

Two Lanthanide–nitronyl nitroxide radicals compounds with slow magnetic relaxation behavior



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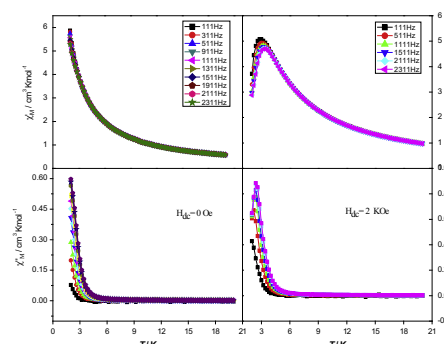
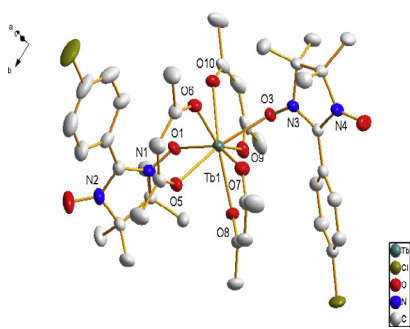
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HIGHLIGHTS

- Synthesize two mononuclear tri-spin complexes based on lanthanide ions and nitronyl nitroxide radicals.
- Complex **1** is dodecahedral (DD) geometry; while in complex **2**, the geometry is square antiprism (SAPR).
- Complexes **1** and **2** exhibit slow magnetic relaxation, suggesting single-molecule magnet behavior.

GRAPHICAL ABSTRACT

Two Lanthanide-radical compounds were synthesized. Complex **1** is dodecahedral geometry; while complex **2** is square antiprism geometry. Two complexes show intramolecular antiferromagnetic interactions and exhibit slow magnetic relaxation behavior.



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ABSTRACT

Two Lanthanide compounds with nitronyl nitroxide radicals [Dy(hfac)₃(NITPh-*p*-Cl)₂·0.5CH₃(CH₂)₅CH₃] (**1**) (hfac = hexafluoroacetylacetonate; NITPh-*p*-Cl = 4'-chlorophenyl-4,4,5,5-tetramethylimida-zoline-1-oxyl-3-oxide, CH₃(CH₂)₅CH₃ is heptane as solvent molecule) and [Tb(hfac)₃(NITPh-*p*-Cl)₂] (**2**) were synthesized and structurally characterized. The X-ray crystallographic analyses show that the structures of the two compounds are similar and all consist of isolated molecules, in which central Ln(III) ions are coordinated to six oxygen atoms from three hexafluoroacetylacetonate ligands and two oxygen atoms from nitronyl nitroxide radicals. Ac magnetic susceptibility studies show complexes **1** and **2** exhibit slow magnetic relaxation, suggesting single-molecule magnet behavior.

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Introduction

The study of single molecular magnets (SMMs) and single chain magnets (SCMs) is currently one of the special hot topics in the field of molecular magnetism and magnetic materials [1–3]. SMMs and SCMs exhibit slow magnetic relaxation, which arises from the combination of a large ground state spin *S* and a strong Ising-type

Table 1
Crystal data and structure refinements for **1** and **2**.

| Compound | 1 | 2 |
|---|---|--|
| Formula | C _{44.50} H ₄₃ Cl ₂ DyF ₁₈ N ₄ O ₁₀ | C ₄₁ H ₃₅ Cl ₂ TbF ₁₈ N ₄ O ₁₀ |
| F _w | 1369.23 | 1315.55 |
| T(K) | 113(2) | 113(2) |
| Crystal syst | Triclinic | Triclinic |
| Space group | <i>P</i> 1̄ | <i>P</i> 1̄ |
| <i>a</i> (Å) | 11.426(4) | 11.450(13) |
| <i>b</i> (Å) | 12.764(4) | 12.775(14) |
| <i>c</i> (Å) | 19.224(7) | 19.256(18) |
| α (deg) | 91.263(6) | 91.320(13) |
| β (deg) | 105.548(8) | 105.277(7) |
| γ (deg) | 95.243(7) | 95.251(11) |
| <i>V</i> (Å ³) | 2686(16) | 2702.5(5) |
| <i>Z</i> | 2 | 2 |
| ρ [g cm ⁻³] | 1.693 | 1.617 |
| μ [mm ⁻¹] | 1.610 | 8.406 |
| θ (deg) | 1.60–27.92 | 2.38–72.39 |
| Index ranges | –15 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 16 –25 ≤ <i>l</i> ≤ 25 | –14 ≤ <i>h</i> ≤ 13 –15 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 23 |
| Refins collected | 34511 | 30332 |
| independent data/ restraints | 12789 12789/465/903 | 10086 10086/0/694 |
| GOF on <i>F</i> ² | 1.010 | 1.055 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.0388, 0.0736 | 0.0511, 0.1325 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.0468, 0.0763 | 0.0537, 0.1357 |

anisotropy [4,5]. The strong magnetic anisotropy provides an energy barrier for the reversal of magnetization. Therefore, SMMs

and SCMs can be used as potential candidates in high-density magnetic memories, quantum computing devices and molecular spintronics [6].

