

## Synthesis of Novel Lanthanide Complexes with Quinone-containing Ligands and Their Redox Controlled Magnetic Interaction

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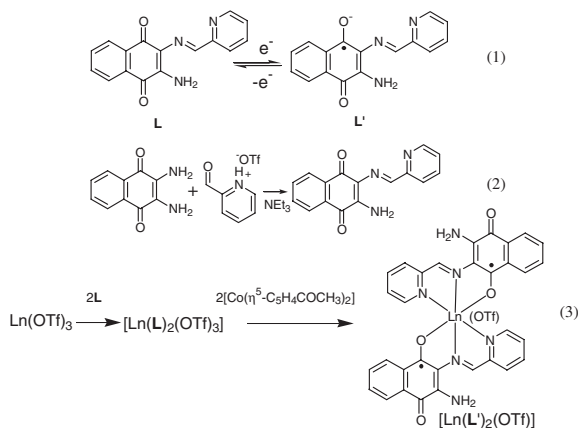
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New lanthanide-quinone and semiquinone complexes with the formula  $[\text{Ln}(\text{L})_2(\text{OTf})_3]$  and  $[\text{Ln}(\text{L}')_2(\text{OTf})]$  ( $\text{Ln} = \text{La}, \text{Gd}, \text{and Yb}$ ;  $\text{OTf} = \text{CF}_3\text{SO}_3^-$ ;  $\text{L} = \text{aminoquinone ligand}$ ;  $\text{L}' = \text{aminosemiquinone ligand}$ ), respectively, were synthesized, and the magnetic interaction between f-electrons and organic radicals was revealed.

Lanthanide ions have attracted much recent attention because of the uniqueness of their spectroscopic<sup>1,2</sup> and magnetic properties. The rather large and anisotropic magnetic moments of most of the lanthanide ions make these ions tempting building blocks of magnetic materials such as  $\text{SmCo}_5$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . However, little is known regarding the nature of the exchange interaction of rare earth ions because few compounds containing magnetically coupled f-block ions have been available. Recently, complexes of lanthanide ions with paramagnetic ligands such as transition metal complexes and organic radicals, have been reported.<sup>3–14</sup>

In the present study, to analyze and control the magnetic properties of lanthanide complexes, we have achieved the synthesis of a new redox-active aminoquinone ligand **L**, which can be altered to **L'** by one-electron reduction, and lanthanide-aminoquinone complexes with the formula  $[\text{Ln}(\text{L})_2(\text{OTf})_3]$  for the metals,  $\text{Ln} = \text{La}, \text{Gd}, \text{and Yb}$  (Scheme 1). By reducing these complexes, we synthesized new lanthanide complexes,  $[\text{Ln}(\text{L}')_2(\text{OTf})]$ , with an organic radical at the ligand. Comparing the magnetic properties of these complexes, we found the exchange interaction of lanthanide ions with semiquinone radicals.<sup>15</sup>



Scheme 1.

Quinone ligand **L** was synthesized through a reaction of 2-acetylpyridinium trifluoromethanesulfonate and 2,3-diamino-1,4-naphthoquinone<sup>16</sup> and neutralized by triethylamine (Scheme 1(2)). By spectrochemical titration of  $\text{La}(\text{OTf})_3$  in acetonitrile with the ligand **L** by monitoring the absorbance at 390 nm, near  $\lambda_{\text{max}}$  of free **L**, we analyzed the stoichiometry of the reaction of  $\text{La}(\text{OTf})_3$  with **L**. The reaction was found to proceed in two steps. First, a ligand coordinates  $\text{La}(\text{OTf})_3$  and forms  $[\text{La}(\text{L})(\text{OTf})_3]$  (stability constant:  $K_1$ ); second, an additional ligand coordinates  $[\text{La}(\text{L})(\text{OTf})_3]$  and

forms  $[\text{La}(\text{L})_2(\text{OTf})_3]$  (stability constant:  $K_2$ ). By the titration, it was estimated that  $K_1 \gg K_2$  and  $K_2 = 1 \times 10^4$ . According to the  $K_2$  value, in an acetonitrile solution of  $1 \times 10^{-5} \text{ mol dm}^{-3}$   $[\text{La}(\text{L})_2(\text{OTf})_3]$ , approximately 5% of **L** does not coordinate to lanthanum ions. It was also revealed that it was difficult for three **L** ligands to simultaneously coordinate to one metal center.

