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Schiff Base Derivatives of Lanthanons—Synthesis of La(III), Pr(III) and Nd(III) Derivatives of β-Ketoimines Derived From 2,4-Pentanedione

S. K. Agarwal and **J. P. Tandon***

Department of Chemistry, University of Rajasthan,
Jaipur-302004, India

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Reactions of the isopropoxides of some of the lighter lanthanons with bidentate β-ketoimines such as *AA*H-*n*-C_4H_9 and *AA*H-C_6H_5 (donor system: N,OH) and tridentate β-ketoimines such as *AA*$(CH_2CH_2)H_2$ and *AA*-$(CH_2CHCH_3)H_2$ (donor system: HO,N,OH) have led to products of the types $Ln(O\text{-}i\text{-}C_3H_7)_{3-n}$ $(AA\text{-}R)_n$, $Ln(O\text{-}i\text{-}C_3H_7)$ (AAR') and $Ln_2(AAR')_3$ [Ln = La(III), Pr(III) or Nd(III); $n = 1$ or 2; $R = \text{-}n\text{-}C_4H_9$ or $\text{-}C_6H_5$ and $R' = \text{-}CH_2CH_2\text{-}$ or $\text{-}CH_2CHCH_3\text{-}$]. Some undergo exchange reactions with an excess of *tert*-butanol leading to the corresponding complexes $Ln(O\text{-}tert\text{-}C_4H_9)_{3-n}$ $(AA\text{-}n\text{-}C_4H_9)_n$ and $Ln(O\text{-}tert\text{-}C_4H_9)$ $(AA\text{-}CH_2CH_2)$. All these have been characterised by elemental analysis, molecular weight determinations and their ir spectra. A thermogravimetric analysis of the diisopropoxy derivatives has also been carried out.

(Keywords: Lanthanides, complexes; β-Ketoimines, complexes)

Schiff-Basen Derivate von Lanthaniden — Synthese von La(III), Pr(III) und Nd(III) Chelaten mit β-Ketoiminen

Reaktionen von Lanthanid-Isopropoxiden mit zweizähnigen β-Ketoiminen [*AA*H-*n*-C_4H_9 und *AA*H-C_6H_5; Donorsystem: N,OH] und dreizähnigen β-Ketoiminen [*AA*$(CH_2CH_2)H_2$ und *AA*$(CH_2CHCH_3)H_2$; Donorsystem: OH, N,OH] führten zu Produkten vom Typ $Ln(O\text{-}i\text{-}C_3H_7)_{3-n}$ $(AA\text{-}R)_n$, $Ln(O\text{-}i\text{-}C_3H_7)$ (AAR') und $Ln_2(AAR')_3$ [Ln = La(III), Pr(III) oder Nd(III); $n = 1$ oder 2; $R = n\text{-}C_4H_9$ oder C_6H_5 und $R' = CH_2CH_2$ oder CH_2CHCH_3]. Einige Komplexe unterliegen bei Behandlung mit einem Überschuß von *tert*-Butanol einer Austauschreaktion, die zu den entsprechenden Butoxid-Komplexen führt [$Ln(O\text{-}tert\text{-}C_4H_9)_{3-n}$ $(AA\text{-}n\text{-}C_4H_9)_n$ und $Ln(O\text{-}tert\text{-}C_4H_9)$ $(AACH_2CH_2)$]. Alle Derivate wurden mittels Elementaranalyse, Molgewichtsbestimmung und IR-Spektroskopie charakterisiert. Eine thermogravimetrische Analyse der Diisopropoxi-Derivate wurde ebenfalls ausgeführt.

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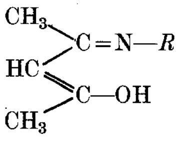
Introduction

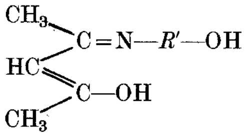
Until recently, studies on complex derivatives of lanthanons were mostly confined to oxo-complexes, particularly β-diketonates. The large cationic radii of the lanthanons and the shielding of their $4f$ electrons make the cation ligand attractions largely electrostatic in nature. One may, therefore, anticipate that stable complexes of lanthanons should be derived from ligands containing strong electronegative donor atoms like oxygen. The lack of N-coordinated complexes was ascribed partly to the fact that nitrogen-donating ligands would form unstable complexes with these metals and also many of them being basic in nature would precipitate their hydroxides.

