Asian Journal of Chemistry Vol. 11, No. 2 (1999), 503–508

Synthesis, Spectral and Thermal Studies of Some Lanthanide(III) Complexes of 4-[N-(Benzalidene) Amino] Antipyrine Thiosemicarbazone

LAKSHMAN SINGH*, (MS.) NEELAM TYAGI, NARESH P. DHAKA and S.K. SINDHU†
Department of Chemistry
Lajpat Rai Post Graduate College, Sahibabad-201 005, India

A new series of sixteen lanthanide(III) complexes of 4-[N-(benzalidene) amino] antipyrine thiosemicarbazone (BAAPTS) with the general composition $LnX_3 \cdot n(BAAPTS)$ ($X = Cl^-$, $n = 2$; $X = NO_3^-$, $n = 1$; Ln = La, Pr, Nd, Sm, Gd, Tb, Dy and Ho) have been synthesized and characterized by chemical analysis, conductance, molar weight, magnetic moments measurements, infrared and electronic spectra. The ligand BAAPTS behaves as neutral tridentate (N, N, S) ligand. The probable coordination number is nine in these complexes.

INTRODUCTION

Due to their medicinal properties, including activity against influenza, protozoa, smallpox, certain kinds of tumour, tuberculosis, leprosy, bacterial and viral infections, psoriasis, rheumatism, tripanosomiasis, coccidiosis, malaria and having possible pesticides and fungicides[1], and their ability to chelate trace metals, the coordination chemistry of thiosemicarbazones was the subject of extensive studies[2, 3]. In the present paper, we describe the coordination behaviour of 4-[N-(benzalidene) amino] antipyrine thiosemicarbazone (BAAPTS) toward lanthanides.

EXPERIMENTAL

The lanthanide(III) chlorides and nitrates were obtained from Rare Earth Products Ltd., India and were used without further purification. The ligand BAAPTS was synthesized and characterized in the laboratory by the known method[4].

Synthesis of the complexes

(i) *$LnCl_3 \cdot 2(BAAPTS)$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho)*: The solution of lanthanide(III) chloride (1 mmol) and BAAPTS (2.1 mmol) in hot ethanol (15 mL each) were mixed and stirred well. After refluxing the reaction mixture on a

---

†Department of Chemistry, S.S.V. College, Hapur, India.

water bath for *ca.* 1 h, the resulting solid complex was obtained, which was filtered and washed with ethanol and finally with diethyl-ether and dried under reduced pressure over P_4O_{10}.

(ii) *$Ln(NO_3)_3$·BAAPTS (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho)*: The corresponding lanthanide(III) nitrate (1.0 mmol) and BAAPTS (1.1 mmol) were dissolved separately in hot ethanol (15 mL each). The solutions were mixed and refluxed for *ca.* 3 h. The resulting solution of the nitrate complex was concentrated to 10 mL and to this diethyl-ether (15 mL) was added with vigorous stirring, whereupon the complex separated out. The finely divided solid mass was finally washed with diethyl-ether and collected. All these complexes were dried *in vacuo* over P_4O_{10}.

All the physical measurements and analyses were performed as reported earlier[5].

RESULTS AND DISCUSSION

The reactions of non-aqueous solution of lanthamide(III) chlorides and nitrates with BAAPTC resulting in complexes of the general composition LnX_3·n(BAAPTS) ($X = Cl^-$, n = 2; $X = NO_3^-$, n = 1; Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The complexes are fairly stable and could be stored for a long time and are non-hygroscopic in nature. The analytical data presented in Table-1 indicate that the complexes are pure and need no further purification. The molar conductance values (2.9–4.0 ohm^{-1} cm^2 mol^{-1}) of these complexes in $PhNO_2$ are too low to account for any dissociation; therefore, the complexes are non-electrolytes. Data on the molecular weight of the complexes in freezing $PhNO_2$ are given in Table-1. The ratio of molecular weight observed for these complexes to that calculated is *ca.* 0.98 which shows that the complexes are monomeric in solution. The magnetic moment values (Table-1) indicate that the lanthanide complexes are diamagnetic, while all the other complexes are paramagnetic as expected. The measured magnetic moments (Table-1) are in good agreement with the theoretical values obtained from the Van Vleck formula[6].

