Asian Journal of Chemistry; Vol. 23, No. 2 (2011), 515-518

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Some Hexa-Coordinated Lanthanide(III) Iodide Complexes with Schiff Bases of Cyanoethylated benzaldehyde

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(*Received*: 4 January 2010; *Accepted*: 20 September 2010) AJC-9097

A series of 16 new complexes of lanthanide(III) iodide, with the Schiff base ligands, 2-methyl-4-NN-*bis*-2'- cyanoethylamino-benzylidineaniline [MCEABAB], 2-methyl-4-NN-*bis*-2'-cyanoethylaminobenzylidine *p*-chloro aniline [MCEABCAB], 2-methyl-4-NN-*bis*-2'-cyanoethylaminobenzylidine *p*-toludine [MCEABPT] and 2-methyl-4-NN-*bis*-2'-cyanoethylamino-benzylidine *p*-fluoroaniline [MCEABFAB] were synthesized. The complexes were characterized on the basis of elemental analyses, molecular weight determinations, conductivity measurements, IR spectra and electronic spectra. Mass spectra and TGA studies for the formation of complexes with general formula $[Ln(L)_4I_2]I$, [where Ln = La, Ce, Sm and Gd; L = MCEABAB, MCEABCAB, MCEABPT and MCEABFAB] were analyzed. Some of the synthesized complexes were tested for biological activity against a variety of test organisms, a few of them were found to be moderately effective.

Key Words: Lanthanide(III) iodide complexes, Synthesis, Structural, Biological properties.

INTRODUCTION

Lanthanides form complexes with variable coordination numbers and mixed geometries. Keeping above in view it is planned to synthesize some new lanthanide(III) metal complexes with nitrogen donor ligands especially Schiff bases with iodide anion[1-5].

EXPERIMENTAL

All the Schiff bases wre synthesized as reported[6].

Synthesis of complexes: Lanthanide(III) iodide (1 mmol) and absolute ethanol (15 mL) were taken in a flask fitted with a stirrer. A solution of corresponding Schiff base (4 mmol) in ethanol (10 mL) was added slowly to the stirred solution. In some cases the complexes were isolated immediately in cold, while in other case in hot solution. The crystal of the complexes were collected under suction, washed with solvent them with ether and finally dried in vacuo over anhyd. $CaCl_2$.

General reaction proposed for the formation of complexes is [Ref. 7]:

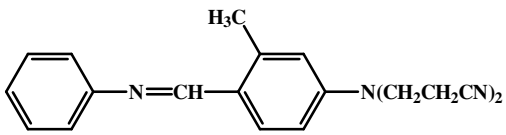
$$M(I)_3 + 4L \xrightarrow[72-75\,^{\circ}C\ Reflux]{Ethanol} M(L)_4(I)_3$$

RESULTS AND DISCUSSION

The analytical data for the complexes are given in Table-1. The complexes are quite stable and can be stored for a long period at room temperature *ca.* 30 °C, however after a few weeks, the complexes have been found to decompose to sticky mass.

The values of molecular weight, magnetic moment, melting points and calculated and found percentages of C, H, N are incorporated in Table-1. The iodide complexes are 1:1 electrolytes as revealed by their conductance values[8,9].

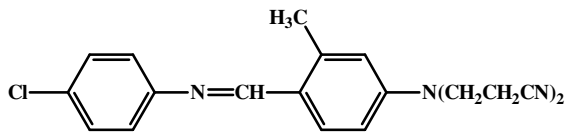
Mass spectral studies of ligands: Mass spectral studies of ligands MCEABAB, MCEABCAB, MCEABPT and MCEABFAB have been done and their molecular weights have been confirmed from the parent and base peaks appeared in the mass spectra of the ligands. The mass spectral study are furnished in Table-2.



