Formation and Structure of Mixed Quaternary Chelates with Late-Lanthanide Metal Ions

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We have newly obtained two series of late-lanthanide metal complexes with three different kinds of chelating ligands (quaternary system), [Ln(dike)$_{3-n}$(NO$_3$)$_n$(terpy)] where Ln(III) = Er(III) or Yb(III), dike = β-diketonate such as acetylacetonate (acac) or 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac), and terpy = 2,2':6',2''-terpyridine; n = 2 (for acac) or 1 (for hfac). Crystal structures for the Yb(III) complexes show that in both series the pentagonal plane around the central Yb^{3+} ion with terpy and one dike ligand is formed. The other chelating ligands coordinate up and down from the plane to form totally 9 coordination around Yb^{3+}.

So far, there were many reports for synthesizing mixed chelate compounds with the transition metal ions, among which ternary complexes, [M(AA)(BB)], were the fundamental system.[1-7] But the quaternary chelating systems with divalent or trivalent d-metal ions, [M(AA)(BB)(CC)], are rather difficult to obtain due to the smaller ionic size of the central metal ion and the rate of ligand substitution reaction.[8-9] We can suppose easily to obtain higher mixed chelate (quaternary or higher) complexes with the metal ion having large ionic radius, i.e., the lanthanide metal ions are usually trivalent cation and larger ionic radius, although the quaternary complexes with these ions have little been reported. Furthermore, we expect that the variation on ionic radius of lanthanide series may cause the variation on the structure of the complexes.

We tried to obtain such kinds of quaternary complexes with a lanthanide metal ion using β-diketonate (dike, i.e., acac or hfac), nitrate, and terpy. In this letter we would report that two series of late-Ln(III) complexes (for Ln = Er^{3+} or Yb^{3+}) containing three kinds of chelating ligands, [Ln(acac)(NO$_3$)$_2$(terpy)] and [Ln(hfac)$_2$(NO$_3$)(terpy)], could be obtained and they have an interesting structure.

For syntheses of the complexes, the procedure as follows: Ln(NO$_3$)$_3$·4H$_2$O salt (10 mmol, Ln = Er^{3+} or Yb^{3+}) was dissolved into the ethanol solution of terpy (10 mmol). After a while, white powder then precipitated, Ln(NO$_3$)$_3$(terpy)·H$_2$O, as a ternary complex. This precipitate was suspended in acetonitrile to which three-molar amounts of β-diketonate (neutralized by NH$_3$) solution was added. The clear solution thus obtained is evaporated slowly to get fine crystals suitable for X-ray structural analysis. Although the molar ratios of Ln(NO$_3$)$_3$(terpy)·H$_2$O and dike were exactly the same in both cases of acac and hfac for synthesis of the quaternary system, the stoichiometry of the complexes depended on the kind of β-diketonate only. For each β-diketonate system the Er(III) and Yb(III) complexes have same composition and the stoichiometry of these complexes did not depend on the kind of lanthnide ions but on the β-diketonate used. For the case of acac, one nitrate of the starting material, Ln(NO$_3$)$_3$(terpy)·H$_2$O, was displaced by one acac to form [Ln(acac)(NO$_3$)$_2$(terpy)]. The elemental analyses are as follows (calculated values shown in parentheses): for [Er(acac)(NO$_3$)$_2$(terpy)] (**I**); C, 38.50(38.52); H, 2.88(2.91); N, 11.23(11.23)%: for [Yb(acac)(NO$_3$)$_2$(terpy)] (**II**); C, 38.56 (38.20); H, 2.86(2.86); N, 10.87(11.10)%. For the case of hfac, two nitrato moieties of the starting material were exchanged by two hfac to form [Ln(hfac)$_2$(NO$_3$)(terpy)]. The elemental analyses are as follows (calculated values shown in parentheses): for [Er(hfac)$_2$(NO$_3$)(terpy)] (**III**); C, 34.40(34.25); H, 1.45 (1.49); N, 6.32(6.39)%: for [Yb(hfac)$_2$(NO$_3$)(terpy)] (**IV**); C, 34.02(34.02); H, 1.42(1.48); N, 6.25(6.34)%.

We could obtain crystal structures of these two Yb(III) complexes **II** [10] and **IV** [11] shown in Figures 1 and 2, respectively. From the structural data, both of the Yb^{3+} ions are 9 coordination which contain a tridentate terpy and two kinds of bidentate ligands, i.e., dike(acac or hfac) and NO$_3^-$. In both cases of acac and hfac, a terpy and a dike are placed in nearly the same plane around a Yb^{3+} ion to form a distorted pentagonal coordination, and residual two bidentate nitrates (for **II**) or a nitrate and a hfac (for **IV**) are coordinated up and down from the distorted pentagonal plane.

