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Synthesis and Characterization of Some 4*f*-Metal Ion Complexes of 4[N-(3′-Nitrobenzalidene)Amino] Antipyrine Thiosemicarbazone

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Some 4*f*-block metal ion coordination compounds of 4[N-(3′-nitrobenzalidene)amino] antipyrine thiosemicarbazone (3′-NO_2BAAPTS) with the general composition [Ln(3′-NO_2BAAPTS)$_2$](ClO_4)$_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho) have been synthesized. The conductance values of these metal coordination compounds in nitrobenzene suggest that the compounds are ionic in nature and all the three perchlorato ions are present outside the coordination sphere. Magnetic, spectral and thermal properties of the compounds have also been investigated. The infrared studies reveal that 3′-NO_2 BAAPTS acts as neutral tridentate (N,N,S) ligand. The coordination number of central metal ion is six in all these compounds.

Key Words: Lanthanides(III), complexes, 4[N-(3′-nitrobenzalidene)-amino] antipyrine thiosemicarbazone.

INTRODUCTION

The coordination chemistry of 4*f*-block metal ions is of comparatively recent origin. In recent years, a number of coordination compounds of lanthanide(III) ions with N,O-donor ligands have been isolated and characterized[1,2]. But comparatively less is known about lanthanide(III) coordination compounds with N,S-donor ligands[3–5]. Thus, in the present work, the author describes the synthesis and characterization of some hexa-coordinated complexes of lanthanide(III) perchlorates with 4[N-(3′-methoxy benzalidene)amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS) (Fig. 1).

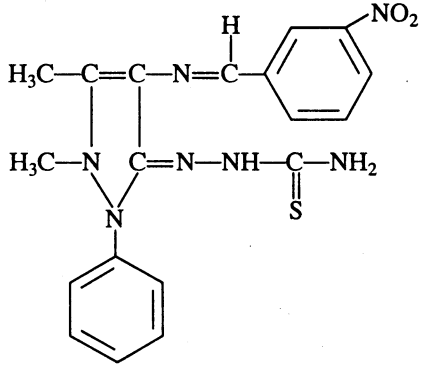


Fig. 1. 4[N-(3′-nitrobenzalidene)amino] antipyrine thiosemicarbazone

EXPERIMENTAL

The lanthanide(III) perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess of acid[6]. The ligand 3′-NO_2BAAPTS was synthesized from 4-aminoantipyrine by the method reported in literature[7].

All the lanthanide(III) perchlorato complexes of 3′-NO_2BAAPTS were synthesized by the following general method. Lanthanide(III) perchlorate (1 mmol) and 3′-NO_2BAAPTS (2.1 mmol) were dissolved separately in hot ethanol and then mixed. The reaction mixture was refluxed for 2 h and the solution was concentrated to a viscous mass which was washed several times with small portions with anhydrous diethyl-ether. The solid mass so obtained was finally washed with ethanol and collected and dried over P_4O_{10} in a vacuum desiccator.

The chemical analyses and physico-chemical studies of the complexes were performed as reported earlier[8, 9].

RESULTS AND DISCUSSION

The reaction of non-aqueous solutions of lanthanide(III) perchlorates with 4[N-(3′-nitrobenzalidene)amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS) resulting in the formation of coordination compounds of the general composition $Ln(ClO_4)_3 \cdot 2$(3′-NO_2BAAPTS) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The analytical data of these coordination compounds are presented in Table-1. In general, these compounds are soluble in common organic solvents. The anlytical data presented in Table-1 indicate that the coordination compounds are generally pure and need no further purification. The pyrolysis curves indicate no change up to 135°C suggesting the absence of either coordinated or uncoordinated aquo ligand in these coordination compounds. The molar conductance values (Table-1) of these complexes indicate that these complexes are 1 : 3 electrolytes in nitrobenzene, suggesting all the perchlorato groups are present outside the coordination sphere[10]. Data on the molecular weight of the present coordination compounds in nitrobenzene are presented in Table-1, allong with values calculated on the basis of established formula of the coordination compounds. The ratio of molecular weight observed for $Ln(ClO_4)_3$ 2(3′-NO_2BAAPTS) to that calculated is found to be approximately 0.25. This data further supports that 4 species are formed in these compounds.

