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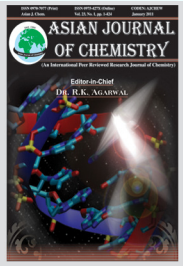

Synthesis and Characterization of Schiff Bases Coordination Compounds of Lanthanide(III) Perchlorates

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Dicyanoethylation of *m*-toluidine was carried out by treating the aromatic primary amine with acryonitrile in acetic acid in presence of cuprous chloride. The cyanoethylated amine on formylation gave 2-methyl-4-NN-*bis*-2'-cyanoethylaminobenzaldehyde. The resulted aldehyde gave Schiff bases 2-methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidineaniline (MCEABAB), 2-methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-chloroaniline (MCEABCAB), 2-methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-toludine (MCEABPT) and 2-methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidine *p*-fluoroaniline (MCEABFAB) with aniline and three different substituted anilines. Lanthanide oxides *viz.*, lanthanum oxide, praseodymium oxide and neodymium oxide were chosen to synthesize new complexes, heaving a general formula $[Ln(L)_6(ClO_4)_3]$ [where Ln = La, Pr and Nd; L = MCEABAB, MCEABCAB, MCEABPT and MCEABFAB]. In all twelve new lanthanide(III) perchlorate complexes of Schiff bases have been prepared. Elemental analyses, molecular weight, melting point, conductivity measurement, spectral studies, thermal analysis and microbial activities of the complexes were carried out.

Key Words: Lanthanide(III) perchlorate complexes, Spectral, TGA and Antimicrobial studies.

INTRODUCTION

The stoichiometery of lanthanides complexes is affected by the ligand-ligand repulsion, metal ligand interaction and also by the anion present in the complexes. These anion compete with the ligand for coordination sites on the central metal ion[1-3].

In the present work, we wish to report lanthanide(III) perchlorate complexes with different Schiff bases.

EXPERIMENTAL

Preparation of Schiff bases: Preparation of 2-methyl-4-NN-*bis*-2'-cyanoethylamino benzaldehyde was moduled on the procedure in the literature[4,5].

NN-*Bis*-2'-cyanoethyl-*m*-toluidine: Freshly distilled *m*-toluidine (10.0 g, 1.0 mol), acrylonitrile (3.3 g, 0.25 mL), glacial acetic acid (14.0 g, 0.25 mol) and freshly prepared, dry cuprous chloride (1.0 g) were gently refluxed for 12 h. The brown coloured liquid was cooled and poured into liquor ammonia (100 mL, 0.88 d). The contents were left overnight, the solid separated was filtered under suction, washed well with water and recrystallized from ethanol in colourless needles (melting point 87 °C, yield 55 %).

2-Methyl-4-NN-*bis*-2'-cyanoethylamino benzaldehyde: NN-*bis*-cyanoethyl-*m*-toluidine (11.6 g, 0.05 mol) was slowly added with manual stirring to cooled mixture of phosphorus oxychloride (9.0 g, 0.05 mol) and dimethyl formamide (15.6 g, 0.2 mol) taken in a round bottom flask provided with a mechanical stirrer and a reflux condenser, carrying a calcium chloride guard tube. The contents were heated with stirring on a steam bath for 3 h. The dark brown liquid was cooled, poured over crushed ice and the clear solution was neutralized with sodium acetate. On keeping over night the solid product separated out. It was collected under suction, washed with little water and recrystallized from ethanol when the aldehyde was obtained as light yellow needles (melting point 146 °C, yield 70 %).

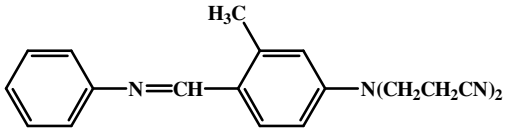
Preparation of Schiff base ligands: Schiff base ligands were prepared by either of the following methods:

Method (i): A solution of the aldehyde (1 mmol) in absolute alcohol (50 mL) was mixed with corresponding amine *i.e.*, (i) aniline (ii) *p*-fluoroaniline (1:1 mmol) in the same solvent and two drops of piperidine were added. The mixture was refluxed for 4.5 h. On cooling dark coloured solidsseparated, which were filtered under suction and recrystallized from ethanol as pale/yellow solids.

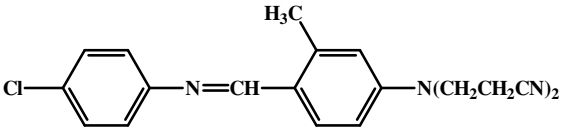
Method (ii): A mixture of the aldehyde (1 mmol) and corresponding amine *i.e.* (i) *p*-chloroaniline (ii) *p*-toludine (1:1 mmol) was taken in a round bottom flask to which two drops of piperidine were added. The contents were heated for 4.5 h in an oil bath maintained at 105-110 °C. The contents first melted and them solidified. The Schiff base were purified by recrystallization from ethanol as pale/yellow solids[6]. Table-1 shows the physical characteristics of the ligands.

