

Reaction of Tris(2-aminoethyl)amine Coordinated to Lanthanum(III) and Gadolinium(III) with Salicylaldehyde

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Reaction of tris(2-aminoethyl)amine coordinated to lanthanum(III) and gadolinium(III) with salicylaldehyde afforded Schiff-base complexes of tris[2-(salicylideneamino)ethyl] amine. In this reaction, a lanthanum(III) complex, which was supposed to be a reaction intermediate, was also obtained and characterized by X-ray crystallography. However, such a reaction intermediate of gadolinium(III) complex was not isolated under similar conditions. This difference was applied to the mutual separation of lanthanum(III) and gadolinium(III).

The physico-chemical properties of the trivalent rare earth ions and their complexes in solution are remarkably similar to each other.¹ It is important to find differences in the reaction behavior of rare earth complexes for the extensive studies of the complexing properties of individual rare earth elements and for the attempts of their mutual separation.

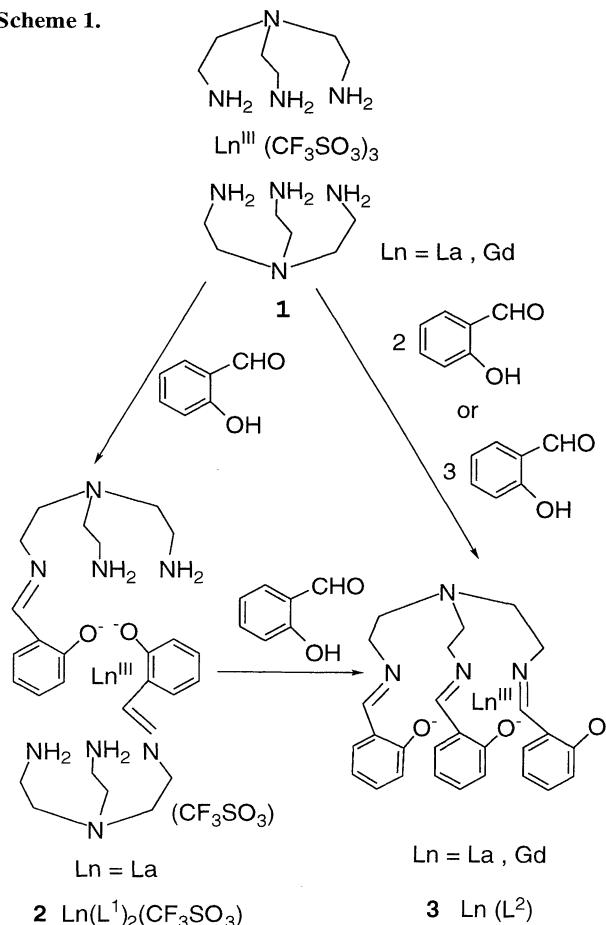
We have prepared praseodymium(III) and neodymium(III) complexes of tripodal heptadentate ligand, tris[2-(salicylideneamino)ethyl] amine (H_3L^2) from the complexes of 1,9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane(L^3)^{2,3} with salicylaldehyde.⁴ The reaction of tris(2-aminoethyl) amine (tren) and salicylaldehyde in the presence of praseodymium(III) or neodymium(III) salt gave identical products. The X-ray crystallographic analysis revealed that $Ln(L^2)$ ($Ln=Pr, Nd$) are novel examples of heptadentate complexes in which all the N_4O_3 donor atoms coordinate to the central metal ions. The first example of this type of complex in lanthanides is {tris(3-aza-4-methyl-6-oxohept-4-en-1-yl)amine}ytterbium(III).⁵ We have also found that the reaction of lanthanum(III) and gadolinium(III) complexes coordinated by the ligand L^3 with salicylaldehyde gave different type of Schiff-base complexes depending on the central metal ions.⁶ The solubility difference of the reaction products was applied to the mutual separation of lanthanum(III) and gadolinium(III).

