Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5519-5525

Schiff Base Complexes for Lanthanide(III) Iodides

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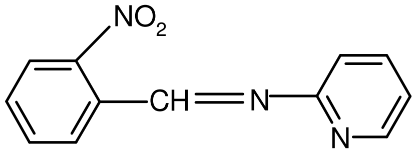
Some newly synthesized lanthanide(III) iodide complexes of Schiff bases having general composition LnL_4I_3 (Ln = La, Ce, Pr or Sm and L = 2N-(2-nitrobenzalidene)aminopyridine (2-NBAPy); 2N-(furfural)aminopyridine (FAPy); 2N-(3,4,5-trimethoxybenzalidene)aminopyridine (TMBAPY); and 2N-(4-chlorobenzalidene)aminopyridine (*p*-ClBAPy). These compounds were characterized on the basis of elemental analysis, molar conductance, molecular weight and spectral data. Coordination number six has been proposed for metal ion in these complexes.

Key Words: Lanthanide(III) iodide complexes, Schiff bases.

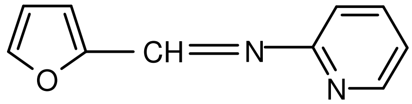
INTRODUCTION

Lanthanide(III) metal ions are appropriate for complex formation because of their size and high formal positive charge and these metal ions generally show coordination number 6 to 10 in their metal complexes[1].

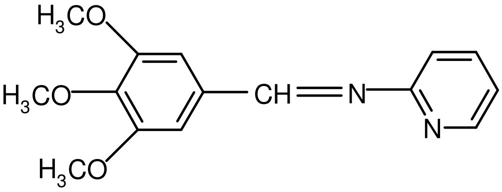
Present communication reports the lanthanide(III) iodide complexes with some Schiff bases ligands *viz.*, 2N-(2-nitrobenzalidene)aminopyridine (2NBAPy), 2N-(furtural)aminopyridine (FAPy), 2N-(3,4,5-trimethoxy benzalidene)aminopyridine (TMBAPy) and 2N-(4-chlorobenzelidene)-aminopyridine (*p*-ClBAPy) (Fig. 1).



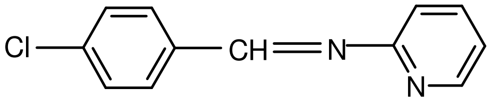
2N-(2-Nitro benzalidene)aminopyridine (2-NBAPy) (**I**)



2N-(Furfural)aminopyridine (FAPy) (**II**)



2N-(3,4,5-Trimethoxy benzalidene)aminopyridine (TMBAPy) (**III**)



2N-(4-Chloro benzalidene)aminopyridine (*p*-ClBAPy) (**IV**)

Fig. 1

EXPERIMENTAL

Lanthanide(III) nitrates were obtained from Rare Earth Products (Ltd.) and lanthanide(III) iodides were prepared from them by treating these nitrate salts with appropriate amount of KI in ethanol[2].

Ligands were prepared as reported earlier[3-6]: A solution of distilled aromatic aldehyde (1 mmol) in absolute alcohol (50 mL) was mixed with corresponding amine *i.e.* 2-amino pyridine (1.1 mmol) in the same solvent and the mixture was refluxed for 3-4 h on cooling yellow to brown products were separated out which were than filtered off and recrystallized using the same solvent.

Mass spectral studies of the ligands were done successfully. The molecular in peaks (or parent peak) appear in the mass spectra of these ligands at the same value at which these are expected to come. These appear at m/e 228, 173, 273 and 217 for 2-NBAPy, FAPy, TMBAPy and *p*-ClBAPy, respectively which confirm the molecular weights of the ligands as compared to their formula weights.

Solvents were obtained from various sources such as BDH, E-Merck and SD chemical and before use these were purified by standard methods[7]. All the physicochemical measurements were made as reported earlier[8-10].

Preparation of complexes: Complexes were prepared by treating corresponding lanthanide(III) iodide (1 mmol) in ethanol with corresponding ligand solution (4.1 mmol) in the same solvent and the resulting mixture was refluxed on the water bath for 0.5 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 $CaCl_2$.

