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Schiff Base Derivatives of Lanthanons

Bifunctional Tridentate Schiff Base Derivatives of La(III), Pr(III), and Nd(III)

By

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Bifunctional tridentate Schiff bases such as,

$$HOC_6H_4C(CH_3):NCH_2CH_2OH,$$
$$HOC_6H_4C(CH_3):NCH_2CH(OH)CH_3,$$
$$HOC_6H_4C(H):NCH_2CH_2OH$$

and $HOC_6H_4C(H):NCH_2CH(OH)CH_3$ react with La(III), Pr(III) and Nd(III) isopropoxides to 1 : 1 and 2 : 3 derivatives of the type, $Ln(O—i\text{-}C_3H_7)(OC_6H_4C[R]:NR'O)$ and $Ln_2(OC_6H_4C[R]:NR'O)_3$ [where, Ln = La(III), Pr(III) or Nd(III); R = CH_3 or H and R′ = $CH_2—CH_2$ or CH_2CHCH_3] in dry benzene. The labile nature of the isopropoxy groups in the 1 : 1 derivatives has been shown by exchange reactions with an excess of *t*-butyl alcohol leading to the formation of $Ln(O—t\text{-}C_4H_9)(OC_6H_4C[R]:NR'O)$; (where R = CH_3 and R′ = CH_2CHCH_3) type derivatives in almost quantitative yield. The IR spectra of the resulting derivatives have been recorded in the range of 4000–400 cm^{-1}. ν C=N frequency bands appear at ≈ 1620 cm^{-1} and almost no change has been noted in their positions on complexation. Some new peaks are, however, observed in the range of 700–600 cm^{-1} and these may be ascribed to the ring deformation coupled with both the *Ln*—O stretching and C—CH_3 stretching modes.

Introduction

Different molar reactions between the isopropoxides of La(III), Pr(III), and Nd(III) and the monofunctional bidentate Schiff bases like benzylidene-2-hydroxy-*n*-alkylamines, benzylidene-o-aminophenol, 2-hydroxy-1-naphthylidene-*n*-butylamine, 2-hydroxy-1-naphthylidene-aniline, o-hydroxy-acetophenone-*n*-butylimine and o-hydroxyacetophenoneanil have been reported in earlier studies from these laboratories and some interesting results regarding the volatility, polymerisation and coordination number of the resulting products described[1–3].

A survey of the literature, however, reveals that studies on the reactions of the lanthanide isopropoxides with bifunctional tridentate Schiff bases have not so far been reported. In the present paper, reactions of lanthanide isopropoxides with bifunctional tridentate Schiff bases, $HOC_6H_4C(R):NR'OH$ [where, $R = CH_3$ or H and $R' = CH_2CH_2$ or CH_2CHCH_3; the resulting Schiff bases are salicylidene-2-hydroxyethylamine (**1**), salicylidene-2-hydroxy-*n*-propylamine (**2**), o-hydroxyacetophenone-2-hydroxyethylimine (**3**) and o-hydroxyacetophenone-2-hydroxy-*n*-propylimine (**4**)] have been investigated.

Experimental

La(III), Pr(III) and Nd(III) isopropoxides were prepared by the sodium alkoxide method[4]. Schiff bases were prepared by the condensation of salicylaldehyde or o-hydroxyacetophenone with the equimolar amount of 2-hydroxyethylamine or 2-hydroxy-*n*-propylamine in benzene; and these were distilled in a high vacuum (1 torr) before use. Salicylidene-2-hydroxyethylamine and salicylidene-2-hydroxy-*n*-propylamine are yellow liquids and o-hydroxyacetophenone-2-hydroxyethylimine and o-hydroxyacetophenone-2-hydroxy-*n*-propylimine are yellow solids.

Salicylidene-2-hydroxyethylamine (**1**), b.p.$_1$ 137–139 °C

$C_9H_{11}NO_2$. Found C 65.30, H 6.50, N 8.45%.
Calc. C 65.44, H 6.71, N 8.48%.

