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## Molecular Crystals and Liquid Crystals

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Toshiaki Tsukuda<sup>a</sup>, Takayoshi Suzuki<sup>a</sup> & Sumio Kaizaki<sup>a</sup>

<sup>a</sup> Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

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## Synthesis and Properties of Lanthanide(III) Complexes Containing Pyridine-Substituted Imino Nitroxide Radical

TOSHIAKI TSUKUDA, TAKAYOSHI SUZUKI  
and SUMIO KAIZAKI

*Department of Chemistry, Graduate School of Science, Osaka University,  
Toyonaka, Osaka, 560-0043, Japan*

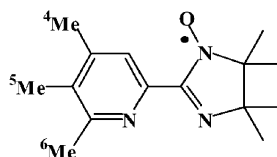
Some lanthanide(III) complexes containing three types of a chelated n-methylpyridine-substituted imino nitroxide radical  $\text{IM}_n\text{Me}_2\text{py}$  ( $n=4,5,6$ ) were synthesized with a small size of the multi-spin system. X-ray structural analysis of  $[\text{Gd}(\text{hfac})_3(\text{IM}_6\text{Me}_2\text{py})]$ ,  $[\text{Dy}(\text{hfac})_3(\text{IM}_4\text{Me}_2\text{py})]$  and  $[\text{Dy}(\text{hfac})_3(\text{IM}_5\text{Me}_2\text{py})]$  demonstrated that they are rigidly eight-coordinated with one  $\text{IM}_n\text{Me}_2\text{py}$  and three hfac ligands. Magnetic susceptibility measurements of the Gd(III) complexes indicate that the antiferromagnetic interaction between Gd(III) and imino nitroxide radical is different from the other lanthanide complexes containing nitronyl nitroxide radicals.

**Keywords:** lanthanide; imino nitroxide radical; crystal structures; magnetic interaction

## INTRODUCTION

In view of the molecular-based magnetic materials, there have been a number of investigations in the multi-spin systems of metal ions and organic radicals which are often utilized to construct assembled complexes. As the metal ions, paramagnetic lanthanide ions attract much attention owing to the rather large magnetic moments. A wide range of complexes from simple mononuclear complexes<sup>[1]</sup> to 1-D chains<sup>[2]</sup> have been described, in which Ln(III) ions are coupled with the organic radicals as other sources of unpaired spin(s). Most of Gd(III) complexes containing radical ligands show ferromagnetic interaction between Gd(III) and the unpaired spin(s) on the radicals<sup>[1]-[3]</sup>. But we have reported that our newly prepared Gd(III) complex containing an imino-type radical, IM2py (Scheme 1), shows antiferromagnetic interaction, in contrast to the nitronyl nitroxide radical complexes<sup>[3]</sup>. Magnetic properties of the complexes containing this type of ligand will show the different aspects of magnetic interactions, expectedly depending on the structural difference.

We prepare three new analogues of the Ln-IM2py complexes using methyl-substituted IM2py, IM*n*Me2py (Scheme 1), and compare the structures and magnetic properties of these analogues with those of IM2py complex.



SCHEME 1 IM*n*Me2py

## EXPERIMENTAL

### Preparations

The imino nitroxide radicals (IM $n$ Me2py)<sup>[5]</sup> and the starting complexes [Ln(hfac)<sub>3</sub>(H<sub>2</sub>O)]<sup>[6]</sup> were prepared according to the literatures. The corresponding [Ln(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (1.0 mmol) was suspended in 10 ml CH<sub>2</sub>Cl<sub>2</sub>. IM- $n$ Me2py (1.37 mmol) in 10 ml CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added to this suspension. After stirring, the red solution was obtained. The solution was poured into 20 ml of *n*-heptane, and allowed to evaporate slowly. Red orange crystals were obtained after overnight. The obtained complexes, [Gd(hfac)<sub>3</sub>(IM6Me2py)] (**Gd-1**), [Gd(hfac)<sub>3</sub>(IM-5Me2py)] (**Gd-2**), [Gd(hfac)<sub>3</sub>(IM4Me2py)] (**Gd-3**), [Dy(hfac)<sub>3</sub>(IM5Me2py)] (**Dy-2**) and [Dy(hfac)<sub>3</sub>(IM4Me2py)] (**Dy-3**), gave the satisfactory elemental analysis.