$[\text{Ln}(\text{L})_2(\text{OTf})_3]$  was obtained by the 1:2 mole-ratio reaction of  $\text{Ln}(\text{OTf})_3$ <sup>17</sup> with **L** (Scheme 1(3)). Recrystallization of  $[\text{Ln}(\text{L})_2(\text{OTf})_3]$  from acetonitrile/diethyl ether afforded red crystals.<sup>18</sup> Semiquinone complexes  $[\text{Ln}(\text{L}')_2(\text{OTf})]$  were obtained by reduction of  $[\text{Ln}(\text{L})_2(\text{OTf})_3]$  with two equivalents of  $[\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{COCH}_3)_2]$ , followed by recrystallization from DMF/diethyl ether.<sup>18</sup>

We used single-crystal X-ray diffraction analysis to determine the molecular structures of  $[\text{Ln}(\text{L})_2(\text{OTf})_3]$  for the metals,  $\text{Ln} = \text{La}, \text{Gd}$  and  $\text{Yb}$ .<sup>19</sup> An ORTEP drawing of  $[\text{Gd}(\text{L})_2(\text{OTf})_3]$  is shown in Figure 1. It is postulated that the naphthoquinone moiety in **L** is so large that three ligands cannot simultaneously coordinate to one metal center, as described above. Four nitrogen atoms and two oxygen atoms of two **L**'s and three triflate oxygen atoms contribute to the first coordination sphere. The coordination structure of  $[\text{Gd}(\text{L})_2(\text{OTf})_3]$  is a distorted tricapped trigonal antiprism (TTP). The molecular structure of  $[\text{La}(\text{L})_2(\text{OTf})_3]$  and that of  $[\text{Yb}(\text{L})_2(\text{OTf})_3]$  were almost identical to that of  $[\text{Gd}(\text{L})_2(\text{OTf})_3]$ . Bond lengths of **L** were almost the same despite the changes in the central metal. According to lanthanide contraction, however, all kinds of bond lengths around the metal center decreased from La to Yb by approximately 0.2 Å. The crystal systems of the three complexes differed from each other, and the coordination structure of  $[\text{La}(\text{L})_2(\text{OTf})_3]$  became a distorted monocapped square antiprism (CASP) in response to the decrease in bond lengths.

In a cyclic voltammogram of **L** in  $\text{Bu}_4\text{NClO}_4\text{-MeCN}$ , two

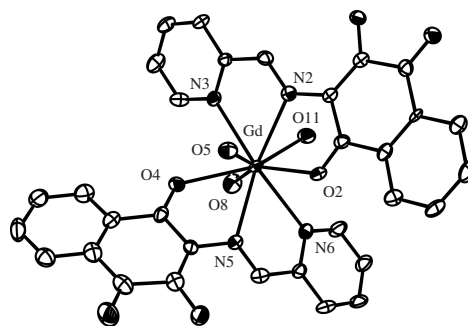


Figure 1. ORTEP drawing of  $[\text{Gd}(\text{L})_2(\text{OTf})_3]$  with a probability of 50%. Triflates are omitted except for coordinating oxygen.

reversible waves were observed at  $-0.72$  and  $-1.30$  V versus ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ), respectively. We attribute these waves to the alternation from quinone (**L**) to semiquinone radical (**L'**) (Scheme 1(1)) and to dianion, respectively. From this perspective, the quasi-reversible wave observed at  $-0.59$  V (vs  $\text{Fc}^+/\text{Fc}$ ) in  $[\text{Gd}(\text{L})_2(\text{OTf})_3]$  is likely a one-electron reduction of **L**,

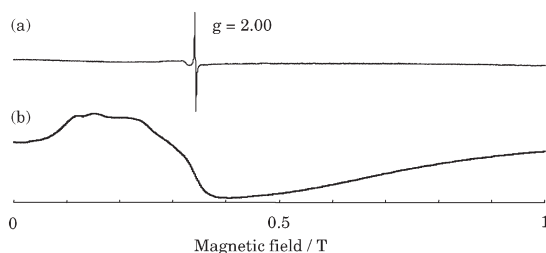
which was altered to  $L'$ . The reduction of  $[Ln(L)_2(OTf)_3]$ , carried out with  $[Co(\eta^5-C_5H_4COCH_3)_2]$ , resulted in a green powder. The elemental analysis data of the powder purified by recrystallization from DMF/diethyl ether coincided with the structure of  $[Ln(L')_2(OTf)] \cdot nH_2O$ . It is postulated that two ligands on a metal were reduced at once, and that two triflates eliminated to neutralize the charge of the complexes. Solvent molecules may be coordinated to the lanthanide ion in order to satisfy the coordination structure, although the coordination structure of  $[Ln(L')_2(OTf)]$  has not been fully revealed.