The magnetic moment values observed for these complexes and presented in Table-1 show that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons. All other tripositive lanthanide ions are paramagnetic due to the presence of 4*f*-electrons which are effectively shielded by $5s^2 5p^6$ electrons. The comparison of these observed values with those observed for 8-hydrated sulphates[11] and those calculated for uncomplexed ions[12], indicates that the 4*f*-electrons do not participate in any bond formation in these complexes. The magnetic moments of the complexes reported herein are within the range.

TABLE-1
ANALYTICAL, CONDUCTIVITY AHD MOLECULAR WEIGHT DATA OF LANTHANIDE(III) PERCHLORATO COMPLEXES OF 3′-NO_2BAAPTS

Complex	Analysis %, Found (Calcd.)				Ω_m (ohm^{-1} cm^2 mol^{-1})	Average m.w. (formula weight)	μ_{eff} (B.M).
	Ln	N	S	ClO_4			
$La(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	10.96 (11.07)	15.45 (15.61	5.04 (5.09)	23.58 (23.77)	76.9	310 (1255.5)	Dia-mag
$Pr(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	11.10 (11.21)	15.44 (15.58)	5.04 (5.08)	23.55 (23.73)	77.8	312 (1257.5)	363
$Nd(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	11.30 (11.42)	15.40 (15.54)	5.03 (5.07)	23.50 (23.68)	78.3	314 (1260.5)	359
$Sm(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	11.72 (11.84)	15.33 (15.47)	5.00 (5.05)	23.48 (23.56)	79.0	315 (1266.5)	1.66
$Gd(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	12.20 (12.32)	15.27 (15.39)	4.96 (5.02)	23.27 (23.43)	76.8	317 (1273.5)	7.89
$Tb(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	12.33 (12.46)	15.22 (15.36)	4.97 (5.01)	23.27 (23.40)	79.2	318 (1275.5)	9.39
$Dy(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	12.58 (12.70)	15.20 (15.32)	4.95 (5.00)	23.20 (23.33)	76.9	320 (1279)	10.57
$Ho(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	12.73 (12.87)	15.18 (15.29)	4.93 (4.99)	23.16 (23.29)	78.3	321 (1281.5)	10.33

Infrared spectra: The strong bands observed at 3440–3270 cm^{-1} region in free ligand have been assigned to ν(NH) vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption at *ca.* 1600 cm^{-1} in free ligand can be attributed to (C=N) stretching vibrations of imine nitrogen which is in agreement with the observations of previous reports[13, 14]. On complexation these frequencies were observed to be shifted to lower wavenumbers (Table-2). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the metal ions. In the spectra of 3′-NO_2BAAPTS the bands observed in 1330–1305 cm^{-1}, 1120–1098 cm^{-1} and 822–762 cm^{-1} region are assigned to [ν(C=S) + ν(C=N) + ν(C—N)], [δ(NCS) + δ(C=S)] and ν(C=S) stretching respectively.[15, 16] Coordination of sulphur with these metal ions would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation (C=S) stretching vibrations should decrease and that of (CN) should increase[17, 18]. In all the present complexes of Ln^{3+} with 3′-NO_2 BAAPTS, the frequencies in the range 1330–1305 cm^{-1} get an increase by nearly 40–50 cm^{-1}. Similarly bending modes of (N—C—S) and (C=S) also get increased but in lesser amount. On the other hand, on complexation the frequencies in 822–762 cm^{-1} are shifted to lower wavenumber and intensities of the bands are also reduced. All these peculiar changes on complexation confidently preclude any umambiguous ascertain of metal-sulphur bonding. The possibility of thione-thiol tautomerism