A survey of the literature revealed that except for a few publications on the β-ketoamine derivatives of lanthanons with tetradentate[1-2] ligands, systematic studies on other types of β-ketoimine derivatives are lacking. *Dutt* and *Nag*[2] have recently synthesized some ionic complexes of lanthanons with ethylenediamine—bis-2,4-pentanedione—*Schiff* base (*enac*) of the type $[Ln(enac)_2]X_3$ (Ln = La, Ce, Pr, Nd, and Sm, $X = Cl^-, NO_3^-, SCN^-$) and $[Ln_2(enac)_3]X_6$ (Ln = Gd, Dy, Er, Y, and $X = Cl^-, NO_3^-$).

It was, therefore, considered of interest to synthesize some new lanthanon derivatives of bi- and tri-dentate β-ketoimines and to study their main characteristics. The bi- and tridentate β-ketoimines used in the present investigations may be represented by the general structures (I) and (II):



(I)



(II)

$R = n\text{-}C_4H_9, C_6H_5$; $R' = CH_2CH_2, CH_2CHCH_3$.

Experimental

As both lanthanon isopropoxides and the β-ketoimine complexes are moisture sensitive, all the reactions have been carried out under strictly anhydrous conditions. The lanthanon isopropoxides were prepared as described earlier[1,3].

Preparation of β-Ketoimines

The β-ketoimines were prepared by taking equimolar amounts of butylamine, 2-hydroxyethylamine or 2-hydroxy-propylamine and 2,4-pentanedione in benzene and refluxing for 4-5 h. The water formed in the reaction was removed azeotropically with benzene and the resulting products analyzed before use.

4-(*N*-Butylimino)-2-penten-2-ol, *AA*H-*n*-C_4H_9.

($C_9H_{17}NO$). Calcd. C 69.63, H 10.96, N 9.02.
Found C 69.61, H 10.92, N 8.96.

Pale yellow liquid; bp 79-80° (0.4-0.5 mm).

4-[*N*-(2-Hydroxyethyl)-imino]-2-penten-2-ol, *AA*(CH_2CH_2)H_2.

($C_7H_{13}NO_2$). Calcd. C 58.75, H 9.09, N 9.77.
Found C 58.62, H 8.96, N 9.51.
Yellow solid; bp 113-115° (0.2 mm).

4-[*N*-(2-Hydroxypropyl)-imino]-2-penten-2-ol, *AA*(CH_2CHCH_3)H_2.

($C_8H_{15}NO_2$). Calcd. C 61.15, H 9.55, N 8.90.
Found C 61.01, H 9.47, N 8.81.
Yellow solid; bp 111-112° (0.3 mm).

4-(*N*-Phenyl)-2-penten-2-ol, *AA*H-C_6H_5, was prepared as reported earlier[4].

Analytical Methods and Physical Measurements

Infrared spectra were recorded in the range of 4,000-400 cm^{-1} with a Perkin Elmer 337 grating infrared spectrophotometer as nujol mulls and in some cases as neat liquids. In a few cases, ir spectra were also recorded in the range of 500-200 cm^{-1} using a UR 10 double beam infrared spectrophotometer. The molecular weights were determined in boiling benzene by means of an ebulliometer (Gallenkamp) using thermistor sensing. Thermogravimetric analysis was carried out on a Stanton (mass flow type) Automatic Recording Thermogravimetric Balance.