We measured and compared the UV-vis, IR, and ESR spectra for all  $[Ln(L)_2(OTf)_3]$  and  $[Ln(L')_2(OTf)]$  compounds. The UV-vis spectra did not change in response to changing the metal center, suggesting that the electronic states of the ligand are not influenced by the metal center, as indicated by the bond lengths of  $L$  not depending on the central metals. The spectra of  $[Ln(L)_2(OTf)_3]$  showed three peaks: the first, around 270 nm, is assigned to the  $\pi-\pi^*$  transition of the pyridine moiety; the second, around 370 nm, is assigned to the  $\pi-\pi^*$  transition of the naphthoquinone moiety; and the third, around 500 nm, is assigned to the charge transfer from the imine to the naphthoquinone moiety in the ligand  $L$ . The spectra of  $[Ln(L')_2(OTf)]$  showed four peaks: the first around 280 nm, is assigned to the  $\pi-\pi^*$  transition of the pyridine moiety; the second around 460 nm, the third around 480 nm, and the fourth broad peak from around 500 to 750 nm are assigned to the naphthosemiquinone moiety.<sup>20</sup>

IR spectra of the  $[Ln(L)_2(OTf)_3]$  compounds were almost the sum of the spectral features of the ligand  $L$  and  $[Ln(OTf)_3]$ . For example, the C=O stretching vibration of  $[La(L)_2(OTf)_3]$  appears as four peaks at 1624, 1603, 1558, and 1540  $cm^{-1}$ . The C=O stretching vibration of  $[La(L')_2(OTf)]$  appears as three peaks at 1608, 1589, and 1535  $cm^{-1}$ . The stretching vibration shifts to the lower wave number in response to the reduction.

ESR spectra of the  $[La(L')_2(OTf)]$  at 250 K show a sharp signal at  $g = 2.00$  due to the organic radical of the semiquinone ligand  $L'$  (Figure 2). In  $[Gd(L')_2(OTf)]$  at 242 K, only a broad signal was observed. This signal may come from the paramagnetic relaxation of an organic radical by lanthanide ions. In the case of  $[Gd(L')_2(OTf)]$  at 2 K, however, still only a broad signal was observed. This should be caused by the exchange interaction of the gadolinium ion.

In order to elucidate the magnetic interaction depending on the metal center, the magnetic susceptibility of the complexes at 300 K was measured. The  $\chi T = 0.724$  ( $cm^3 K mol^{-1}$ ) for  $[La(L')_2(OTf)]$ , indicating the existence of two  $S = 1/2$  states of the ligands in a complex (ideally,  $\chi T = 0.75$ ). The  $\chi T = 7.98$  ( $cm^3 K mol^{-1}$ ) for  $[Gd(L)_2(OTf)_3]$ , denoting the  $S = 7/2$  state of the gadolinium ion (ideally,  $\chi T = 7.88$ ). The  $\chi T = 8.47$  ( $cm^3 K mol^{-1}$ ) for  $[Gd(L')_2(OTf)]$ , indicating the existence of one  $S = 7/2$  state of the gadolinium ion and two  $S = 1/2$  states of the ligands (ideally  $\chi T = 8.63$ ). Preliminary results on the temperature dependence of



**Figure 2.** ESR spectra of  $[La(L')_2(OTf)]$  at 250 K (a), and  $[Gd(L')_2(OTf)]$  at 2 K (b).

$\chi T$  indicated that the  $\chi T$  value of  $[Gd(L')_2(OTf)]$  decreased to below 50 K, suggesting the manifestation of an antiferromagnetic interaction. This result is consistent with the results of the ESR spectroscopy, as noted above.

