

A chelate nitronyl nitroxide ligand based mononuclear gadolinium composite

Peng Hu, Fengping Xiao, Jangfei Cao and Yanhua Zhao*

Environment and Chemical Engineering College, Zhaoqing University, Zhaoqing, China.

*Corresponding author e-mail: 254152734@qq.com

Abstract. A new mononuclear gadolinium complex: $[\text{Gd}(\text{tfac})_3(\text{NIT-2thz})]$ (tfac = trifluoroacetylacetonate; NIT-2thz = 2-(2'-thiazolyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was synthesized, structurally and magnetically characterized. Single-crystal X-ray structural analysis reveals that this complex crystallized in the $C2/c$ space groups. Each central Gd ion is eight-coordinated by three bischelate tfac ligands and one radical ligand. Through magnetic study, ferromagnetic Gd (III)–radical coupling of this complex were observed.

1. Introduction

These years, one of the research hotspots is to design and synthesis of lanthanide (Ln) based single-molecule magnets (SMMs) due to their huge magnetic anisotropy arising from the large, unquenched orbital angular momentum [1]. Till now, a lot of Ln (III) ions based SMMs have been reported [2]. However, the intrinsic drawbacks of Ln (III) ions always reduce the effective relaxation energy barrier, leading to the loss of remnant magnetization [3]. Magnetic exchange coupling which generally exist in molecular paramagnetic species has been found to be an effective method to increase the effective relaxation energy barrier. Under this view, stable radical ligands like nitronyl nitroxide, thioaminy, thiazyl and verdazyl are ideal candidates to construct SMMs since this type of ligands can generate strong intramolecular magnetic exchange coupling [4]. Among them, nitronyl nitroxide (NIT) radicals are widely used due to their relative stability and easily to obtain derivatives [5]. However, NIT radicals are not good donating ligands, therefore, the utilization of strong electron withdrawing coligands such as hexafluoroacetylacetonate (hfac) and trifluoroacetylacetonate (tfac) are necessary to strengthen their coordinate ability with metallic ions [6].

In our group's previous study, we have obtained number of NIT-Ln complexes by using chelate benzimidazole substituted nitroxide radicals (NIT-BzImH) as ligands and tfac as coligands [7]. To further study the effect of substitution of the radical ligands on magnetic properties, herein, we adopted thiazole substituted nitronyl nitroxide (NIT-2thz) as a chelate ligand to construct NIT-Ln complexes. In this paper, we report a novel radical–Gd complex $[\text{Gd}(\text{tfac})_3(\text{NIT-2thz})]$ (tfac= trifluoroacetylacetonate; NIT-2thz = 2-(2-thiazolyl)-4,4,5,5-tetramethylimidazoline-1-oxyl) and its structure magnetic properties were studied. .



2. Experimental

2.1. Materials and measurements

All the starting chemicals were bought from Sigma-Aldrich and used without further purification. The radical ligand of NIT-2thz was synthesized according to literature [8]. Elemental analyses (C, H, N) were carried out using a Perkin–Elmer 240 elemental analyzer. IR spectra were recorded in the range of 400–4000 cm^{-1} from KBr pellets with a Shimadzu Tracer-100 IR spectrometer. The direct-current (dc) magnetic susceptibilities and alternating-current (ac) magnetic susceptibility data were measured on MPMSXL–7 SQUID magnetometer. Diamagnetic corrections were made with Pascal’s constants for all the constituent atoms.

2.2. Synthesis of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$

0.08 mmol $\text{Gd}(\text{tfac})_3 \cdot 2\text{H}_2\text{O}$ were added in 25 mL n-heptane, then the mixture were heated to boil and stirred for about 100 minutes. A solution of NIT-2thz (0.06 mmol) in 10 mL of CHCl_3 was added. The resulting dark blue mixture was stirred for about 10 minutes then cooled the solution to room temperature for slow evaporation. After three days, blue plate crystals were obtained.

3. Results and discussion

3.1. Crystal structure of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$

The crystal structure of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$ is shown in Fig.1. This asymmetric unit is composed of two crystallographic independent $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$ moieties. Each Gd atom is eight-coordinated with three bidentate tfac coligands. The coordination sphere of the Gd(III) ions are completed by one O atom from the NO group and one N atom from the thiazole ring. The Gd1–O (radical), Gd 2–O(radical), Gd1–N(thz) and Gd2–N(thz) distances are 2.463(3), 2.482(4), 2.739(4) and 2.715(4) Å, respectively. The Gd–O (tfac) bond lengths are in the range of 2.410(3)–2.462(3) Å. The coordinated N–O and uncoordinated N–O bond lengths of the NIT radical ligands are 1.373(6)/1.382(6) and 1.374(5)/1.375(5) Å, respectively.

