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Structure and Bonding of Some Newly Synthesized Complexes of Lanthanide(III) Complexes of 4[N-(*p*-dimethylaminobenzalidene) Amino] Antipyrine Thiosemicarbazone

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A series of complexes of the type $LnX_3 \cdot 2$(DABAAPTS), where Ln = La, Pr, Nd, Sm, Gd, Tg, Dy and Ho, X = ClO_4^-, or NCS^-, DABAAPTS= 4[N-(*p*-dimethylaminobenzalidene) amino] anti pyrine thiosemicarbazone have been synthesized and characterized on the basis of elemental analysis, molecular weight measurements, molar conductance, room temperature magnetic moment, infrared and electronic spectral data. The ligand DABAAPTS behaves as neutral tridentate (N_2S) ligand.

INTRODUCTION

In recent years, a large number of coordination compounds of lanthanides(III) with various Schiff bases having N,O-donor ligands have been prepared and characterized.[1–3] But comparatively very little is known about thiosemicarbazone complexes of lanthanides(III).[4] In view of highly coordinated compounds formed by lanthanide metal ions, the authors report here the synthesis and characterization of some six and nine coordinated complexes formed by lanthanides(III) with 4[N-(*p*-dimethylaminobenzalidene) amino] antipyrine thiosemicarbazone.

EXPERIMENTAL

The lanthanide(III) oxides and nitrates were obtained from Rare Earth Products Ltd., India. The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid (AR) and evaporating off the excess of acid. The lanthanide isothiocyanates were prepared by adding a warm ethanolic solution of lanthanide nitrates to warm ethanolic solution of KCNS. The precipitate of KNO_3 rapidly coagulated. The volume of the solution was reduced on a water bath, cooled, filtered and the filtrate was used for complexation. The ligand was synthesized and characterized by the known method[5].

Synthesis of the Complexes

(i) $Ln(NCS)_3 \cdot 2$(DABAABTS) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho): The absolute ethanolic solution (10 mL) of lanthanide isothiocyanate (1 mmol) was

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added in drops to the hot ethanolic solution (15 mL) of ligand (2.1 mmol) for 10 min with vigorous stirring. The solution was then allowed to stand for 24 h at room temp. (37°C). The precipitate was filtered, washed with absolute ethanol and dried in *vacuo*.

(ii) $Ln(ClO_4)_3$·2(DABAAPTS) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho): Lanthanide(III) perchlorate (1 mmol) and DABAAPTS (2.1 mmol) were dissolved separately in hot ethanol (15 mL each). The reaction mixture was refluxed for *ca.* 3 h and the solution was concentrated to a viscous mass, which was washed several times with small portions of hot ethanol to remove the excess of ligand. The finely divided solid mass was finally washed with diethyl ether and collected and dried over P_4O_{10}.

All the physical measurements and analyses were performed as reported earlier.[6]

RESULTS AND DISCUSSION

The reactions of non-aqueous solution of lanthanide(III) isothiocyanates and perchlorates with DABAAPTS resulting in complexes of the general composition LnX_3·2(DABAAPTS) (Ln = La, Pr, Nd, Sm, Gd, Tg, Dy or Ho; X = NCS^- or ClO_4^-). The analytical data of these complexes are given in Table-1. The complexes are generally stable and could be stored for a long time and are non-hygroscopic in nature. The molar conductance values of isothiocyanato complexes are too low to account for any dissociation; therefore, the complexes are non-electrolytes. The molar counductance values of $Ln(ClO_4)_3$·2L complexes are in the range 78.9–81.3 ohm^{-1} cm^2 $mole^{-1}$ which suggest the perchlorato complexes are 1 : 3 electrolytes in nitrobenzene.[7] Data on the molecular weight of the complexes in $PhNO_2$ (Table 1) indicate that the ratio of molecular weight observed for $Ln(NCS)_3$·2(DABAAPTS) to that calculated is *ca.* 0.98, which suggest the complexes are monomeric in nature. In case of $Ln(ClO_4)_3$·2(DABAAPTS) the ratio is found to be *ca.* 0.25, which supports that 4 species are formed in the perchlorato complexes. The magnetic moment values (Table-1) indicate that the lanthanum(III) complexes are diamagnetic, while all the other complexes are paramagnetic as expected. The measured magnetic moments are in good agreement with the theoretical values obtained from Van Vleck formula[8].