Synthesis of La(III), Pr(III), *and* Nd(III) *β-Ketoimine Complexes*

On treating La(III), Pr(III) or Nd(III) isopropoxides (in amounts of 0.5-0.7 g per run) with the β-ketoimine in the desired ratio in benzene, a clear solution was obtained. The reaction mixture was refluxed at the bath temperature of ~ 100 °C followed by the slow fractionation of the liberated isopropanol with benzene, which was estimated oxidimetrically (in all cases the theoretical amount was observed). The residual benzene was then removed under reduced pressure and the resulting products were finally dried at 50-60 °C (0.5 mm) for 2-3 h. The details of synthesis and elemental analyses are recorded in Tables 1 and 2. All complexes of this type were yellow solids.

Alcohol Exchange Reactions of Mono- and Diisopropoxy Lanthanon Derivatives With an Excess of tert-Butanol

The exchange reactions of mono- and diisopropoxy derivatives (0.55-0.7 g per run) of La(III), Pr(III) or Nd(III) with an excess of *tert*-butanol (2.3-3.2 g per run) were carried out in anhydrous benzene. The reaction mixture was fractionated and the ternary azeotrope of isopropanol with *tert*-butanol and benzene collected. The remaining solvent was then removed under reduced

Table 1. *Reactions of lanthanon isopropoxides* [$Ln(ipr)_3$] *with Schiff bases of type* CH_3—$COH=CH$—$CCH_3=NR$ [$R=n$—C_4H_9 (**A**) *and* $R=C_6H_5$ (**B**)]

Ln $(ipr)_3$	*Schiff* base	Molar ratio	Refl. time (h.)	Compound type formed	*Ln* found (calcd.)	N found (calcd.)	Mol. wt. found (calcd.)	Molec. assoc.
La	**A**	1:1	7	$La(ipr)_2$ **A**	33.79 (33.73)	3.39 (3.40)	831 (411)	2.0
La	**A**	1:2	10	$La(ipr)$ $\mathbf{A}_2$	27.46 (27.41)	5.52 (5.54)	721 (506)	1.4
Pr	**A**	1:1	7	$Pr(ipr)_2$ **A**	34.17 (34.10)	3.30 (3.38)	834 (413)	2.0
Pr	**A**	1:2	10	$Pr(ipr)$ $\mathbf{A}_2$	27.68 (27.71)	5.58 (5.50)	726 (508)	1.4
Nd	**A**	1:1	7	$Nd(ipr)_2$ **A**	34.60 (34.62)	3.42 (3.36)	842 (416)	2.0
Nd	**A**	1:2	10	$Nd(ipr)$ $\mathbf{A}_2$	28.24 28.19	5.44 (5.47)	732 (511)	1.4
La	**B**	1:1	8	$La(ipr)_2$ **B**	32.18 (32.21)	3.31 (3.24)	872 (431)	2.0
La	**B**	1:2	11	$La(ipr)$ $\mathbf{B}_2$	25.39 (25.43)	5.15 (5.12)	771 (546)	1.4
Pr	**B**	1:1	8	$Pr(ipr)_2$ **B**	32.58 32.52	3.18 (3.23)	878 (433)	2.0
Pr	**B**	1:2	11	$Pr(ipr)$ $\mathbf{B}_2$	25.72 (25.69)	5.04 (5.10)	776 (548)	1.4
Nd	**B**	1:1	8	$Nd(ipr)_2$ **B**	33.12 (33.03)	3.16 (3.20)	883 (436)	2.0
Nd	**B**	1:2	11	$Nd(ipr)$ $\mathbf{B}_2$	26.09 (20.13)	5.11 (5.07)	781 (551)	1.4

Table 2. *Reactions of lanthanon isopropoxides* $[Ln(ipr)_3]$ *with Schiff bases of type* $CH_3—COH=CH—CCH_3=NR'OH$ $[R'=CH_2CH_2$ (**C**) *and* $R'=CH_2CHCH_3$ (**D**)$]$

