

## NOTE

**Studies on Lanthanide(III) Iodide Complexes of Some Schiff Bases**

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Some newly synthesized lanthanide(III) iodide complexes with Schiff bases having general composition  $\text{LnL}_4\text{I}_3$  ( $\text{Ln} = \text{La, Ce, Gd, Sm}$ , and  $\text{L} = 2[\text{N}(\text{-benzalidene) amino}]$ pyridine (BAPy), 2[N-(4'-dimethylamino benzalidene) amino]pyridine (pBAPy); 2[N-(3'-nitrobenzalidene) amino]pyridine (3-NBAPy) and 2[N-(2'-hydroxybenzalidene) amino]pyridine (SAPy). pBAPy, 3-NBAPy and SAPy). These compounds were characterized on the basis of elemental analysis, molar conductance, molecular weight and spectral data. The coordination number six of central metal ion is proposed on the basis of conductance value.

**Key Words:** Lanthanide(III), Iodide, Schiff bases.

Lanthanide(III) metal ions are appropriate for complex formation because of their size and high positive charge. These ions form generally the coordination compounds<sup>1</sup> with coordination numbers 6 to 10. In the present communication we wish to present the studies on lanthanide(III) iodide complexes with some Schiff bases, viz., 2[N-(benzalidene) amino]pyridine (BAPy); 2[N-(4'-dimethylamino benzalidene) amino]pyridine (pBAPy); 2[N-(3'-nitrobenzalidene) amino]pyridine (3-NBAPy) and 2[N-(2'-hydroxybenzalidene) amino]pyridine (SAPy).

Lanthanide(III) nitrates were obtained from Rare Earth Products (Ltd) and lanthanide(III) iodides were prepared from them by treating them with appropriate amount of KI in ethanol<sup>2</sup>. Ligands were prepared as reported earlier<sup>3-6</sup>. Solvents were obtained from various sources such as B.D.H., E. Merck and S.D. Chemicals and before use these were purified by standard methods<sup>7</sup>. The metal content was estimated by reported method<sup>8</sup> and all other physio-chemical measurements were made as reported earlier<sup>9</sup>.

Complexes were prepared by treating corresponding lanthanide(III) iodides (1 mmol) in ethanol with corresponding ligand solution (4.1 mmol) in the same solvent and the resulting mixture was refluxed on a water bath for 1/2 to 1 h (at ca. 70–75°C). On cooling, the desired complex formation takes place. The compounds were filtered and collected, washed with solvent and finally with ether and dried *in vacuo* over  $\text{CaCl}_2$ .

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The analytical data for these compounds are given in Table-1. The complexes are stable and can be stored for some period. After a long time period these complexes become sticky. These complexes are soluble in common organic solvents. On the basis of conductance and molecular weight data the general composition  $[\text{Ln}(\text{L})_4\text{I}_2]\text{I}$  is suggested for these complexes as conductance data support 1 : 1 electrolytic nature of the complexes showing that one iodide is present outside the coordination sphere. Some observations can be made from the molecular weight data as the ratio of formula weight to observed molecular weight is *ca.* 0.5 for these complexes.

TABLE-1  
PHYSICO-CHEMICAL DATA AND IR SPECTRAL BANDS ( $\text{cm}^{-1}$ ) OF  
LANTHANIDE(III) IODIDE COMPLEXES OF SCHIFF BASE LIGANDS

