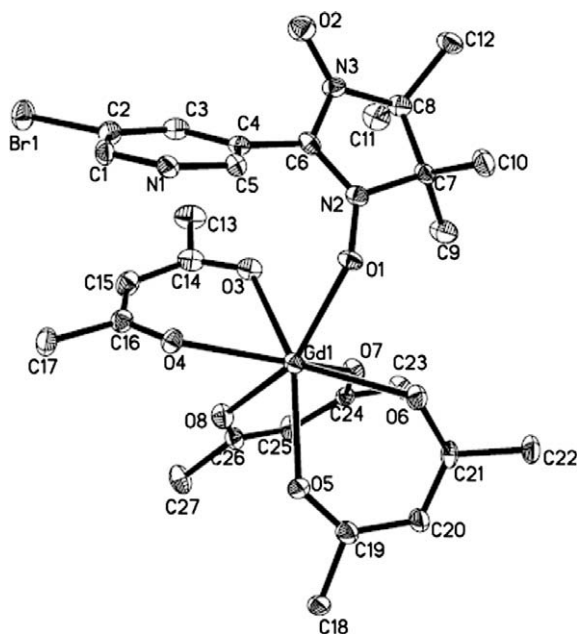
Fig. 1. ORTEP draw of Gd(hfac)$_3$(NIT-5-Br-3py) with 30% thermal ellipsoids. Fluorine atoms and hydrogen atoms are omitted for the sake of clarity.
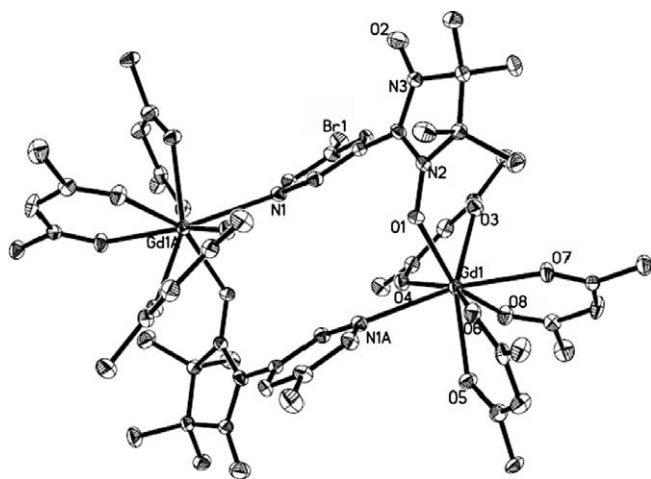
Fig. 2. ORTEP draw of [Gd(hfac)$_3$(NIT-5-Br-3py)]$_2$ with 30% thermal ellipsoids. Fluorine atoms and hydrogen atoms are omitted for the sake of clarity.
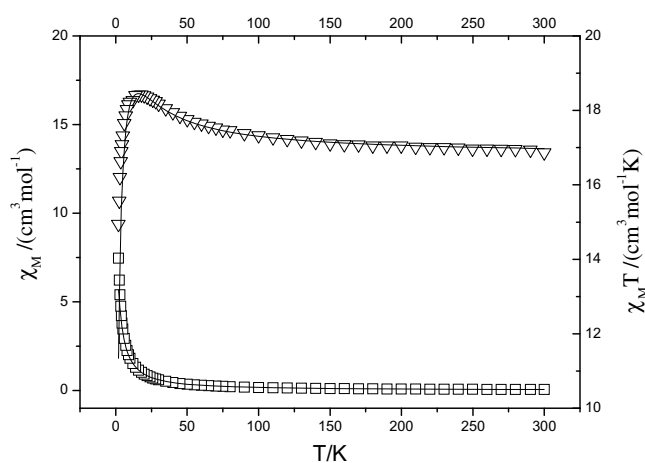
Fig. 3. χ_M (□) vs. T and $\chi_M T$(▽) vs. T plots for the complex. The solid lines represent the theoretical values.

