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Mono-, Di- and Tri-ethanolamine Derivatives of Samarium

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Reactions of samarium isopropoxide with mono-, di- and tri-ethanolamines have been studied in presence of benzene. The reaction between samarium isopropoxide and monoethanolamine in different molar ratios gave mono-, di- and tri- derivatives. Compound Sm(dieth. am)(OPr^{i}) is formed when samarium isopropoxide (1 mol) reacted with diethanolamine (1 mol), whereas the reaction in the molar ratio of 2 : 3 yielded Sm_2(dieth. am)$_3$. All the three moles of isopropanol were liberated when an equimolecular quantities of samarium isopropoxide and triethanolamine were allowed to react with the isolation of samarium triethanolaminate. The only soluble compounds being Sm(monoeth.am) $(OPr^{i})_2$ and its corresponding tertiary butanol derivative, Sm(moneth. am)$(OBu^{t})_2$. Attempts to distil some of these compounds were unsuccessful, as these decompose on being heated under reduced pressure.

A considerable amount of work has been carried out on the ethanolamine derivatives of boron[1], aluminum[2], titanium[3], tin[4], germanium[5], niobium and tantalum[6]. Further, it has been observed that the amino ($-NH_2$) and imino ($\rangle NH$) groups of the mono- and diethanolamines do not appear to take part in the replacement reactions with the alkoxides of boron, aluminium and titanium and only the hydroxylic hydrogen was reported to be reactive. However, with germanium, tin, niobium and tantalum alkoxides, both the hydroxyl as well as amino or imino hydrogen of mono- or di-ethanolamines have been reported active in the replacement reactions.

A survey of the literature reveals that no study has been made on the ethanolamine derivatives of samarium. It was, therefore, considered of interest to carry out the reactions of samarium isopropoxide with mono-, di- and tri- ethanolamines.

The reactions between samarium isopropoxide and monoethanolamine were found to proceed stoichiometrically in the following manner:

$$Sm(OPr^{i})_3 + H_2NCH_2CH_2OH \rightarrow$$
$$Sm(OPr^{i})_2(OCH_2CH_2NH_2) + Pr^{i}OH$$

soluble in benzene

(I)

$$Sm(OPr^{i})_3 + 2H_2NCH_2CH_2OH \rightarrow$$
$$Sm(OPr^{i})(OCH_2CH_2NH_2)_2 + 2Pr^{i}OH$$

Sparingly soluble in benzene

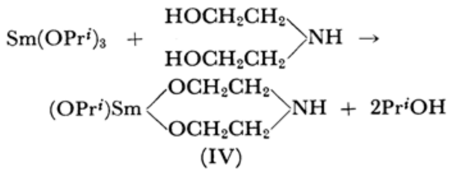
(II)

$$Sm(OPr^{i})_3 + 3H_2NCH_2CH_2OH \rightarrow$$
$$Sm(OCH_2CH_2NH_2)_3 + 3Pr^{i}OH$$

insoluble in benzene

(III)

The reactions between samarium isopropoxide and diethanolamine in the molar ratio of 1 : 1 liberated 2 mol of isopropanol forming the product (IV), insoluble in benzene. However, when the above reaction was carried out with molar ratio of 2 : 3, amost all the isopropanol was liberated yielding a benzene insoluble product (V). The reaction in molar ratio of 1 : 2 also liberated all the 3 mol of isopropanol, yielding a similar type of benzene insoluble product (VI). These reactions, thus, can be represented by the following equations:



$$Sm(OPr^{i})_3 + \begin{matrix} HOCH_2CH_2 \\ HOCH_2CH_2 \end{matrix}\rangle NH \rightarrow (OPr^{i})Sm\langle\begin{matrix} OCH_2CH_2 \\ OCH_2CH_2 \end{matrix}\rangle NH + 2Pr^{i}OH$$

(IV)

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1) R. C. Mehrotra and G. Srivastava., *J. Indian Chem. Soc.*, **39**, 521 (1962).

