

## IMINE DERIVATIVES OF LANTHANONS

## Part I. Reactions of Neodymium(III) Isopropoxide with Monofunctional Bidentate and Bifunctional Tridentate Aldimines and Ketamines

S. P. MITAL, R. V. SINGH AND J. P. TANDON

*Department of Chemistry, University of Rajasthan, Jaipur 302 004 (India)*

## ABSTRACT

$\text{Nd}(\text{OPr}^i)_2(\text{SB})$  and  $\text{Nd}(\text{OPr}^i)(\text{SB})_2$  [where SBH represents the molecule of monofunctional bidentate aldimine] type of derivatives have been synthesised by 1 : 1 and 1 : 2 molar reactions of neodymium isopropoxide with the aldimines having the donor system NOH and formed by the condensation of salicylaldehyde with alkylamines. However, bifunctional tridentate Schiff bases ( $\text{LH}$ )<sub>3</sub> have been found to yield  $\text{Nd}(\text{OPr}^i)(\text{L})$  and  $\text{Nd}_2(\text{L})_3$  type of complexes in 1 : 1 and 2 : 3 molar ratio respectively. The isopropoxy groups of the 1 : 1 complexes have been found to undergo replacement reactions with excess of *t*-butanol and the resulting complexes are hydrolytically stable. All the newly synthesized complexes have been characterized on the basis of elemental analyses, molecular weight determinations, conductance measurements and infrared and proton magnetic resonance spectral studies.

## INTRODUCTION

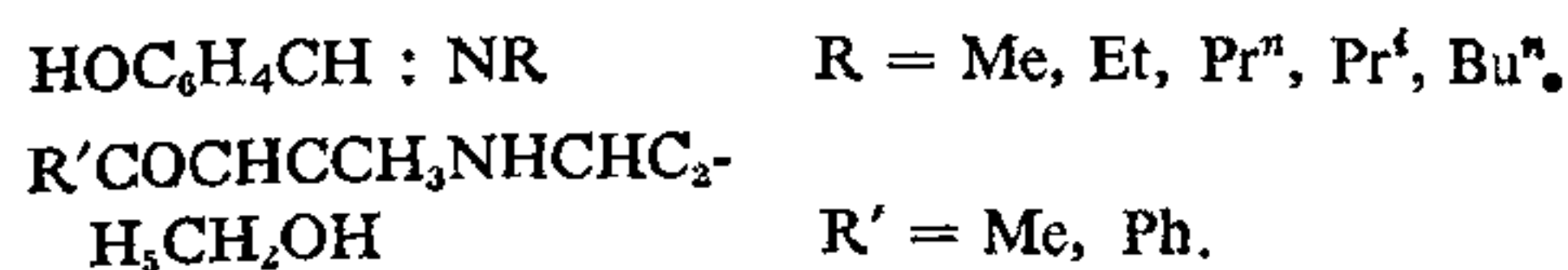
IN view of the industrial importance of metal nitrogen bonded complexes of lanthanides, a number of new derivatives have been prepared<sup>1-3</sup>. The Schiff bases, obtained by the condensation of aldehydes or ketones with primary amines also constitute an important class of N-donor ligands and have the characteristic azomethine group ( $>\text{C}=\text{N}$ ). The results of the reactions of such nitrogen donor ligands, namely, the monofunctional bidentate and bifunctional tridentate Schiff bases with  $\text{Nd}(\text{OPr}^i)_3$  have been reported during the present investigations.

## EXPERIMENTAL

Benzene (B.D.H.) was refluxed over sodium wire for several hours and then distilled azeotropically with ethanol. Isopropanol (B.D.H.) was refluxed over sodium metal and then distilled over aluminium isopropoxide.  $\text{Nd}_2\text{O}_3$  (Schuchardt, Germany) was used and its isopropoxide was prepared by the sodium alkoxide method<sup>4</sup>.

Schiff bases were prepared by the method reported earlier and purified either by distillation under reduced pressure or recrystallization with absolute alcohol.

The general formulae of the Schiff bases used are as follows :

*Preparation of the Complexes*

Neodymium isopropoxide was dissolved in benzene and the appropriate amount of the Schiff base added. The mixture was refluxed and the isopropanol liberated was collected azeotropically with benzene. The progress of the reaction could thus be monitored by the estimation of isopropanol in the azeotrope. After distilling out the solvent benzene, the residual benzene was removed under vacuum and the resulting solid products were finally dried at 50–60° C/0.5 mm for 2–3 hours. Their elemental analyses agreed with the calculated values within the limits of experimental error.

