Synthesis and properties of the complexes of lanthanides with nitronyl nitroxide biradical

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Five novel complexes of formula $[Ln(hfac)_3] \cdot BNPhOM$, where Ln = Gd, Ho, Dy, Y, Er; hfac = hexfluoracetylacetonate; BNPhOM = 1,3-[bis-2,2'-(4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide)phenoxy] propane, have been prepared and characterized by elemental analysis, molar conductances, IR and electronic spectra. The temperature dependence of the magnetic susceptibility for Gd(III) and radical was measured (2—300 K). The observed data were successfully simulated giving the exchange integral $J = 0.28$ cm^{-1}, $J' = -0.33$ cm^{-1}. These results indicate a weak ferromagnetic spin exchange interaction between Gd(III) ion and the radical and a weak antiferromagnetic spin exchange interaction between the radical and radical.

Keywords Rare earth complexes, nitronyl nitroxide biradical, magnetism

Introduction

Metal-radical is an effective approach to synthesize magnetic molecular materials.[1] Beyond transition metal ions, rare earth ions are attracting interest in the synthesis of molecular based materials.[2] In this case the interest is associated with the possibility of understanding the nature of the magnetic interactions involving rare earth ions, which is much less well known than those involving transition metal ions. Further, it is hoped to exploit the large magnetic anisotropy associated with rare earth ions. It is possible to give rise to magnetically ordered materials with relatively high critical temperatures. In order to synthesize compounds with higher critical temperatures we are currently trying to vary both the radicals and the co-ligands. A logical evolution of this approach seems to be the use of nitronyl nitroxide biradicals as ligands towards metal ions. To our knowledge, little work has been devoted to investigating the magnetism of the complexes of lanthanides with nitronyl nitroxides biradical. In this paper, we describe the synthesis and properties of five novel complexes of formula $[Ln(hfac)_3] \cdot BNPhOM$, where Ln = Gd, Ho, Dy, Y, Er; hfac = hexfluoracetylacetonate; BNPhOM = 1,3-[bis-2,2'-(4,4,5,5- tetramethyl - 4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide)phenoxy] propane. We discuss here the magnetic properties of $[Gd(hfac)_3] \cdot BNPhOM$ complex.

Experimental

General

Hfac was purchased and used as received. Ln(hfac)$_3 \cdot 3H_2O$ were prepared as previously described.[3] All solvents and other reagents were of analytical grade and used with further purification. Analyses for C, H, and N were carried out with a Perkin-Elmer Model 240 elemental analyzer. Metal contents were determined by EDTA titration. The IR spectra were recorded on an IR-408 infrared spectrophotometer with KBr disks. Electronic spectra were measured on a Shimadzu UV-vis-

Scanning spectrophotometer. Molar conductances were performed using DDS-11A conductometer. The measurement of the variable temperature magnetic susceptibility was carried out at the Physics Department of Beijing University, using vibrating sample magnetometer CF-1 (sensitivity $m = 10^{-4}$ emu). Diamagnetic corrections were made with Pascal's constants for all the constituent atoms and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$.

Synthesis

Synthesis of BNIPhOM: the synthetic route of BNIPhOM is shown in scheme 1.

Scheme 1

1   2

3
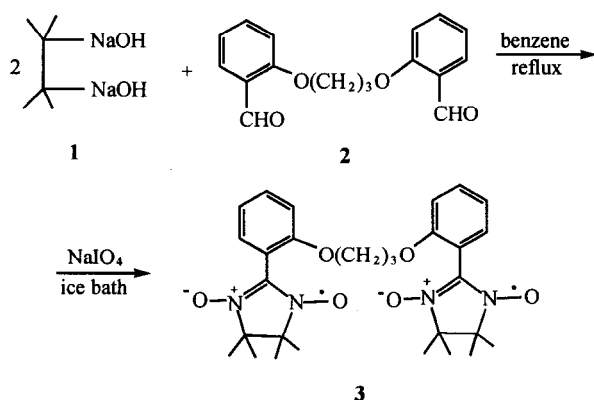
2,3-Bis(hydroxylamino)-2,3-dimethylbutane (1) (2 g) and 1, 3-bis-2, 2'-dimethanylphenoxyl-propane (2) (3.64 g) were dissolved in anhydrous benzene (60 mL). The mixture was heated under gentle reflux for 12 h. After filtration, the precipitate was added CH$_2$Cl$_2$ (100 mL) and stirred at room temperature for 10 min. A solution containing 2 g of sodium metaperiodate in 20 mL of water was added at 5 ℃. Instantaneously a blue-purple color developed; after stirring for 10 min, extraction with methylene chloride, the combined organic phase was dried and evaporated in vacuo. The residue recrystallized from CH$_2$Cl$_2$/petroleum ether (1:1) to give the nearly pure BNIPhOM (3) crystal, mp 163—165 ℃. Anal. C$_{29}$H$_{38}$N$_4$O$_6$. Calcd: C, 64.46; H, 7.11; N, 10.40. Found: C, 64.31; H, 6.84; N, 10.69. The structure of BNIPhOM has been evidenced by X-ray diffraction studies.[4]