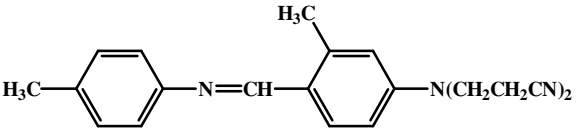
2-Methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidineaniline (MCEABAB) (I)

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

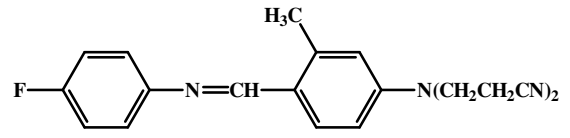
S. No.	Complexes (Colour)	Yield, % (m.p., ºC)	Elemental analysis (%): Found (calcd.)			Λ_m (ohm^{-1} cm^2 mol^{-1})	m.w. found (calcd.)	Magnetic moment (BM)
			C	H	N			
1	$[La(MCEABAB)_4I_2]I$ (Light brown)	72 (168)	48.03 (53.81)	3.86 (4.48)	11.21 (12.55)	51.5	895 (1784)	Diamag.
2	$[Ce(MCEABAB)_4I_2]I$ (Light brown)	75 (170)	50.01 (53.78)	3.92 (4.48)	11.22 (12.54)	52.0	894 (1785)	2.51
3	$[Sm(MCEABAB)_4I_2]I$ (Light brown)	74 (152)	49.50 (53.48)	3.82 (4.45)	11.29 (12.47)	52.6	900 (1795)	1.69
4	$[Gd(MCEABAB)_4I_2]I$ (Orange)	75 (156)	49.64 (53.27)	3.96 (4.43)	10.98 (12.43)	52.8	904 (1802)	7.81
5	$[La(MCEABCAB)_4I_2]I$ (Dark brown)	74 (175)	50.20 (49.81)	4.01 (3.94)	10.99 (11.62)	52.1	969 (1927)	Diamag.
6	$[Ce(MCEABCAB)_4I_2]I$ (Chocolate)	73 (154)	50.26 (49.79)	4.00 (3.94)	10.85 (11.61)	54.9	970 (1928)	2.40
7	$[Sm(MCEABCAB)_4I_2]I$ (Brown)	80 (156)	50.31 (49.51)	4.03 (3.91)	10.89 (11.55)	53.3	971 (1939)	1.41
8	$[Gd(MCEABCAB)_4I_2]I$ (Light brown)	75 (180)	51.01 (49.33)	4.10 (3.90)	11.02 (11.51)	53.2	976 (1946)	7.60
9	$[La(MCEABPT)_4I_2]I$ (Light brown)	74 (220)	51.55 (54.75)	4.80 (4.78)	12.13 (12.16)	51.9	925 (1841)	Diamag.
10	$[Ce(MCEABPT)_4I_2]I$ (Dark brown)	75 (184)	52.03 (54.72)	4.73 (4.77)	12.10 (12.16)	54.6	926 (1842)	2.45
11	$[Sm(MCEABPT)_4I_2]I$ (Dark brown)	78 (210)	49.30 (54.39)	4.01 (4.74)	12.00 (12.08)	52.4	930 (1853)	1.38
12	$[Gd(MCEABPT)_4I_2]I$ (Brown)	73 (200)	49.10 (54.19)	4.10 (4.73)	11.95 (12.04)	53.3	936 (1860)	7.78
13	$[La(MCEABFAB)_4I_2]I$ (Light brown)	70 (166)	48.20 (51.66)	3.25 (4.09)	11.21 (12.05)	52.3	934 (1858)	Diamag.
14	$[Ce(MCEABFAB)_4I_2]I$ (Dark brown)	68 (200)	48.18 (51.64)	3.38 (4.08)	11.25 (12.04)	55.4	933 (1859)	2.41
15	$[Sm(MCEABFAB)_4I_2]I$ (Brown)	70 (190)	48.36 (51.36)	4.01 (4.06)	10.32 (11.98)	53.1	939 (1869)	1.45
16	$[Gd(MCEABFAB)_4I_2]I$ (Light brown)	71 (165)	49.11 (51.17)	3.98 (4.05)	10.35 (11.94)	52.9	942 (1876)	7.74



2-Methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-chloroaniline (MCEABCAB) (II)



2-Methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-toludine (MCEABPT) (III)



2-Methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-fluoroaniline (MCEABFAB) (IV)

Structure of Schiff base ligand I to IV

TABLE-2

S. No.	Schiff base ligands	Peaks appear at m/e	
		Parent peaks	Base peaks
1	MCEABAB	316	317
2	MCEABCAB	351	351
3	MCEABPT	330	331
4	MCEABFAB	335	335

Infrared spectral studies: Metal-iodide band appears usually in far IR region below 200 cm^{-1}, since the region of the spectra currently studied for the complexes is 4000-400 cm^{-1}, the metal-iodide band could not be studied.