### Crystallography

X-ray diffraction was made on a Rigaku AFC5R diffractometer. Crystal data are as follows: **Gd-1**; C<sub>28</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>F<sub>18</sub>Gd, triclinic, space group P $\bar{1}$ , FW = 1010.71,  $a$  = 12.201(3) Å,  $b$  = 16.482(3) Å,  $c$  = 11.960(3) Å,  $\alpha$  = 93.67(2)°,  $\beta$  = 118.93(1)°,  $\gamma$  = 83.35(2)°,  $V$  = 2090.8(1) Å<sup>3</sup>,  $Z$ =2,  $R$ <sub>1</sub>=0.070,  $R$ <sub>w</sub> =0.197. **Dy-2**; C<sub>28</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>F<sub>18</sub>Dy, monoclinic, space group P2<sub>1</sub>/n, FW = 1015.96,  $a$  = 14.556(3) Å,  $b$  = 23.826(5) Å,  $c$  = 11.003(2) Å,  $\beta$  = 96.38(2)°,  $V$  = 3792(1) Å<sup>3</sup>,  $Z$ =4,  $R$ <sub>1</sub>= 0.052,  $R$ <sub>w</sub> =0.177. **Dy-3**; C<sub>28</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>F<sub>18</sub>Dy, monoclinic, space group P2<sub>1</sub>/n, FW = 1015.96,  $a$  = 11.588(2) Å,  $b$  = 23.301(4) Å,  $c$  = 14.508(2) Å,  $\beta$  = 93.97(1)°,  $V$  = 3907.8(9) Å<sup>3</sup>,  $Z$ =4,  $R$ <sub>1</sub> = 0.078,  $R$ <sub>w</sub> =0.293.

## RESULTS AND DISCUSSION

### The **Gd-1** complex

The molecular structure as well as the space group of the **Gd-1** complex

(Figure 1) is different considerably from those of the IM2py complex. Space group  $P\bar{1}$  ( $Z=2$ ) for (**Gd-1**) versus  $P2_1/n$  ( $Z=4$ ) for  $[\text{Gd}(\text{hfac})_3(\text{IM2py})]$ <sup>[4]</sup>. The distance of Gd–N(IM) in **Gd-1** is 2.623 (6) Å, which is longer by *ca.* 0.07 Å than that in the IM-2py complex. In addition, the coordination geometry

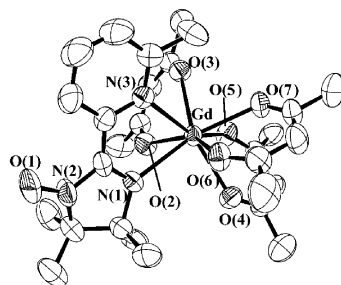


FIGURE 1 Molecular structure of  $[\text{Gd}(\text{hfac})_3(\text{IM-6Me2py})]$

of the **Gd-1** is found to be dodecahedron(DD) rather than bicapped trigonal prism(TPRS) to which the IM2py complex is close in terms of the semiquantitative method of polytopal analysis<sup>[7]</sup>.

#### The IM4Me2py and IM5Me2py complexes

Instead of the **Gd-2** and **Gd-3** of which suitable crystals for X-ray analysis were not obtained so far, the X-ray structures of **Dy-2** and **Dy-3** of which the structures are similar to the Gd(III) complexes have been determined. **Dy-2** and **Dy-3** are formed with similar structures to the Dy–IM2py complex<sup>[4]</sup> in the same crystal system. (Figure 2). The bond lengths of the Dy–N(IM) (2.518(5) Å for the **Dy-2** and 2.522(5) Å for **Dy-3**) are close to those of the Dy–IM2py complex (2.520(5) Å). The methyl proton of the 5- or 4-methyl in the pyridyl group is close to the fluorine atom of the  $\text{CF}_3$  in the neighboring molecule. Since the lengths of  $\text{H}\cdots\text{F}$  (2.94 Å for **Dy-2** and 3.02 Å for **Dy-3**) are longer than the sum of the van der Waals radii of hydrogen and fluorine (2.69 Å), there is no hydrogen bond between the molecules. However, nonexistence of the disordered  $\text{CF}_3$  moieties in contrast to  $[\text{Ln}(\text{hfac})_3(\text{IM2py})]$  with disordered  $\text{CF}_3$  suggests the presence of weak electrostatic interaction

