Preparation of a Novel Schiff Base Complex of Lanthanum(III)

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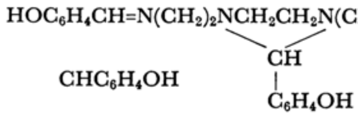
A Schiff base,



$$HOC_6H_4CH{=}N(CH_2)_2\underbrace{NCH_2CH_2N}_{\substack{CH\\|\\C_6H_4OH}}(CH_2)_2N{=}CHC_6H_4OH$$

$(TS_3)H_3$

from triethylenetetramine and salicylaldehyde was reported as a multidentate ligand by Mukkerjee.¹⁾ Sarma et al.²˒³⁾ have found that when the base, $(TS_3)H_3$, reacts with such metal ions as cobalt(III), iron(III), manganese(III), gallium(III), aluminum(III), cobalt(II), nickel(II) and copper(II), one molecule of salicylaldehyde is hydrolyzed and a metal complex of a sexadentate ligand, HOC_6H_4-$CH{=}N(CH_2)_2NH(CH_2)_2NH(CH_2)_2N{=}CHC_6H_4$-$OH$ $(TS_2)H_2$, is formed. No metal complexes of TS_3 have ever been obtained as pure crystals, in spite of the elaborated investigations.

In this paper we report the preparation of a metal complex of $(TS_3)^{3-}$ using lanthanum(III) ion as a central metal.

White crystals, which were prepared from lanthanum(III) perchlorate and $(TS_3)H_3$ in methanol, were found by the elementary analysis to have the formula of $La(TS_3)$ (Found: C, 54.23; H, 4.63; N, 9.50; La, 23.2. Calcd. for $LaC_{27}H_{27}N_4O_3$: C, 54.55; H, 4.58; N, 9.42; La, 23.3%). The infrared spectrum supported our present conclusion, since no N–H, O–H and ClO_4^- bands were observed in 3500—3000 and 1100 cm^{-1} region. Although this ligand has seven coordination atoms, it is sterically impossible for this ligand to form a heptadentate chelate with one metal ion. The molecular weight determination by the use of the "Vapor Pressure Osmometer" has shown that this compound is dimeric, and the structure as shown in Fig. 1 is assumed as the most probable one.

It appears that the formation of TS_3 complex is due to the fact that the coordination number and coordination place are not so rigid in lanthanide(III) ions as in other metal ions, since metal-ligand linkage of the lanthanum(III) complex is mainly ionic and the ionic radius of lanthanum(III) ion is relatively large.

The preparation of similar complexes of a series of lanthanide ions is in progress. The results will be reported shortly with the more detailed discussion on the structures of this type of compounds.

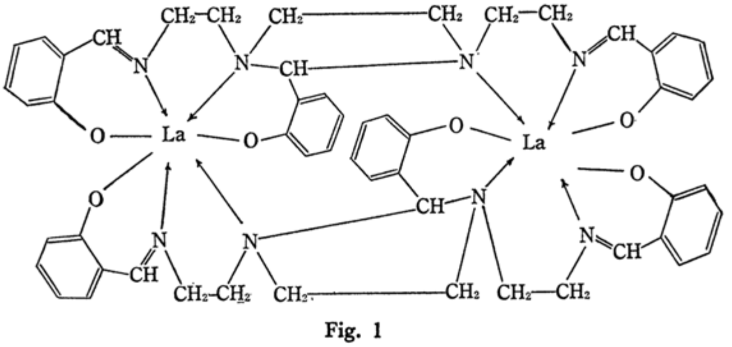


Fig. 1

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