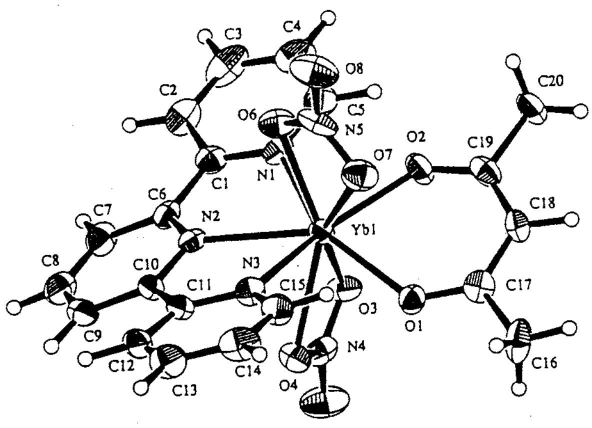

Figure 1. ORTEP drawing of [Yb(acac)(NO$_3$)$_2$(terpy)] (**II**) with 30% probability ellipsoids giving atomic numbering. Selected bond lengths (Å) and angles (°) are as follows: Yb(1)-O(1), 2.221(5); Yb(1)-O(2), 2.204(5); Yb(1)-O(3), 2.414(6); Yb(1)-O(4), 2.470(6); Yb(1)-O(5), 2.377(6); Yb(1)-O(6), 2.479(6); Yb(1)-N(1), 2.529(6); Yb(1)-N(2), 2.454(6); Yb(1)-N(3), 2.464(6); O(1)-Yb(1)-O(2), 77.2(2) ; N(1)-Yb(1)-N(2), 65.0(2) ; N(2)-Yb(1)-N(3), 66.0(2).

In complex **II**, the Yb-N bond distance to the central pyridyl moiety, 2.454(6) Å, and one side of terminal pyridyl moiety, 2.464(6) Å, are similar with each other and that to the other terminal one, 2.529(6) Å, is larger than those shown just before. The terpy ligand forms asymmetric Yb-N coordinate bonds as like consisting of a bipyridyl and a pyridyl moieties (see in Figure 1). The terpy ligand in complex **IV** shown in Figure 2 binds to Yb^{3+} ion also in the similar manner as that observed in **II**. The unsymmetrical coordination of terpy indicates that the ionic radius of Yb^{3+} is smaller than the bite of terpy ligand. The dihedral angles between two adjacent chelate rings of the terpy ligand in **II** and **IV** are 14.0 and 4.2 °, respectively. The larger distortion of terpy ligand in **II** than that in **IV** suggests that **II** has more steric hindrance (probably between the protons on the positions C5 and C15 of terpy and O atoms of dike ligand in same pentagonal plane).

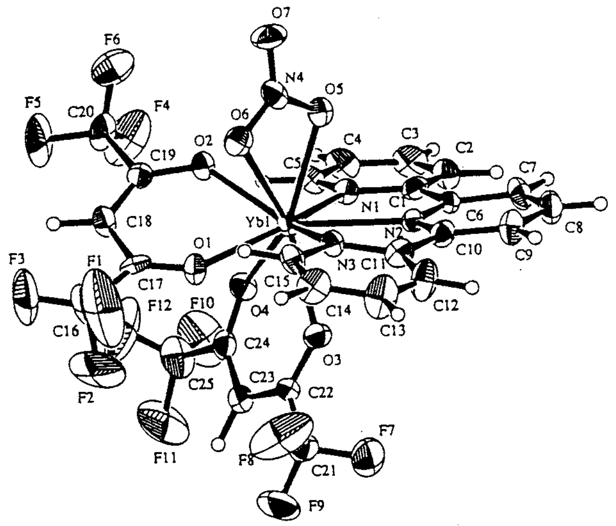

Figure 2. ORTEP drawing of $[Yb(hfac)_2(NO_3)(terpy)]$ (**IV**) with 30% probability ellipsoids giving atomic numbering. Selected bond lengths (Å) and angles (°) are as follows: Yb(1)-O(1), 2.261(7); Yb(1)-O(2), 2.312(7); Yb(1)-O(3), 2.309(7); Yb(1)-O(4), 2.339(8); Yb(1)-O(5), 2.381(8); Yb(1)-O(6), 2.537(8); Yb(1)-N(1), 2.476(8); Yb(1)-N(2), 2.477(8); Yb(1)-N(3), 2.509(8); O(1)-Yb(1)-O(2), 76.7(3) ; O(3)-Yb(1)-O(4), 70.7(3) ; N(1)-Yb(1)-N(2), 65.3(3) ; N(2)-Yb(1)-N(3), 65.9(3).

The bond distances of Yb-O(acac) placed at the trans position of terpy in **II**, 2.221(5) and 2.204(5) Å, is a little bit shorter than those in $[Yb(acac)_3(H_2O)]$ (the average value is 2.23 Å)[12] and are rather shorter than those of corresponding Yb-O(hfac) ones in **IV**, 2.261(7) and 2.312(7) Å, which means that the hfac ligand in **IV** is bound to the Yb^{3+} ion with weaker interaction. In other words, the combination of terpy-acac system is more convenient to form a π-base and a π-acid interaction than that of terpy-hfac system. These bond differences between Yb-acac and Yb-hfac reflects to the difference of dihedral angles of the terpy ligand described above. Consequently, these factors (shorter bond lengths of Yb-acac and therefore larger steric repulsion) prevent exchanging of NO_3^- ligand by another acac ligand to yield the bis-acac complex; $[Ln(acac)_2(NO_3)(terpy)]$.