*Exchange Reactions of Mono- and Diisopropoxy Neodymium Derivatives with an Excess of *tert*-Butanol*

The exchange reactions of mono- and diisopropoxy derivatives of Nd(III) with an excess of *t*-butanol were carried out in anhydrous benzene. The reaction mixture was fractionated and the ternary azeotrope of isopropanol with *t*-butanol and benzene collected. The remaining solvent was then removed under reduced pressure and the products were finally dried at 50–60° C (0.5 mm) for 2–3 hrs.

*Analytical Methods and Physical Measurements*

Neodymium was determined by complexometric titrations with EDTA using bromopyrogallol red as the indicator<sup>5</sup>. Nitrogen was estimated by Kjeldahl's method and isopropanol by oxidation with normal potassium dichromate solution in 12.5% sulphuric acid<sup>6</sup>. Molecular weights were determined ebullioscopically in benzene.

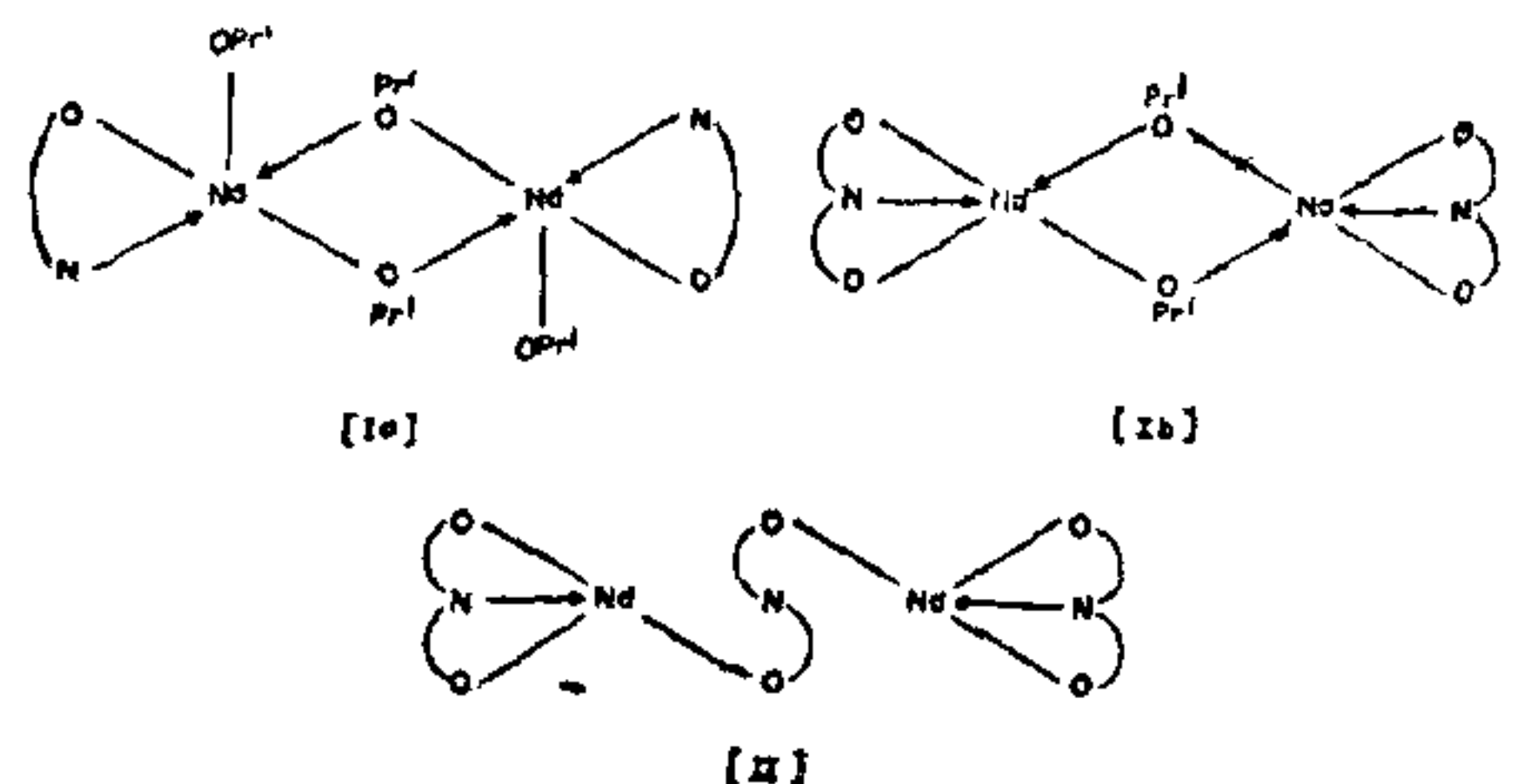
The infrared spectra of the Schiff bases and their metal derivatives were recorded in the region 4000–

200  $\text{cm}^{-1}$  as nujol mulls using Perkin-Elmer model 577, grating infrared spectrophotometer and the PMR spectra on a Perkin-Elmer RB-12 spectrometer using TMS as the internal reference.