2) R. C. Mehrotra and R. K. Mehrotra., *ibid.*, **39**, 677 (1962).

3) D. M. Puri and R. C. Mehrotra., *ibid.*, **39**, 447 (1962).

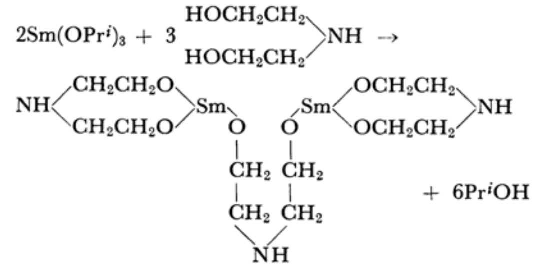
4) V. D. Gupta., Ph. D. Thesis, Rajasthan University (1965).

5) G. Chandra., Ph. D. Thesis, Rajasthan University (1963).

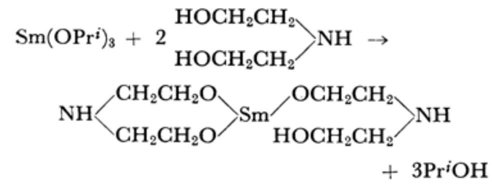
6) P. N. Kapoor., Ph. D. Thesis, Rajasthan University (1965).

TABLE 1. REACTIONS OF SAMARIUM ISOPROPOXIDE WITH MONO-, DI- AND TRIETHANOLAMINES IN THE PRESENCE OF BENZENE

Reaction mixture in benzene	Molar ratio	Products and State	Amount of alcohol in the azeotrope		Analysis of the compounds			
					Found		Calcd.	
			Found g	Calcd. g	Sm %	N %	Sm %	N %
$Sm(OPr^i)_3$ + Monoethanolamine (1.251 g) (0.232 g)	1 : 1	$Sm(OPr^i)_2(OC_2H_6N)$ Faint yellowish brown solid (1.26 g)	0.231	0.233	45.2	4.12	45.7	4.26
$Sm(OPr^i)_3$ + Monoethanolamine (1.899 g) (0.748 g)	1 : 2	$Sm(OPr^i)(OC_2H_6N)_2$ Faint yellowish brown solid (1.91 g)	0.742	0.744	44.9	8.38	45.6	8.48
$Sm(OPr^i)_3$ + Monoethanolamine (1.791 g) (1.032 g)	1 : 3	$Sm(OC_2H_6N)_3$ Yellowish brown solid (1.84 g)	1.020	1·029	45.0	12.61	45.5	12.70
$Sm(OPr^i)_3$ + Diethanolamine (1.141 g) (0.372 g)	1 : 1	$Sm(OPr^i)(C_4H_9O_2N)$ Faint yellow solid (1.03 g)	0.427	0.420	49.2	4.37	48.1	4.48
$Sm(OPr^i)_3$ + Diethanolamine (1.229 g) (0.603 g)	2 : 3	$Sm_2(C_4H_9O_2N)_3$ Faint yellow solid (1.13 g)	0.664	0.676	50.1	6.80	49.3	6.88
$Sm(OPr^i)_3$ + Diethanolamine (1.233 g) (0.802 g)	1 : 2	$Sm(C_4H_9O_2N)(C_4H_{10}O_2N)$ Faint yellow solid (1.30 g)	0.622	0.676	41.2	7.77	42.0	7.83
$Sm(OPr^i)_3$ + Triethanolamine (1.034 g) (0.550 g)	1 : 1	$Sm(C_6H_{12}O_3N)$ Faint yellow solid (0.90 g)	0.568	0.568	49.2	4.41	50.1	4.79
$Sm(OPr^i)_2(OC_2H_6N)$ + Bu^tOH (0.95 g) (10.2 g)	1 : excess	$Sm(OBu^t)_2(OC_2H_6N)$ Withish yellow solid (0.96 g)	0.342	0.347	43.2	3.86	42.2	3.93

