Single Crystal X-Ray Analyses of a Series of Hexamethylphosphoramide-Coordinated Complexes of Rare Earth Triflates: Existence of Tetrad Effects in the Coordinate Bonds

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The molecular structures of $[M(OTf)_2(hmpa)_4]OTf\cdot CHCl_3$ (OTf = OSO_2CF_3; M = Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $[Sc(OTf)_2(hmpa)_4]OTf$, and $[La(\eta^2\text{-}OTf)(OTf)(hmpa)_4]OTf\cdot CHCl_3$ were accurately determined by single crystal X-ray analyses. Tetrad effects are manifested in the series of the coordinate bond lengths.

Rare earth complexes are known to exhibit characteristic reactivities, and some of them have become indispensable reagents or catalysts for highly selective functional group transformations and stereocontrolled polymerizations.[1,2] The origin of the unique reactivities of the complexes, however, has not yet been sufficiently elucidated, although several factors such as strong oxophilicity, long ionic radius, large coordination number, and lanthanide contraction are often employed in the qualitative explanations of the reactivities. We have envisioned that it is necessary to clarify the precise coordinative nature of a series of rare earth complexes in order to obtain detailed information on the structure–reactivity relationships of the complexes. For this purpose we have chosen hexamethylphosphoramide (HMPA)-coordinated complexes of rare earth(III) triflates as the model substrates, and have determined their accurate crystal structures by single crystal X-ray analyses.

All the HMPA complexes, except the radioactive promethium complex, were prepared by treatment of anhydrous rare earth triflates with five equivalents of HMPA in dry tetrahydrofuran.[3] The single crystals for X-ray analyses were obtained by recrystallization from a mixed solvent of chloroform and ethyl acetate. The crystals were extremely air sensitive and were sealed in a glass capillary. The data collection for the X-ray analyses was carried out at 173 K by the use of the two dimensional area detector equipped with laser-stimulated image plate fluorescence.

Accurate structural analyses revealed the following three types of molecular structures: $[M(OTf)_2(hmpa)_4]OTf\cdot CHCl_3$ (M = Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $[Sc(OTf)_2(hmpa)_4]OTf$, and $[La(\eta^2\text{-}OTf)(OTf)(hmpa)_4]OTf\cdot CHCl_3$. The ORTEP drawings of $[La(\eta^2\text{-}OTf)(OTf)(hmpa)_4]OTf\cdot CHCl_3$ and $[Ce(OTf)_2(hmpa)_4]OTf\cdot CHCl_3$ are shown in Figures 1 and 2.[4] All complexes, except the lanthanum complex, show almost the same hexacoordinated octahedral structure. Four HMPA molecules are coordinated to the central metal ion forming an equatorial plane. Two triflate anions are located at the trans position, while a third triflate anion is not coordinated to the metal but interacts with chloroform through a hydrogen bond.[5] Compared with other complexes, the scandium complex dose not contain chloroform in this crystal structure. The lanthanum complex forms a distorted hepta-coordinated mono(face-capped) octahedral structure in that one of the triflate anions acts as a bidentate ligand. The chloroform molecule in this complex is located between the free triflate anion and one of the HMPA molecules.

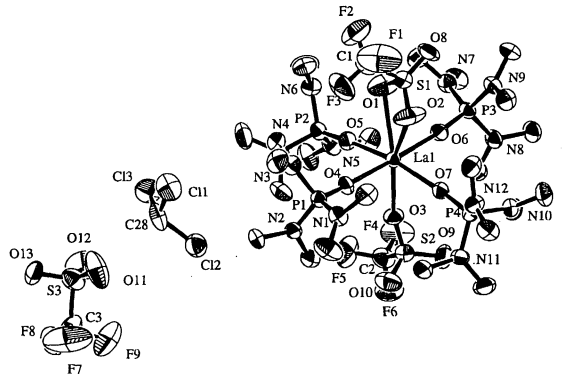

Figure 1. ORTEP drawing of $[La(\eta^2\text{-}OTf)(OTf)(hmpa)_4]OTf\cdot CHCl_3$.

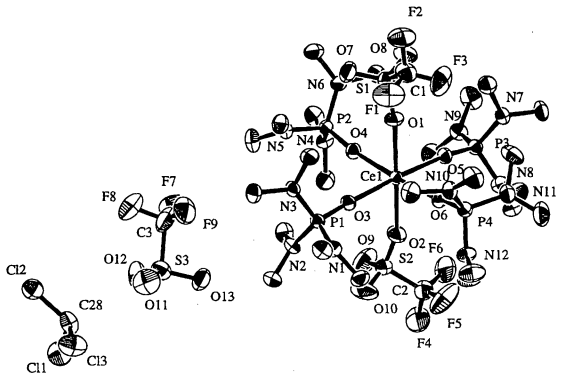

Figure 2. ORTEP drawing of $[Ce(OTf)_2(hmpa)_4]OTf\cdot CHCl_3$.

The thirteen HMPA complexes from cerium to lutetium are considered to constitute an ideal model system for elucidating the coordinative nature of a series of lanthanide complexes, because the crystal structures of these complexes closely resemble each other, being almost superimposable except for the coordinate bond lengths. The respective coordinative bond lengths have been plotted *vs.* atomic number, and the two representative plots are shown in Figure 3. It is apparent that the bond lengths between the HMPA oxygen atom and the central metal are 0.05~0.10Å shorter than the bond lengths between the triflate oxygen atom and the metal. These facts indicate that HMPA coordinates to the metal ion more strongly than the triflate anion.