$\chi_M T$ value is 16.86 cm^3 mol^{-1} K, slightly higher than the value (16.5 cm^3 mol^{-1} K) expected for an uncoupled system for two Gd(III) ions (S = 7/2) and two organic radicals (S = 1/2). On decreasing the temperature, the $\chi_M T$ values increase steadily and reach a maximum of 18.42 cm^3 mol^{-1} K at 18 K, then decrease sharply to 14.95 cm^3 mol^{-1} K at 2.0 K.

For the four-spin system as shown in Scheme 1, there are two kinds of magnetic interactions in the complex: (1) the interaction between Gd(III) ion and the nitronyl nitroxide radical through N–O group (J_1) and (2) the coupling of the Gd(III) ion with the nitronyl
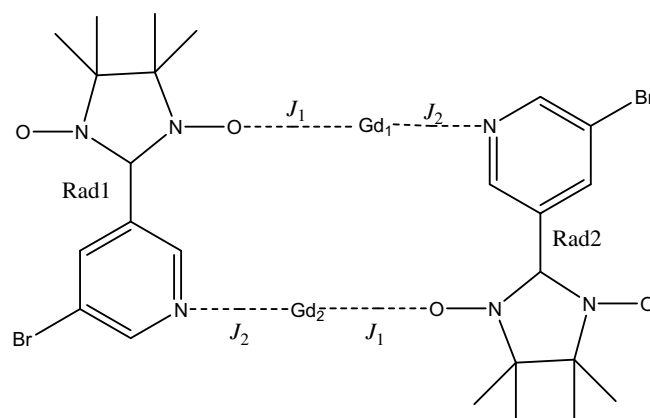
Scheme 1. [Gd(hfac)$_3$(NIT-5-Br-3py)]$_2$.

nitroxide radical through the pyridine ring (J_2). The magnetic pathways $[\hat{H} = -2J_1(\hat{S}_{Gd1}\hat{S}_{Rad1} + \hat{S}_{Gd2}\hat{S}_{Rad2}) - 2J_2 \ (\hat{S}_{Gd1}\hat{S}_{Rad2} + \hat{S}_{Gd2}\hat{S}_{Rad1})]$ of the topology of this kind preclude a simple calculation of the spin levels by Kambe's methods [21], hence the MAGPACK program has been used [22]. Numerical simulations for the complex give $g = 2.018$ cm^{-1}, $J_1 = +2.60$ cm^{-1}, $J_2 = -0.24$ cm^{-1}. There is no way to experimentally assign J_1 and J_2 to the two different exchange pathways through the N–O and pyridine nitrogen. However, comparison with the J values observed in other NITR complexes (Table 1) suggests that J_1 can be associated with the interaction through the N–O group [13]. It is worth noting that the signs of the two coupling constants (J_1,J_2) are opposite, which is different from the analogous complexes (Table 1) having only either antiferromagnetic or ferromagnetic interaction between Gd(III) and free radical. In Table 1, the magnetic behavior of compounds 1–7 shows the ferromagnetic interactions between Gd(III) and radical ($J_{Gd-rad} > 0$), and especially for the compound 5 there were two J positive values. In contrast, in the case of the complexes 8–13 the Gd(III)-radical interaction is found antiferromagnetic and the complex 10 possessed two J negative values. To our knowledge, the complex reported here is first example that showed two different kinds of magnetic interactions (ferromagnetic and antiferromagnetic) between Gd(III) and free radical because of the different bridging mode (N–O group and pyridine ring). Further investigation is going on for understanding the mechanism.

The weak ferromagnetic coupling can be explained by the following mechanism: the unpaired electron of radical transfers into the empty 5d orbit of the Gd(III) ion, and the alignment of the 4f and 5d electrons is parallel on the basis of Hund's rule [16]. While the much weaker antiferromagnetic coupling between Gd(III) ion and radical is presumably due to the dominance of the direct overlap of 4f orbital of Gd(III) ion with the SOMOπ^* orbit of NIT-5-Br-3py [23].

Supplementary material

CCDC 634994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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