The azomethine stretching frequency which appears 1599-1584 cm^{-1} region in ligands, shifts toward 1516-1501 cm^{-1} in complexes which shows that the azomethine nitrogen is involved in the formation of complexes. This is also confirmed by the appearance of new band at about 497-475 cm^{-1} which is signal for a metal ligand band. The partial infrared spectral data for lanthanide(III) iodide complexes of Schiff base ligands are given in Table-3.

Electronic spectral studies: Electronic spectra studies of some of the representative complexes of lanthanide(III) iodide with Schiff bases have also been carried out successfully.

Typical spectral data for solution of the complexes were investigated in non-aqueous media. The shift of hypersensitive

TABLE-3
PARTIAL INFRARED SPECTRAL DATA FOR LANTHANIDE(III) IODIDE COMPLEXES OF SCHIFF BASE LIGANDS

S. No.	Complexes	ν(C=N) stretching (azomethine)	ν(Ln-N) (Metal-ligand vibration)
1	MCEABAB	1584 s	–
2	$[La(MCEABAB)_4I_2]I$	1502 sh	480 w
3	$[Ce(MCEABAB)_4I_2]I$	1510 w	482 w
4	$[Sm(MCEABAB)_4I_2]I$	1512 m	497 w
5	$[Gd(MCEABAB)_4I_2]I$	1512 m	480 w
6	MCEABCAB	1599 s	–
7	$[La(MCEABCAB)_4I_2]I$	1509 m	485 w
8	$[Ce(MCEABCAB)_4I_2]I$	1514 sh	483 w
9	$[Sm(MCEABCAB)_4I_2]I$	1516 sh	490 w
10	$[Gd(MCEABCAB)_4I_2]I$	1511 m	492 w
11	MCEABPT	1591 s	–
12	$[La(MCEABPT)_4I_2]I$	1512 s	485 w
13	$[Ce(MCEABPT)_4I_2]I$	1510 w	490 w
14	$[Sm(MCEABPT)_4I_2]I$	1511 m	495 w
15	$[Gd(MCEABPT)_4I_2]I$	1511 m	480 w
16	MCEABFAB	1590 s	–
17	$[La(MCEABFAB)_4I_2]I$	1506 m	480 w
18	$[Ce(MCEABFAB)_4I_2]I$	1505 w	490 w
19	$[Sm(MCEABFAB)_4I_2]I$	1501 w	475 w
20	$[Gd(MCEABFAB)_4I_2]I$	1507 m	485 w

bands has been utilized to calculate the nephlauxatic effect (β) in the complexes. From β values the covalency factor ($b^{1/2}$), Sinha's covalency parameter (δ %) and covalency angular overlap parameter (η) have been evaluated.

The values of (1-β) and δ % have been found to be positive for the complexes. This suggests covalent bonding between the metal and the ligand is covalent[10,11]. The electronic spectral data are furnished in Table-4.

Thermogravimetric analysis: Thermogravimetric analysis for checking the thermal stability and liberate in ligand in complexes.

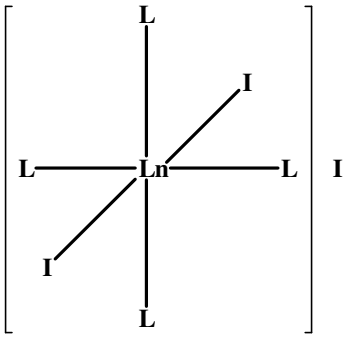
Thermal studies of two representative complexes *viz.*, $[LaI_3{\cdot}4(MCEABFAB)]$ and $[CeI_3{\cdot}4(MCEABPT)]$ have been carried out. Thermograms of the complexes showed that in different stages of decomposition they partly liberated ligands and ultimately metal oxide were formed as end products in all cases[12,13].

$$LaI_3{\cdot}4(MCEABFAB) \xrightarrow{230-320\,^\circ C} LaI_3{\cdot}1.07(MCEABFAB) \xrightarrow{510-575\,^\circ C} LaI_3{\cdot}0.688(MCEABFAB) \xrightarrow{720-745\,^\circ C} La_2O_3 \quad (1)$$

$$CeI_3{\cdot}4(MCEABPT) \xrightarrow{80-120\,^\circ C} CeI_3{\cdot}3.88(MCEABPT) \xrightarrow{220-310\,^\circ C} CeI_3{\cdot}1.46\,(MCEABPT) \xrightarrow{710-790\,^\circ C} Ce_2O_3 \quad (2)$$

Probable coordination structures of the complexes: Based on conductance and molecular weight data of lanthanide(III) iodo complexes, showed that one out of the three iodo ions should be present outside the coordination sphere. Hence coordination number six is suggested for metal ion in these lanthanide(III) iodide complexes[14].