## RESULTS AND DISCUSSION

The reactions of  $\text{Nd}(\text{OPr}^i)_3$  with SBH in 1 : 1 and 1 : 2 molar ratios yielded  $\text{Nd}(\text{OPr}^i)_2(\text{SB})$  and  $\text{Nd}(\text{OPr}^i)(\text{SB})_2$  type of derivatives respectively, whereas similar reactions with  $\text{LH}_2$  in 1 : 1 and 2 : 3 molar ratios yielded  $\text{Nd}(\text{OPr}^i)(\text{L})$  and  $\text{Nd}_2(\text{L})_3$  type of derivatives, respectively. These are coloured solids, soluble in DMF and non-electrolytes in DMF. The determination of molecular weights of these complexes in boiling chloroform show that  $\text{Nd}(\text{OPr}^i)_2(\text{SB})$  and  $\text{Nd}(\text{OPr}^i)(\text{L})$  types of derivatives are dimeric, whereas  $\text{Nd}_2(\text{L})_3$

type of derivatives are monomeric in nature. This shows the possibility of penta ( $\text{I}_a$ ,  $\text{I}_b$ ) and tetra ( $\text{II}$ ) coordination state of neodymium atoms respectively in these complexes as shown below :



(where  $\text{N}^{\text{OH}}$  and  $\text{HO}^{\text{N}}^{\text{OH}}$  represent the ligand molecule).

TABLE I  
PMR spectral data ( $\delta$ , PPM) of the ligands and their metal complexes

Compound	R	R'	a (aryl)	b (OH)	c (methine)	d	e	f	g	h	i	j
(i)	H	$-\text{CH}_2\text{CH}_2\text{CH}_3$ d e f	6.50– 7.40m	12.90bs	7.62s	2.9t	1.1s'	0.5t	..	..	..	..
(ii)	H	$-\text{CH}_2\text{CH}_2\text{CH}_2$ d e f	6.60– 7.60m	..	7.8s	3.0t	1.45s'	0.7t	..	1.1	4.18	..
(iii)	H	$-\text{CH}_2\text{CH}_2\text{CH}_3$ d e f	6.50– 7.30m	..	7.98s	3.0t	1.40s'	0.85t	..	1.15	4.20	..
(iv)	H	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.95– 7.70m	9.45bs	8.55s	3.5d	1.90	1.22t	3.98	..	..	3.5bs
(v)	$\text{CH}_3$	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.42– 7.45m	16.4bs	2.30s	3.63d	1.6	0.9t	3.63	..	..	2.9bs
(vi)	H	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.50– 7.30m	..	9.0s	3.9d	1.75	1.3t	4.0	1.05	4.2	..
(vii)	$\text{CH}_3$	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.40– 7.20m	..	2.55s	3.75d	1.5	1.35t	3.75	1.35	4.3	..
(viii)	H	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.45– 7.0m	..	8.85s	3.8d	2.0	1.20t	4.0	..	..	..
(ix)	$\text{CH}_3$	$-\text{CH}-\text{CH}_2$   g d $\text{CH}_2-\text{CH}_3$ e f	6.45– 7.0m	..	2.35s	3.8d	1.78	1.30t	3.80	..	..	..

s = singlet, d = doublet, t = triplet, s' = sextet, bs = broad signal and m = complex multiplet



The monoisopropoxy bis-Schiff base complexes have been found to have a molecular association,  $\sim 1.5$ , showing that an equilibrium exists between the monomeric and dimeric species, the polymerization probably occurring through the bridging isopropoxy groups.

The  $\text{Nd}(\text{OPr}^i)_2(\text{SB})$ ,  $\text{Nd}(\text{OPr}^i)(\text{SB})_2$  and  $\text{Nd}(\text{OPr}^i)(\text{L})$  complexes undergo exchange in reactions with excess of *t*-butanol ( $\text{HOBu}^t$ ) and yield  $\text{Nd}(\text{OBu}^t)_2(\text{SB})$ ,  $\text{Nd}(\text{OBu}^t)(\text{SB})_2$  and  $\text{Nd}(\text{OBu}^t)(\text{L})$  types of derivatives, respectively. The resulting butoxy derivatives are non-volatile, coloured solids, soluble in DMF, non-electrolytes in DMF and monomeric in boiling chloroform.