TABLE-1
PHYSICAL CHARACTERISTICS OF THE LIGANDS

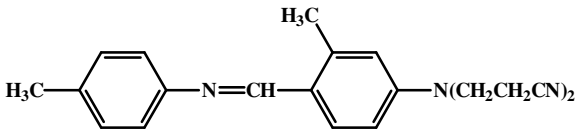
Name of ligands	Yield (%)	State	Colour	m.p. (ºC)
MCEABAB	85.0	Solid	Light yellow	140-142
MCEABCAB	80.0	Solid	Light yellow	142-144
MCEABPT	82.0	Solid	Pale yellow	143-146
MCEABFAB	87.5	Solid	Pale yellow	138-140



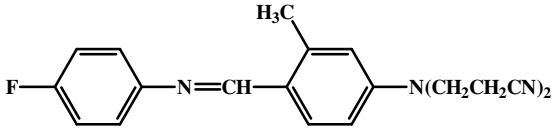
2-Methyl-4-NN-*bis*-2′-cyanoethylaminobenzylidineaniline (MCEABAB) (I)



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

Synthesis of complexes: The reactions of lanthanide(III) perchlorate salts solution in ethanol (1 mmol) with four Schiff base ligands solutions in the required molar concentrations [1:6], resulted the formation of new complexes of lanthanide perchorate having general formula. $[M(L)_6(ClO_4)_3]$ (M = La, Pr and Nd; L = MCEABAB, MCEABCAB, MCEABPT and MCEABFAB). The general equation for the preparation of the complexes is shown below[7]:

$$M(ClO_4)_3 + 6L \xrightarrow[72-75\ ^\circ C\ reflux]{Ethanol} M(L)_6(ClO_4)_3$$

RESULTS AND DISCUSSION

Analytical, conductance, molecular weight, melting point and magnetic moment data for lanthanide(III) perchlorate complexes with are presented in Table-2. Lanthanide(III)

TABLE-2
ANALYTICAL CONDUCTANCE, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA FOR LANTHANIDE(III) PERCHLORATE COMPLEXES OF SCHIFF BASE LIGANDS

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			
$La(MCEABAB)_6(ClO_4)_3$	Chocolate	60	194	37.51 (42.00)	3.53 (3.42)	10.21 (9.60)	100	586 (2333)	Diamag.
$Pr(MCEABAB)_6(ClO_4)_3$	Dark brown	62	193	36.25 (41.97)	3.75 (3.42)	10.15 (9.59)	110	585 (2335)	3.51
$Nd(MCEABAB)_6(ClO_4)_3$	Dark brown	58	204	35.39 (41.89)	3.50 (3.42)	9.98 (9.57)	118	589 (2339)	3.52
$La(MCEABCAB)_6(ClO_4)_3$	Light brown	65	208	32.44 (38.44)	3.50 (2.98)	9.45 (8.78)	1.07	640 (2549)	Diamag.
$Pr(MCEABCAB)_6(ClO_4)_3$	Raddish brown	62	198	31.97 (38.41)	3.32 (2.97)	9.81 (8.78)	115	641 (2551)	3.54
$Nd(MCEABCAB)_6(ClO_4)_3$	Dark brown	60	194	33.79 (38.35)	3.30 (2.97)	10.05 (8.76)	120	645 (2555)	3.58
$La(MCEABPT)_6(ClO_4)_3$	Light brown	60	200	37.51 (41.65)	3.46 (3.30)	10.41 (9.25)	118	610 (2420)	Diamag.
$Pr(MCEABPT)_6(ClO_4)_3$	Raddish brown	70	188	36.32 (41.62)	3.29 (3.30)	10.30 (9.25)	120	611 (2422)	3.48
$Nd(MCEABPT)_6(ClO_4)_3$	Blackish brown	65	198	34.92 (41.56)	3.41 (3.29)	9.80 (9.23)	119	613 (2425)	3.59
$La(MCEABFAB)_6(ClO_4)_3$	Orange	62	202	34.21 (40.09)	3.41 (3.10)	10.44 (9.16)	99	616 (2444)	Diamag.
$Pr(MCEABFAB)_6(ClO_4)_3$	Blackish	55	192	34.20 (40.08)	2.93 (3.10)	11.01 (9.16)	116	618 (2445)	3.46
$Nd(MCEABFAB)_6(ClO_4)_3$	Raddish black	59	194	33.98 (40.00)	3.30 (3.10)	10.19 (9.14)	122	617 (2450)	3.51

perchlorate complexes are electrolytic in nature and behave as 1:3 electrolytes (in $PhNO_2$)[8,9].