Synthesis of complexes: all complexes were prepared in a similar fashion and it will suffice to detail the typical preparation of [Gd(hfac)$_3$] · BNIPhOM. Gd-

(hfac)$_3$·3H$_2$O (1 mmol) was dissolved in 10 cm^3 of n-heptane at 60 ℃, and BNIPhOM (1 mmol) was added. The solution was stirred for 20 min, then it was cooled to room temperature and stirred for 10 h to give a violet ~ red precipitate and then filtered. The precipitate was washed successively with n-heptane and dried in vacuo. Anal. C$_{44}$H$_{41}$O$_{12}$F$_{18}$N$_4$Gd. Calcd: C, 40.13; H, 3.14; N, 4.25; Gd, 11.94. Found: C, 40.67; H, 2.92; N, 4.10; Gd, 12.15. C$_{44}$H$_{41}$O$_{12}$F$_{18}$N$_4$Ho. Calcd: C, 39.89; H, 3.12; N, 4.22; Ho, 12.45. Found: C, 39.80; H, 2.94; N, 3.81; Ho, 12.70. C$_{44}$H$_{41}$O$_{12}$F$_{18}$N$_4$Er. Calcd: C, 39.79; H, 3.33; N, 4.11; Er, 12.60. Found: C, 39.86; H, 3.30; N, 4.10; Er, 12.18. C$_{44}$H$_{41}$O$_{12}$F$_{18}$N$_4$Dy. Calcd: C, 39.93; H, 3.10; N, 4.23; Dy, 12.29. Found: C, 40.00; H, 3.02; N, 4.12; Dy, 11.87. C$_{44}$H$_{41}$O$_{12}$F$_{18}$N$_4$Y. Calcd: C, 42.28; H, 3.28; N, 4.48; Y, 7.12). Found: C, 42.00; H, 3.30; N, 4.50; Y, 7.54.

Results and discussion

Elemental analyses have indicated that the ratio of Ln(III) salt to biradical in the complex is 1:1, [Ln(hfac)$_3$] · BNIPhOM. The IR spectra show that N—O stretching vibration for BNIPhOM (1365 cm^{-1}) shifted to lower frequency of ca 1340 cm^{-1} for the complexes. This indicates that the N—O group of BNIPhOM is coordinated. The IR spectra of the complexes exhibit two characteristic strong bands of 1650 cm^{-1} and 1440 cm^{-1} attributed to $\nu_{c=o}$ and $\nu_{c=c}$ stretching vibrations of the hfac, respectively, suggesting an enol coordination mode for hfac ligands[5] (see Table 1).

Table 1 Selected absorption in IR spectra for the complexes

Complexes	$\nu_{c=o}$ (cm^{-1})	$\nu_{c=c}$ (cm^{-1})	$\nu_{N\rightarrow O}$ (cm^{-1})
Gd(hfac)$_3$BNIPhOM	1645	1440	1341
Er(hfac)$_3$BNIPhOM	1650	1447	1344
Ho(hfac)$_3$BNIPhOM	1645	1434	1348
Y(hfac)$_3$BNIPhOM	1648	1445	1342
Dy(hfac)$_3$BNIPhOM	1646	1442	1340

The molar conductance of the complexes in n-heptane solution is close to zero, which suggests that the complexes are non-electrolyte.

The UV-vis reflectance spectra of the complexes for solid sample are similar to each other. The strongest ab-

sorptions (a broad band centered around 550 nm) can be safely attributed to $n \rightarrow \pi^*$ transition, and the absorptions around 340 nm can be attributed to $n \rightarrow \pi^*$ of ON-CNO conjugate group of the radical.[6] The f-f transition were observed for complexes of Ho(III), Er(III) and Dy (III). According to relevant absorption peaks of aqua ion of Ln(III),[7,8] the parameters $b^{1/2}$ were obtained,

given in Table 2, which show that the covalency decreases as the atomic ordinal number of the rare earth metal increases for the same ligand. This is in agreement with the general observation that the nepheloauxetic effect is more pronounced in the beginning of the 4f ground than for the later members.