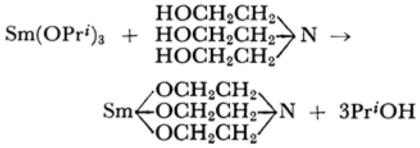


(V)



(VI)

When the reaction of samarium isopropoxide with tri-ethanolamine was carried out in equimolar quantities in the presence of benzene, all the three moles of isopropanol was liberated giving benzene insoluble triethanolaminate (VII) according to the equation:



(VII)

The technique of the above reactions was to add the required amounts of ethanolamines to a benzene solution of samarium isopropoxide. The contents were refluxed under a column for about five hours after which the binary azeotrope of isopropanol liberated during the course of each reaction was fractionated out carefully with benzene. It was observed in the reactions with di- and tri- ethanolamines that the product was thrown out as the reaction proceeds and after two hours most of the products were isolated from the reaction mixture.

The interchange reaction of the benzene soluble product (I) with *t*-butanol was also carried out in the presence of benzene when all the isopropoxide groups were replaced by tertiary butoxide groups yielding the corresponding product (VIII), soluble in benzene:

$$\mathrm{Sm(OPr^{\mathit{i}})_2(OCH_2CH_2NH_2) + 2Bu^{\mathit{t}}OH \rightarrow}$$
$$\mathrm{Sm(OBu^{\mathit{t}})_2(OCH_2CH_2NH_2) + 2Pr^{\mathit{i}}OH}$$

Attempts to distil these compounds were unsuccessful and these derivatives decomposed on being heated to a high temperature under reduced pressure. On account of the insoluble nature of the most of these products, their molecular weights could not be determined ebullisocopically.

Experimental

An all glass apparatus with 'Quickfit' interchangeable joints was used. Fractionations were carried out in a column packed with Raschig rings and fitted to a total condensation variable take-off stillhead.

Samarium isopropoxide was prepared from samarium chloride (Johnson & Matthey, London) as described by Sankhla, Misra and Kapoor[7] and was analysed before use. Mono-, di- and triethanolamines (Dr. Theodor Schuchardt GMBH & Co) were distilled before use. Tertiary butanol was dried by distilling over sodium *t*-butoxide.

Samarium was estimated by igniting the compounds to its sesquioxide (Sm_2O_3). Isopropanol in the azeotrope was estimated by oxidation with normal $K_2Cr_2O_7$ in 12.5% sulphuric acid[8]. Nitrogen was estimated by the Kjeldahl's method.

Reactions

1) Reaction between Samarium Isopropoxide and Monoethanolamine in the Presence of Benzene (Molar Ratio 1 : 1).

Monoethanolamine (0.232 g) was added to a light yellow solution of samarium isopropoxide (1.251 g) in benzene (56 g). The contents were refluxed under a column at low bath temperature for about 6 hr and the isopropanol liberated during the course of above reaction was fractionated out carefully with benzene. The excess benzene was then collected into a separate flask at 80°C. On drying the product under reduced pressure at the room temperature, a benzene soluble light yellowish brown compound was obtained (yield, 1.26 g).

Found: Sm, 45.2; N, 4.12%. Calcd for $\mathrm{Sm(OPr^{\mathit{i}})_2(OCH_2CH_2NH_2)}$: Sm, 45.7; N, 4.26%. Alc. (Lib), 0.231 g: Alc. (Calcd), 0.233 g.

The above compound was tried for sublimation when on heating under reduced pressure at 280°C/0.1 mmHg, a deep brown residue was left. (% of samarium in the decomposed product, 68.95.)

Other reactions of mono-, di- and tri-ethanolamines with samarium isopropoxide in different molar ratios and the interchange reaction are given in Table 1.

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[7] B. S. Sankhla, S. N. Misra and R. N. Kapoor., *Chem. & Ind.*, **1965**, 382.

[8] D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, **1950**, 3450.