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Schiff Base Derivatives of Lanthanons, La(III), Pr(III), Nd(III) and Sm(III) Complexes of Bifunctional Tetradentate *Schiff* Base

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Reactions of La(III), Pr(III), Nd(III) or Sm(III) nitrate with bifunctional tetradentate *Schiff* base, $[o\text{-}HOC_6H_4C(CH_3):NCH_2]_2$, having the donor system HO—N—N—OH in 1 : 2 molar ratio have been investigated and found to yield new derivatives of the type $[Ln(SBH_2)_2](NO_3)_3$ [where *Ln* = La(III), Pr(III), Nd(III) or Sm(III) and SBH_2 = *Schiff* base molecule, $[o\text{-}HOC_6H_4C(CH_3):NCH_2]_2$. On the basis of elemental analyses, conductivity and magnetic measurements and infrared spectra, plausible structures for the resulting complexes have been indicated.

Introduction

In earlier publications of these laboratories[1–6], different molar reactions of the isopropoxides of La(III), Pr(III), Nd(III) and Sm(III) with the bi-, tri- and tetradentate *Schiff* bases in the medium of dry benzene have been reported and some interesting results regarding the volatility, polymerization and coordination numbers of the resulting products described.

In the aquo complex, the water molecule is a pertaining strong ligand towards the lanthanide ions and thus competes effectively for the coordination sites unless other ions or ligands having a strong structure-breaking influence are also present. *Frank* et al.[7] and *Freed*[8] have shown that nitrate ions have large structure breaking tendency over Cl^- ions.

In view of this, reactions of lanthanon nitrates with the bifunctional tetradentate *Schiff* bases, $(o\text{-}HOC_6H_4CCH_3:NCH_2)_2$ have been attempted and the results of these studies discussed in the present paper.

Experimental

Materials. Lanthanum, praseodymium, neodymium, samarium nitrates (hydrated) were prepared by dissolving their respective oxides (Dr. *Theodor Schuchardt*, Germany) in concentrated nitric acid (A.R.) and then evaporated to dryness. The product so obtained was crystallised in water to remove excess of nitric acid and then washed several times with ether.

Preparation of the *Schiff* Base

Schiff base, bis(o-hydroxyacetophenone)ethylenediimine, was prepared by the condensation of two moles of o-hydroxyacetophenone with one mole of ethylenediamine in absol. ethanol. It was then purified by recrystallisation and analysed before use.

Bis(o-hydroxyacetophenone)ethylenediimine, m. p. 188–189 °C.

$C_{18}H_{20}O_2N_2$. Found N 9.33, C 72.91, H 6.83.
Calc. N 9.45, C 72.98, H 6.80.

Reactions of Lanthanon Nitrates with Bifunctional Tetradentate *Schiff* Bases in the Acetone Medium

To a solution of 1.50 g bis(o-hydroxyacetophenone) ethylenediimine was added an acetone solution of $La(NO_3)_3 \cdot 6\,H_2O$ (1.10 g) (molar ratio 2: 1) with continuous stirring.

Solid yellow $[La(C_{18}H_{20}O_2N_2)_2](NO_3)_3$ soon separated out, which was filtered, washed with acetone and dried.

Calc. La 15.15, N 10.68. Found La 15.08, N 10.61.

Molar conductance 230 $ohm^{-1}\,cm^2\,mole^{-1}$.

Pr(III), Nd(III) and Sm(III) reacted in a similar way.

Analytical Methods and Physical Measurements

Lanthanum, praseodymium, neodymium and samarium were determined by complexometric titration with *EDTA* using Eriochrome Black T as the indicator.

Nitrogen was estimated by *Kjeldahl*'s method.

Conductivity measurements were made at 25 + 1 °C with a RLC bridge with a cell having cell constant 0.74 cm^{-1}.

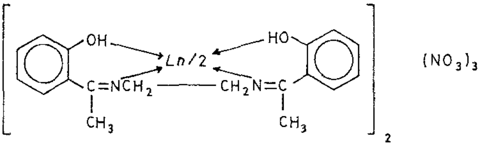
Magnetic data were determined by the *Gouy* method at the room temperature (35 ± 1 °C) using a semi-micro analytical balance.

Infrared spectra of the *Schiff* bases and the lanthanon derivatives were recorded in the range of 4,000–400 cm^{-1} with a Perkin Elmer 337 grating infrared spectrophotometer as nujol mulls. The wavelengths at 1,601 and 1,028 cm^{-1} of polystyrene were used as calibrants.