Infrared: 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 absorptions at *ca.* 1600 cm^{-1} in free ligand can be attributed to (C=N) stretchings of imine nitrogen, which is in agreement with the observations of previous workers[7, 8]. On complexation, this frequency was observed to be shifted to lower wave number, which suggests involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the Ln^{3+}. The bands observed in 1330–1305, 1120–1095 and 820–760 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) stretching respectively[9, 10]. Coordination of sulphur with the metal 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[11]. In all the present complexes of Ln^{3+} with BAAPTS, the frequencies in the range 1330–1095 cm^{-1} suffer a positive increase by nearly 50–40 cm^{-1}. On the other hand, on complexation, the frequencies in 820–760 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. The possibility of thione-thiol tautomerism (H—N—C=S) $\rightleftharpoons$ (C=N—SH) in BAAPTS has been ruled out, for no bands around 2700–2500 cm^{-1} characteristics of thiol group are displayed in the infrared absorption[12]. The far infrared spectral bands in 440–330 cm^{-1} region are assigned to ν(Ln—N)/ν(Ln—S) modes[13].

TABLE-1

ANALYTICAL AND MAGNETIC MOMENT DATA OF Ln^{3+} COMPLEXES OF BAAPTS

Complex	% Analysis, found (calcd.)			Mol. weight found (calcd.)	μ_{eff} (B.M.)
	M	N	S		
$La(BAAPTS)_2Cl_3$	14.01 (14.27)	17.01 (17.25)	6.49 (6.57)	967 (973.5)	Diamag
$Pr(BAAPTS)_2Cl_3$	14.22 (14.45)	16.98 (17.22)	6.48 (6.56)	969 (975.5)	3.51
$Nd(BAAPTS)_2Cl_3$	14.39 (14.62)	16.91 (17.16)	6.47 (6.54)	970 (978.5)	3.59
$Sm(BAAPTS)_2Cl_3$	15.04 (15.23)	16.80 (17.06)	6.43 (6.50)	975 (984.5)	1.66
$Gd(BAAPTS)_2Cl_3$	15.62 (15.83)	16.72 (16.94)	6.38 (6.45)	982 (991.5)	7.89
$Tb(BAAPTS)_2Cl_3$	15.80 (16.00)	16.67 (16.90)	6.36 (6.44)	983 (993.5)	9.78
$Dy(BAAPTS)_2Cl_3$	16.03 (16.29)	16.60 (16.85)	6.34 (6.41)	990 (997)	10.50
$Ho(BAAPTS)_2Cl_3$	16.33 (16.50)	16.56 (16.86)	6.33 (6.40)	991 (999.5)	10.45
$La(BAAPTS)(NO_3)_3$	19.96 (20.17)	18.16 (18.28)	4.57 (4.64)	683 (689)	Diamag
$Pr(BAAPTS)(NO_3)_3$	20.27 (20.40)	18.12 (18.23)	4.56 (4.63)	685 (691)	3.41
$Nd(BAAPTS)(NO_3)_3$	20.53 (20.74)	18.00 (18.15)	4.53 (4.61)	686 (694)	3.52
$Sm(BAAPTS)(NO_3)_3$	21.27 (21.42)	17.82 (18.00)	4.48 (4.57)	690 (700)	1.60
$Gd(BAAPTS)(NO_3)_3$	22.02 (22.20)	17.69 (17.82)	4.42 (4.52)	701 (707)	7.80
$Tb(BAAPTS)(NO_3)_3$	22.20 (22.42)	17.50 (17.77)	4.43 (4.51)	702 (709)	9.42
$Dy(BAAPTS)(NO_3)_3$	22.51 (22.80)	17.53 (17.68)	4.40 (4.49)	706 (712.5)	10.59
$Ho(BAAPTS)(NO_3)_3$	22.89 (23.07)	17.49 (17.62)	4.39 (4.47)	707 (715)	10.39