RESULTS AND DISCUSSION

The analytical data for these complexes are given in Table-1.

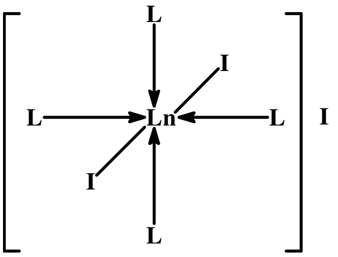
Complexes are stable and can be stored for some period. After a long time period some of these complexes become sticky. The complexes are soluble in common organic solvents. On the basis of conductance and molecular weight data for general composition $[Ln(L_4)I_2]I$ is suggested for these complexes as conductance data support 1:1 electrolytic nature of the complexes showing that one iodide is present outside the coordination sphere. Same observation can be made from the molecular weight data as the ratio of the formula weight to observed molecular weight cryoscopically is *ca.* 0.5 for these complexes.

On the basis of IR spectral studies, it is observed that ν(C=N) azomethine group frequency shift towards lower frequency side thereby suggesting that the linkage of ligands to the metal is through (C=N) azomethine nitrogen atom[11] (Table-2).

All other peaks as ν(C=C) and ν(C-N) *i.e.* pyridine ring deformation and breathing bands remains practically unchanged on complex formation. A new band ν(Ln-N) appears at *ca.* 522-512 cm^{-1} in the present complexes ν(Ln-I) band is beyond the scope of studies as this band appears usually at ca 200-100 cm^{-1} in far IR region.

Electronic spectral data of some of the complexes have been performed successfully and the shift of hypersensitive bands has been utilized to calculate the nephelauxatic effect (β) in these complexes. From β values the covalency factor (b½) Sinha's covalency parameter (δ %) (metal ligand covalency percentage) and covalency angular overlap parameter (η) have been calculated and are reported in (Table-3). The reported values of these parameters are similar to the previous observations[12].

On the basis of above discussion coordination number six is suggested for the central metal atom, which is supported by conductance, molecular weight and IR spectral data of these complexes. Proposed structure of the complexes is given in Fig. 2.



[Ln = La, Ce, Sm or Pr ; L = 2-NBAPy, FAPy, TMBAPy and *p*-ClBAPy] (CN = 6)

Fig. 2

TABLE-1
ANALYTICAL CONDUCTANCE, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA FOR LANTHANIDE(III) IODIDE COMPLEXES OF SCHIFF BASE LIGANDS