In the present work, we have isolated a novel ten-coordinate lanthanum(III) complex **2** by the reaction of tren coordinated to lanthanum(III) with salicylaldehyde, while a gadolinium(III) complex **2** was not obtained (Scheme 1). The isolated lanthanum(III) complex **2** was supposed to be a reaction intermediate. The difference was applied to the mutual separation of lanthanum(III) and gadolinium(III).

Tren (4 mmol) was added to a solution of 2 mmol of $La(CF_3SO_3)_3$ in methanol (20 cm³) and stirred for 1 min at 40-50 °C. Then salicylaldehyde (6 or 4 mmol) was added to this solution ($La : tren : salicylaldehyde = 1 : 2 : 3$ or $1 : 2 : 2$) and stirred for 5 min at 40-50 °C. Yellow solid was precipitated while stirring. This product gave an IR band at 1623 cm⁻¹ due to C=N stretching vibration, but no bands corresponding to a primary amine nor to a trifluoromethanesulfonate anion were observed. The IR spectrum of this product is similar to those of the praseodymium(III) and neodymium(III) complexes of the tripodal ligand L^2 whose structures have been confirmed by X-ray

analysis.⁴ This information together with the elemental analysis⁷ suggested that the compound formed was **3**. Since **3** does not contain a trifluoromethanesulfonate anion, the ligand L^2 forms an inner-complex in which the ligand functions as a trivalent anionic ligand. Under lower salicylaldehyde ratio ; i.e., $La : tren : salicylaldehyde = 1 : 2 : 1$, yellow crystals of **2** were preferentially obtained in place of **3**. This product gave characteristic IR bands at 1628 cm⁻¹ ($\nu_{C=N}$), 3345 and 3289 cm⁻¹ (ν_{NH_2}). In addition, a broad band at 1260 cm⁻¹ associated with trifluoromethanesulfonate anion was observed. This information together with the elemental analysis⁸ suggested that the compound formed was **2** in which two sets of L^1 were coordinated to La^{3+} . The structure of **2** was determined by X-ray structural analysis.⁹ Molecular structure, atomic numbering scheme, and the selected bond distances of **2** are shown in Figure 1 where La^{3+} is coordinated by the eight nitrogen atoms and the two oxygen atoms. The apical nitrogen atoms (N1 and N5) cap the triangular face formed by the other three coordinating N

Scheme 1.



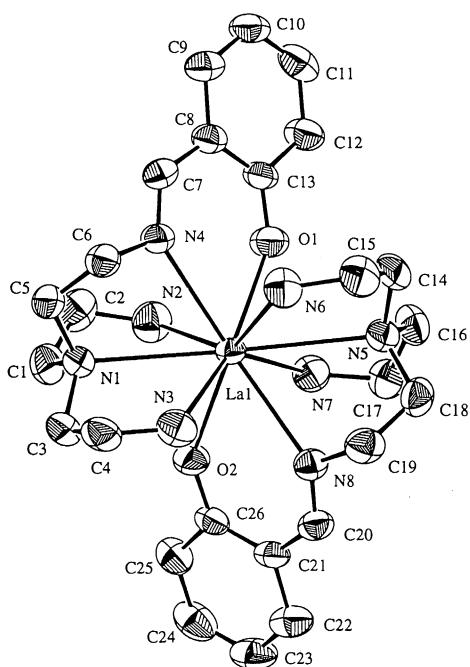


Figure 1. Molecular structure and atomic numbering of **2**. The counter anion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) : La1-O1, 2.423(4) ; La1-O2, 2.416(4) ; La1-N1, 2.939(4) ; La1-N2, 2.718(6) ; La1-N3, 2.773(6) ; La1-N4, 2.708(4) ; La1-N5, 2.952(5) ; La1-N6, 2.825(5) ; La1-N7, 2.707(5) ; La1-N8, 2.716(4).

atoms. The distances of apical nitrogens, N1 and N5, from the metal ion are greater than those of the other nitrogens, which has been commonly observed in other rare earth complexes with tren derivatives.^{3,4}

The lanthanum(III) complex **2** was supposed to be a reaction intermediate since **3** was obtained upon addition of salicylaldehyde to a solution of **2**.

