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Synthesis and Characterization of Lanthanide(III) Perchlorate Complexes of Some Schiff Base Ligands

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In the present work the lanthanide(III) perchlorate complexes with some Schiff base ligands with the general composition $Ln(L)_6(ClO_4)_3$ (Ln = La and Sm) (L = 2[N-(benzalidene)amino]-pyridine (BAPy), 2[N-(4′-dimethylaminobenzalidene)amino] pyridine (PBAPy), 2[N-(3-nitrobenzalidene)amino] pyridine (3-NBAPy), and 2[N-(2-hydroxybenzalidene)amino] pyridine (SAPy) were isolated and characterized by elemental analysis, molar conductance, m.w. and spectral data. The coordination number of central metal ion is proposed as six based on the conductive nature of perchlorate ion.

Key Words: Lathanide(III), Perchlorate, Schiff bases, Complexes.

INTRODUCTION

Lanthanide(III) ions because of their size and charge are the best ions to form stable complexes with high coordination numbers[1] generally in the coordination number 6 to 10. In this paper the studies on lanthanide(III) perchlorate complexes with some Schiff base ligands, *viz.*, 2[N-(benzalidene)amino]pyridine (BAPy), 2[N-(4′-dimethylaminobenzalidene)amino] pyridine (PBAPy), 2[N-(3-nitrobenzalidene)amino] pyridine (3-NBAPy), and 2[N-(2-hydroxybenzalidene)-amino] pyridine (SAPy) have been presented.

EXPERIMENTAL

The lanthanide oxides were obtained from Rare Earth Products Ltd. (India). The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess of acid[2]. The ligands were prepared by reported methods[3–6]. Solvents used were of BDH, E. Merck and S.D. Chemicals. Before use they were purified by standard methods[7]. All the physico-chemical measurements were performed by the reported methods[8].

Preparation of complexes

The solutions of respective lanthanide(III) perchlorates (1.1 mmol) and Schiff

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base ligand (6.2 mmol) in hot methanol (25 mL each) were mixed and refluxed on a water bath for 1–2 h. These were then concentrated to about 10 mL and diethyl ether (*ca.* 25 mL) was added with constant stirring to separate the desired product, which was collected and washed with ether and dried *in vacuo* over $CaCl_2$.

RESULTS AND DISCUSSION

The reaction of lanthanide(III) perchlorate salts with the respective Schiff base ligands results in the formation of complexes with the general composition $[Ln(ClO_4)_3(L)_6]$ (Ln = La and Sm, L = BAPy, PBAPy, 3-NBAPy and SAPy). The analytical data for these complexes is given in Table-1. The complexes are fairly stable and could be stored for a long period and non-hygroscopic in nature. These complexes behave as 1 : 3 electrolytes in $PhNO_2$ suggesting that all the perchlorate groups are present outside the coordination sphere[9]. Data on molecular weight of these complexes suggested that 4 species are formed for these complexes in solution as the ratio of observed m.w. to the calculated one is approximately 0.25. Magnetic moment values are also given in Table-1, which shows that only lanthanum complexes are diamagnetic in nature but all other lanthanide(III) ions are paramagnetic in nature due to presence of 4*f* electrons, which are effectively shielded by $5s^2p^6$ electrons[10, 11].