Table 2   f-f transition of the complexes and Ln^{3+} aquo ions

Ln^{3+}	f-f transition (cm^{-1})		Assignment		β	$b_{1/2}$
	Aquo ions	Complex	Ground state	Exiting state		
Dy^{3+}	35336	34136	$^6H_{15/2}$	$^4L_{17/2}$	0.9667	0.129
	27946	27093		$^6P_{5/2}$		
Ho^{3+}	29826	29047	$^5I_8$	$^3L_9$	0.9730	0.116
	22768	22134		$^5F_1$		
Er^{3+}	31882	31163	$^4I_{15/2}$	$^2K_{13/2}$	0.9838	0.090
	25180	24932		$^2H_{9/2}$		

The magnetic susceptibility of [Gd(hfac)$_3$] · BN-PhOM at different temperatures (2—300 K) was measured. The reason for the choice of gadolinium(III) complex is the relative simplicity of its magnetic properties, which do not exhibit the large anisotropy effects observed for other lanthanides.[9] Gadolinium(III) is a f^7 ion, its ground state is $^8S_{7/2}$. The zero field splitting in the ground state is fairly small since the excited states are relatively high in energy. Thus $S = 7/2$ is a good quantum number. The temperature dependence of the magnetic susceptibility of Gd(III) complex is shown in Fig. 1. The effective magnetic moments per molecule is 8.41 B.M. at room temperature, which is slightly larger than the spin-only value of 8.12 B.M. As the temperature was lowered, the magnetic moments decreased gradually. When the temperature decreased to under 10 K, the effective magnetic moments decreased sharply, implying the existence of antiferromagnetic spin-exchange coupling. In order to further assess the strength of this

magnetic interaction quantitatively, we build a model of the magnetic coupling in [Gd(hfac)$_3$] · BNIPhOM, which is the following
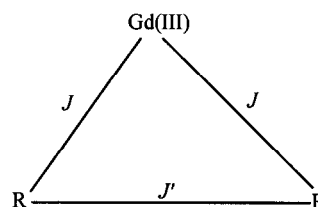
Where J is the exchange integral between Gd(III) and radical, J' is the exchange integral between radical and radical. The magnetic analysis was carried out with the susceptibility equation based on the spin Hamiltonian operator,

$$\hat{H} = -2J(\hat{S}_{Gd}\hat{S}_R + \hat{S}_{Gd}\hat{S}_{R'}) - 2J'\hat{S}_R\hat{S}_{R'}$$

The molar magnetic susceptibility for [Gd(hfac)$_3$] · BN-PhOM complex is given by Eq. (1).

$$\chi_M = [Ng^2\beta^2/6KT][A/B] \tag{1}$$

$$A = 105 + 497\exp(16J/KT) + 252\exp(7J/KT) + 252\exp[(9J/KT) - 2J'/KT]$$

$$B = 6 + 10\exp(16J/KT) + 8\exp(7J/KT) + 8\exp[(9J/KT) - 2J'/KT]$$

Where χ_M is the molar susceptibility and other symbols have their usual meanings. The experiment data (2— 300 K) were fitted with a theoretical expression using least-square method. The agreement factor (R) is defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma(\chi_M)_{obs}$. The best-fit values are $g = 2.05$, $J = 0.28$ cm^{-1}, $J' = -0.33$ cm^{-1}, $R = 3.8 \times 10^{-3}$. The very small positive

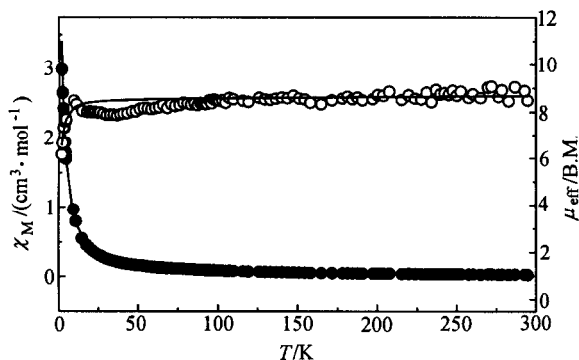**Fig. 1**   Plots of $\chi_M(\bullet)$ and $\mu_{eff}(\bigcirc)$ *vs*. temperature for [Gd-(hfac)$_3$] · BNPhOM. The solid line represents the best fitting.

value of J indicates that there exists a very weak ferromagnetic spin exchange interaction between the Gd(III) and the radical. The very small negative value of J' indicates that there exists a very weak antiferromagnetic spin exchange interaction between radical and radical.[10,11] According to elemental analysis, spectra character, molar conductances and magnetic behavior, we assume that the coordination environment of [Ln-(hfac)$_3$] · BNPhOM is as shown in Fig. 2.

This hypothesis is also in qualitative agreement with the previously reported.[2,10-12] Then, the most direct and forceful evidence for the above assumption may come from X-ray crystallographic studies. Unfortunately, all our efforts to obtain single crystals were unsuccessful.
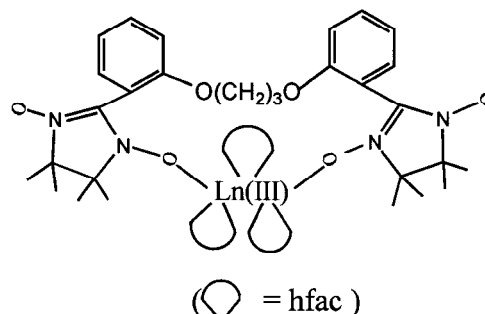

($\bigcirc$ = hfac)

Fig. 2   Coordination evironment of [Ln(hfac)$_3$] · BNPhOM.

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