TABLE-2

INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF $Ln(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$

Assignments	2′-NO_2 BAAPTS	$La(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Pr(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Nd(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Sm(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Gd(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Tb(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Dy(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)	$Ho(ClO_4)_3 \cdot$ 2(3′-NO_2 BAAPTS)
ν(NH)	3442 s 3270 s	3440 s 3275 m	3445 m 3272 m	3442 s, 3270 m	3445 s, 3270 m	3440 s 3270 s	3442 m 3272 m	3445 s 3270 m	3442 s 3275 m
ν(C═N)	1600 vs	1575 m	1572 m	1560 m	1565 m	1570 s	1565 m	1560 m	1562 s
ν(C═S) + ν(C═N) + ν(C—N)	1330 s, 1305 s	1345 m	1335 m	1342 m	1345 m	1342 m	1335 m	1345 m	
δ(NCS) + CS-bending	1120 m, 1098 m	1150 m, 1130 m	1660 m, 1135 m	1160 m, 1135 m	1165 m, 1140 m	1155 m, 1130 m	1162 m, 1132 m	1165 m, 1140 m	1165 m 1132 m
ν(N—N)	1050 m	1065 m	1068 m	1062 m	1065 m	1065 m	1062 m	1065 m	1165 m
ν(C═S)	822 s 762 s	782 s, 730 m	785 s, 725 m	790 s, 710 m	782 s, 722 m	792 s 710 m	782 s, 725 m	785 s, 710 s	782 s 720 m
ν(Ln—N)	—	420 m	415 m	425 m	435 m	440 m	445 m	450 m	445 m
ν(Ln—S)	—	340 w	325 w	315 w	320 w	322 w	325 w	330 w	332 w

(H—N—C=S) ⇌ (C=N—S—H) in this ligand has been ruled out, for no bands around 2700–2500 cm^{-1}, characteristic of thiol group, are displayed in the infrared absorption.[19, 20] In far infrared region ν(Ln—N) and ν(Ln—S) were also assigned[21].

Hence, the ligand behaves as neutral tridentate group and the lanthanide ions are coordinated through N and N of two azomethine group and of S of thio-keto group.

In all the lanthanide(III) perchlorato complexes only two strong ν_3 and ν_4 bands are observed at 1100–1085 cm^{-1} and 630–620 cm^{-1} region respectively (Table-3) for perchlorate ion indicating that tetrahedral symmetry has not been disturbed on complexation, and the perchlorate ions are not bonded to lanthanide metal ion[22, 33]. This conclusion has also been supported by conductance and molecular weight data.

TABLE-3
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ClO_4^- ION IN $Ln(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$

Complex	ν_3	ν_4
$La(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1085 s	625 s
$Pr(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1088 s	622 s
$Nd(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1095 s	620 s
$Sm(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1100 s	629 s
$Gd(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1092 s	630 s
$Tb(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1095 s	625 s
$Dy(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1090 s	630 s
$Ho(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	1088 s	625 s

Electronic spectra

Typical spectral data for solutions of the present complexes investigated in CH_3CN are recorded in Table-4 and for comparison, data for an aqueous salt solution have also been given. Lanthanum(III) has no significant absorption in the visible region. The absorption bands of Pr(III), Nd(III), Sm(III) and Ho(III) complexes in the visible and near infrared region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^6H_{3/2}$ and $^5I_8$ respectively to the excited J-levels of 4*f*-configuration. Some red shifts or nephelauxetic effect is observed in CH_3CN solution of these coordination compounds. This red shift is usually accepted as evidence of a higher degree of covalency than existing in the aquo compounds[24, 25]. In all the complexes marked enhancement in the intensity of the bands has been observed. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes from the β values. The covalence factor ($b^{1/2}$), Sinha parameter (δ%) (metal-ligand covalency per cent) and the covalency angular overlap parameter (η) have been calculated. The positive values for (1 – β) and δ% in these coordination compounds suggest that the bonding between the metal and the thiosemicarbazone is