Ln $(ipr)_3$	*Schiff* base	Molar ratio	Refl. time (h.)	Compound type formed	*Ln* found (calcd.)	N found (calcd.)	Mol. wt. found (calcd.)	Molec. assoc.
La	**C**	1:1	15	La(*ipr*) **C**	40.98 (40.96)	4.08 (4.12)	693 (339)	2.0
La	**C**	2:3	24	La_2 $\mathbf{C}_3$	39.59 (39.62)	5.95 (5.98)	—	—
Pr	**C**	1:1	15	Pr(*ipr*) **C**	41.22 (41.29)	4.04 (4.10)	697 (341)	2.0
Pr	**C**	2:3	24	Pr_2 $\mathbf{C}_3$	39.89 (39.95)	5.98 (5.95)	—	—
Nd	**C**	1:1	15	Nd(*ipr*) **C**	41.84 (41.86)	4.01 (4.06)	705 (344)	2.0
Nd	**C**	2:3	24	Nd_2 $\mathbf{C}_3$	40.48 (40.51)	5.88 (5.89)	725 (712)	1.0
La	**D**	1:1	15	La(*ipr*) **D**	39.30 (39.33)	3.95 (3.99)	717 (353)	2.0
La	**D**	2:3	24	La_2 $\mathbf{D}_3$	37.32 (37.38)	5.60 (5.65)	— —	— —
Pr	**D**	1:1	15	Pr(*ipr*) **D**	39.70 (39.68)	3.95 (3.94)	—	—
Pr	**D**	2:3	24	Pr_2 $\mathbf{D}_3$	37.66 (37.70)	5.59 (5.61)	—	—
Nd	**D**	1:1	15	Nd(*ipr*) **D**	40.20 (40.23)	3.88 (3.90)	738 (358)	2.0
Nd	**D**	2:3	24	Nd_2 $\mathbf{D}_3$	38.21 (38.24)	5.59 (5.56)	—	—

Table 3. *Alcohol exchange reactions of mono- and diisopropoxy-Schiff base derivatives of lanthanons* [*Ln*(*ipr*)$_2$ **A**] *with an excess of tert-butanol* [*tbut*]

Compound type	Compound type formed	*Ln* found (calcd.)	N found (calcd.)	Mol. wt. found (calcd.)	Molec. assoc.
La(*ipr*)$_2$ **A**	La(*tbut*)$_2$ **A**	31.60 (31.64)	3.20 (3.18)	451 (439)	1.0
La(*ipr*) **A**$_2$	La(*tbut*) **A**$_2$	26.68 (26.72)	5.39 (5.38)	531 (520)	1.0
Pr(*ipr*)$_2$ **A**	Pr (*tbut*)$_2$ **A**	31.92 (31.97)	3.20 (3.17)	447 (441)	1.0
Pr(*ipr*) **A**$_2$	Pr(*tbut*) **A**$_2$	27.10 (27.05)	5.31 (5.37)	537 (522)	1.0
Nd(*ipr*)$_2$ **A**	Nd(*tbut*)$_2$ **A**	32.51 (32.48)	3.11 (3.15)	458 (444)	1.0
Nd(*ipr*) **A**$_2$	Nd(*tbut*) **A**$_2$	27.45 (27.47)	5.30 (5.33)	542 (525)	1.0

Table 4. *Alcohol exchange reactions of monoisopropoxy-Schiff base derivatives of lanthanons* [*Ln*(*ipr*) **C**] *with an excess of tert-butanol* [*tbut*]

Compound type	Compound type formed	*Ln* found (calcd.)	N found (calcd.)
La(*ipr*) **C**	La(*tbut*) **C**	39.29 (39.33)	3.92 (3.96)
Pr(*ipr*) **C**	Pr(*tbut*) **C**	39.62 (39.68)	3.90 (3.94)
Nd(*ipr*) **C**	Nd(*tbut*) **C**	40.21 (40.23)	3.88 (3.90)

pressure and the products were finally dried at 50-60 °C (0.5 mm) for 2-3 h. See Tables 3 and 4. All complexes in this series were yellow or yellowish brown solids.

