Lanthanum(III) and praseodymium(III) complexes with bidentate and tetradeutate Schiff base ligands containing indole ring

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Complexes of lanthanum(III) and praseodymium(III) with Schiff bases, prepared from isatin with aniline, 4-chloroaniline, 2-bromoaniline, 2-nitroaniline (HL), ethylenediamine, α-phenylenediamine and 4-methyl-α-phenylenediamine (H₂L') have been synthesised and their physico-chemical properties investigated using elemental analysis, molar conductivities, magnetic susceptibility measurements and spectral (visible, infrared and 'H NMR) data. The Schiff bases HL bind in a bidentate manner while Schiff bases H₂L' bind in a tetradeutate manner. The probable structures of the complexes are proposed.

Isatin (I) also known as indole-2,3-dione, can be considered to be the o-quinone of 2,3-dihydroxyindole. It is a unique molecule possessing both amide and ketocarbonyl groups. Apart from this, it has an active hydrogen atom attached to nitrogen (or oxygen) and an aromatic ring which should substitute at 5- and 7- positions. It exists in a tautomeric form (II) and these functional characteristics play an important role in governing the various reactions of the molecule¹.

The C-3 carbonyl group of isatin is strongly electrophilic. As a result, isatins are readily involved in condensation and addition reactions. However, the coordination behaviour of Schiff bases derived from isatin is practically unknown. Hassaan et al. reported nickel(II) chelates of Schiff bases derived from isatin with amino acids and substituted hydrazines². The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes since it has been recognised that many of these complexes may serve as models for biologically important species³. In recent years, extensive investigations of lanthanide complexes have been studied⁴-⁶ for their interesting and important properties, for example, their ability reversibly to bind oxygen, catalytic activity in hydrogenation of olefins, structural probes in biological systems and the development of shift reagents.

In the present note, we report the preparation and characterisation of lanthanum(III) and praseodymium(III) complexes with some bidentate and tetradeutate Schiff base ligands derived from isatin. The structures of the ligands are shown below (III and IV).

![Schiff base structures](image)

Experimental

The reagents and solvents were analytical of grade. Lanthanum (III) and praseodymium(III) chlorides were purchased from BDH. The ligands were prepared by the condensation of isatin with appropriate amine as reported in the literature². The details of the analytical methods and physical
measurements were the same as those described earlier.

Reaction of lanthanum(III)/praseodymium(III) chloride with Schiff base derived from isatin and aniline

To a refluxing solution of Schiff base (0.03 mol) in methanol (30 cm$^3$) was added a methanolic solution (20 cm$^3$) of lanthanum (III) chloride or praseodymium (III) chloride (0.01 mol). To this, saturated ethanolic potassium hydroxide solution (5 cm$^3$) was added. The solution was refluxed for 20 h. The resulting mixture was concentrated to about 10 cm$^3$ and pet-ether (10 cm$^3$) was added which resulted yellow coloured precipitate. The precipitate was filtered off, washed with ether and dried in vacuo.

The same synthetic procedure was adopted for the reactions with other Schiff bases derived from isatin and 4-chloroaniline, 2-bromoaniline and 2-nitroaniline. These reactions are summarised in Table 1.

Reaction of lanthanum(III) chloride / praseodymium(III) chloride with Schiff base derived from isatin and ethylenediamine

To a methanolic solution (20 cm$^3$) of lanthanum (III) chloride or praseodymium (III) chloride (0.01 mol), an ethanolic solution (20 cm$^3$) of Schiff base (0.01 mol) containing potassium hydroxide (0.02 mol) was added. The resulting mixture was refluxed for 10 h. The solid complex so obtained was filtered off, washed repeatedly with ethanol and dried in vacuo.

The same synthetic procedure was adopted for the reactions of lanthanum (III) chloride or praseodymium (III) chloride with Schiff bases derived from isatin and 4-phenylenediamine or 4-methyl-4-phenylenediamine. The details of these reactions along with the analytical data of the products are given in Table 1.

Results and discussion

The reactions of LnCl$_3$ (Ln = La (III) or Pr (III)) with various Schiff bases led to the formation of two types of complexes as shown below:

\[
\text{LnCl}_3 + 3 \text{ LH} \overset{\text{methanol}}{\underset{\text{KOH}}{\longrightarrow}} [\text{Ln(L)}_3] + 3 \text{KCl} + 3 \text{H}_2\text{O}
\]

\[
\text{LnCl}_3 + \text{L'H}_2 \overset{\text{methanol}}{\underset{\text{KOH}}{\longrightarrow}} [\text{Ln(L'H)}\text{Cl(H}_2\text{O)}]
\]

where Ln = La (III) or Pr (III); LH = Schiff bases derived from isatin and aniline, 4-chloroaniline, 2-bromoaniline and 2-nitroaniline; L'H$_2$ = Schiff bases derived from isatin and ethylenediamine, 4-phenylenediamine and 4-methyl-4-phenylenediamine.