Infrared Spectra: The strong lands observed at 3360–3330 cm^{-1} region in the 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 1600 cm^{-1} in free ligand can be attributed to ν(C=N) of imine nitrogen, which is in agreement with early reports[9, 10]. On complexation this frequency was observed to be shifted to lower wave number, which suggests involvement of unsaturated N-atoms of the two azomethine groups in bonding with Ln^{3+}. The bands observed in 1360–1130 cm^{-1}, 1115–1095 cm^{-1} and 830–730 cm^{-1} region are assigned to [ν(C=S) + ν(C=N) + ν(C—N)], [δ(N—C—S) + δ(C=S)] and ν(C=S) stretchings respectively[11, 12]. Coordination of sulphur with the Ln^{3+} ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence, on complexation ν(C=S) vibrations should decrease and those of

ν(CN) should increase. In all the present complexes of Ln^{3+} with DABAAPTS, the frequencies in the range 1360–1130 cm^{-1} and 1115–1095 cm^{-1} suffer a positive increase by nearly 40–50 cm^{-1} Similarly δ(N—C—S) and δ(C=S) frequencies also get increased but in lesser amount. On the other hand, on complexation, the frequencies in 830–730 cm^{-1} are shifted to lower wave numbers and intensity of the bands is also reduced. All these peculiar changes on complexation confidently confirm the metal-sulphur bonding in these complexes.

TABLE-1
ANALYTICAL AND MAGNETIC MOMENT DATA OF Ln^{3+} COMPLEXES OF DABAAPTS

Complex	% Analysis, Found (Calcd)			m.w. Found (Calcd)	μ_{eff} (B.M.)
	M	N	S		
$La(NCS)_3 \cdot 2(DABAAPTS)$	12.22 (12.33)	20.86 (21.11)	14.00 (14.19)	1122 (1127)	Diamag
$Pr(NCS)_3 \cdot 2(DABAAPTS)$	12.36 (12.48)	20.83 (21.08)	13.97 (14.17)	1124 (1129)	3.53
$Nd(NCS)_3 \cdot 2(DABAAPTS)$	12.60 (12.72)	20.79 (21.02)	13.93 (14.13)	1126 (1132)	3.52
$Sm(NCS)_3 \cdot 2(DABAAPTS)$	13.03 (13.18)	20.70 (20.91)	13.84 (14.05)	1130 (1138)	1.61
$Gd(NCS)_3 \cdot 2(DABAAPTS)$	13.59 (13.71)	20.54 (20.78)	13.77 (13.97)	1138 (1145)	7.82
$Tb(NCS)_3 \cdot 2(DABAAPTS)$	13.69 (13.86)	20.50 (20.74)	13.75 (13.94)	1139 (1147)	9.50
$Dy(NCS)_3 \cdot 2(DABAAPTS)$	13.96 (14.12)	20.43 (20.68)	13.70 (13.90)	1140 (1150.5)	10.61
$Ho(NCS)_3 \cdot 2(DABAAPTS)$	14.17 (14.31)	20.40 (20.64)	13.69 (13.87)	1142 (1153)	10.33
$La(ClO_4)_3 \cdot 2(DABAAPTS)$	10.92 (11.10)	15.46 (15.66)	5.06 (5.11)	308 (1251.5)	Diamag
$Pr(ClO_4)_3 \cdot 2(DABAAPTS)$	11.05 (11.24)	15.44 (15.63)	5.05 (5.10)	309 (1253.5)	3.41
$Nd(ClO_4)_3 \cdot 2(DABAAPTS)$	11.27 (11.46)	15.39 (15.59)	5.04 (5.09)	310 (1256.5)	3.52
$Sm(ClO_4)_3 \cdot 2(DABAAPTS)$	11.70 (11.88)	15.32 (15.52)	5.02 (5.06)	313 (1262.5)	1.61
$Gd(ClO_4)_3 \cdot 2(DABAAPTS)$	12.16 (12.36)	14.25 (15.43)	4.98 (5.04)	314 (1269.5)	7.82
$Tb(ClO_4)_3 \cdot (DABAAPTS)$	12.32 (12.50)	15.22 (15.41)	4.97 (5.03)	314 (1271.5)	9.47
$Dy(ClO_4)_3 \cdot 2(DABAAPTS)$	12.55 (12.74)	15.20 (15.37)	4.95 (5.01)	315 (1275)	10.59
$Ho(ClO_4)_3 \cdot 2(DABAAPTS)$	12.72 (12.91)	15.17 (15.34)	4.94 (5.00)	315 (1277.5)	10.43

The possibility of thione-thiol tautomerism (H—N—C=S) ⇌ (C=N—SH) in DABAAPTS has been ruled out, for no bands around 2700–2500 cm^{-1} characteristic of thiol group are displayed in the infrared absorption[13] The far infrared spectral bands in 450–332 cm^{-1} region are assigned to ν(Ln—N)/ν(Ln—S) modes[14].