TABLE-4

ELECTRONIC SPECTRAL DATA (cm^{-1}) AND BONDING PARAMETERS OF LANTHANIDE(III) PERCHLORATO COMPLEXES OF 3'-NO_2BAAPTS

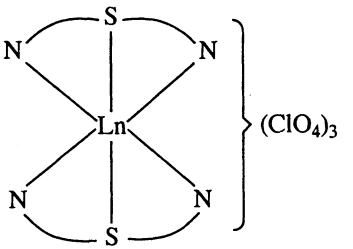
Complex	$Ln(ClO_4)_3$ electronic spectral bands	$Ln(ClO_4)_3 2L$ electronic spectral bands	Energy levels	$(1-\beta)$	β	$b^{1/2}$	$\delta\%$	η
$Pr(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	22470	22300	$^4H_4 \rightarrow {}^3P_2$	0.00756	0.99244	0.04347	0.76175	0.00380
	21325	21200	$\rightarrow {}^3P_1$	0.00586	0.99414	0.03827	0.58945	0.00294
	20750	20550	$\rightarrow {}^3P_0$	0.00963	0.99037	0.04906	0.97236	0.00483
	17000	16800	$\rightarrow {}^1D_2$	0.01176	0.98824	0.05422	1.18999	0.00593
$Nd(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	19600	19400	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.01020	0.98980	0.05049	1.03051	0.00514
	17380	17250	$\rightarrow {}^4G_{5/2}{}^2G_{7/2}$	0.00747	0.98253	0.04321	0.75262	0.00376
	13680	13500	$\rightarrow {}^2S_{3/2}{}^4F_{7/2}$	0.01315	0.98685	0.05733	1.33252	0.00664
	12470	12420	$\rightarrow {}^4F_{5/2}{}^4H_{9/2}$	0.00400	0.99599	0.04472	0.40161	0.00201
$Sm(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	24870	24700	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.00683	0.99317	0.04132	0.68769	0.00344
	24000	23800	$\rightarrow {}^6P_{5/2}$	0.00804	0.99196	0.04483	0.81051	0.00404
	21550	21400	$\rightarrow {}^4I_{13/2}$	0.00696	0.99304	0.04171	0.70087	0.00350
$Ho(ClO_4)_3 \cdot 2(3'\text{-}NO_2BAAPTS)$	22400	22260	$^5I_8 \rightarrow {}^5G_6{}^5F_1$	0.00625	0.99375	0.05590	0.62893	0.00313
	19310	18980	$\rightarrow {}^5F_4$	0.01708	0.98291	0.09241	1.73769	0.00865
	15740	15610	$\rightarrow {}^5F_5{}^5S_2$	0.00825	0.99174	0.06422	0.83187	0.00415
	13510	13380	$\rightarrow {}^5I_4$	0.00962	0.99037	0.06935	0.97135	0.00485

covalent compared with the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were found to be positive indicating covalent bonding.

Thermal studies

A careful analysis of all the pyrolysis curves of the coordination compounds indicates virtually no change in weight up to 170°C. At 170–260°C a loss of 33.46–34.21% is observed which corresponds to one molecule of the organic ligand followed by a further loss of 67–68.4% in 290–405°C temperature region showing the complete loss of 3′-NO_2BAAPTS. The lanthanide oxide (La_2O_3,Nd_2O_3 or Dy_2O_3) was finally formed at *ca.* 830°C. Above this temperature there is no measuable change in weight.[26, 27]

Stereochemistry: Infrared spectral data confirm the ionic nature of perchlorate ions and tridentate (N,N,S) nature of 3′-NO_2BAAPTS and hence in these coordination compounds the trivalent lanthanide ions are bonded by four nitrogen atoms and two sulphur atoms and thus produce a coordination number six in these coordination compounds. The tentative structure of these coordination compounds may be presented as:



(Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). (C.N. = 6)

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