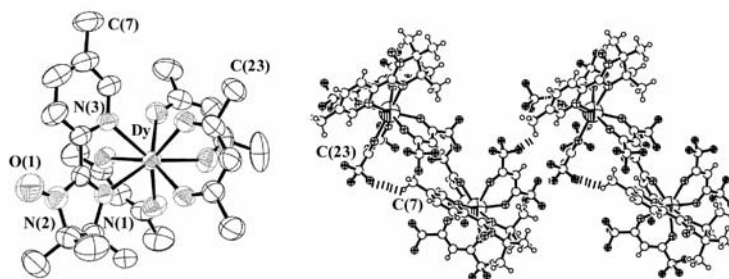


FIGURE 2 Molecular structure and packing of  $[\text{Dy}(\text{hfac})_3(\text{IM5Me2py})]$

between hydrogen and fluorine atom. It is likely that the variation of the substituted pyridine makes it possible to form hydrogen bonded 1-D chain.

In summary, there is significant structural change from the IM2py complex to **Gd-1** probably due to the steric repulsion between the methyl group in IM6Me2py and  $[\text{Ln}(\text{hfac})_3]$  moiety, whereas the IM2py, IM4Me2py, IM5Me2py complexes show a similar molecular structure.

### Magnetic Properties

There is found to be some influence to the magnetic properties from the substituted methyl group. The temperature dependences of the magnetic susceptibilities in **Gd-1**, **Gd-2** and **Gd-3** are shown in Figure 3. The analysis in terms of the Van Vleck equation based on the Heisenberg model ( $H = -2JS_1 \cdot S_2$ )<sup>[8]</sup> indicates that they give an antiferromagnetic interaction between Gd(III) and IM $n$ Me2py. The estimated exchange coupling constants in the IM $n$ Me2py complexes ( $J = -4.0 \text{ cm}^{-1}$  for **Gd-1**,  $J = -3.8 \text{ cm}^{-1}$  for **Gd-2** and **Gd-3**) are slightly larger than that of the IM2py complex ( $J = -3.0 \text{ cm}^{-1}$ ), showing a small substitution effect on the magnetic interaction. Apparently, the interaction between the

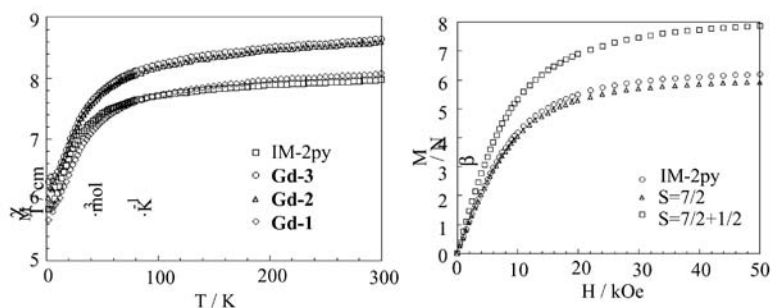


FIGURE 3 Temperature (left) and field (right) dependence of lanthanide complexes containing IM-radical.

Gd(III) and the imino nitroxide radical is always antiferromagnetic in contrast to the ferromagnetic interaction between the Gd(III) and the nitronyl nitroxide<sup>[3]</sup>. It is noted that the magnetic nature of the IM2py and IM $n$ Me2py complexes is opposite to that of the nitronyl nitroxide radical complexes. The elucidation for this reverse character has to wait further study which is in progress in our laboratory.

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