In lanthamide(III) nitrate complexes, the occurrence of two strong absorptions at 1525–1515 cm^{-1} and 1310–1290 cm^{-1} region is attributed to ν_4 and ν_1 modes of vibration of covalently bonded nitrate group respectively[14, 15]. If the $(\nu_4 - \nu_1)$ difference is taken as an approximate measure of the covalency of the nitrate groups[15], a value of *ca.* 200 cm^{-1} for the complexes studied suggests strong covalency for the metal-nitrate bonding. According to Lever *et al.*[16], bidentate coordination of NO_3^- groups involves a greater distortion from D_{3h} symmetry than unidentate coordination; therefore bidentate complexes should show a large separation of $(\nu_1 + \nu_4)$. In the present study, a separation of *ca.* 55–35 cm^{-1} in the combination bands in the 1800–1700 cm^{-1} region suggests the bidentate nitrate coordination. Further the bidentate character of nitrate groups has been established by X-ray[17] and neutron diffraction studies[18]. Thus, it is inferred that in the present study the nitrate groups may be bidentate in nature[18]. In chloro complexes, the ν(Ln—Cl) has been assigned to 285–270 cm^{-1} region.

Electronic spectra: Typical spectra for solutions (0.001 M) of $Ln(NO_3)_3\cdot$BAAPTS investigated in CH_3CN are recorded in Table-2. 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 4f-configuration respectively[19]. 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 complexes. From the β-values, the covalence factor ($b^{1/2}$), the Sinha's parameter (δ%) and the covalency angular overlap parameter (η) were also calculated. The positive value for $(1 - \beta)$ and δ% in these compounds suggest that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and water. The values of parameter of bonding ($b^{1/2}$) were found to be positive indicating covalent bonding[19, 20].

Thermal studies: The pyrolysis curves of $[Ln(BAAPTS)_2Cl_3]$ (Ln = La, Pr, Gd or Tb) indicate that the complexes do not possess water of crystallization. The complexes are stable up to 200°C beyond which they start to lose mass up to a temperature of 280°C corresponding to loss of one molecule of BAAPTS. The remaining organic ligand was lost in 350–450°C temperature again. The residue obtained at *ca.* 815°C is due to formation of stable lanthanide oxides.

Thermoanalytical results of $[Ln(BAAPTS)(NO_3)_3]$ (Ln = La, Nd, Gd or Tb) suggest the complexes are stable up to 250°C. In 250–320°C temperature range, a loss of 26.48–27.39% is due to evaporation of 0.5 molecule of BAAPTS and from 340–380°C, a loss of 52.20–53.19% is observed because of the complete loss of BAAPTS. The residue obtained after heating at *ca.* 825°C to constant weight is very close to that expected for the lanthanide oxide (La_2O_3, Nd_2O_3, Gd_2O_3 or Tb_4O_7). In conclusion, the present studies of these complexes reveal that the coordination number of Ln^{3+} may be nine in all the complexes.

TABLE-2
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELATED BONDING PARAMETERS OF $Ln(NO_3)_3 \cdot (BAAPTS)$

