

Synthesis and Characterization of Lanthanum(III) Complexes of Schiff Base Derived from Pyridine-2-Carboxaldehyde and Benzidine

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Complexes of trivalent lanthanum with Schiff base derived from pyridine-2-carboxaldehyde and benzidine have been synthesized and characterized. The IR spectrum shows that the ligand bis(pyridine-2-carboxaldehyde)benzidine acts as a bidentate ligand. The thermal analyses prove the presence of two coordinated water molecules. The complexes have been assigned the general formula $[La\{(P_2CA)_2B\}(H_2O)_2X_3]$.

Key Words: Synthesis, Lanthanum(III), Benzidine, Schiff base, Pyridine-2-carboxaldehyde.

INTRODUCTION

A number of lanthanide(III) complexes and their behaviour as Schiff reagents^{1,2} and also the complexes of trivalent lanthanide ions with the ligand bis(acetylaceton)benzidine³ have been reported. The present investigation is concerned with the synthesis and characterization of the complexes of trivalent lanthanum ion with the ligand bis(pyridine-2-carboxaldehyde)benzidine $(P_2CA)_2B$ and their characterization on the basis of estimation of metal and anion content, determination of molar mass, measurement of molar conductance, magnetic moment, IR and UV spectra and thermal (TGA and DTA) studies.

EXPERIMENTAL

Lanthanum oxide (Indian Rare Earths Ltd., Kerala) was converted to the corresponding nitrate and chloride. Pyridine-2-carboxaldehyde and benzidine were used as such.

The ligand $(P_2CA)_2B$ was prepared by mixing methanolic solutions of benzidine and pyridine-2-carboxaldehyde in the molar ratio 1 : 2. The reaction mixture was refluxed on a water bath for 2 h. The resulting solution was then poured into ice-cold water when a yellow crystalline solid separated. It was filtered and recrystallized from ethanol (m.p. 149°C).

For the preparation of the nitrate and chloro complexes, a methanolic solution of the ligand was refluxed for 1 h and then a methanolic solution of the metal

salt was added (1 : 1). The reaction mixture was refluxed for 6 h and concentrated to a viscous mass. It was washed several times with chloroform and ethanol to remove any excess metal salt and/ or ligand. Finally, the complexes were dried *in vacuo* over P_2O_5 .

The acetato and thiocyanato complexes were prepared by substitution method. Lanthanum nitrate complex with $(P_2CA)_2B$ was dissolved in methanol, which was mixed with an aqueous methanol solution of each of the different anionic salts such as sodium acetate or ammonium thiocyanate in the stoichiometric ratio. Each of the reaction mixtures was refluxed on a water bath for 4 h in order to replace the nitrate ions with the respective anions. The resulting solution was then concentrated and the concentrate was cooled to get the complex precipitated. The complex obtained was collected, washed with aqueous methanol and dried *in vacuo* over P_2O_5 .

The IR spectra of the ligand and complexes were recorded in KBr and in a few cases, in polyethylene on a Perkin-Elmer-621 grating infrared spectrophotometer in the range $4000-75\text{ cm}^{-1}$. The electronic spectra of the ligand and the complexes were recorded in the range 185–900 nm. The magnetic susceptibilities of the complexes were measured on a Gouy balance or vibrating sample magnetometer. Thermogravimetric analysis were carried out on Shimadzu DT-40 and DuPont-2000 thermal analyzers in an atmosphere of nitrogen with a sample mass *ca.* 5 mg and heating rate of 10 or $20^\circ\text{C min}^{-1}$. The molar conductances of the complexes, having concentration 10^{-3} M , in acetonitrile, methanol and nitrobenzene, were determined at room temperature using an Elico conductivity bridge (type CM 82 T) with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm^{-1}).

RESULTS AND DISCUSSION

The IR spectrum of $(P_2CA)_2B$ exhibits a very strong band at 1564 cm^{-1} which is attributed to $\nu(\text{C}=\text{N})$ of the azomethine group in the ligand³. This band appears at a lower wavenumber region around 1497 cm^{-1} in the complexes. This signifies that the two-azomethine nitrogen atoms are involved in coordination.

The bands appearing at 1468 and 744 cm^{-1} in the spectrum of the ligand are assigned respectively to the stretching and the out-of-plane bending vibrations of the pyridine ring. These bands are retained in the complexes in the same regions. This suggests that pyridine nitrogen is not coordinated to the lanthanum ion⁴. Hence $(P_2CA)_2B$ acts as a neutral bidentate ligand towards the lanthanum ion, the donor atoms being the two nitrogen atoms of the two-azomethine group.