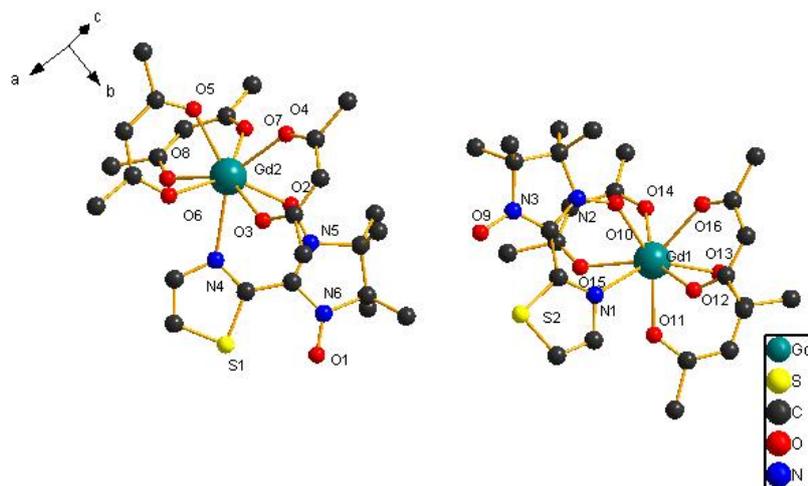


Figure 1. Crystal structure of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$. All hydrogen atoms are omitted for clarity

3.2. Magnetic properties of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$

The magnetic susceptibilities of $\text{Gd}(\text{tfac})_3\text{NIT-2thz}$ under variable-temperatures were measured from 300 to 2.0 K in an applied field of 1 kOe. As shown in Fig.2, the χ_{MT} value for this complex at 300 K is 8.15 $\text{cm}^3 \text{K} \cdot \text{mol}^{-1}$. This value is close to the theoretical one of 8.25 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for one uncoupled

Gd(III) ion ($^8S_{7/2}$, $S = 7/2$, $L = 0$) plus one radical ligand ($S = 1/2$). While cooling, the $\chi_M T$ value increases gradually to $9.66 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 5.5 K, and then decreases to $9.49 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. Based on previous work, the increase of $\chi_M T$ value from 300 K to 5.5 K indicates ferromagnetic interaction dominates in Gd complex while the decrease of $\chi_M T$ value from 5.5 K to 2 K is due to antiferromagnetic intermolecular interactions. Based on the characteristics of the molecular structure, the variable-temperature magnetic susceptibilities data were analyzed by Equation 1 and 2 which deduced from the spin Hamiltonian $H = -J S_{\text{rad}} S_{\text{Gd}}$ (considering one Gd(III)-radical interaction ($J_{\text{Gd-Rad}}$)). The possible interactions between mononuclear molecules are treated in the mean field approximation (zJ') at low temperature. A fit of the experimental data was obtained with $g = 1.89$, $J = 2.74 \text{ cm}^{-1}$, $J' = -0.012 \text{ cm}^{-1}$, $R = 1.24 \times 10^{-5}$ where R is defined as $R = \sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \sum(\chi_M)_{\text{obs}}^2$.

$$c_{\text{GdRad}} = \frac{4Ng^2\beta^2}{kT} \frac{7 + 15 \exp(4J_{\text{GdRad}} / kT)}{7 + 9 \exp(4J_{\text{GdRad}} / kT)} \quad (1)$$

$$c_M = c_{\text{RadGd}} / [1 - (zJ' c_{\text{radGd}} / Ng^2\beta^2)] \quad (2)$$

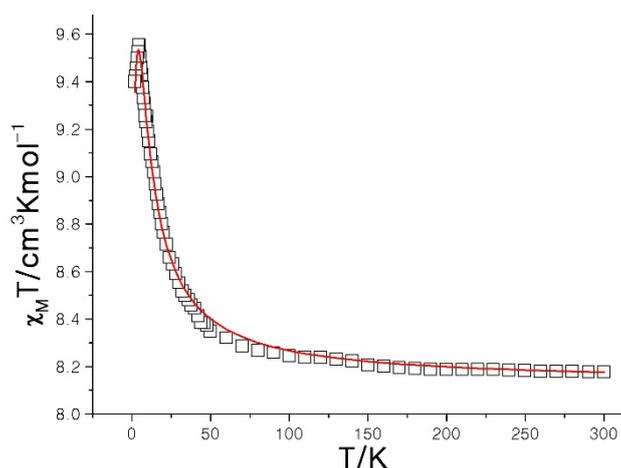


Fig. 2 Temperature dependence of $\chi_M T$ for Gd(tfac)₃NIT-2thz. The solid line represents the theoretical values based on the corresponding equations.

4. Conclusion

We have synthesized a mononuclear Gd-radical complex base on NIT-2thz radical ligand. Single crystal X-ray analyses reveal that each NIT-2thz ligand act as a chelate ligand to link one Gd(III) ion. Magnetic studies reveal that the magnetic interaction between NIT-2thz ligands and Gd ions are ferromagnetic.

Acknowledgments

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