For IR spectra of these complexes, we could obtain characteristic bands as C=C and C=O of β-diketonate at 1575 and 1520 cm^{-1} (for **I**), 1599 and 1521 cm^{-1} (for **II**), 1652 and 1602 cm^{-1} (very strong bands, for **III**), and 1664 and 1603 cm^{-1} (very strong bands, for **IV**). It is also interesting to note the nitrate coordination mode[13,14] by the IR bands in the region 1700-1800 cm^{-1}. For the acac series, there are two weak bands at 1778 and 1737 cm^{-1} (fot **I**) or 1782 and 1739 cm^{-1} (for **II**), which means the nitrate in the chelate acts as a bidentate ligand.[15] In case of the hfac series, unfortunately, there are rather strong absorption bands due to the hfac ligand in this region which obscure weak bands of the coordinated nitrate.

Finally, from the points of view concerned stereochemistries of ligands used and their coordination abilities (nitrate, hfac, acac and terpy), the behaviors of ligand exchange reactions for the lanthanide complexes are summarized as follows: (i) We could not obtain any ternary complexes, $[Ln(acac)_3(terpy)]$, when we tried to synthesize the chelates by using $Ln(acac)_3H_2O$ and terpy as starting materials. (ii) It is quite reasonable that the exchange reaction of NO_3^- ligand in the complex $Ln(terpy)(NO_3)_3 \cdot H_2O$ by β-diketonate one (hfac or acac) occurs to form the quaternary system. (iii) In the present study of quaternary systems (Yb-terpy-NO_3-acac or hfac), they contain two hfac (for **III** and **IV**) or one acac ligand (for **I** and **II**) by exchanging two or one nitrate, respectively. These behaviors are rather strange because the coordination ability of hfac is weaker than that of acac. We consider that the hardness of Ln^{3+} (Er^{3+} or Yb^{3+}) and hfac ligands are the cause that two nitrate ions may be displaced by two hfac ligands to give **III** or **IV**.

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References and Notes

1 G. A. L. Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481(1966).
2 Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, **43**, 556(1970).
3 Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, **43**, 2282(1970).
4 H. Sigel, *Angew. Chem., Int. Ed. Engl.*, **14**, 394(1975).
5 C. Tsiamis, C. Y-Tsochatzi, A. Hartzimitrion, and A. Gourdon, *Inorg. Chim. Acta*, **237**, 93(1995).
6 G. Malandrio, R. Licata, F. Castelli, I. L. Fragala, and C. Benelli, *Inorg. Chem.*, **34**, 6233(1995).
7 M. Frechatte and C. Bensimon, *Inorg. Chem.*, **34**, 3520(1995).
8 (a) S. Wang, Z. Pang, K. D. L. Smith, Y. Hua, C. Deslippe, and M. J. Wagner, *Inorg. Chem.*, **34**, 908(1995). (b) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 1257(1966).
9 (a) N. Sabbatini and M. Guardigli, *Coord. Chem. Rev.*, **123**, 201(1993). (b) U. Kilimann and F. T. Edelmann, *ibid.*, **141**, 1(1995). (c) F. T. Edelmann and Y. K. Gun'ko, *ibid.*, **165**, 163(1997).
10 Crystal Structure data for **II**: $YbN_5C_{20}O_8H_{18}$ (*FW* = 629.43), monoclinic, space group $P2_1/n$ (#14), $a = 10.917(4)$ Å, $b = 14.263(4)$ Å, $c = 14.915(5)$ Å, $\beta = 102.38(3)$ °, $V = 2268(1)$ Å^3, $Z = 4$, D(calcd) = 1.843 g/cm^3, μ(MoKα) = 41.78 cm^{-1}, $R = 0.034$ ($R_w = 0.022$) on 2376 reflections ($I > 3\sigma(I)$).
11 Crystal Structure data for **IV**: $YbN_4C_{25}O_7F_{12}H_{13}$ (*FW* = 882.42), triclinic, space group P-1 (#2), $a = 12.012(3)$ Å, $b = 15.695(2)$ Å, $c = 8.280(1)$ Å, $\alpha = 95.08(1)$ °, $\beta = 107.70(2)$ °, $\gamma = 88.39(2)$ °, $V = 1481.2(5)$ Å^3, $Z = 2$, D(calcd) = 1.978 g/cm^3, μ(MoKα) = 32.83 cm^{-1}, $R = 0.053$ ($R_w = 0.039$) on 3123 reflections ($I > 3\sigma(I)$).
12 J. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, *Inorg. Chem.*, **8**, 22(1969).
13 Y. Ihara, Y. Fukuda, and K. Sone, *Inorg. Chem.*, **26**, 3745(1987).
14 A. B. P. Lever, E. Montovami, and B. S. Ramaswamy, *Can. J. Chem.*, **49**, 1957(1971).
15 For **III** and **IV**, we could not assign the nitrate bands due to the existence of very strong diketonate bands in the same region.