Salicylidene-2-hydroxy-n-propylamine (**2**), b.p.$_1$ 136–139 °C

$C_{10}H_{13}NO_2$. Found C 66.97, H 7.62, N 7.79%.
Calc. C 67.01, H 7.31, N 7.81%.

o-Hydroxyacetophenone-2-hydroxyethylimine (**3**), m.p. 95–96 °C, b.p.$_1$ 160 °C

$C_{10}H_{13}NO_2$. Found C 67.20, H 7.91, N 7.73%.
Calc. C 66.96, H 7.31, N 7.81%.

o-Hydroxyacetophenone-2-hydroxy-n-propylimine (**4**), m.p. 90–92 °C, b.p.$_1$ 161 °C

$C_{11}H_{15}NO_2$. Found C 68.98, H 8.35, N 7.15%.
Calc. C 68.42, H 7.83, N 7.24%.

Analytical Methods

La(III), Pr(III) and Nd(III) were determined by complexometric titrations with *EDTA* using Eriochrome Black T as the indicator[5] and nitrogen was estimated by *Kjeldahls'* method. The isopropylalcohol liberated in the reaction was estimated by an oxidation method[6].

Molecular weights were determined by semimicro ebulliometer (Gallenkamp) using thermistor sensing. The IR spectra were recored by Perkin-Elmer 337 Grating Infrared spectrophotometer using KBr optics.

Reactions

Synthesis of La(III), Pr(III) and Nd(III) Schiff base complexes

On mixing Schiff bases with the lanthanide isopopoxide in 1 : 1 and 2 : 3 molar ratios in dry benzene, slight heat was produced. The experimental technique was the same as described earlier[1–3].

The details of these reactions as well as the resulting products are summarized in Table 1.

Exchange reactions of isopropoxy lanthanide Schiff base derivatives

t-Butyl alcohol (in excess) was mixed with the solution of the isopropoxy lanthanide Schiff base derivatives in presence of dry benzene. The solution was refluxed under a fractionation column and the azeotrope collected slowly, till the distillate attained a constant temperature of 80 °C. The resulting compounds (Table 2) were dried under reduced pressure.

Results and Discussion

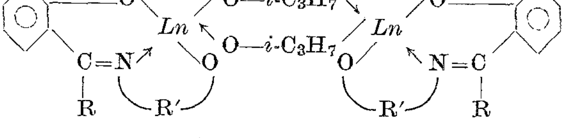
1 : 1 and 2 : 3 molar reactions of bifunctional tridentate Schiff bases with the isopropoxides of lanthanide may be represented by the following equations:

$$Ln(O\text{—}i\text{-}C_3H_7)_3 + OHC_6H_4C(R):NR'OH \rightarrow$$
$$\rightarrow Ln(O\text{—}i\text{-}C_3H_7)(OC_6H_4C[R]:NR'O) + 2\, i\text{-}C_3H_7OH$$

$$2\, Ln(O\text{—}i\text{-}C_3H_7)_3 + 3\, OHC_6H_4C(R):NR'OH \rightarrow$$
$$\rightarrow Ln_2(OC_6H_4C[R]:NR'O)_3 + 6\, i\text{-}C_3H_7OH$$

The reactions leading to the formation of isopropoxy Schiff base derivatives of salicylidene-2-hydroxyethylamine and salicylidene-2-hydroxy-*n*-propylamine were found to be exothermic, followed by the separation of a yellow compound immediately after mixing the reactants.

The ebullioscopic determinations of molecular weights in boiling benzene show it to be dimeric, the dimerisation possibily taking place through isopropoxy bridges as shown below:



[where, Ln = La(III) or Nd(III); R = CH_3 and R′ = CH_2CH_2 or CH_2CHCH_3].

The bis-lanthanide tris-Schiff base derivatives are also non-volatile and yellow solids. The soluble ones have been found to be monomeric

Table 1. *Reactions of La(III), Pr(III), and Nd(III) Isopropoxides with Schiff Bases*