All the newly synthesised complexes are coloured solids and soluble in DMF, DMSO, chloroform and nitrobenzene. The analytical data are in good agreement with the proposed stoichiometry of the complexes. Molar conductance values of $10^{-3}$ M solutions of the complexes indicate the non-electrolytic nature of the complexes. The presence of water molecule in second type complexes is inferred from thermogravimetric analysis which show the loss of one water molecule at 150-165°C.

The lanthanum(III) complexes as expected, have no resultant magnetic moments whereas the magnetic moments of praseodymium(III) complexes (3.49-3.62 μ$_B$) show little deviation from Van Vleck value and that of hydrated sulphate.

The electronic absorption bands of praseodymium(III) appear due to the transitions from the ground level $^3H_4$ to the excited J level of the 4f configuration. Praseodymium(III) complexes show bands ~16780, 20280-20500, 20960-21230 and 22000-22350 cm$^{-1}$ corresponding to the transitions from $^3H_4$ to $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$ energy levels, respectively. It has been observed that on complexation, the electronic spectral bands shift to lower energy side (naphelauxetic effect). Jorgenson has attributed the slight shift in the bands to the effect of crystal field upon the interelectronic repulsion between the 4f electrons, i.e. to lowering of the interelectron repulsion parameter in the complexes. Further a marked enhancement in the intensity of the bands upon complexation is also observed. Values of naphelauxetic ratio (β) which is defined as $\nu_e/\nu_i$, where $\nu_e$ and $\nu_i$ are energies (in cm$^{-1}$) of the transitions in complex and free ion, respectively, for the present derivatives are given in Table 2. From the mean (β) values, the covalency parameter (δ) and bonding parameter (b$^{1/2}$) were determined using standard procedures. The values of which β are less than unity and positive values of δ and (b$^{1/2}$) support partial covalent nature of bonding between metal and ligands.

The IR spectra of the ligands and their complexes are complicated because of coupling between various

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of the azomethine linkage. This band shifts to lower

frequency (1620 -1610 cm⁻¹) in the complexes. The lowering in frequency of this band is an indication of the coordination of the unsaturated nitrogen of azomethine linkage. The coordination of nitrogen to lanthanum or praseodymium is also confirmed by the appearance of new bands in the region 390 - 370 cm⁻¹ assignable to v(Ln-N). The spectra of the ligands also show bands at ca. 3200 and 1680 cm⁻¹ which are assigned to v(N-H) and v(C=O) vibrations of the isatin moiety. However, in complexes, these bands disappear suggesting the enolization of keto group. This is also confirmed by the appearance of bands at ca. 1490 and 1580 cm⁻¹ which may be assigned to v(C=O) and newly formed v(C=N) vibrations, respectively. Conclusive evidence regarding the bonding of lanthanum(III) and praseodymium(III)

bands. However, attempts have been made to identify some important bands which furnish information regarding the mode of bonding. The IR spectra of isatin schiff base ligands show one strong band at ca. 1640-1630 cm⁻¹ which may be assigned to v(C=N) of the azomethine linkage. This band shifts to lower
with enolic oxygen is provided by the appearance of bands at ca. 480 cm\(^{-1}\) due to \(v(Ln-O)\). The infrared spectra of complexes of type \([Ln(L')ClH_2O]\) show bands at ca. 3420 - 3380 cm\(^{-1}\) which are assigned to \(v(OH)\) vibration of the coordinated water molecule.

The proton magnetic resonance spectra of lanthanum(III) complexes have been recorded in deuterated chloroform or dimethyl sulphoxide. The intensities of all the resonance lines were determined by planimetric integration. A comparison of the spectra of ligands with those of complexes led to the following conclusion:

(a) The peak due to NH of isatin ring appears at ca. 11.2 ppm in the spectra of the ligands which disappears in the complexes further confirming the enolization of keto group.

(b) The chemical shifts due to aromatic ring proton appear at ca. 7.8 - 8.4 ppm in the ligands which shift slightly downfield in the complexes. This may be due to the decrease of electron density after forming the complexes.

(c) The spectrum of complexes \([La(SIE)Cl(H_2O)]\) shows a singlet at \(\delta 2.40\) due to (CH\(_2\))\(_2\) group. The spectra of complexes \([La(SIP)Cl(H_2O)]\) and \([La(SIM)Cl(H_2O)]\) show signals at ca. \(\delta 6.80 - 7.10\) due to phenyl ring. The spectra of the complexes \([La(SIM)Cl(H_2O)]\) also shows one singlet at \(\delta 2.10\) due to methyl group attached to \(C_6H_3\) ring. These complexes show signals at \(\delta 12.4\) due to OH group.

Thus, on the basis of above studies the following structures are tentatively proposed for \([Ln(L_3)]\) (V) and \([Ln(L')ClH_2O]\) (VI) complexes.

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References