CHEMISTRY LETTERS, pp. 2331-2334 1994.

Reaction of Lanthanum(III) and Gadolinium(III) Complexes Coordinated by Pendant-armed Macrocyclic Ligand with Salicylaldehyde

Masatoshi KANESATO,* Toshiro YOKOYAMA, and Osamu ITABASHI
Tohoku National Industrial Research Institute, 4-2-1, Nigatake, Miyagino-ku, Sendai 983

In the reaction of Lanthanum(III) and Gadolinium(III) complexes coordinated by the ligand 1, 9-bis(2-aminoethyl)-1, 4, 6, 9, 12, 14-hexaazacyclohexadecane with salicylaldehyde, only Gd^{3+} was led to an unexpected complex with the ligand tris{2-(salicylideneamino)ethyl}amine. The difference of the reactivity was applied to the separation of La^{3+} and Gd^{3+}.

The chemical properties of the trivalent rare earth ions and their complexes in solution are very similar to each other. Because of the remarkable similarities of the rare earth elements, their mutual separation usually requires tedious procedures.[1)]

It is important to find a different behavior in the reaction of rare earth complexes for the extensive studies of the complexing properties of each rare earth element and for the attempts to separate and purify the individual elements effectively.

Recent reports have described the synthesis of macrocyclic complexes of Y^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Eu^{3+}, and Yb^{3+} with the ligand 1, 9-bis(2-aminoethyl)-1, 4, 6, 9, 12, 14-hexaaza-

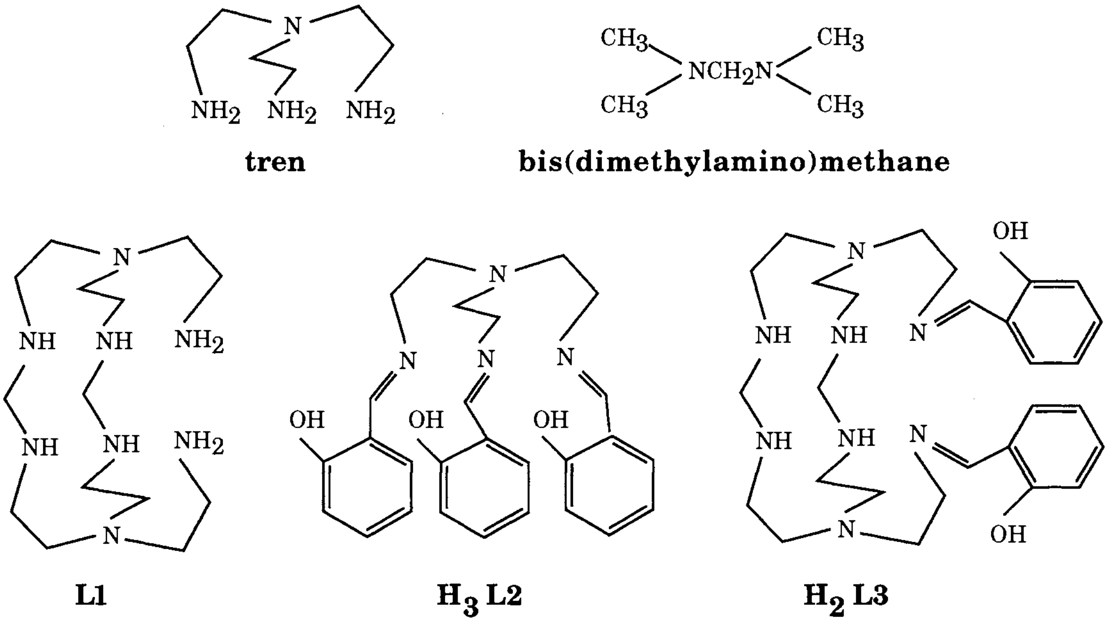


Fig. 1. Illustrations of the reagents and ligands discussed in this work.