Ln(O—*i*-C_3H_7)$_3$ (g)	Schiff base (g)	Molar ratio	Refluxing time (hrs.)	Product and Characteristics	2-Propanol in the azeotrope Found (Calcd.)	Analysis, % *Ln* Found (Calcd.)	Analysis, % N Found (Calcd.)	Molecular weight Found (Calcd.)	Molecular Association
La(O—*i*-C_3H_7)$_3$ 0.64	**1**, $C_9H_{11}NO_2$ 0.33	1 : 1	16	La(O—*i*-C_3H_7)($C_9H_9NO_2$) Yellow solid insoluble in benzene	0.24 (0.24)	38.44 (38.48)	3.97 (3.87)	—	—
La(O—*i*-C_3H_7)$_3$ 1.30	**1**, $C_9H_{11}NO_2$ 1.20	2 : 3	24	$La_2(C_9H_9NO_2)_3$ Yellow solid, insoluble in benzene	0.70 (0.74)	36.20 (36.21)	5.38 (5.47)	—	—
La(O—*i*-C_3H_7)$_3$ 0.57	**2**, $C_{10}H_{13}NO_2$ 0.32	1 : 1	16	La(O—*i*-C_3H_7)($C_{10}H_{11}NO_2$) Yellow solid, insoluble in benzene	0.21 (0.21)	37.06 (37.02)	3.80 (3.73)	—	—
La(O—*i*-C_3H_7)$_3$ 0.68	**2**, $C_{10}H_{13}NO_2$ 0.57	2 : 3	24	$La_2(C_{10}H_{11}NO_2)_3$ Yellow solid, insoluble in benzene	0.37 (0.38)	34.34 (34.34)	5.15 (5.18)	—	—
La(O—*i*-C_3H_7)$_3$ 0.54	**3**, $C_{10}H_{13}NO_2$ 0.30	1 : 1	16	La(O—*i*-C_3H_7)($C_{10}H_{11}NO_2$) Yellow solid, soluble in benzene	0.20 (0.20)	37.10 (37.02)	3.69 (3.73)	768 (375)	2.0

$La(O—i\text{-}C_3H_7)_3$	**3**, $C_{10}H_{13}NO_2$	1 : 2	24	$La_2(C_{10}H_{11}NO_2)_3$	0.35	34.38	5.21	—	—
0.63	0.53			Yellow solid, sparingly soluble in benzene	(0.35)	(34.34)	(5.18)		
$La(O—i\text{-}C_3H_7)_3$	**4**, $C_{11}H_{15}NO_2$	1 : 1	16	$La(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$	0.24	35.62	3.63	792	2.0
0.51	0.31			Yellow solid, soluble in benzene	(0.24)	(35.71)	(3.59)	(389)	
$La(O—i\text{-}C_3H_7)_3$	**4**, $C_{11}H_{15}NO_2$	1 : 2	24	$La_2(C_{11}H_{13}NO_2)_3$	0.32	32.66	4.88	—	—
0.56	0.51			Yellow solid, sparingly soluble in benzene	(0.32)	(32.63)	(4.93)		
$Pr(O—i\text{-}C_3H_7)_3$	**1**, $C_9H_{11}NO_2$	1 : 1	16	$Pr(O—i\text{-}C_3H_7)(C_9H_9NO_2)$	0.31	38.70	3.97	—	—
0.85	0.44			Yellow solid, insoluble in benzene	(0.32)	(38.78)	(3.85)		
$Pr(O—i\text{-}C_3H_7)_3$	**1**, $C_9H_{11}NO_2$	1 : 2	24	$Pr_2(C_9H_9NO_2)_3$	0.40	36.54	5.37	—	—
0.72	0.56			Yellow solid, insoluble in benzene	(0.40)	(36.55)	(5.44)		
$Pr(O—i\text{-}C_3H_7)_3$	**2**, $C_{10}H_{13}NO_2$	1 : 1	16	$Pr(O—i\text{-}C_3H_7)(C_{10}H_{11}NO_2)$	0.23	37.35	3.67	—	—
0.62	0.35			Yellow solid, insoluble in benzene	(0.23)	(37.37)	(3.71)		
$Pr(O—i\text{-}C_3H_7)_3$	**2**, $C_{10}H_{13}NO_2$	2 : 3	24	$Pr_2(C_{10}H_{11}NO_2)_3$	0.30	34.62	5.21	—	—
0.58	0.49			Yellow solid, insoluble in benzene	(0.32)	(34.64)	(5.16)		
$Pr(O—i\text{-}C_3H_7)_3$	**3**, $C_{10}H_{13}NO_2$	1 : 1	16	$Pr(O—i\text{-}C_3H_7)(C_{10}H_{11}NO_2)$	0.23	37.39	3.75	—	—
0.62	0.35			Yellow solid, sparingly soluble in benzene	(0.23)	(37.37)	(3.71)		