The thermogram of the complexes shows a weight loss of about 5% at 165°C . This loss is consistent with the loss of two water molecules. The DTA of the complexes shows a strong endothermic peak at 180°C . It is an evidence for the coordinated nature of water.

All complexes absorb at 3369 cm^{-1} , which is assigned to stretching, and at 1619 cm^{-1} bending modes of water molecule⁵. Nakamoto⁶ suggested that the most diagnostic band for coordinated water lies in the region $1000-800\text{ cm}^{-1}$. A new band appearing in the spectra of these complexes around 818 cm^{-1} that does not

have its equal in the ligand is assigned to the rocking mode of vibration, around 739 cm^{-1} is assigned to the wagging mode and that around 618 cm^{-1} is assigned the $\nu(\text{M—O})$ (H_2O) mode⁷.

The IR spectra of the nitrate complexes exhibit three additional bands at 1384, 1303 and 1009 cm^{-1} , which are assigned to ν_4 , ν_1 and ν_2 modes of coordinated nitrate ion⁴. The separation between ν_4 and ν_1 bands is *ca.* 81 cm^{-1} , which indicates that the nitrate ions are coordinated unidentately⁷.

The spectrum of chloro complex shows an additional weak band in the far infrared region at 285 cm^{-1} assigned to $\nu(\text{M—Cl})$ vibration⁸.

The spectrum of acetato complex showing two bands at 1566 and 1381 cm^{-1} is assigned to asymmetric and symmetric stretching vibrations of carboxylate ion⁹. In the spectrum of the complex ν_{sym} is shifted to higher frequency region whereas ν_{asym} is shifted to lower frequency region. These shifts indicate that acetate ion is coordinated unidentately to the lanthanum ion.

The IR spectrum of thiocyanato complex exhibits bands at 2044, 811 and 512 cm^{-1} is assigned to $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of N-coordinated thiocyanate ion¹⁰ respectively.

The electronic spectrum of the ligand exhibiting three bands at 250, 300 and 350 nm. The weak band at 350 nm is assigned to $n \rightarrow \pi^*$ transition. The other two intense bands at 300 and 250 nm are assigned to $\pi \rightarrow \pi^*$ transition. The spectra of all these complexes are more or less similar to that of the ligand ensuring that the electronic transitions are exclusively localized ones on the ligand moiety.

The magnetic moments show that the complexes are diamagnetic as expected from their noble gas configuration¹¹.

TABLE-1
ELEMENTAL ANALYSES AND CHARACTERIZATION DATA OF THE COMPLEXES

Complexes	Mol. mass found (calcd.)	Metal % found (calcd.)	C found (calcd.)	H found (calcd.)	N found (calcd.)	Wt. loss due to water in TGA found (calcd.)	Anion % found (calcd.)
[La{(P ₂ CA) ₂ B}(H ₂ O) ₂ (NO ₃) ₃]	718 (723)	19.11 (19.20)	39.97 (39.85)	3.15 (3.07)	13.45 (13.56)	4.90 (4.98)	25.60 (25.72)
[La{(P ₂ CA) ₂ B}(H ₂ O) ₂ Cl ₃]	640 (644)	21.50 (21.58)	44.70 (44.78)	3.40 (3.44)	8.70 (8.71)	5.50 (5.60)	16.49 (16.52)
[La{(P ₂ CA) ₂ B}(H ₂ O) ₂ (CH ₃ COO) ₃]	719 (715)	19.34 (19.44)	50.34 (50.43)	4.30 (4.37)	7.75 (7.84)	5.00 (5.04)	—
[La{(P ₂ CA) ₂ B}(H ₂ O) ₂ (NCS) ₃]	708 (712)	19.45 (19.52)	45.69 (45.57)	3.21 (3.12)	13.90 (13.79)	5.10 (5.06)	24.40 (24.49)

Molar conductance values indicate non-electrolytic behaviour of the complexes¹². Thus the anions present in these complexes are inside the coordination sphere. On the basis of the above observations and discussions the following general formula is suggested for the complexes [La{(P₂CA)₂B}(H₂O)₂X₃], where

X represents monovalent anions such as acetate, chloride, nitrate and thiocyanate. In these complexes, $(P_2CA)_2B$ acts as a neutral bidentate ligand coordinating the metal ion through the two-azomethine nitrogen atoms. Water molecules and the anions are coordinated unidentately. Thus, lanthanum ion in the present complexes has a coordination number 7.

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