BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1862—1863 (1967)

Preparation of the Schiff Base Complexes of Lanthanide(III) Ions

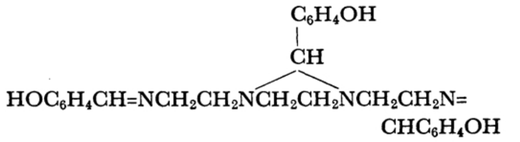
Toshiyuki Isobe,* Sigeo Kida** and Seizo Misumi*

**Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Fukuoka*
***Department of Chemistry, Wakayama University, Wakayama*

(Received February 6, 1967)

The 1 : 1 complexes of lanthanide(III) ions such as La(III), Pr(III), Nd(III), Gd(III) and Er(III) with tris-(salicylidene amino)-triethylenetetramine have been prepared. Among these complexes, the lanthanum(III) complex is unique in infrared spectra and solubility to the solvents; it is soluble in chloroform and nitrobenzene and found to be dimeric in chloroform solution. The other lanthanide(III) complexes are practically insoluble in any available solvents, and are assumed to be polymeric.

Tris - (salicylidene amino) - triethylenetetramine, (which will be abbreviated as (trien-S_3)H_3) was prepared from salicylaldehyde and triethylenetetramine as a multidentate ligand by Mukherjee,[1]



$$\begin{array}{c} C_6H_4OH \\ | \\ CH \\ HOC_6H_4CH{=}NCH_2CH_2NCH_2CH_2NCH_2CH_2N{=} \\ \qquad\qquad\qquad\qquad CHC_6H_4OH \end{array}$$

(trien-S_3)H_3.

However, Sarma *et al.*[2,3] found that when this compound reacts with metal ions such as, Co(III), Fe(III), Mn(III), Ga(III), Al(III), Co(II), Ni(II) and Cu(II), one molecule of salicylaldehyde is hydrolyzed from it, and the metal complexes of sexadentate ligand, $HOC_6H_4CH{=}NCH_2CH_2NHCH_2CH_2NHCH_2CH_2N{=}CHC_6H_4OH$, (which will be abbreviated as (trien-S_2)H_2), are formed. No metal complexes of (trien-S_3)$^{3-}$ have ever been obtained, in spite of their elaborated investigations.

In this investigation we have isolated and characterized (trien-S_3)$^{3-}$ complexes of La(III), Pr(III), Nd(III), Gd(III) and Er(III).

Experimental

Preparation. *(trien-S_3)H_3.* The methanol solutions of triethylenetetramine and salicylaldehyde were mixed in 1 : 3 mol ratio. After heating at 60°C for a few minutes, ether was added to this mixture, and the yellow crystals were separated, filtered and recrystallized from methanol solution. Mp 103—104°C.

Found: C, 70.15; H, 6.59; N, 12.32%. Calcd for $C_{27}H_{30}N_4O_3$: C, 70.72; H, 6.59; N, 12.22%.

La(trien-S_3). One millimole (0.458 g) of (trien-S_3)H_3 was dissolved in 20 m*l* of ammoniacal methanol (~pH 8). To this solution was added 1 mmol (0.448 g) of lanthanum(III) perchlorate dissolved in 5 m*l* of methanol, and heated at 60°C for a few minutes unitl the white precipitate was formed. After cooling, the precipitate was filtered, washed with methanol, and purified by recrystallization from chloroform solution. This compound was also obtained by adding the methanol solution of 1 mmol of triethylenetetramine to the mixture of 1 mmol of lanthanum(III) perchlorate and 3 mmol of salicylaldehyde in methanol, and boiling the mixed solution for a few minutes.

The compound is colorless plates, and slightly soluble in methanol, fairly soluble in chloroform and nitrobenzene and practically insoluble in other solvents.

Found: La, 23.2; C, 54.23; H, 4.63; N, 9.50%. Calcd for $LaC_{27}H_{27}N_4O_3$: La, 23.3; C, 54.55; H, 4.58; N, 9.50%.

M(trien-S_3), M=Pr, Nd, Gd, and Er. These compounds were prepared by the same method as described above except using Pr(III)-, Nd(III)-, Gd(III)- and Er(III)-perchlorate instead of lanthanum(III) perchlorate. However, since these compound were practically insoluble in any available solvents, purification through recrystallization was not in practice.

Found: Pr, 23.4; C, 53.09; H, 4.73; N, 9.20%. Calcd for $PrC_{27}H_{27}N_4O_3$: Pr, 23.6; C, 54.37; H, 4.56; N, 9.39%.

Found: Nd, 23.5; C, 52.90; H, 4.65; N, 9.32%. Calcd for $NdC_{27}H_{27}N_4O_3$: Nd, 24.0; C, 54.07; H, 4.54; N, 9.34%.

Found: Gd, 25.5; C, 51.00; H, 4.59; N, 8.97%. Calcd for $GdC_{27}H_{27}N_4O_3$: Gd, 25.7; C, 52.92; H, 4.44; N, 9.14%.

Found: Er, 26.0; C, 50.51; H, 4.41; N, 8.87%. Calcd for Er $C_{27}H_{27}N_4O_3$: Er, 26.9; C, 52.07; H, 4.37; N, 9.00%.