Infrared spectral studies: In the IR spectra of the complexes a negative shift in [-C=N-] azomethine stretching frequency of the ligand has been observed which shows that the coordination is from nitrogen of [-C=N-] (azomethine) group.

In all the complexes, the occurrence of two strong bands at *ca.* 1098-1061 cm^{-1} and 670-623 cm^{-1} region in the spectra of lanthanide perchlorate complex[8,9].

The partial IR data for Schiff base ligands and complexes are given in Table-3.

TABLE-3
PARTIAL INFRARED SPECTRAL DATA AND INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF PERCHLORATE ANION IN THE LANTHANIDE(III) PERCHLORATE COMPLEXES OF SCHIFF BASE LIGANDS

Complexes	ν(C=N) stretching (azo-methine)	ν(Ln–N) metal-ligand vibration	Perchlorate anion vibrations	
			ν_3	ν_4
MCEABAB	1584 s	–	–	–
$La(MCEABAB)_6(ClO_4)_3$	1540 w	530 w	1089 s	628 s
$Pr(MCEABAB)_6(ClO_4)_3$	1542 m	525 w	1068 sh	635 m
$Nd(MCEABAB)_6(ClO_4)_3$	1545 w	520 w	1090 w	629 s
MCEABCAB	1599 s	–	–	–
$La(MCEABCAB)_6(ClO_4)_3$	1542 w	535 w	1095 sh	630 m
$Pr(MCEABCAB)_6(ClO_4)_3$	1542 w	530 w	1061 w	670 s
$Nd(MCEABCAB)_6(ClO_4)_3$	1543 w	520 w	1084 s	623 s
MCEABPT	1591 s	–	–	–
$La(MCEABPT)_6(ClO_4)_3$	1541 w	522 w	1098 s	629 s
$Pr(MCEABPT)_6(ClO_4)_3$	1546 w	538 w	1086 s	628 s
$Nd(MCEABPT)_6(ClO_4)_3$	1543 sh	518 w	1085 s	629 s
MCEABFAB	1590 s	–	–	–
$La(MCEABFAB)_6(ClO_4)_3$	1541 w	520 w	1095 s	629 s
$Pr(MCEABFAB)_6(ClO_4)_3$	1543 w	528 w	1085 s	629 s
$Nd(MCEABFAB)_6(ClO_4)_3$	1544 sh	520 w	1087 s	628 s

Thermogravimetric analysis: Thermal study of one representative complexes *viz.* $[La(ClO_4)_3 \cdot 6(MCEABAB)]$ has been done successfully. These thermal studies show that ligand in different stage of decomposition partely liberate from complexes and final step metal oxide is found at high temperature[10,11].

$$La(ClO_4)_3 \cdot 6(MCEABAB) \xrightarrow{260-310\,^\circ C}$$

$$La(ClO_4)_3 \cdot 5.80(MCEABAB) \xrightarrow{310-345\,^\circ C}$$

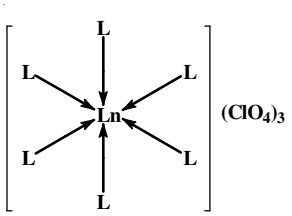
$$La(ClO_4)_3 \cdot 1.28(MCEABAB) \xrightarrow{380-425\,^\circ C} La_2O_3$$

Proposed structure of the complexes: These complexes were characterized on the bases of melting point, elemental analysis, conductance, magnetic measurement, IR and TGA study.

In case of lanthanide(III) perchlorate complexes high conductance values (in $PhNO_2$) clearly indicate that all the perchlorate ions present outside the coordination sphere.

This fact is also supported by the IR spectral data of these complexes which indicate the presence of perchlorate ions outside the coordination sphere with T_d symmetry. The coordination number in lanthanide(III) perchlorate is 6[11].

The probable structure of the complexes are show in Fig. 1.



[Ln = La, Pr and Nd; L = MCEABAB, MCEABCAB, MCEABPT and MCEABFAB] (C.N. = 6)

Fig. 1

Antimicrobial studies: Antimicrobial *viz.* antibacterial study of representative lanthanide(III) perchlorate $[La(MCEABCAB)_6(ClO_4)_3]$ complexes was carried out on *E. coli* species in bacteria. The growth of bacterial species were checked using paper disc method on nutrient agar medium and the colonies diameters were measured[12,13] the complexes was not found effective. The growth of bacterial colonies are reported in Table-4.

TABLE-4
ANTIBACTERIAL ACTIVITIES OF $Ln(MCEABCAB)_6(ClO_4)_3$ (AFTER 48 h OF INCUBATION)

Bacteria	$La(MCEABCAB)_6(ClO_4)_3$			
	0	1 mg/10 mL	2 mg/10 mL	3 mg/10 mL
E. coli	0.1* cm	0.1 cm	0.0 cm	0.0 cm

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