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COMPLEXES OF YTTRIUM AND LANTHANIDE PERCHLORATES WITH 4-N-(2'-FURFURYLIDENE)AMINOANTIPYRINE

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ABSTRACT

Yttrium and lanthanide perchlorate complexes with 4-N-(2'-furfurylidene)aminoantipyrine (FAA) of the composition $[Ln(FAA)_3(ClO_4)_2]ClO_4$ (where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er) have been synthesised and characterized by elemental analyses, molar conductance in non-aqueous solvents, magnetic susceptibility measurements, infrared, electronic as well as proton NMR spectra and thermogravimetric analyses. In these complexes the ligand FAA acts as a neutral tridentate one coordinating through the carbonyl oxygen, azomethine nitrogen and oxygen of the furan ring. Two of the perchlorate ions are coordinated monodentately and the third one being ionic.

INTRODUCTION

Antipyrine and its derivatives are well known for their pharmaceutical applications[1]. Schiff bases of furfural, nitrofurfural and their semicarbazones were investigated earlier for their antifungal and antimicrobial activity[2,3]. Hence, the Schiff base derived from 4-aminoantipyrine and furfural would be expected to be exhibiting enhanced physiological properties. In continuation of our studies on Schiff base complexes of yttrium and lanthanide perchlorates[5,7,8], we report here the preparation and characterization of the complexes of yttrium and lanthanide perchlorates with a Schiff base derived from furfural and 4-aminoantipyrine, *viz.*, 4-N-(2'-furfurylidene)aminoantipyrine, abbreviated as FAA (Fig. 1). This ligand is expected to function as a neutral tridenate one coordinating through the carbonyl oxygen, azomethine nitrogen and the oxygen of the furan ring.

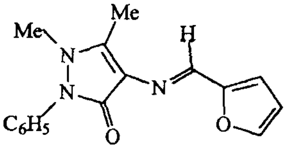


Fig. 1. 4-N-(2'-Furfurylidene)aminoantipyrine

RESULTS AND DISCUSSIONS

The present complex formation is given by the general equation shown below,

$$Ln(ClO_4)_3 + 3FAA \rightarrow [Ln(FAA)_3(ClO_4)_2]ClO_4$$

The complexes are dark brown, slightly hygroscopic solids which are soluble in acetonitrile, acetone, methanol and nitrobenzene and insoluble in benzene, chloroform, ethyl acetate and toluene. The analytical data (Table I) indicate that the complexes have the general compositions $Ln(FAA)_3(ClO_4)_3$. The molar conductivities of the complexes (Table II) in DMF are in the range expected for 1:1 electrolytes[9]. Slightly higher values were observed in nitrobenzene, methanol and acetonitrile, probably due to the partial displacement of coordinated perchlorate ions by solvent molecules[9]. Hence, the complexes may be formulated as $[Ln(FAA)_3(ClO_4)_2]ClO_4$, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.

Infrared Spectra

The IR spectra of the ligand and the complexes are presented in Table III. The IR spectrum of the ligand FAA indicates a strong band at 1645 cm^{-1} which is assigned to the stretching vibration of the carbonyl group[4]. In the complexes this band is shifted to 1618 cm^{-1} indicating the coordination of the carbonyl oxygen[5,10]. FAA shows a strong band around 1590 cm^{-1} which is attributed to the ν(C=N) mode of the azomethine group. This band is shifted to about 1575 cm^{-1} in the complexes which shows the coordination of the azomethine nitrogen[5]. The antisymmetric bands due to ν_a(C -O -C) observed at 1215 and 1132 cm^{-1} in FAA are lowered to 1180 and 1110 cm^{-1}, respectively, in the complexes[6]. Also, the ν(C-H) out-of-plane bending mode observed at 820 cm^{-1} is shifted to 800 cm^{-1} in the complexes[11,12]. All these results indicate the coordination of the furan oxygen to the metal ion in the complex. The complexes show the doubly split strong band with band maxima at about 1142 and 1120 cm^{-1} (ν_4 vibrations C_{3v}), a medium band at 928 cm^{-1} (ν_2 vibration C_{3v}) and a medium band at 630 cm^{-1} (ν_5 vibration C_{3v})

Table I Analytical Data[a] of Yttrium and Lanthanide Perchlorate Complexes of FAA