In conclusion, we synthesized new lanthanide-quinone and semiquinone complexes with the formulas  $[Ln(L)_2(OTf)_3]$  and  $[Ln(L')_2(OTf)]$  ( $Ln = La, Gd$ , and  $Yb$ ), performed single crystal X-ray diffraction analysis of the  $[Ln(L)_2(OTf)_3]$  complexes, and found magnetic interactions between the organic radicals and the lanthanide ion.

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- 18 *Characterization Data*:  $[La(L)_2(OTf)_3]$ ; Anal. Calcd for  $C_{35}H_{22}F_9N_6O_{13}S_3La \cdot 2H_2O$ : C, 35.94; H, 2.63; N, 7.01. Found: C 35.72; H, 2.23; N, 7.14%.  $[Gd(L)_2(OTf)_3]$ ; Anal. Calcd for  $C_{35}H_{22}F_9N_6O_{13}S_3Gd \cdot 2.8H_2O$ : C, 35.13; H, 2.49; N, 6.68. Found: C 34.86; H, 2.27; N, 6.97%.  $[Yb(L)_2(OTf)_3]$ ; Anal. Calcd for  $C_{35}H_{22}F_9N_6O_{13}S_3Yb \cdot 1.4H_2O$ : C, 35.31; H, 2.34; N, 6.73. Found: C 35.03; H, 2.08; N, 7.00%.  $[La(L')_2(OTf)]$ ; Anal. Calcd for  $C_{33}H_{22}F_3N_6O_7SLa \cdot 9H_2O$ : C, 39.45; H, 4.01; N, 8.36. Found: C 39.70; H, 4.34; N, 8.48%.  $[Gd(L')_2(OTf)]$ ; Anal. Calcd for  $C_{33}H_{22}F_3N_6O_7SGd \cdot 7.6H_2O$ : C, 39.72; H, 3.76; N, 8.42. Found: C 39.95; H, 3.60; N, 8.16%.  $[Yb(L')_2(OTf)]$ ; Anal. Calcd for  $C_{33}H_{22}F_3N_6O_7SYb \cdot 6H_2O$ : C, 40.25; H, 3.48; N, 8.53. Found: C 40.13; H, 3.63; N, 8.57%.
- 19 *Crystallographic Data*:  $[La(L)_2(OTf)_3] \cdot 2MeCN$ :  $C_{39}H_{28}F_9LaN_8O_{13}S_3$ ,  $M_r = 1222.77$ , triclinic,  $P\bar{1}$ ,  $a = 11.203(9)$ ,  $b = 11.179(9)$ ,  $c = 19.29(2)$  Å,  $\alpha = 87.93(3)$ ,  $\beta = 86.12(3)$ ,  $\gamma = 72.46(3)$  (deg),  $V = 2298.5(36)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 293$  K,  $\mu(Mo K\alpha) = 1.175$  mm<sup>-1</sup>. Of a total of 17378 collected reflections, 9968 were independent ( $R_{int} = 0.046$ ).  $R(F_0)/R_w(F_0) = 0.140/0.196$ . (CCDC 196471).  $[Gd(L)_2(OTf)_3] \cdot 4MeCN$ :  $C_{43}H_{34}F_9GdN_{10}O_{13}S_3$ ,  $M_r = 1323.22$ , orthorhombic,  $Pbca$ ,  $a = 20.411(5)$ ,  $b = 20.692(5)$ ,  $c = 23.921(6)$  Å,  $V = 10103.1(43)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 133$  K,  $\mu(Mo K\alpha) = 1.544$  mm<sup>-1</sup>. Of a total of 81195 collected reflections, 11502 were independent ( $R_{int} = 0.095$ ).  $R(F_0)/R_w(F_0) = 0.043/0.048$ . (CCDC 196472).  $[Yb(L)_2(OTf)_3] \cdot 3MeCN$ :  $C_{41}H_{31}F_9N_9O_{13}S_3Yb$ ,  $M_r = 1297.95$ , monoclinic,  $P2_1/c$ ,  $a = 12.1461(5)$ ,  $b = 19.7165(8)$ ,  $c = 20.3672(9)$  Å,  $\beta = 90.092(2)$  (deg),  $V = 4952.2(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 293$  K,  $\mu(Mo K\alpha) = 2.110$  mm<sup>-1</sup>. Of a total of 41116 collected reflections, 11570 were independent ( $R_{int} = 0.036$ ).  $R(F_0)/R_w(F_0) = 0.030/0.042$ . (CCDC 196473).
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