Results and Discussion

The reactions of La(III), Pr(III) or Nd(III) chlorides with β-ketoimines in aqueous or alcoholic medium at room temperature as well as under refluxing conditions were carried out. These, however, yielded lanthanon tris-2,4-pentanedionate derivatives only:

$$Ln\mathrm{Cl}_3 + 3\,AA\mathrm{H}—R + \mathrm{H_2O} \rightarrow Ln(AA)_3 \cdot \mathrm{H_2O} + 3\,R\mathrm{NH_2HCl}.$$

Even attempts to synthesize *Schiff* base derivatives by refluxing the preformed lanthanon-tris-2,4-pentanedionate with an excess of amine remained unsuccessful. In earlier publications from these laboratories[5–10], reactions of metal alkoxides of III(Al,Ga), IV(Ti,Zr) and V(Nb,Ta) group elements with β-ketoimines have been shown to be quite facile, resulting in the isolation of pure products in almost quantitative yields. Further, lanthanon isopropoxides have been used as useful starting materials for the synthesis of a variety of lanthanon derivatives with ligands such as β-diketones[11], β-ketoesters[12], glycols[13] and hydroxy acids[14].

In the present investigation reactions of La(III), Pr(III), and Nd(III) isopropoxides with β-ketoimines are studied.

*Lanthanon(III) Derivatives With Ligands of Type AA*H—*R*

Reactions of lanthanon isopropoxides with $AA—R$ in 1:1 and 1:2 molar ratios can be represented as follows:

$$Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})_3 + n\,AA\mathrm{H}—R \rightarrow Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})_{3-n}\,(AA—R)_n + n\,i\text{-}\mathrm{C_3H_7OH}$$

$(n = 1$ or 2; $Ln = $ La, Pr or Nd; $R = n\text{-}\mathrm{C_4H_9}$ or $\mathrm{C_6H_5}$.)

Above reactions in the 1:3 molar ratio were also attempted but the analysis of the resulting products always corresponded to $Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})(AA—R)_2$ type of derivatives and the excess of the ligand was found unreacted; this may be due to the lower concentration (≈ 5 mol %) of the enolic form initially present.

The reactions of lanthanon isopropoxides with β-ketoimines in 1:1 and 1:2 molar ratios have yielded the diisopropoxy-mono-β-ketoimine, $Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})_2\,(AA—R)$ and mono isopropoxy-bis-β-ketoimine, $Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})\,(AA—R)_2$ derivatives respectively.

The resulting complex derivatives are non-volatile, light to deep yellow solids, semi-solids and crystalline in nature. These derivatives are extremely sensitive to moisture.

The diisopropoxy-mono-β-ketoimine derivatives have been found to be dimeric and the monoisopropoxy-bis-β-ketoimine derivatives have a molecular association ~ 1.5, showing that an equilibrium exists between the monomeric and dimeric species, the polymerization probably occuring through the bridging isopropoxy groups.

The diisopropoxy-mono-β-ketoimine and the monoisopropoxy bis-β-ketoimine derivatives undergo exchange reactions and yield the dibutoxy-mono-β-ketoimine and monobutoxy-bis-β-ketoimine derivatives as shown by the following general equations:

$$Ln(\text{O-}i\text{-C}_3\text{H}_7)_{3-n}(AA\text{—}R)_n + (3\text{—}n)\ tert\text{-C}_4\text{H}_9\text{OH} \rightarrow$$
$$\rightarrow Ln(\text{O-}tert\text{-C}_4\text{H}_9)_{(3-n)}(AA\text{—}R)_n + (3\text{—}n)\ i\text{-C}_3\text{H}_7\text{OH}$$

$$(n = 1 \text{ or } 2;\ Ln = \text{La, Pr, Nd};\ R = n\text{-C}_4\text{H}_9).$$

The resulting butoxy derivatives have been found to be monomeric in boiling benzene and this may be attributed to the steric hindrance caused by the *tert*-butyl group. These compounds are also non-volatile, light to deep yellow solids and crystalline in nature.