Complex[b]	% Metal	% ClO_4	% C	% H	% N	% Yield	Mp (°C)
$[Y(FAA)_3(ClO_4)_2]ClO_4$	7.22	24.31	46.81	3.69	10.24	66	240
	(7.21)	(24.23)	(46.82)	(3.68)	(10.23)		
$[La(FAA)_3(ClO_4)_2]ClO_4$	10.86	23.35	44.94	3.54	9.82	71	251
	(10.84)	(23.29)	(44,94)	(3.54)	(9.83)		
$[Pr(FAA)_3(ClO_4)_2]ClO_4$	10.97	23.37	44.91	3.53	9.83	74	262
	(10.97)	(23.25)	(44.91)	(3.54)	(9.84)		
$[Nd(FAA)_3(ClO_4)_2]ClO_4$	11.31	22.90	44.75	3.54	9.80	69	230
	(11.21)	(23.19)	(44.75)	(3.51)	(9.79)		
$[Sm(FAA)_3(ClO_4)_2]ClO_4$	11.75	23.25	44.63	3.52	9.74	63	248
	(11.62)	(23.08)	(44.60)	(3.51)	(9.75)		
$[Eu(FAA)_3(ClO_4)_2]ClO_4$	11.84	22.91	44.56	3.49	9.73	72	230
	(11.74)	(23.06)	(44.54)	(3.50)	(9.74)		
$[Gd(FAA)_3(ClO_4)_2]ClO_4$	11.96	23.04	44.36	3.48	9.71	66	261
	(12.10)	(22.96)	(44.36)	(3.49)	(9.70)		
$[Dy(FAA)_3(ClO_4)_2]ClO_4$	12.31	22.80	44.20	3.49	9.67	73	256
	(12.44)	(22.87)	(44.18)	(3.48)	(9.66)		
$[Ho(FAA)_3(ClO_4)_2]ClO_4$	12.54	22.58	44.08	3.46	9.64	71	210
	(12.62)	(22.83)	(44.10)	(3.47)	(9.64)		
$[Er(FAA)_3(ClO_4)_2]ClO_4$	12.59	22.98	44.11	3.45	9.61	69	232
	(12.77)	(22.79)	(44.00)	(3.46)	(9.62)		

a. Calculated values in parenthesis

b. Empirical formulae: $C_{48}H_{45}N_9O_{18}Cl_3M$

Table II. Molar Conductance and Magnetic Moment Data of Yttrium and Lanthanide Perchlorate Complexes of FAA

Complex	Molar conductance[a]				
	$C_6H_5NO_2$	MeOH	MeCN	DMF	(B.M)
$[Y(FAA)_3(ClO_4)_2]ClO_4$	41.40	131.84	196.73	79.07	-
$[La(FAA)_3(ClO_4)_2]ClO_4$	35.51	131.20	200.92	88.00	-
$[Pr(FAA)_3(ClO_4)_2]ClO_4$	30.36	148.64	187.52	84.14	3.62
$[Nd(FAA)_3(ClO_4)_2]ClO_4$	31.52	105.46	188.00	92.00	3.17
$[Sm(FAA)_3(ClO_4)_2]ClO_4$	32.02	110.57	179.69	76.00	2.03
$[Eu(FAA)_3(ClO_4)_2]ClO_4$	37.75	96.87	193.74	81.13	3.61
$[Gd(FAA)_3(ClO_4)_2]ClO_4$	34.71	117.50	185.27	77.62	7.82
$[Dy(FAA)_3(ClO_4)_2]ClO_4$	28.54	125.56	209.27	73.04	10.59
$[Ho(FAA)_3(ClO_4)_2]ClO_4$	41.90	102.50	191.02	69.12	10.23
$[Er(FAA)_3(ClO_4)_2]ClO_4$	37.44	112.02	196.03	81.81	9.44

[a] 10^{-3} M solutions used; $ohm^{-1}cm^2 mole^{-1}$

characteristic of monodentately coordinated perchlorate groups. The complexes also show a strong band at 1080 cm^{-1} and a medium band at 626 cm^{-1} which are attributed to the ν_3 and ν_4 vibrations (Td) of the ionic perchlorate group [13-15]. The new bands observed at 475, 410 and 550 cm^{-1} are attributed to the ν(M-O) (furan), ν(M-N) and ν(M-O) (carbonyl) bands, respectively[16,17].