Table 1 (continued)

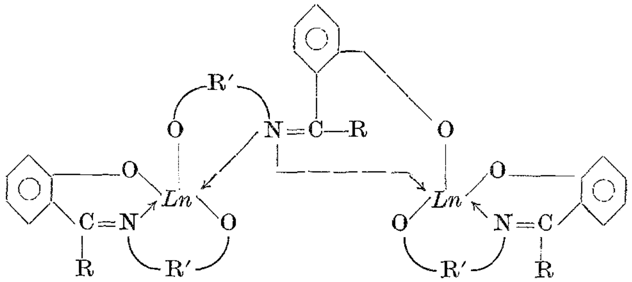
Ln(O—*i*-C_3H_7)$_3$ (g)	Schiff base (g)	Molar ratio	Refluxing time (hrs.)	Product and Characteristics	2-Propanol in the azeotrope	Analysis, %		Molecular weight	Molecular Association
						Ln	N		
					Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	
Pr(O—*i*-C_3H_7)$_3$ 0.66	**3**, $C_{10}H_{13}NO_2$ 0.55	2 : 3	24	$Pr_2(C_{10}H_{11}NO_2)_3$ Yellow solid, sparingly soluble in benzene	0.36 (0.37)	34.59 (34.64)	5.19 (5.16)	—	—
Pr(O—*i*-C_3H_7)$_3$ 0.72	**4**, $C_{11}H_{15}NO_2$ 0.43	1 : 1	16	Pr(O—*i*-C_3H_7)($C_{11}H_{13}NO_2$) Yellow solid, sparingly soluble in benzene	0.27 (0.27)	36.07 (36.01)	3.61 (3.57)	—	—
Pr(O—*i*-C_3H_7)$_3$ 0.74	**4**, $C_{11}H_{15}NO_2$ 0.67	2 : 3	24	$Pr_2(C_{11}H_{13}NO_2)_3$ Yellow solid, sparingly soluble in benzene	0.40 (0.41)	32.98 (32.94)	4.86 (4.89)	—	—
Nd(O—*i*-C_3H_7)$_3$ 0.85	**1**, $C_9H_{11}NO_2$ 0.43	1 : 1	16	Nd(O—*i*-C_3H_7)($C_9H_9NO_2$) Yellow solid, insoluble in benzene	0.30 (0.31)	39.36 (39.34)	3.79 (3.83)	—	—
Nd(O—*i*-C_3H_7)$_3$ 0.74	**1**, $C_9H_{11}NO_2$ 0.57	2 : 3	24	$Nd_2(C_9H_9NO_2)_3$ Yellow solid, insoluble in benzene	0.40 (0.41)	36.95 (36.98)	5.41 (5.39)	—	—

$Nd(O—i\text{-}C_3H_7)_3$ 0.72	**2**, $C_{10}H_{13}NO_2$ 0.40	1 : 1	16	$Nd(O—i\text{-}C_3H_7)(C_{10}H_{11}NO_2)$ Yellow solid, insoluble in benzene	0.26 (0.27)	37.82 (37.89)	3.73 (3.68)	—	—
$Nd(O—i\text{-}C_3H_7)_3$ 0.76	**2**, $C_{10}H_{13}NO_2$ 0.63	2 : 3	24	$Nd_2(C_{10}H_{11}NO_2)_3$ Yellow solid, insoluble in benzene	0.41 (0.42)	35.23 (35.18)	5.17 (5.12)	—	—
$Nd(O—i\text{-}C_3H_7)_3$ 0.52	**3**, $C_{10}H_{13}NO_2$ 0.27	1 : 1	16	$Nd(O—i\text{-}C_3H_7)(C_{10}H_{11}NO_2)$ Yellow solid, soluble in benzene	0.19 (0.19)	37.91 (37.89)	3.67 (3.68)	798 (380)	2.0
$Nd(O—i\text{-}C_3H_7)_3$ 0.64	**3**, $C_{10}H_{13}NO_2$ 0.53	2 : 3	24	$Nd_2(C_{10}H_{11}NO_2)_3$ Yellow solid, soluble in benzene	0.35 (0.35)	35.21 (35.18)	5.11 (5.12)	830 (820)	1.0
$Nd(O—i\text{-}C_3H_7)_3$ 0.70	**4**, $C_{11}H_{15}NO_2$ 0.42	1 : 1	16	$Nd(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ Yellow solid, soluble in benzene	0.25 (0.26)	36.51 (36.56)	3.61 (3.54)	800 (394)	2.0
$Nd(O—i\text{-}C_3H_7)_3$ 0.58	**4**, $C_{11}H_{15}NO_2$ 0.52	2 : 3	24	$Nd_2(C_{11}H_{13}NO_2)_3$ Yellow solid, soluble in benzene	0.32 (0.32)	33.41 (33.46)	4.91 (4.87)	883 (862)	1.0