The most significant discovery is that a couple of tetrad effects are manifested in the series of the coordinate bond lengths; plot A displays four downward curvatures and plot B shows four upward curvatures.[6] The tetrad effect represents the periodical change in physical and chemical properties of the lanthanide(III)

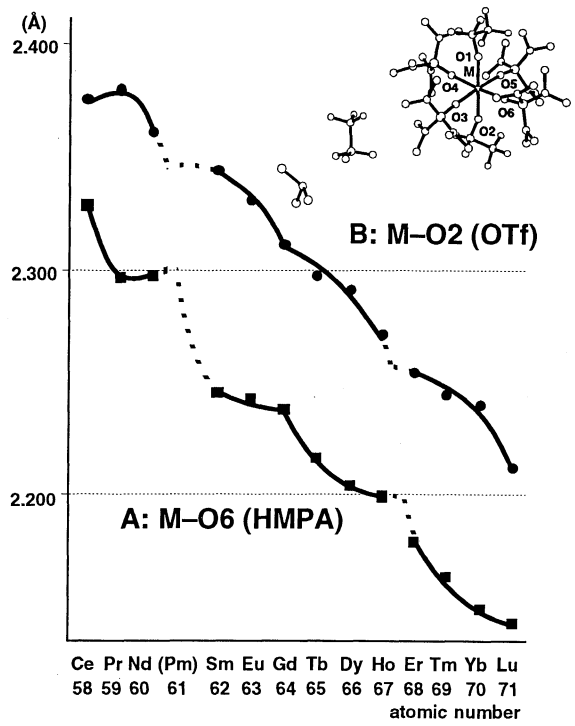

Figure 3. Plot A: M–O6 bond lengths vs. atomic number. Plot B: M–O2 bond lengths vs. atomic number.

series as four tetrads [(La, Ce, Pr, Nd), (Pm, Sm, Eu, Gd), (Gd, Tb, Dy, Ho), (Er, Tm, Yb, Lu)] are formed with increasing atomic number. Some distinct tetrad effects have been already observed in the partition constants of lanthanide(III) salts in liquid-liquid systems,[7] and they are attributed to the ion stabilities which originate mainly from the quantum mechanical interelectronic repulsion energy of 4f electrons.[8,9] The tetrad effects found in our study can be explained by considering the stability of the lanthanide(III) ions. Thus, relatively less stable ions bond to the electron-donating ligand HMPA more strongly than the more stable ions, with shortening of bond lengths to form four downward curvatures. The strong coordination of HMPA elevates the electron density at the central metal and also brings about steric crowding around the metal. These electronic and steric factors are responsible for the elongation of the distance between the triflate oxygen atom and the central metal, resulting in the formation of the four upward curvatures.

It is also worth mentioning that the scandium and ytterbium complexes possess relatively long P–O bond lengths in the ligand HMPA.[10] These P–O bond elongations may reflect the strong oxophilicity of Sc^{3+} and Yb^{3+} ions and they may be largely ascribed to their relatively short ionic radii in the rare earth(III) ions.[11] It is noted that these facts are consistent with the exceptionally high catalytic activities of Sc(III) and Yb(III) compounds in many Lewis acid promoted reactions.[12,13]

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4 Crystal data for $[La(\eta^2\text{-}OTf)(OTf)(hmpa)_4]OTf\cdot CHCl_3$: formula $C_{28}H_{73}O_{13}Cl_3F_9N_{12}P_4S_3La$, colorless prism, triclinic, space group $P\bar{1}$, a = 15.336(7) Å, b = 17.328(4) Å, c = 12.051(2) Å, α = 103.24(2)°, β = 102.38(3)°, γ = 90.76(3)°; V = 3044.4 Å^3; D_{calc} = 1.551 g cm^{-1}; Z = 2; 659 parameters; 5906 reflections with $I_0 > 4.50\sigma(I_0)$; R = 0.069; R_w = 0.090. Crystal data for $[Ce(OTf)_2(hmpa)_4]OTf\cdot CHCl_3$: formula $C_{28}H_{73}O_{13}Cl_3F_9N_{12}P_4S_3Ce$, colorless prism, triclinic, space group $P\bar{1}$, a = 15.223(6) Å, b = 17.497(3) Å, c = 12.032(1) Å, α = 103.887(10)°, β = 102.52(3)°, γ = 90.30(3)°; V = 3037.1 Å^3; D_{calc} = 1.556 g cm^{-1}; Z = 2; 659 parameters; 5852 reflections with $I_0 > 4.50\sigma(I_0)$; R = 0.057; R_w = 0.072. Details of the all molecular structures have been deposited at the Cambridge Crystallographic Centre.

5 The atomic distances (3.17~3.44 Å) between the chloroform carbon and the oxygen atoms of the triflate anion indicate that the hydrogen atom of chloroform interacts with the two oxygen atoms of the triflate anion.

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11 We consider that the exceptionally strong oxophilicity of Yb^{3+} in lanthanide(III) ions originates also from the 4f electron configuration of ytterbium(III). Namely, ytterbium(III) possesses thirteen electrons in seven 4f orbitals, and this insufficiently filled state, which has a tendency to become a filled state (f^{14}), renders the ytterbium(III) ion more electron-attracting in all lanthanide(III) ions.

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