Proton NMR Spectra

The proton NMR spectrum of the ligand FAA shows the azomethine proton resonance at about δ 7.70 ppm with respect to TMS. It is shifted to δ 8.16 ppm in the case of the

Table III. Important Infrared Spectral Bands of FAA and its Rare Earth Perchorate Complexes

Compound	ν (C=O)	ν (C=N)	ν (C-O-C)	$\nu_4(ClO_4)$ Coord.	$\nu_5(ClO_4)$ Coord. $\nu_4(ClO_4)$ Ionic	$\nu_2(ClO_4)$ Coord	ν_3(ionic) (ClO_4)	Furan ν (Ln-O)	ν (Ln-N)	ν (Ln-O)
FAA	1645 s	1590 s	1132 s	-	-	-	-	-	-	-
$[Y(FAA)_3(ClO_4)_2]ClO_4$	1622 s	1580 m	1108 s	1142 s	630 m	928 m	1080 s	475 w	410 w	550 w
$[La(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1575 m	1110 s	1120 s	626 m	928 m	1080 s	475 w	410 w	550 w
$[Pr(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1578 m	1115 s	1142 s	630 m	928 m	1080 s	475 w	410 w	550 w
$[Nd(FAA)_3(ClO_4)_2]ClO_4$	1618 s	1580 m	1110 s	1120 s	626 m	928 m	1080 s	475 w	410 w	550 w
$[Sm(FAA)_3(ClO_4)_2]ClO_4$	1619 s	1578 m	1115 s	1142 s	630 m	928 m	1080 s	475 w	410 w	550 w
$[Eu(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1576 m	1108 s	1120 s	626 m	928 m	1080 s	475 w	410 w	550 w
$[Gd(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1575 m	1110 s	1142 s	630 m	928 m	1080 s	475 w	410 w	550 w
$[Dy(FAA)_3(ClO_4)_2]ClO_4$	1622 s	1575 m	1110 s	1120 s	626 m	928 m	1080 s	475 w	410 w	550 w
$[Ho(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1575 m	1108 s	1142 s	630 m	928 m	1080 s	475 w	410 w	550 w
$[Er(FAA)_3(ClO_4)_2]ClO_4$	1620 s	1575 m	1100 s	1120 s	626 m	928 m	1080 s	475 w	410 w	550 w

s: strong; m: medium; w: weak

yttrium perchlorate complex and to δ 8.03 ppm in the case of the lanthanum perchlorate complex, indicating the coordination of the azomethine nitrogen[18]. The resonance of the *ortho* hydrogen of the furan ring observed at δ 7.4 ppm in the ligand[19] is shifted to δ 7.6 ppm in the lanthanum complex and to δ 7.7 ppm in the yttrium complex. This confirms the coordination of the furan oxygen. Other relevant bands observed in the case of the ligand and the complexes are as follows; phenyl multiplet at δ 7.33 ppm, $=C-CH_3$ at δ 2.42 ppm and $-N-CH_3$ at δ 3.17 ppm.

Electronic Spectra

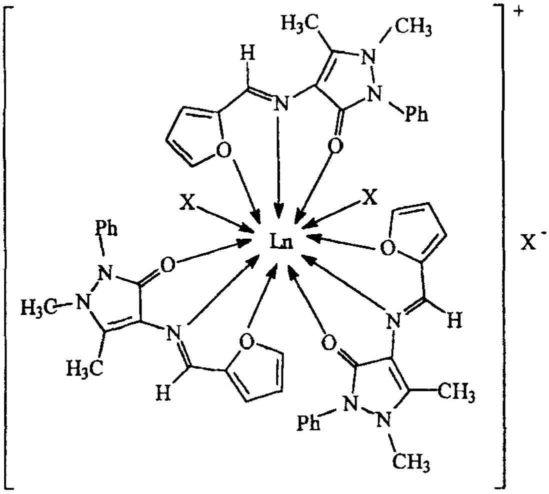
The electronic spectra of the ligand and the complexes in acetonitrile do not give much structural details. The ligand has the following absorption maxima in acetonitrile. One $n \longrightarrow \pi^*$ transition at 29.49 kK and two $\pi \longrightarrow \pi^*$ transitions at 38.76 and 47.85 kK. In the complexes the $n \longrightarrow \pi^*$ transition is almost unchanged. The low energy $\pi \longrightarrow \pi^*$ transition is red-shifted to the region ranging from 38.95 to 40.05 kK. The compounds are intensely coloured and most of the f-f transitions of the lanthanide ions in the visible region are obscured in the complexes by the broad metal-ligand charge transfer transitions. Hence, electronic spectra are not very useful in the investigation of f-f transitions of the present complexes.