In the I.R. spectra of the bidentate Schiff bases, no absorption band appears in the region,  $3400\text{--}3100\text{ cm}^{-1}$  on account of strong hydrogen bonding and a broad band is simply observed in the region,  $3050\text{--}2850\text{ cm}^{-1,8}$ . However, in tridentate Schiff bases, broad absorption bands of strong to weak intensity are observed in the region,  $3400\text{--}3100\text{ cm}^{-1}$  and these may be assigned to OH or NH stretching modes<sup>9</sup>.

In the neodymium derivatives, no absorption band of the OH or NH group is observed in the region  $3400\text{--}2850\text{ cm}^{-1}$ , indicating coordination through oxygen of the phenolic as well as the alcoholic groups. Further, a strong band observed in the region  $1630\text{--}1610\text{ cm}^{-1}$  in the spectra of Schiff bases and their metal derivatives is a characteristic absorption band of the azomethine ( $>\text{C}=\text{N}-$ ) group<sup>10</sup>.

The far infrared spectra of the resulting derivatives show a medium intensity band at  $390 \pm 10\text{ cm}^{-1}$  which may be assigned to Nd-N coordinate linkage.

The bonding of neodymium metal to azomethine nitrogen as well as oxygen (phenolic and alcoholic) is further confirmed by the PMR spectral studies (Table I) of N-(*n*-propyl) salicylalimine (i), N-(1-hydroxy-2-butyl) salicylalimine (iv), N-(1-hydroxy-2-butyl)-2-hydroxyacetophenoneimine (v) and their corresponding Schiff base complexes (ii, iii, vi, vii, viii, ix). The chemical shift values ( $\delta$ ) of the different protons are recorded in Table I and the main points suggestive of the proposed structures are as follows:

1. The bonding of the phenolic oxygen moiety in compounds (ii, iii, vi, vii, viii and ix) is substantiated by the disappearance of OH proton signals, which are observed in the ligands (i), (iv) and (v) at 12.90, 9.45 and 16.4 ppm respectively.
2. The 3.5 and 2.9 ppm resonances due to alcoholic OH protons of the ligands (iv) and (v) disappear in compounds (vi), (vii), (viii) and (ix) indicating the chelating nature of the ligands.
3. In the compounds (ii, iii, vi, vii, viii and ix), methyl, methylene and methine proton peaks are shifted down-field as compared to the ligand indicating the coordination of nitrogen of the ligand moieties to neodymium atom.
4. New proton signals at 4.18, 4.20 and 4.30 and 1.1, 1.15, 1.05 and 1.35 in neodymium complexes are due to the methine and methyl protons respectively of the isopropoxy groups; these do not appear in the corresponding ligands.

#### ACKNOWLEDGEMENT

One of the authors (SPM) wishes to thank the U.G.C., New Delhi, for the financial assistance.

1. Williams, R. J. P., *Quart. Rev. Chem. Soc.*, 1970, 24, 331.
2. Dutt, N. K. and Nag, K., *J. Inorg. Nucl. Chem.*, 1968, 30, 249.
3. Isoble, T. and Kida, S., *Bull. Chem. Soc. (Japan)*, 1966, 39, 2561; 1967, 40, 1862.
4. Misra, S. N., Misra, T. N., Kapoor, R. N. and Mehrotra, R. C., *Chem. and Ind.*, 1963, p. 120; Richard, A. Anderson, David, H. Templeton and Allan Zalkin, *Inorg. Chem.*, 1978, 17(7), 1962.
5. Welcher, F. J., *The Analytical Uses of E.D.T.A.*, D. Van Nostrand Company, Inc., Princeton, New Jersey, New York.
6. Bradley, D. C., Abd-el Halim, F. M. and Wardlaw, W., *J. Chem. Soc. (London)*, 1950, p. 3450.
7. Rasmussen, R. S., Tunnicliffe, D. D. and Brat-tain, R. R., *J. Am. Chem. Soc.*, 1949, 71, 1068.
8. Nuttall, R. H., Sharp, D. W. A. and Waddington, T. C., *J. Chem. Soc.*, 1960, p. 4965.
9. Agrawal, S. K. and Tandon, J. P., *Mh. Chem.*, 1975, 106, 261.
10. Sharma, B. D. and Bailar, J. C. (Jr.), *J. Am. Chem. Soc.*, 1955, 77, 5476.