Complex	$Ln(NO_3)_3$ electronic spectral bands	Complex electronic spectral bands	Energy levels	(1 – β)	β	$b^{1/2}$	δ%	η
$Pr(NO_3)_3 \cdot BAAPTS$	22470	22300	$^3H_4 \rightarrow {}^3P_2$	0.0075	0.9924	0.0615	0.7617	0.0038
	21280	21100	$\rightarrow {}^3P_1$	0.0084	0.9915	0.0650	0.8522	0.0042
	20830	20680	$\rightarrow {}^3P_0$	0.0072	0.9928	0.0600	0.7252	0.0036
	16950	16800	$\rightarrow {}^1D_2$	0.0088	0.9912	0.0665	0.8919	0.0044
$Nd(NO_3)_3 \cdot BAAPTS$	19420	19280	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	0.0072	0.9928	0.0600	0.7252	0.0036
	17390	17200	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.0109	0.9891	0.0739	1.1040	0.0055
	13420	13210	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.0156	0.9846	0.0884	1.5888	0.0079
	12500	12340	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.0128	0.9872	0.0800	1.2966	0.0065
$Sm(NO_3)_3 \cdot BAAPTS$	24850	24730	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.0048	0.9952	0.0491	0.4843	0.0024
	24100	23800	$\rightarrow {}^6P_{5/2}$	0.0124	0.9876	0.0788	1.2597	0.0063
	21600	21480	$\rightarrow {}^4I_{3/2}$	0.0055	0.9945	0.0527	0.5581	0.0028
$Ho(NO_3)_3 \cdot BAAPTS$	22500	22290	$^5I_8 \rightarrow {}^5G_6, {}^5F_1$	0.0093	0.9907	0.0683	0.4918	0.0047
	19300	19050	$\rightarrow {}^5F_4$	0.0129	0.9871	0.0805	1.3120	0.0065
	15720	15600	$\rightarrow {}^5F_5, {}^5S_2$	0.0076	0.9924	0.0618	0.7689	0.0038
	13500	13370	$\rightarrow {}^5I_4$	0.0096	0.9904	0.0693	0.9713	0.0048

ACKNOWLEDGEMENT

One of us (L.S.) is thankful to UGC, New Delhi for award of minor research project.

REFERENCES

1. S.E. Livingstone, *Quart. Rev. Chem. Soc.*, **19,** 386 (1965) and references therein.
2. S. Padhye and G.B. Kauffman, *Coord. Chem. Rev.*, **63,** 127 (1985).
3. D.X. West, S.B. Padhye, P.B. Sonawane and R.C. Chi-Kate, *Asian J. Chem. Revs.*, **1,** 125 (1990).
4. R.K. Agarwal, Bharat Bhushan and G. Singh, *J. Inst. Chemists (India)*, **65,** 131 (1993).
5. R.K. Agarwal, R.K. Sarin and Himanshu Agarwal, *Bull. Chem. Soc. Ethiop.*, **9,** 23 (1995).
6. J.H. Van Vleck and N. Frank, *Phys. Rev.*, **34,** 1494 (1929).
7. P.S. Radhakrishnan, P. Indrasenan and C.G.R. Nair, *Polyhedron*, **3,** 67 (1984).
8. R.K. Agarwal, Himanshu Agarwal and Indranil Chakraborti, *Synth. React. Inorg. Met.-Org. Chem.*, **25,** 679 (1995).
9. K. Swaminathan and H.M.N.H. Irving, *J. Inorg. Nucl. Chem.*, **26,** 1291 (1964).
10. D. Banerjee and I.P. Singh, *Indian J. Chem.*, **6,** 34 (1968).
11. V.B. Rana, *J. Inorg. Nucl. Chem.*, **37,** 1826 (1975).
12. B.D. Sharma and J.C. Bailer (Jr.), *J. Am. Chem. Soc.*, **77,** 5476 (1955).
13. J.R. Ferrao, Low Frequency Vibrations of Inorganic and coordination compounds, Plenum, New York (1971).
14. J.R. Ferraro, *J. Mol. Spectra*, **4,** 99 (1960).
15. C.C. Addison and N. Logan, *Adv. Inorg. Chem. and Radiochem.*, **6,** 95 (1964).
16. A.B.P. Lever, E. Mantiovani and B.S. Ramaswamy, *Canad. J. Chem.*, **49,** 1957 (1971).
17. T. Ueki, A Zalkin and D. Templeton, *Acta Crystallogr.*, **20,** 836 (1966).
18. J.I. Bullock, *J. Inorg. Nucl. Chem.*, **29,** 2257 (1967).
19. S.S.L. Surana, M. Singh and S.N. Misra, *J. Inorg. Nucl. Chem.*, **42,** 610 (1980).
20. S.P. Sinha, Complexes of Rare Earths, Pergamon Press, New York (1966).

(*Received*: 5 October 1998; *Accepted*: 4 December 1998) AJC-1647