Compound	Colour	Yield (%)	Decomp. temp (ºC)	Elemental analysis (%): Found (Calcd.) C	H	N	Λ_m (ohm^{-1} cm^2 mol^{-1})	Average m.w. (f.w.)	μ_{eff} (BM)
[La(2-NBAPy)$_4$I$_2$]I	Brownish black	61	159	27.04 (35.9)	2.14 (2.24)	14.19 (10.49)	50.3	612 (1201)	Diamag.
[Ce(2-NBAPy)$_4$I$_2$]I	Dark brown	60	158	27.20 (35.7)	2.13 (2.24)	13.32 (10.48)	51.9	602 (1202)	2.32
[Sm(2-BAPy)$_4$I$_2$]I	Dark brown	62	162	27.02 (35.6)	2.13 (2.22)	12.32 (10.39)	51.2	610 (1212)	1.60
[Pr(2-NBAPy)$_4$I$_2$]I	Dark brown	61	161	28.04 (35.8)	2.14 (2.24)	14.19 (10.48)	52.3	614 (1203)	3.62
[La(FAPy)$_4$I$_2$]I	Blackish brown	63	160	29.02 (34.7)	2.13 (2.31)	11.32 (8.10)	50.3	510 (1036)	Diamag.
[Ce(FAPy)$_4$I$_2$]I	Brown	65	159	28.30 (34.6)	2.12 (2.31)	12.13 (8.10)	51.9	512 (1037)	2.33
[Sm(FAPy)$_4$I$_2$]I	Black	64	158	28.35 (34.3)	2.19 (2.29)	12.32 (8.02)	52.9	514 (1047)	1.63
[Pr(FAPy)$_4$I$_2$]I	Brownish black	63	157	29.35 (34.5)	2.13 (2.31)	13.12 (8.09)	52.3	516 (1038)	3.61
[La(TMBAPy)$_4$I$_2$]I	Yellow	63	155	29.42 (40.4)	3.29 (3.59)	7.38 (6.28)	51.3	642 (1336)	Diamag.
[Ce(TMBAPy)$_4$I$_2$]I	Brown	64	156	46.35 (40.3)	3.59 (3.59)	2.72 (6.27)	52.3	648 (1337)	2.42
[Sm(TMBAPy)$_4$I$_2$]I	Yellow	65	157	30.98 (40.0)	3.53 (3.56)	7.83 (6.23)	51.3	652 (1347)	1.63
[Pr (TMBAPy)$_4$I$_2$]I	Light brown	66	158	33.50 (40.2)	2.39 (3.59)	4.05 (6.27)	50.3	647 (1338)	3.62
[La(*p*-ClBAPy)$_4$I$_2$]I	Yellow crystalline	67	159	29.60 (36.9)	2.20 (2.30)	8.27 (7.17)	51.4	520 (1170)	Diamag.
[Ce(*p*-ClBAPy)$_4$I$_2$]I	Dark brown	68	152	30.90 (36.8)	2.21 (2.30)	9.15 (7.15)	52.4	528 (1171)	2.32
[Sm(*p*-ClBAPy)$_4$I$_2$]I	Yellow	63	151	25.23 (36.6)	2.12 (2.28)	13.13 (7.11)	51.9	522 (1181)	1.60
[Pr(*p*-ClBAPy)$_4$I$_2$]I	Light yellow	66	153	23.45 (36.7)	1.96 (2.30)	11.93 (7.16)	50.3	524 (1172)	3.61

TABLE-2
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF LANTHANIDE(III) IODIDE COMPLEXES OF SCHIFF BASE LIGANDS

Assignment Compound	ν(C=N) *str.* (azomethine)	ν(C-N)/ν(C=C) Pyridine ring breathing & deformation	ν(Ln-N) metal ligand vibration
2-NBAPy	1600s	1530s 1091m	-
[La(2-NBAPy)$_4$I$_2$]I	1595s	1530sh 1090w	512w
[Ce(2-NBAPy)$_4$I$_2$]I	1589s	1528s 1090sh	515w
[Sm(2-NBAPy)$_4$I$_2$]I	1590s	1527s 1088w	515w
[Pr(2-NBAPy)$_4$I$_2$]I	1594s	1525sh 1085w	512w
FAPy	1602s	1528s 1089m	-
[La(FAPy)$_4$I$_2$]I	1595s	1525sh 1090sh	515w
[Ce(FAPy)$_4$I$_2$]I	1599s	1479m 1090sh	515w
[Sm(FAPy)$_4$I$_2$]I	1583s	1480m 1090w	520w
[Pr(FAPy)$_4$I$_2$]I	1590s	1478m 1090sh	520w
TMBAPy	1686s	1503s 1038m	-
[La(TMBAPy)$_4$I$_2$]I	1595s	1503sh 1040w	512w
[Ce(TMBAPy)$_4$I$_2$]I	1591s	1505sh 1464m 1035sh	515w
[Sm(TMBAPy)$_4$I$_2$]I	1621s	1505sh 1462w 1041w	520w
[Pr(TMBAPy)$_4$I$_2$]I	1622s	1465sh 1040sh	515w
p-ClBAPy	1598s	1522m 1087m	-
[La(*p*-ClBAPy)$_4$I$_2$]I	1531s	1525w 1483m 1088m	514w
[Ce(*p*-ClBAPy)$_4$I$_2$]I	1586s	1525sh 1475w 1085sh	515w
[Sm(*p*-ClBAPy)$_4$I$_2$]I	1588s	1520sh 1484w 1091w	512w
[Pr(*p*-ClBAPy)$_4$I$_2$]I	1581s	1484w 1090m	522w