On the other hand, in the case of a gadolinium(III) complex, only **3** was obtained as a yellow solid¹⁰ under the condition of Gd : tren : salicylaldehyde = 1 : 2 : 3 or 1 : 2 : 2. Several attempts including change of salicylaldehyde ratio and solvents were not successful to isolate the gadolinium(III) complex corresponding to **2**. Ten-coordinate gadolinium(III) complexes are less popular than the corresponding lanthanum(III) complexes. Ten-coordinate gadolinium(III) complex of **2** might be rather unstable due to a smaller ionic size of gadolinium(III) compared to that of lanthanum(III). Since the lanthanum(III) complex was preferentially precipitated under lower salicylaldehyde ratio, this system can be applicable to the mutual separation of lanthanum(III) and gadolinium(III).

Tren (8 mmol) was added to a solution of the mixture of $\text{La}(\text{CF}_3\text{SO}_3)_3$ and $\text{Gd}(\text{CF}_3\text{SO}_3)_3$ (2 mmol each) in hot methanol (20 cm³) and stirred for 1 min at 40-50 °C. Then salicylaldehyde

(4 mmol) was added to this solution (Ln : tren : salicylaldehyde = 1 : 2 : 1) and stirred for 5 min at 40-50 °C. This solution was evaporated to about 10 cm³. The product was precipitated as yellowish crystals on cooling for 3 days. The purity of La in the crystals was 91.9% for Gd (yield, 46.2%).

In conclusion, reaction of tren coordinated to lanthanum(III) and gadolinium(III) with salicylaldehyde gave Schiff-base complexes **3**. A lanthanum(III) complex **2**, which was supposed to be a reaction intermediate, was obtained as crystals at lower salicylaldehyde ratio. X-ray crystallographic analysis of **2** revealed that La^{3+} is coordinated by the eight nitrogen atoms and the two oxygen atoms. Under the condition of Ln : tren : salicylaldehyde = 1 : 2 : 1 (Ln = La, Gd), lanthanum(III) complex **2** was preferentially precipitated from the mixture, while gadolinium(III) complex remained in the solution.

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References and Notes

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- 7 **3** (Ln=La) : Yield, 72.2%. Anal. Found : C, 51.49 ; H, 5.04 ; N, 8.87%. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_4\text{O}_3\text{La} \cdot 2\text{H}_2\text{O}$: C, 51.44 ; H, 4.96 ; N, 8.89%.
- 8 **2** : Yield, 44.3%. Anal. Found : C, 41.07 ; H, 5.80 ; N, 13.53%. Calcd for $\text{C}_{26}\text{H}_{42}\text{N}_8\text{O}_2\text{La} \cdot \text{CF}_3\text{SO}_3 \cdot \text{CH}_3\text{OH}$: C, 41.08 ; H, 5.66 ; N, 13.69%.
- 9 Crystal data for **2** : $\text{C}_{26}\text{H}_{42}\text{N}_8\text{O}_2\text{La} \cdot \text{CF}_3\text{SO}_3 \cdot \text{CH}_3\text{OH}$, $M = 818.68$, monoclinic, space group $P2_1/a$, $a=19.491(5)$ Å, $b=18.493(9)$ Å, $c=19.533(4)$ Å, $\beta=95.52(2)^\circ$, $Z=8$, $V=7007(2)$ Å³, $D_c=1.552$ g/cm³. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda=0.71069$ Å). The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to $R = 0.037$ and $R_w = 0.053$ for 9788 observed reflections with $I \geq 3\sigma(I)$.
- 10 **3** (Ln=Gd) : Yield, 88.9%. Anal. Found : C, 51.24 ; H, 4.82 ; N, 8.48%. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_4\text{O}_3\text{Gd} \cdot \text{H}_2\text{O}$: C, 51.41 ; H, 4.63 ; N, 8.88%.