The Synthesis of Lanthanide(III) Complexes with Schiff Bases Obtained from Salicylaldehyde

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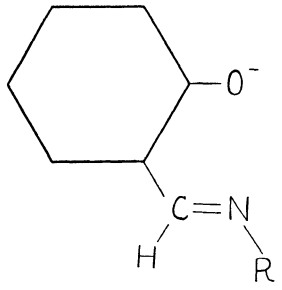
(Received March 22, 1971)

There have been only a few papers available on lanthanide(III) complexes with Schiff bases as ligands.[1-3] Complexes with *N*-*n*-alkylsalicylideneiminates (I,



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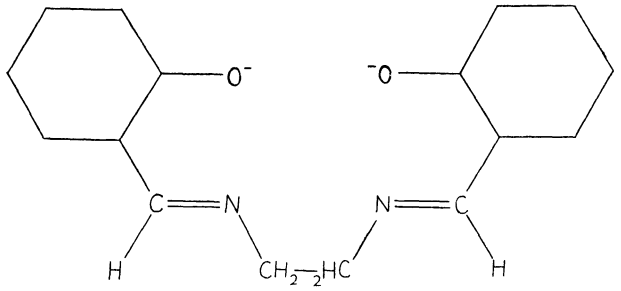
abbreviated as SAL·R) have not been reported in literature. With *N*,*N*′-ethylenebis(salicylideneiminate) (II, abbreviated as SALen), complexes of types $Ln_2(SALen)_3$ and $Ln_2(SALen)_3 \cdot nL$ were previously reported, L being H_2O and C_2H_5OH, and Ln a lanthanide(III)



II

ion. However, some properties, such as colour, solubility and melting point, widely differ from those of the complexes of a similar composition obtained in the present work. The method of preparation employed in the previous work differs from the present one, and recrystallization was not possible in the previous work, whereas the complexes were purified by recrystallization from organic solvents in our case. The present communication deals with tris(*N*-methylsalicylideneiminato)- and *N*,*N*′-ethylenebis(salicylideneiminato)-lanthanide(III) complexes.

Complexes of the type $Ln(SAL \cdot CH_3)_3 \cdot nH_2O$ were synthesized in the following way. To preformed *N*-methylsalicylideneimine (0.033 mol) was added lanthanide(III) chloride hydrate (0.01 mol), and the mixture was ground for about 1 hr, until it nearly solidified. No solvent was used in this process. The powder obtained was recrystallized from methanol or ethanol. They are soluble in methanol and ethanol, and slightly soluble in acetone and chloroform. The cerium(III) and neodymium(III) complexes are brownish orange and yellowish orange, respectively.

TABLE 1. ANALYTICAL DATA OF THE COMPLEXES OF THE TYPES $Ln(SAL \cdot CH_3)_3 \cdot nH_2O$ (COMPLEX I) AND $Ln_2(SALen)_3 \cdot nH_2O$ (COMPLEX II)

Ln	*n*	mp °C	Found, %			Calcd, %		
			C	H	N	C	H	N
Complex I								
Ce	4	159—161	46.40	5.05	6.55	46.90	5.25	6.84
Nd	3	259—261	48.21	4.94	6.90	47.98	5.03	6.99
Complex II								
Nd	4	227—229	46.61	4.54	6.44	46.81	4.75	6.83
Sm	4	275—277	45.56	4.53	7.14	46.35	4.70	6.76
Eu	4	164—166	45.98	4.50	6.22	46.23	4.69	6.74
Tb	3	167—169	47.37	4.33	6.71	47.07	4.44	6.86
Er	3	178—180	45.88	4.32	7.10	46.40	4.38	6.76

The complexes of the type $Ln_2(SALen)_3 \cdot nH_2O$ were prepared as follows. To a solution of *N*,*N*′-ethylenebis(salicylideneimine) (0.005 mol) in ethanol (10 ml) was added lanthanide(III) chloride hydrate (0.015 mol), and the resulting solution was stirred for 1 hr at about 40°C. The precipitate was filtered off and purified by recrystallization from methanol or ethanol. The complexes are soluble in methanol and ethanol, but slightly soluble in chloroform and acetone. They are yellow and show melting points as given in Table 1. The complexes reported previously melted with decomposition above 300°C, and were not soluble in common organic solvents.

Analytical data of the complexes are shown in Table 1.

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2) T. Isobe, S. Kida, and S. Misumi, This Bulletin, **40**, 1862 (1967).
3) S. Yamada, K. Yamanouchi, and H. Kuma, *Synth. Inorg. Metalorg. Chem.*, **1**, 9 (1971).