Nitronyl nitroxides radicals have used as widespread ligands to synthesize molecular magnetic materials [7–9]. A large number of metal-radical complexes with various structures have been synthesized and magnetically characterized [10–12]. At the same time, lanthanide metal ions, especially heavy lanthanide ions, such as terbium(III) and dysprosium(III), have large magnetic anisotropies, which arise from the large, unquenched orbital angular momentum [13]. Therefore, lanthanide ions become good candidates for synthesizing SMMs and SCMs [14–16]. Especially since the first 4f–2p SMM [Dy(hfac)₃NITpPy] [17] and SCM [Co(hfac)₂(NITPhOMe)] [18] was discovered, the “metal-radical” strategy of combining organic radicals with lanthanide ions has been particularly successful employed to construct SCMs and SMMs [19]. However, nitronyl nitroxide radicals are poorly donating ligands, the use of strongly electron-withdrawing coligands at the metal, like hexafluoroacetylacetonate(hfac) [20,21], is often required, such as Dy(hfac)₃(NIT-3Brthien) [22], Ln(hfac)₃(NITNapOMe)₂ [23] and so on. To many lanthanide-nitronyl nitroxide radicals complexes, the slightly different ligand field can drastically affect the magnetic relaxation of the magnetization [24,25].

To develop the new magnetic coupling systems of 4f-radicals and better understand the nature of 4f–2p magnetic interaction, we use nitronyl nitroxide radicals and lanthanide ions to construct novel 4f–2p SMMs. Herein we report two new 4f–2p complexes: [Dy(hfac)₃(NITPh-*p*-Cl)₂·0.5CH₃(CH₂)₅CH₃] (**1**), (hfac = hexafluoroacetylacetonate; NITPh-*p*-Cl = 4'-chlorophenyl-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide) and [Tb(hfac)₃(NITPh-*p*-Cl)₂] (**2**).

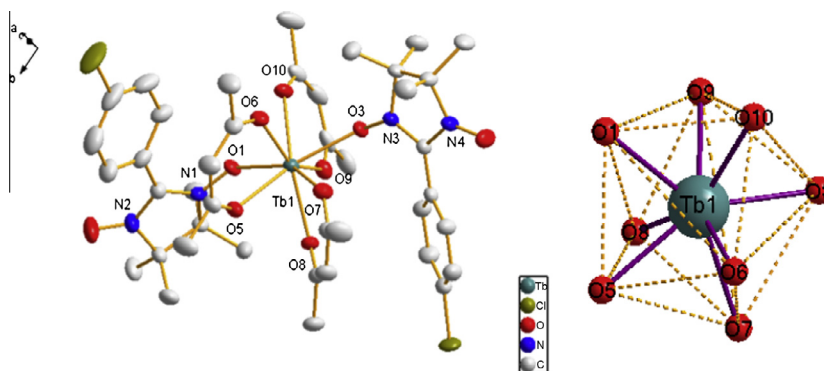


Fig. 1. (a) The molecular structure of **2**. Fluorine and hydrogen atoms are not shown for the sake of clarity. Thermal ellipsoids are scaled to enclose 50% probability. (b) The coordination geometry of Tb(III) ion in compound **2**.

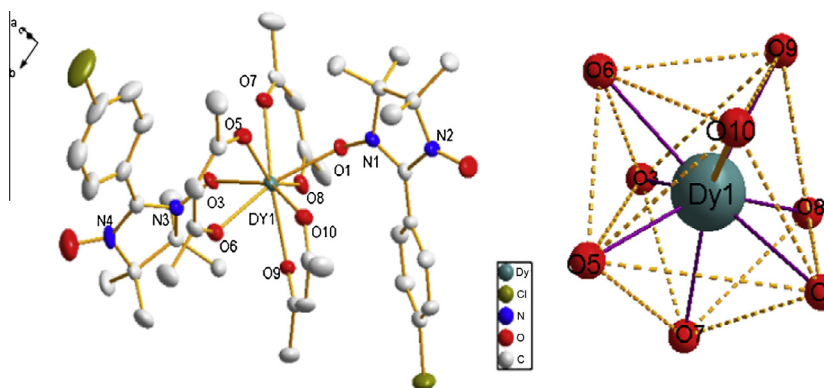


Fig. 2. (a) The molecular structure of **1**. Fluorine and hydrogen atoms are not shown for the sake of clarity. Thermal ellipsoids are scaled to enclose 50% probability. (b) The core in compound **1**.

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