Magnetic Studies

All of the complexes, except those of yttrium and lanthanum, are paramagnetic. The measured magnetic moments of the complexes (Table II) show only a small deviation from the van Vleck values, indicating the non-participation of the well shielded 4f-electrons in bonding [20].

Thermal Studies

The thermogravimetric analyses of the perchlorate complexes of FAA in nitrogen atmosphere indicate that the complexes are stable up to 150° C. The complexes decompose in two stages. The first stage starts at 150-170° C and ends in the range 360-380° C (the corresponding DTG peak being observed at about 305° C) which involves a mass loss of 26.4 to 28% corresponding to the loss of one ligand and the decomposition of one perchlorate to chloride. The presence of chloride after the first stage is confirmed by conventional qualitative chloride analysis of the intermediate compound. The second stage starts at 360-380°C and the slow decomposition is complete by 700° C. This stage involving the decomposition of the ligands and perchlorate groups is not well characterized. The final residue consists of the metal chloride and traces of carbon.



Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

Fig. 2. Tentative Structure of the Complexes.

EXPERIMENTAL

Materials

The complexes are fairly stable under laboratory conditions. A very small quantity of the complex, which is far below the explosion limits, was used for the analyses. Hence, no special safty measure is needed in handling the perchlorate complexes.

The perchlorates of yttrium and lanthanides were prepared by dissolving the respective oxides (99.99 % pure) in 50% perchloric acid. The salts were crystallised by evaporating the resulting solution over a water bath and dried under vacuum over P_4O_{10}. The ligand was prepared by condensation of 4 g (19.7 mmol) of 4-aminoantipyrine and 1.9 g (11.8 mmol) of furan-2-carboxaldehyde in 30 mL ethanol. These were mixed on a steam bath for 4 h, kept overnight and the formed yellow brown crystals of the Schiff base were filtered and recrystallised repeatedly from hot ethanol. (yield:80% (4.5 g), m.p. 206 °C).The purity of the ligand was ascertained by TLC, IR spectrum and elemental analysis [found: C, 67.9%; H, 5.27 % and N,15.0%; calculated for $C_{16}H_{15}N_3O_2$ (formula weight : 281.3): C, 68.31% ; H, 5.37% and N, 14.93].

Preparation and Analysis of the Complexes

The complexes were prepared as follows: a solution of the ligand (3.2 mmol, 0.9 g) in ethyl acetate (60 mL) and the metal perchlorate (1 mmol 0.55 g) in ethyl acetate (10 mL) were mixed and refluxed for 3 h. The solid complex precipitated on cooling, was filtered, washed several times with hot benzene and dried *in vacuo* over P_4O_{10}. The complexes were analysed for metal[21] and perchlorate[22] contents by conventional methods. Conductivities of the complexes in nitrobenzene, acetonitrile, methanol and DMF (10^{-3} M solution) were measured at room temperature using a Toshniwal conductivity bridge with a dip-type conductance cell and platinum electrode. Magnetic susceptibilities were measured at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The IR spectra of the ligand and the complexes were recorded in the 4000-400 cm^{-1} range on a Shimadzu-IR-470 spectrophotometer using KBr discs. Electronic spectra of the ligand and the complexes in acetonitrile (10^{-4} M solutions) were recorded in the range 200-1000 nm on a Shimadzu-UV-160 A spectrophotometer. Thermal studies were carried out using a DuPont 2000 thermal analyser in nitrogen atmosphere (sample mass: 10 mg; heating rate; 10° /min).

CONCLUSION

The ligand FAA acts as a neutral tridentate ligand in the complexes coordinating through the carbonyl oxygen, azomethine nitrogen and oxygen of the furan ring. Two of the perchlorate ions are coordinated monodentately, the third one being ionic. Hence, a coordination number of eleven may be assigned to the metal in these complexes. The complexes are stable up to 150° C and undergo decomposition in two stages resulting in the formation of the respective metal chloride.

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