Lanthanon(III) Derivatives With Ligands of Type AAR'H$_2$

The 1:1 molar ratio reactions of $AAR'\text{H}_2$ with the isopropoxides of La(III), Pr(III), and Nd(III) may be represented by following equations:

$$Ln(\text{O-}i\text{-C}_3\text{H}_7)_3 + AAR'\text{H}_2 \rightarrow Ln(\text{O-}i\text{-C}_3\text{H}_7)\ (AAR') + 2\,i\text{-C}_3\text{H}_7\text{OH}$$

$$(\text{R}' = \text{CH}_2\text{CH}_2 \text{ or } \text{CH}_2\text{CHCH}_3).$$

The resulting monoisopropoxy-β-ketoimine derivatives have been obtained as yellow solids and are non-volatile. The ebullioscopic determination of molecular weights in boiling benzene shows them to be dimeric, the dimerization possibly taking place through the isopropoxy bridges.

The 2:3 molar reactions of lanthanon isopropoxide have also been carried out and dilanthanon tris-β-ketoimine complexs have been isolated in almost quantitative yields:

$$2\,Ln(\text{O-}i\text{-C}_3\text{H}_7)_3 + 3\,AAR'\text{H}_2 \rightarrow Ln_2(AAR')_3 + 6\,i\text{-C}_3\text{H}_7\text{OH}$$

$$(\text{R}' = \text{CH}_2\text{CH}_2 \text{ or } \text{CH}_2\text{CHCH}_3).$$

The dilanthanon tris-β-ketoimine derivatives have almost similar properties, but are monomeric in benzene.

Similar to the isopropoxy derivatives of bidentate β-ketoimines, the isopropoxy group of monoisopropoxy β-ketoimine derivatives has also been shown to undergo exchange reactions with an excess of *tert*-butanol:

$$Ln(\text{O-}i\text{-C}_3\text{H}_7)\,(AAR') + tert\text{-C}_4\text{H}_9\text{OH} \rightarrow Ln(\text{O-}tert\text{-C}_4\text{H}_9)\,(AAR') + i\text{-C}_3\text{H}_7\text{OH}$$

$$(\text{R}' = \text{CH}_2\text{CH}_2).$$

Table 5. *Infrared absorption frequencies (in* cm^{-1}*) of lanthanon complexes of Schiff bases*

La(*ipr*)$_2$ **A**	La(*ipr*) **A**$_2$	Pr(*ipr*)$_2$ **A**	Pr(*ipr*) **A**$_2$	Nd(*ipr*) **A**	Nd(*ipr*) **A**$_2$
2900 Sb	2900 Sb	2900 Sb	2900 Sb	2900 Sb	2900 Sb
1620 vs	1620 vs	1620 vs	1620 vs	1620 vs	1610 vs
1565 m	1560 m	1560 m	1560 m	1570 m	1570 m
1450 m	1450 m	1450 m	1450 m	1450 m	1450 m
1370 m	1370 m	1370 m	1370 m	1370 m	1370 m
1240 m	1240 m	1240 m	1240 m	1240 m	1245 m
1200 w	1198 w	1198 w	1198 w	1198 w	1198 w
1150 m	1150 m	1150 m	1150 m	1150 m	1150 m
1110 w	1111 w	1110 w	1110 w	1110 w	1108 w
1085 w	1090 w	1085 w	1085 w	1085 w	1090 w
1020 S	1022 S	1022 S	1022 S	1020 S	1020 S
975 Sh	975 m	975 m	975 m	980 m	982 m
925 mb	925 mb	925 mb	925 mb	925 mb	925 mb
860 Sh	860 w	855 Sh	855 Sh	855 w	855 w
775 m	775 m	775 m	775 m	775 m	775 m
740 s	740 s	740 s	740 s	740 s	740 s
660 m	660 m	660 m	660 m	660 m	660 m
610 w	610 w	612 w	612 w	615 w	610 w