Results and Discussion

Derivatives of the type $[Ln(SBH_2)_2](NO_3)_3$ (Ln = La(III), Pr(III), Nd(III) or Sm(III) and SBH_2 = bis(o-hydroxyacetophenone)ethylenediimine are yellow solids and soluble in dimethylformamide and dimethyl sulphoxide. On heating, their colour changes to dark brown at ~ 230 °C.

The molar conductance values as determined in *DMF* at the concentration 10^{-3} *M* and 25 ± 1 °C lie in the range of 224–231 $\mathrm{ohm^{-1}\,cm^2\,mole^{-1}}$ indicating their behaviour as 1 : 3 electrolytes[9]. The cation species may, therefore, be formulated as $[Ln(SBH_2)_2]^{3+}$ [where *Ln* = La(III), Pr(III), Nd(III) or Sm(III) and SBH_2 = bis(o-hydroxyacetophenone)ethylenediimine] showing that all the three nitrate groups lie outside the coordination sphere and behave as monodentate ligands. The resulting *Schiff* base complexes may be structurally represented as follows:



The magnetic susceptibilities of *Schiff* base derivatives of La(III), Pr(III), Nd(III) or Sm(III) have been determined by the *Gouy* method and recorded in Table 1. The *Schiff* base derivatives of La(III) have been shown to be diamagnetic, whereas in the case of the derivatives of praseodymium, neodymium and samarium, the magnetic moments have been found to be of the order of 3.48, 3.53 and 1.26 μ_B resp. indicating their paramagnetic nature.

The experimental and theoretical values of the magnetic moments in the case of Pr^{3+} and Nd^{3+} have been found to be almost of the same order, whereas in the case of Sm^{3+} the theoretical and experimental magnetic moments are 0.84 and 1.26 μ_B resp. This anomalous behaviour may be due to the fact that while the state above the ground state is well separated in Pr^{3+}, this is not the case in Sm^{3+}. Further, the second order *Zeeman* effect is of appreciable importance in Sm^{3+} but of very small importance in Pr^{3+} [10].

The infrared absorption frequencies of the *Schiff* bases as well as the corresponding lanthanon derivatives were measured.

In the case of the *Schiff* base, bis(o-hydroxyacetophenone)ethylenediimine, no band is observed in the 3,500–3,200 $\mathrm{cm^{-1}}$ region on account of strong hydrogen bonding. The stretching frequency of the hydrogen bonded OH is shifted considerably to lower frequency in the *Schiff* bases and overlaps with the ν CH vibrations in the region 2,950–2,850 $\mathrm{cm^{-1}}$ [11, 12].

However, a medium broad band is observed in the region 3,300–3,200 $\mathrm{cm^{-1}}$ and this may be due to the presence of ν OH or ν NH group. In the case of *Schiff* bases no such band is observed.

Table 1. *Magnetic data of lanthanon derivatives of bis(o-hydroxyacetophenone)ethylenediimine*, $(HOC_6H_4CCH_3 : NCH_2)_2$

Compound	Ground state of the metal ion	g	$s \cdot 10^{-6}$ (c. g. s.)	$\mu_{\text{eff.calcd.}}$ μ_B	$\mu_{\text{eff.exp.}}$ μ_B
$[La(C_{18}H_{20}O_2N_2)_2](NO_3)_3$	$^1S_0$	1	— 0.20	—	—
$[Pr(C_{18}H_{20}O_2N_2)_2](NO_3)_3$	$^3H_4$	4/5	4.65	3.58	3.48
$[Nd(C_{18}H_{20}O_2N_2)_2](NO_3)_3$	$^4I_{9/2}$	9/11	4.99	3.62	3.53
$[Sm(C_{18}H_{20}O_2N_2)_2](NO_3)_3$	$^6H_{5/2}$	2/7	0.80	0.84	1.26

A characteristic band at ~ 1,607 cm^{-1} may be attributed to the ν C=N of the *Schiff* bases. This is observed in almost the same region (1,608–1,610 cm^{-1}) in the case of *Schiff* base complexes[13, 14].

A strong intensity band at ~ 1385 cm^{-1} and a medium intensity band at ~ 816 cm^{-1} may be assigned to the ionic nitrate (D_{3h}) in the *Schiff* base complexes[15]. Further, the band in the region, 700–600 cm^{-1} may be due to the ring deformation coupled with *Ln*—O stretching and C—CH_3 stretching modes and CH out of plane deformation coupled with *Ln*—O stretching modes[16].

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