TABLE-3

ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELATED BONDING PARAMETERS OF LANTHANIDE(III) COMPLEXES OF SCHIFF BASE LIGANDS

Complex	Lanthanide salt's electronic spectral band (cm^{-1})	Complex electronic spectral band (cm^{-1})	Energy level	(1-β)	β	b^{½}	δ %	η
[Sm(2-NBAPy)$_4$)I$_2$]I	24900	24570	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.01325	0.98670	0.11510	1.3428	0.006620
	24000	23040	$\rightarrow {}^6P_{5/2}$	0.04000	0.96000	0.20000	4.1660	0.019700
	21600	21530	$\rightarrow {}^4I_{13/2}$	0.00324	0.99600	0.05690	0.3250	0.001990
[Sm(FAPy)$_4$I$_2$]I	24900	24700	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.00800	0.99100	0.08940	0.8072	0.004480
	24000	23050	$\rightarrow {}^6P_{5/2}$	0.03950	0.96040	0.19870	4.1128	0.019600
	21600	21550	$\rightarrow {}^4I_{13/2}$	0.00231	0.99760	0.04800	0.2315	0.001190
[Sm(TMBAPy)$_4$I$_2$]I	24900	24500	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.01405	0.98595	0.11853	1.4250	0.010448
	24000	23070	$\rightarrow {}^6P_{5/2}$	0.03875	0.96125	0.19685	4.0312	0.019183
	21600	21520	$\rightarrow {}^4I_{13/2}$	0.00370	0.99630	0.06082	0.3713	0.003700
[Sm[*p*-ClBAPy)$_4$I$_2$]I	24900	24450	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.01807	0.98193	0.13442	1.8402	0.008990
	24000	23150	$\rightarrow {}^6P_{5/2}$	0.03540	0.96460	0.18814	3.6699	0.017540
	21600	21530	$\rightarrow {}^4I_{13/2}$	0.00324	0.99670	0.05692	0.3250	0.001648

TABLE-4

ANTIFUNGAL ACTIVITIES OF SOME OF THE REPRESENTATIVE COMPLEXES OF LANTHANIDE(III) METAL IONS WITH SCHIFF BASES LIGANDS

Compound no.	Complex	*Aspergilus* sp.			*Mucor* sp.		
		Concentrations (mg/mL)			Concentrations (mg/mL)		
		10	20	30	10	20	30
I	[Sm(TMBAPy)$_4$I$_2$]I	–	–	–	3.0	2.5	1.1
II	[La(*p*-ClBAPy)$_4$I$_2$]I	0.5*	0.7	0.5*	2.4	2.0	1.0*
III	[Pr(*p*-ClBAPy)$_4$I$_2$]I	–	–	–	2.4	2.0	1.2

*Minimum value.

Antifungal activities were also performed by some of these complexes on *Aspergilus* sp. and *Mucor* sp. on PDA culture medium using disc method taking solution of complexes in DMF in varied concentrations. Radial growth of fungal colonies are given (Table-4). Antibacterial studies of some of the representative complexes were also performed on *E. coli* sp. on NA culture medium using disc methods Radial growth results are given in Table-5.

TABLE-5
ANTIBACTERIAL ACTIVITIES OF SOME OF THE REPRESENTATIVE COMPLEXES OF LANTHANIDE(III) METAL IONS WITH SCHIFF BASES LIGANDS

Compd. no.	Complex	*E. coli*		
		Concentrations (mg/mL)		
		10	20	30
IV	$[Sm(TMBAPy)_4I_2]I$	1.0	0.7	0.4
V	$[La(p\text{-}ClBAPy)_4I_2]I$	0.9	0.7	0.7
VI	$[Pr(p\text{-}ClBAPy)_4I_2]I$	1.3	1.0	1.1

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(*Received*: 25 September 2007; *Accepted*: 8 May 2008) AJC-6571