In lanthanide(III) isothiocyanate complexes the presence of the three fundamental absorptions ν(C—N)(ν_1), ν(C—S)(ν_3) and δ(N—C—S)(ν_2) are identified in 2040–2030 cm^{-1}, 840–832 cm^{-1} and 4.82–465 cm^{-1} region respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions.[15] In lanthanide(III) perchlorato complexes only two strong ν_3 and ν_4 bands are observed at 1110–1080 cm^{-1} and 628–620 cm^{-1} region respectively for perchlorate ion indicating that tetrahedral symmetry has not been disturbed on complexation, and the perchlorate ions are not bonded to metal ion.[16]

Electronic spectra: Typical spectral data for solutions of $Ln(NCS)_3 \cdot 2(DABAAPTS)$ (Ln = Pr, Nd, Sm, Ho) investigated in CH_3CN are recorded in Table-2 and for comparison, data for an aqueous salt solution are also given. Lanthanum(III) has no significant absorption in the visible region. The absorption bands of praseodymium(III), neodymium(III), samarium(III) and holmium(III) in the visible and near IR region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^4H_{5/2}$ and $^5I_8$ respectively to the excited J-levels of 4*f*-configuration respectively[17]. Some red-shift or nephelauxetic effect is observed in acetonitrile solution of these coordinating compounds. The red-shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate compounds. From the β-values the covalence factor ($b^{1/2}$), Sinha parameter (δ%) and the covalency angular overlap parameter (η) were also calculated. The positive value for $(1 - \beta)$ and δ% in these chelate compounds suggest that 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[17, 18].

Thermal studies: Due to explosive nature of perchlorato complexes, we have not studied the thermal properties of these complexes; but the thermoanalytical results of $[Ln(DABAAPTS)_2(NCS)_2]$ indicate that at *ca.* 220°C, the complexes start to lose mass with partial evaporation of the organic ligand up to 300°C, the loss of mass (34.9–35.7%) corresponds to loss of one molecule of DABAAPTS. At temperature 430°C, the remaining DABAAPTS is also lost. The residues obtained after heating at *ca.* 810°C, to constant weight, are very close to that expected for lanthanide oxides.[19]

In conclusion, in case of $[Ln(DABAAPTS)_2(NCS)_3]$, the lanthanide ions are surrounded by seven nitrogen atoms (three of isothiocyanate ions and four from azomethine groups of DABAAPTS) and two sulphur atoms of thioketo group. Hence a coordination number nine has been suggested for lanthanide ions in these complexes. In $[Ln(DABAAPTS)_2](ClO_4)_3$ complexes the trivalent lanthanide ions are bounded by four nitrogen atoms and two sulphur atoms from the azomethine and thioketo group respectively of the two organic ligans. Conclusively a coordination number six is suggested in these complexes.

TABLE-2

ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELATED BONDING PARAMETERS OF LANTHANIDE(III) ISOTHIOCYANATE COMPLEXES OF DABAAPTS

Complesx	$Ln(NCS)_3$ electronic spectral bands	Complex electronic spectral bands	Energy levels	$(1-\beta)$	β	$b^{1/2}$	δ %	η
$Pr(NCS)_3 \cdot 2(DABAAPTS)$	22400	22240	$^3H_4 \rightarrow {}^3P_2$	0.00714	0.99285	0.05974	0.71914	0.00360
	21230	21040	$\rightarrow {}^3P_1$	0.00894	0.99105	0.06685	0.90207	0.00451
	20800	20620	$\rightarrow {}^3P_0$	0.00865	0.99134	0.06576	0.87255	0.00435
	16900	16730	$\rightarrow {}^1D_2$	0.01006	0.98994	0.07092	1.01622	0.00507
$Nd(NCS)_3 \cdot 2(DABAAPTS)$	19400	19230	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.00876	0.99123	0.06618	0.88375	0.00441
	17400	17210	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.01091	0.98608	0.07385	1.10304	0.00702
	13400	13240	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.01194	0.98805	0.07726	1.20844	0.00603
	12500	12230	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.02160	0.97840	0.10392	2.20768	0.01097
$Sm(NCS)_3 \cdot 2(DABAAPTS)$	24900	24730	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.00682	0.99317	0.05839	0.68669	0.00344
	24000	23810	$\rightarrow {}^6P_{5/2}$	0.00791	0.99208	0.06288	0.79731	0.00398
	21600	21470	$\rightarrow {}^4I_{13/2}$	0.00601	0.99398	0.05481	0.60463	0.00302
$Ho(NCS)_3 \cdot 2(DABAAPTS)$	22500	22270	$^5I_8 \rightarrow {}^5G_6, {}^5F_1$	0.01022	0.98977	0.07148	1.03256	0.00515
	19350	19100	$\rightarrow {}^5F_4$	0.01291	0.98708	0.08034	1.30789	0.00652
	15700	15530	$\rightarrow {}^5F_5, {}^5S_2$	0.01082	0.98917	0.07355	1.09384	0.00545
	13550	13370	$\rightarrow {}^5I_4$	0.01328	0.98670	0.08148	1.34590	0.00671

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