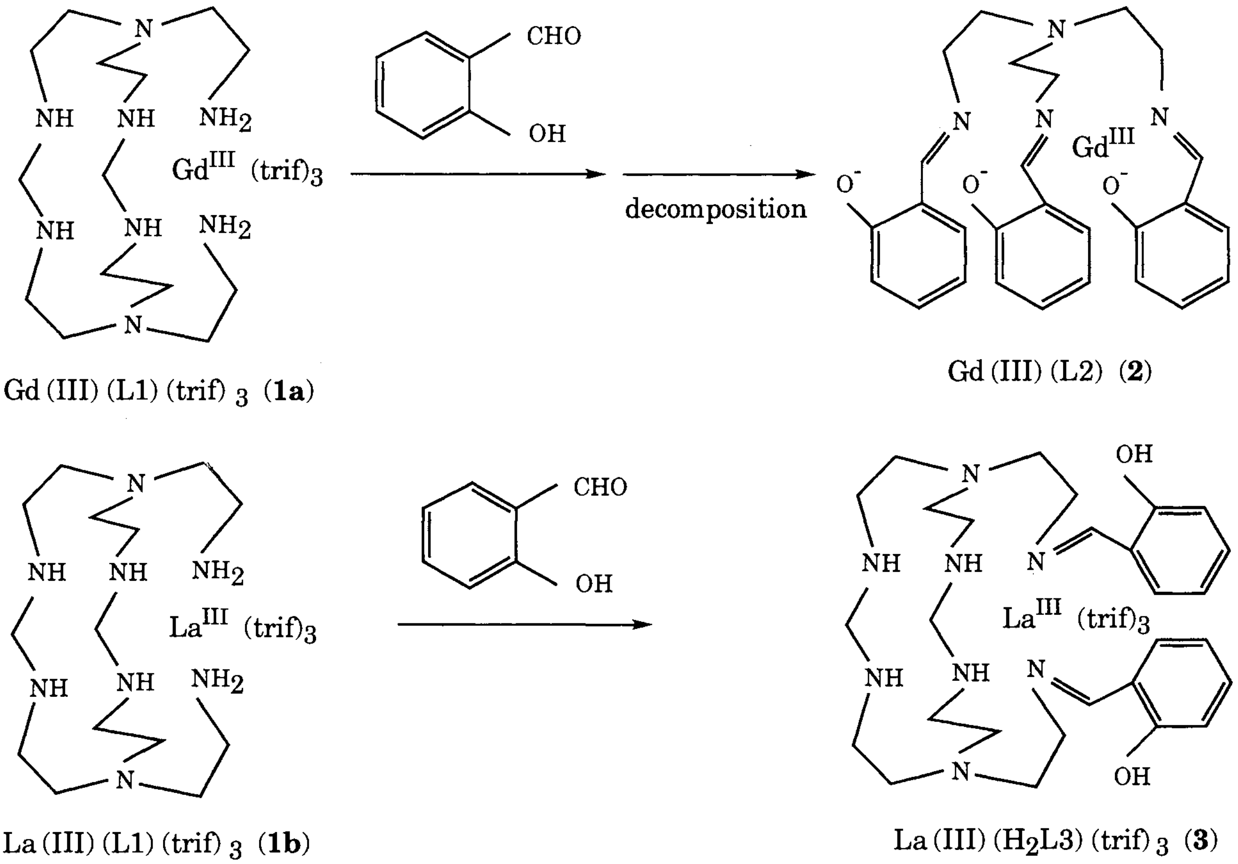
cyclohexadecane (**L1**) by using the template approach involving the combination of the metal trifluoromethanesulfonate(trif) salt as the template source, 2 equiv of the tetradentate amine tris(2-aminoethyl)amine(tren), and an excess of bis(dimethylamino)methane.[2,3] A macrocyclic complex of Gd^{3+} with the ligand **L1** has been prepared as white crystals by using a procedure similar to that described in the previous paper.[2] This product was found to be $Gd(III)(L1)(trif)_3$ (**1a**) by IR spectrum and elemental analysis.[4]

These rare earth complexes, $Ln(III)(L1)(trif)_3$ (Ln=Y, La, Ce, Pr, Eu, Gd, and Yb), have two pendant arms which contain two primary amines. It is well known that a primary amine reacts with an aldehyde to give a Schiff-base compound. We are interested in the reactivity of the primary amines of these rare earth complexes.