Compound (Colour)	m.p. (°C)	Found (Calcd.) %		$\Omega_m$ ( $\text{ohm}^{-1} \text{cm}^2$ $\text{mol}^{-1}$ )	Average m.w. (formula weight)	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{Ln}-\text{N})$
		M	N				
BAPy (Light yellow)	180–185	—	—	—	—	1664 s	—
[La(BAPy) <sub>4</sub> I <sub>2</sub> ] (Yellow)	129	10.20 (11.13)	7.17 (8.97)	51.9	625 (1248)	1624 s	514 m
[Gd(BAPy) <sub>4</sub> I <sub>2</sub> ] (Orange)	168	10.39 (12.40)	7.27 (8.84)	52.3	648 (1266)	1629 s	520 m
[Sm(BAPy) <sub>4</sub> I <sub>2</sub> ] (Orange)	121	10.19 (11.91)	7.72 (8.89)	50.3	684 (1259)	1628 s	525 m
[Ce(BAPy) <sub>4</sub> I <sub>2</sub> ] (Orange)	153	10.29 (11.20)	7.16 (8.96)	51.6	629 (1249)	1627 s	516 m
PBAPy (Yellowish orange)	185–187	—	—	—	—	1667 s	—
[La(PBAPy) <sub>4</sub> I <sub>2</sub> ] (Pale yellow)	142	8.27 (9.78)	10.38 (11.83)	50.3	758 (1420)	1627 s	525 w
[Gd(PBAPy) <sub>4</sub> I <sub>2</sub> ] (Pale yellow)	168	9.19 (10.91)	10.18 (11.68)	51.5	718 (1438)	1625 s	522 w
[Sm(PBAPy) <sub>4</sub> I <sub>2</sub> ] (Pale yellow)	144	8.98 (10.48)	9.28 (11.74)	52.5	713 (1431)	1624 s	518 m
[Ce(PBAPy) <sub>4</sub> I <sub>2</sub> ] (Brown)	128	8.12 (9.85)	9.82 (11.82)	53.6	718 (1421)	1622 s	512 m
[3-NBAPy] (Yellow)	202–205	—	—	—	—	1675 s	—
[La(3-NBAPy) <sub>4</sub> I <sub>2</sub> ] (Red)	143	8.13 (9.73)	9.62 (11.76)	52.3	782 (1428)	1630 s	520 w
[Gd(3-NBAPy) <sub>4</sub> I <sub>2</sub> ] (Red)	162	9.15 (10.85)	9.78 (11.61)	53.1	742 (1446)	1630 s	525 w
[Sm(3-NBAPy) <sub>4</sub> I <sub>2</sub> ] (Dark Orange)	160	9.21 (10.42)	9.87 (11.67)	51.4	729 (1439)	1624 s	521 w

Compound (Colour)	m.p. (°C)	Found (Calcd.) %		$\Omega_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Average m.w. (formula weight)	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{Ln}-\text{N})$
		M	N				
[Ce(3-NBAPy) <sub>4</sub> I <sub>2</sub> ]I (Orange)	170	8.22 (9.79)	10.57 (11.75)	55.1	722 (1429)	1627 s	521 w
SAPy (Reddish orange)	190–192	—	—	—	—	1660 s	—
[La(SAPy) <sub>4</sub> I <sub>2</sub> ]I (Yellow)	139	9.19 (10.59)	7.39 (8.53)	51.5	626 (1312)	1624 s	519 m
[Gd(SAPy) <sub>4</sub> I <sub>2</sub> ]I (Black)	125	10.18 (11.80)	7.93 (8.42)	52.3	658 (1330)	1624 s	514 m
[Sm(SAPy) <sub>4</sub> I <sub>2</sub> ]I (Black)	146	10.23 (11.33)	7.13 (8.46)	53.1	672 (1323)	1625 s	519 m
[Ce(SAPy) <sub>4</sub> I <sub>2</sub> ]I (Yellowish green)	149	9.16 (10.66)	7.24 (8.53)	54.1	628 (1313)	1626 s	521 m

On the basis of IR spectral studies, it is observed that the  $\nu(\text{C}=\text{N})$  azomethine group frequency shifts towards lower frequency side thereby suggesting that the linkage of ligands to the metal is through  $(\text{C}=\text{N})$  azomethine N-atom<sup>10</sup>. All other peaks as  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}-\text{N})$ , i.e., pyridine ring deformation and breathing bands remain practically unchanged on complexation. A new band  $\nu(\text{Ln}-\text{N})$  appears in 525–510 cm<sup>-1</sup> region in the present complexes.  $\nu(\text{Ln}-\text{I})$  band is beyond the scope of studies as this band appears usually at ca. 200–100 cm<sup>-1</sup> in far IR region.

On the basis of this discussion coordination number six is suggested for the central metal which is supported by the conductance, molecular weight and IR spectral data of these complexes.

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