La(*ipr*) **C**	Pr(*ipr*) **C**	Nd(*ipr*) **C**	La(*ipr*) **D**
2950-2850 Sb	2950-2850 Sb	2950-2850 Sb	2950-2850 Sb
1620 vs	1620 vs	1622 vs	1625 vs
1575 vs	1575 vs	1580 vs	1578 vs
1475 vs	1470 vs	1468 vs	1470 vs
1450 Sh	1450 S	1450 S	1450 S
1435 m	1432 m	1435 m	1435 m
1390 vs	1390 vs	1390 vs	1388 vs
1260 S	1265 S	1265 S	1262 S
1250 Sh	1255 m	1250 mb	1250 mb
1190 m	1188 m	1190 m	1190 m
1160 m	1165 m	1165 m	1166 m
1080 mb	1080 mb	1080 m	1080 w
1015 m	1025 m	1025 m	1028 m
960 m	955 m	958 m	960 m
935 m	935 m	937 m	940 m
890 m	890 m	885 m	884 m
850 m	850 m	835 m	840 m
800 Sb			
740 m	740 m	738 m	735 m
675 m	675 m	678 m	677 m
625 m	620 m	628 m	630 m
550 m	555 m	552 m	558 m
475 Sh	470 m	472 m	475 w

However, these exchange reactions are quite slow and could be completed only in presence of an excess of *tert*-butanol and on refluxing for about 30 h. The resulting butoxy derivatives are obtained as yellow solids and are non-volatile and sparingly soluble in benzene.

To have an idea about the thermal stability, a thermogravimetric analysis of $Ln(\mathrm{O}\text{-}i\text{-}\mathrm{C_3H_7})_2(AA\text{-}n\text{-}\mathrm{C_4H_9})$ has also been carried out. A weighed quantity of a sample was heated under a controlled rate of heating (4 °C/min). The complex derivatives have been found to be thermally stable up to 110 °C and thereafter, a continuous loss in weight is observed resulting in the formation of $Ln_2\mathrm{O}_3$ at 830 °C.

Infrared Spectra

The ir spectra of the *Schiff* bases as well as the corresponding lanthanon derivatives have been recorded. The frequencies and relative intensities of the lanthanon complexes are summarized in Table 5.

In the case of bidentate *Schiff* bases, no absorption band appears in the region 3,400-3,100 cm^{-1} on account of strong hydrogen bonding and a broad band is simply observed in the region 2,975-2,850 cm^{-1}[15–16]. However in the case of tridentate *Schiff* bases used in the present investigations broad absorption bands of strong to weak intensity are observed in the region 3,400-3,100 cm^{-1} and these may be assigned to OH or NH stretching modes respectively[17].

In the lanthanon derivatives of these *Schiff* bases, no absorption band of the OH or NH group is observed in the region 3,400-3,100 cm^{-1}, indicating coordination through the oxygen of the phenolic as well as the alcoholic groups. This type of bonding is also substantiated by the appearance of a number of new absorption bands of medium intensity in the 700-600 cm^{-1} region. These bands may be assigned to the ring deformation coupled with Ln-O stretching and $\mathrm{C—CH_3}$ stretching modes and also the CH out of plane deformation coupled with Ln-O stretching modes[18,19].

A strong band is observed in the region 1,630-1,610 cm^{-1} in the spectra of *Schiff* bases and this is a characteristic absorption band of the azomethine ($>\mathrm{C=N}—$) group. In the IR spectra of lanthanon complexes of *Schiff* bases, $\nu(\mathrm{C=N})$ is observed at almost the same position[20].

Far infrared spectra of a few complex derivatives have also been recorded in order to substantiate the bonding of lanthanon to the nitrogen of the azomethine and oxygen of the alcoholic group. The $\nu(Ln\text{-}\mathrm{N})$ frequencies have been observed at different positions by different workers. In the 1,10-phenanthroline complexes of lighter and heavier lanthanides, bands at 200 and 235 cm^{-1} respectively have been assigned to ν(*Ln*-N). *Forsberg et al.*[21] have observed bands at ~ 360 cm^{-1} in the ethylenediamine complexes of lanthanons whereas in the lanthanon (III) β-diketonates, bands at ~ 200 and ~ 235 cm^{-1} have been assigned to ν(*Ln*-O) and ν(*Ln*-O) coupled with ring deformation vibrations[18]. In the lanthanon complexes of the *Schiff* bases, a strong band at ~ 200 cm^{-1} may be attributed to ν(*Ln*-N) and/or ν(*Ln*-O) vibrations.

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