The probable structure suggested for the complexes is given the Fig. 1.



[Ln = La, Ce, Sm and Gd; L = MCEABAB, MCEABCAB, MCEABPT and MCEABFAB] (C.N. = 6)

Fig. 1.

Antimicrobial studies: Antimicrobial *viz.* antifungal and antibacterial studies of representative lanthanide(III) iodide complexes have also been carried out successfully.

These studies were carried out on *Aspergillus fumigatus*, *Aspergillus niger* and *Mucor* species among fungi and *E. coli* species in bacteria using paper disc method on appropriate nutrient medium. The colony diameters were measured after 48 h of inculated[15,16].

TABLE-4
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELATED BONDING PARAMETERS OF LANTHANIDE(III) IODIDE COMPLEXES OF SCHIFF BASES

S. No.	Complexes	Lanthanide salts electronic spectral band (cm^{-1})	Complex electronic spectral band (cm^{-1})	Energy levels	(1-β)	β	$b^{1/2}$	δ %	η
1	$[Sm(MCEABAB)_4I_2]I$	24850	24271	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0232990	0.976700	0.1526400	2.384520	0.0115813
		24100	23809	$\rightarrow {}^6P_{5/2}$	0.0120746	0.987920	0.1098800	1.222200	0.0060216
		21600	20920	$\rightarrow {}^4I_{13/2}$	0.0314810	0.965510	0.1774290	3.250450	0.0156191
2	$[Sm(MCEABCAB)_4I_2]I$	24850	24330	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0209250	0.979070	0.1446540	2.137270	0.0104097
		24100	23696	$\rightarrow {}^6P_{5/2}$	0.0170124	0.982980	0.1304318	1.730690	0.0084646
		21600	20496	$\rightarrow {}^4I_{13/2}$	0.0513425	0.948657	0.2265880	5.412122	0.0252310
3	$[Sm(MCEABPT)_4I_2]I$	24850	24096	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0303420	0.969658	0.1741890	3.129140	0.0150541
		24100	23584	$\rightarrow {}^6P_{5/2}$	0.0214100	0.978590	0.1463210	2.187840	0.0106471
		21600	20833	$\rightarrow {}^4I_{13/2}$	0.0355090	0.964491	0.1884380	3.681630	0.0175940
4	$[Sm(MCEABFAB)_4I_2]I$	24850	24330	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0209250	0.979070	0.1446540	2.137270	0.0104097
		24100	23809	$\rightarrow {}^6P_{5/2}$	0.0120740	0.987926	0.1098840	1.222150	0.0060187
		21600	20920	$\rightarrow {}^4I_{13/2}$	0.0314814	0.968518	0.1774290	3.250400	0.0156151

Results are summarized in Table-5 MIC (minimum inhibitory concentration) in these ranges for these complexes are denoted by astericks (*). The complexes selected are found to be moderately effective against fungal and bacterial species.

TABLE-5
ANTIFUNGAL AND ANTIBACTERIAL ACTIVITIES OF SOME OF THE REPRESENTATIVE COMPLEXES OF LANTHANIDE(III) MEAL IONS WITH SCHIFF BASE LIGANDS (AFTER 48 h OF INCUBATION)

	0	1 mg/10 mL	2 mg/10 mL	3 mg/10 mL
		$La(MCEABCAB)_4(I)_3$		
A. fumigatus	0.4 cm	0.2 cm	0.2* cm	0.2 cm
A. Niger	0.3 cm	0.2 cm	0.2* cm	0.2 cm
Mucor sps.	1.0 cm	0.5 cm	0.5* cm	0.5 cm
		$Gd(MCEABFAB)_4(I)_3$		
A. fumigatus	0.5 cm	0.5 cm	0.2* cm	No growth
A. Niger	0.5 cm	0.5 cm	0.1* cm	No growth
Mucor sps.	0.5 cm	0.4 cm	0.3 cm	0.1* cm
		$Ce(MCEABFAB)_4(I)_3$		
E. coli sps.	0.1* cm	0.1 cm	0.1 cm	0.1 cm
		$Sm(MCEABPT)_4(I)_3$		
E. coli sps.	0.2 cm	0.2 cm	0.1 cm	0.3 cm

*Minimum value

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