6 mmol of salicylaldehyde was added to a solution of 2 mmol of **1a** in acetonitrile (100 cm^3) and stirred for 5 mins at room temperature. This solution was evaporated to about 20 cm^3 and then allowed to cool in a refrigerator for 10 h. The resulting yellowish crystals were collected by filtration, washed with cold acetonitrile and then dried under vacuum. The crystals gave a band at 1626 cm^{-1} in the IR spectrum due to C=N stretching vibration, but no bands corresponding to a primary amine or to the presence of a trifluoromethanesulfonate anion were found. The IR spectrum of this product is similar to that of the known tripodal ligand tris{2-(salicylideneamino)ethyl}amine($\mathbf{H_3L2}$), [5,6] which is prepared from tren and 3 equiv of salicylaldehyde. This information together with the microanalysis suggested that the compound formed was Gd(III)(L2)[7] (**2**) (Scheme 1). Although the precise mechanism of the present reaction is still an open question, the fact that **2** was synthesized reveals that decomposition of macrocyclic structure of **1a** was caused by salicylaldehyde. Because this product doesn't contain the trifluoromethanesulfonate anion, the ligand **L2** may form an inner-complex compound in which it functions as a trivalent anionic polydentate ligand.

On the other hand, in the case of a lanthanum complex , $La(III)(L1)(trif)_3$ (**1b**), such a reaction was not observed under the same condition as that of **1a** with salicylaldehyde. The solution of acetonitrile (20 cm^3) containing **1b** and salicylaldehyde, which was prepared by the same procedure as described above, was allowed to cool in a refrigerator for 3 days, but no solid was precipitated. The solution of acetonitrile was added to much amount of diethyl ether to give an orange solid. This product gave a band at 1626 cm^{-1} in the IR spectrum due to C=N stretching vibration with no band corresponding to a primary amine but with a strong band at 1255 cm^{-1} indicating the presence of a trifluoromethanesulfonate anion. This together with the microanalysis indicated that the compound formed was $La(III)(H_2L3)(trif)_3$[8] (**3**) (Scheme 1).

The difference of the reactivity between La^{3+} and Gd^{3+} complexes of the ligand **L1** with salicylaldehyde was monitored by UV-visible spectroscopy. Figure 2 shows the spectral change of the reaction of **1a** with salicylaldehyde. The absorbance in the region of about 350 to 370 nm gradually increased and finally a shoulder appeared, which reveals that **2** was produced because it was observed that **2** has the absorption maxima at 357 nm in acetonitrile. In the case of the reaction of **1b** with salicylaldehyde, such a shoulder at 357 nm was not observed in 10 h (Fig. 3).



Gd (III) (L1) (trif) 3 (**1a**)

Gd (III) (L2) (**2**)

La (III) (L1) (trif) 3 (**1b**)

La (III) (H_2L3) (trif) 3 (**3**)

Scheme 1.

The difference of reactivity of **1a** and **1b** with salicylaldehyde can be applied to the mutual separation of Gd^{3+} and La^{3+}. In the reaction of **1a** and **1b** with salicylaldehyde, only Gd^{3+} was led to a complex with the ligand **L2** and it was easily precipitated from acetonitrile on the basis of the very low solubility of **2** in acetonitrile because the ligand **L2** forms inner-complex compound in which it functions as a trivalent anionic polydentate ligand. On the other hand the solubility of **3** in acetonitrile is very high compared to that of **2**.

A mixture of **1a** (2 mmol) and **1b** (2 mmol) was dissolved in 100 cm^3 of acetonitrile. Then 6 mmol of salicylaldehyde was added and stirred for 5 mins at room temperature. This solution was evaporated to about 20 cm^3 and then allowed to cool in a refrigerator for 10 h. The resulting yellowish crystals were collected by filtration, washed with cold acetonitrile and then dried under vacuum. The crystals were dissolved in an acidic solution and then the concentrations of La^{3+} and Gd^{3+} in this solution were determined by an ICP-atomic emission spectrometer. The purity of Gd^{3+} in the crystals was 99.9% for La^{3+}. This method was also found to be effective for the separation of a mixture of Lanthanum(III) and Gadolinium(III) oxide.