TABLE-1.
ANALYTICAL, CONDUCTANCE AND MOLECULAR WEIGHT DATA FOR COMPLEXES

Compound, Colour (Yield %)	m.p. (°C)	Found (Calcd.) % Ln	N	Ωm (ohm^{-1} cm^2 mol^{-1})	Average m.w. (formula weight)	μ_{ff} (B.M.)
$La(ClO_4)_3(BAPy)_6$	160	8.98	10.17	79.8	38.3	Diamag.
Orange (50)	163	(9.07)	(10.97)		(1521)	
$Sm(ClO_4)_3(BAPy)_6$	168	9.20	10.19	79.3	378	1.57
Brown (55)	172	(9.72)	(10.89)		(1542)	
$La(ClO_4)_3(PBAPy)_6$	165	7.16	13.92	78.2	448	Diamag.
Brownish black (55)	168	(7.76)	(14.08)		(1789)	
$Sm(ClO_4)_3(PBAPy)_6$	160	7.99	13.29	78.3	440	1.58
Brown (50)	164	(8.33)	(14.00)		(1800)	
$La(ClO_4)_3(3NBAPy)_6$	163	7.12	12.98	79.3	442	Diamag.
Brownish black (55)	167	(7.71)	(13.99)		(1801)	
$Sm(ClO_4)_3(3NBAPy)_6$	168	9.12	12.92	78.1	450	1.59
Brown (50)	171	(8.28)	(13.90)		(1812)	
$La(ClO_4)_3(SAPy)_6$	172	8.14	10.15	79.1	422	Dimag.
Orange (75)	176	(8.54)	(10.35)		(1627)	
$Sm(ClO_4)_3(SAPy)_6$	170	8.25	9.98	79.3	408	1.58
Brownish black (60)	175	(9.15)	(10.25)		(1638)	

The partial IR data for these compounds are given in Table-2. The IR spectra of these complexes when compared with those of the ligands show a considerable shift in ν(C=N) azomethine absorption to lower frequency side indicating a decrease in the stretching force constant of (C=N) as a consequence of the coordination through azomethine nitrogen, the double bond character in the carbon and nitrogen is reduced[12–15]. The bands observed at *ca.* 1580–1380 cm^{-1} and 1115–1060 cm^{-1} are tentatively assigned to antisymmetric and symmetric ν(C=C) and ν(C—N) of pyridine ring which remain unchanged in frequency and band intensity revealing non-involvement of pyridine nitrogen and metal bond. Some new medium and weak intensity bands are observed in the range 550–500 cm^{-1} in the complexes where no absorption is there in case of ligands. These bands are assigned to ν(M—N) stretching modes[16, 17]. In these complexes presence of two strong bands at *ca.* 1115–1060 cm^{-1} and 630–610 cm^{-1} regions respectively for perchlorate ion indicates that tetrahedral symmetry has not been disturbed on complexation for perchlorate ions. Therefore these ions are not bonded to metal ion[18, 19]. This conclusion is supported by conductance and molecular weight data.

TABLE-2
PARTIAL IR DATA FOR LANTHANIDE(III) PERCHLORATE COMPLEXES OF SCHIFF BASE LIGANDS

Compound	ν(C=N) (azomethine)	Pyridine ring breathing and deformation bands		ν(Ln—N)
		ν(C=C)	ν(C—N)	
BAPy	1664 s	1576 m	1069 m	—
$La(ClO_4)_3(BAPy)_6$	1599 s	1575 sh	1070 w	520 w
$Sm(ClO_4)_3(BAPy)_6$	1593 s	—	1075 sh	519 w
PBAPy	1667 s	1580 m	1089 m	—
$La(ClO_4)_3(PBAPy)_6$	1597 s	1575 sh	1090 w	538 w
$Sm(ClO_4)_3(PBAPy)_6$	1620 s	—	1088 s	535 w
3NBAPy	1675 s	1380 m	1085 m	—
$La(ClO_4)_3(3\text{-}NBAPy)_6$	1659 s	1379 m	1984 sh	525 w
$La(ClO_4)_3(3\text{-}NBAPy)_6$	1596 s	1380 w	1085 sh	525 w
SAPy	1660 s	1409 w	1100 sh	—
$La(ClO_4)_3(SAPy)_6$	1620 s	—	1115 w	525 w
$Sm(ClO_4)_3(SAPy)_6$	1653 s	1443 w	1109 s	520 w

Configuration of the complexes

Lanthanide metal ions may have coordination number 6, 8 or 10 depending upon the nature of anion present. In the present case conductance, m.w. and IR spectral data support the fact that all the perchlorate ions are present outside the coordination sphere thereby generating six coordination number on the lanthanide(III) metal ion as observed earlier[8].

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