Measurements. The infrared spectra were measured in KBr and in H. C. B. mull in the region of 4000—650 cm^{-1} by using a Hitachi EPI-S2 infrared spectrophotometer.

The UV spectra were obtained by a Hitachi ESP-2 spectrophotometer.

The molecular weight determination was carried out in chloroform solution by a Vapor Pressure Osmometer of Mechrolab Co.

---

[1] A. K. Mukherjee, *Science and Culture,* **19**, 107 (1953).

[2] B. D. Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.,* **77**, 5476 (1955).

[3] B. D. Sarma, K. R. Lay, R. E. Sievers and J. C. Bailar, Jr., *ibid.,* **86**, 14 (1964).

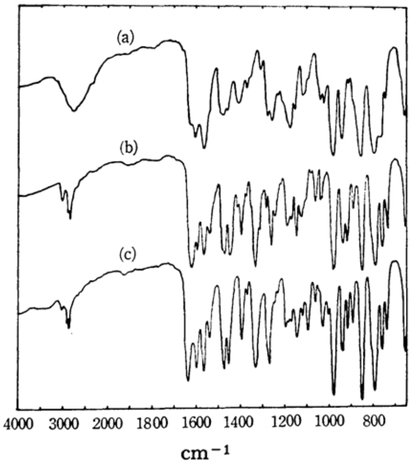


Fig. 1. Infrared spectra.
(a) (trien-S_3)H_3; (b) La(trien-S_3);
(c) Pr(trien-S_3) in HCB mull.
The spectra of the Nd(III), Gd(III) and Er(III) complexes are same as (c).

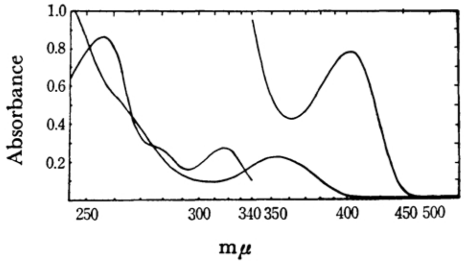
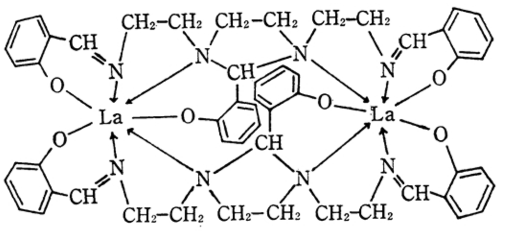


Fig. 2. Electronic spectra.
(a) (trien-S_3)H_3 (a_1: 3.49×10^{-5} mol/l, a_2: 3.49×10^{-4} mol/l) in methanol.
(b) La(trien-S_3) (3.64×10^{-5} mol/l) in chloroform.

Results and Discussion

As is shown in Fig. 1, in the infrared spectra of the lanthanide(III) complexes no absorptions were observed in the regions of $\sim$1100 cm^{-1} and 3000—3500 cm^{-1}. This indicates that ClO_4^-, -OH, H_2O and $\rangle$NH groups do not exsist in those complexes. Thus, the infrared spectra support the experimental formula M(trien-S_3) (where M represents for a lanthanide(III) ion), derived from the elementary analysis, since any alternative constitutions would fail to give rigorous understanding of the spectra.

The steric consideration has led to the conclusion that the ligand, (trien-S_3)$^{3-}$ could not form a heptadentate chelate with one metal ion. In fact, the molecular weight of the lanthanum(III) complex has been determined to be 1172 which is very close to the value, 1188, calculated for the dimeric complex, La_2(trien-S_3)$_2$. The most probable structure of the lanthanum(III) complex may be shown as:



It is remarkable that among the lanthanide(III) complexes of (trien-S_3)$^{3-}$, only the lanthanum(III) complex is soluble in chloroform and nitrobenzene, while the other complexes are insoluble in any available solvents. The infrared spectra of these complexes are practically identical except the lanthanum(III) complex as seen in Fig. 1. These facts suggest that the lanthanide(III) complexes of (trien-S_3)$^{3-}$ other than the lanthanum(III) complex have polymeric structure.

It is interesting that the lanthanide(III) ions react with (trien-S_3)H_3 to form (trien-S_3)$^{3-}$ complexes and there was no indication of the hydrolysis of (trien-S_3)H_3 to form a (trien-S_2)$^{2-}$ complex losing one molecule of salicylaldehyde as was reported[2,3] in the cases of the other metal ions. This seems to be due to the fact that the coordination number and the coordination positions are not so rigid in lanthanide(III) ions as in other metal ions, since metal-ligand linkage of lanthanide(III) complexes is mainly ionic and the ionic radii of lanthanide(III) ions are relatively large. However, it should be noted that the UV spectrum of (trien-S_3)H_3 has been seriously changed upon the complex formation with a lanthanum (III) ion as shown in Fig. 2. This fact implies that the electronic state of the ligand has been considerably affected by the formation of coordination bond with a lanthanum(III) ion.

The authors wish to thank Professor H. Saikachi of Kyushu University for the measurement of the molecular weight. This work was supported in part by the grants of the Ministry of Education and of the Japan Society for the Promotion of Science, to which authors' thanks are due.