In conclusion, a different behavior in the reaction of La^{3+} and Gd^{3+} complexes of pendant-armed macrocyclic ligand with salicylaldehyde was observed and it was applied to the mutual separation of La^{3+} and Gd^{3+}

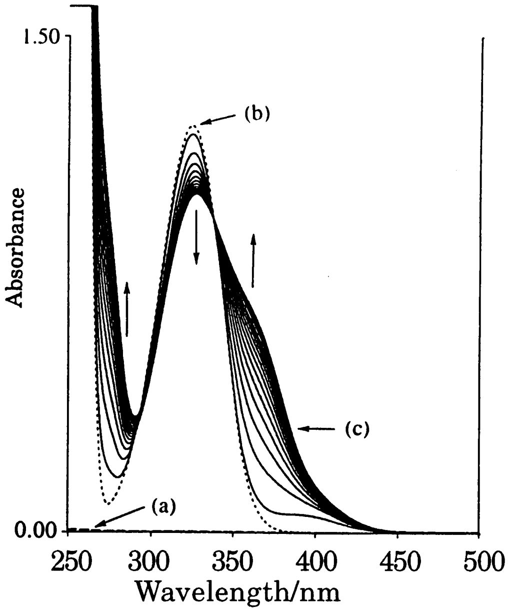


Fig. 2. UV-visible spectrum
(a) **1a** 1.25×10^{-4} M
(b) salicylaldehyde 3.75×10^{-4} M
(c) Spectral changes of reaction of (a) with (b)
Measurements were made every 30 mins.

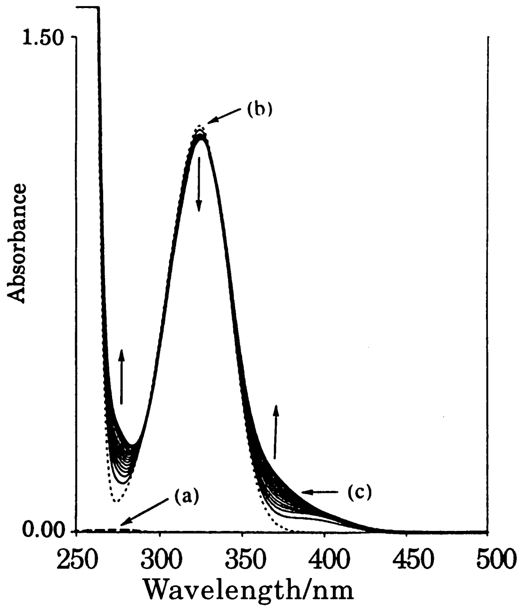


Fig. 3. UV-visible spectrum
(a) **1b** 1.25×10^{-4} M
(b) salicylaldehyde 3.75×10^{-4} M
(c) Spectral changes of reaction of (a) with (b)
Measurements were made every 30 mins.

References

1) F. Szabadvary, "Handbook on the Physics and Chemistry of Rare Earths," ed by K. A. Gschneidner, Jr. and L. Eyring, North-Holland (1988), Vol. 11, P.33.

2) P. H. Smith and K. N. Raymond, *Inorg. Chem.*, **24**, 3469 (1985).

3) P. H. Smith, Z. E. Reyes, Chi-Woo Lee, and K. N. Raymond, *Inorg. Chem.*, **27**, 4154 (1988).

4) **1a** : Yield, 34.7%. Anal. Found : C, 23.58 ; H, 3.89 ; N, 12.96%. Calcd for $GdC_{17}H_{36}N_8O_9S_3F_9\cdot CH_3CN$: C, 23.72 ; H,4.09 ; N,13.10%.

5) S. K. Chandra, P. Chakraborty, and A. Chakravorty, *J. Chem. Soc. Dalton Trans.*, **1993**, 863.

6) A. Malek, G. C. Dey, A. Nasreen, T. A. Chowdhury, and E. C. Alyea, *Synth. React. Inorg. Met.-Org. Chem.*, **9**, 145 (1979).

7) **2** : Yield, 37.9%. Anal. Found : C, 52.72 ; H, 4.47 ; N, 9.83%. Calcd for $GdC_{27}H_{27}N_4O_3\cdot 0.5\,CH_3CN$: C, 53.10 ; H, 4.54 ; N, 9.95%.

8) **3** : Yield, 85.4%. Anal. Found : C, 34.32 ; H, 4.08 ; N, 9.50%. Calcd for $LaC_{31}H_{44}N_8O_{11}F_9S_3\cdot 0.5\,C_2H_5OC_2H_5$: C, 34.53 ; H, 4.30 ; N, 9.76%.

(Received September 9, 1994)