Table 2. *Reactions of Isopropoxy Schiff Base* (**4**) *Derivatives of Ln(III), with t-Butyl Alcohol*

Compound (g)	*t*-Butyl alcohol (in excess) (g)	Product and Characteristics	2-Propanol in the azeotrope Found. (Calcd.)	Analysis % *Ln* (Calcd.) Found	Analysis % N (Calcd.) Found
$La(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ 0.76	3.5	$La(O—t\text{-}C_4H_9)(C_{11}H_{13}NO_2)$ Yellow solid, insoluble in benzene	0.11 (0.11)	34.42 (34.45)	3.51 (3.47)
$Pr(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ 0.80	3.8	$Pr(O—t\text{-}C_4H_9)(C_{11}H_{13}NO_2)$ Yellow solid, insoluble in benzene	0.11 (0.12)	34.75 (34.77)	3.41 (3.45)
$Nd(O—i\text{-}C_3H_7)(C_{11}H_{13}NO_2)$ 0.72	4.1	$Nd(O—t\text{-}C_4H_9)(C_{11}H_{13}NO_2)$ Yellow solid, insoluble in benzene	0.11 (0.11)	35.31 (35.30)	3.39 (3.42)

in boiling benzene and may possibly be represented by the following structure:



Similar to the isopropoxy Schiff base derivatives of monofunctional bidentate Schiff bases such as 2-hydroxy-1-naphthylidene-*n*-butylamine and o-hydroxyacetophenone-*n*-butylimine[1–2], these derivatives have also been shown to undergo exchange reactions with an excess of *t*-butyl alcohol as shown below:

$$Ln(O\text{—}i\text{-}C_3H_7)[OC_6H_4C(CH_3):NCH_2CHCH_3O] + t\text{-}C_4H_9OH \rightarrow$$
$$\rightarrow Ln(O\text{—}t\text{-}C_4H_9)[OC_6H_4C(CH_3):NCH_2CHCH_3O] + i\text{-}C_3H_7OH$$

The resulting butoxy-Schiff base derivatives are also non-volatile, yellow solids and insoluble in benzene.

Infrared Spectra

Infrared spectra of the isopropoxy lanthanide as well as the bis-lanthanide tris-Schiff base derivatives along with the parent Schiff bases were recorded as Nujol mulls in the range of 4,000–400 cm^{-1} using KBr optics. A few characteristic absorption bands with their tentative assignments are as given below:

3,400–3,100 cm^{-1} region: Sharp bands at $\approx$ 3,380 and $\approx$ 3,135 cm^{-1} may be assigned to OH or NH stretching modes, resp.; of the Schiff bases.

1,650–1,600 cm^{-1} region: A characteristic band at 1,620–1,630 cm^{-1} may be attributed to ν CN of the Schiff bases as well as the lanthanide complexes[7].

700–600 cm^{-1} region: The band at $\approx$ 675 cm^{-1} may be assigned to the ring deformation coupled with *Ln*—O stretching and $C\text{—}CH_3$ stretching modes and another one at $\approx$ 635 cm^{-1} to the CH out of plane deformation coupled with *Ln*—O stretching modes[8].

In the resulting derivatives, coordination through the nitrogen of the C=N group and the oxygens of the phenolic as well as alcoholic groups can be substantiated by the following observations:

(i) The disappearence of the characteristic bands of the Schiff bases in the region, 3,400–3,100 cm^{-1}.

(ii) The appearence of some new bands in the region, 700–600 cm^{-1}.

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