Asian Journal of Chemistry Vol. 15, No. 1 (2003), 105–110

Synthesis and Characterisation of Lanthanide(III) 7-[(Amino(4-Hydroxyphenyl) Acetyl) Amino]-3-methyl-8-oxo Complexes

S.R. PINGALKAR* and M.N. DESHPANDE
P.G. Department of Chemistry, Science College, Nanded-431 602, India

Lanthanide(III) complexes of 7-[(amino(4-hydroxyphenyl) acetyl) amino]-3-methyl-8-oxo (AHAAMO) monohydrate with the general composition $[Ln(L_2)(H_2O)_2]Cl$ (where Ln = La, Ce, Pr, Nd, Sm, Gd., Tb or Dy) have been prepared and characterised by the elemental analysis, conductivity measurement, UV-visible, IR, NMR spectra, X-ray diffraction studies, magnetic susceptibility and thermal studies. Infrared studies of these complexes reveal that AHAAMO acts as tetradentate ligand and coordinate through nitrogen and oxygen.

Key Words: Lanthanide(III), Complexes, 7[(amino (4-hydroxyphenyl) acetyl) amino]-3-methyl-8-oxo, characterization.

INTRODUCTION

In the past a number of workers were interested to isolate solid complexes of lanthanide(III) with drugs. But literature survey shows that the solid Ln(III) complexes of 7[(amino (4-hydroxyphenyl) acetyl) amino]-3-methyl-8-oxo (AHAAMO) complexes have not been reported. We report here the synthesis of lanthanide(III) complexes of AHAAMO and their characterisation.

EXPERIMENTAL

The lanthanide(III) chlorides were obtained from Indian Rare Earth Ltd., Kerala, India. The ligand AHAAMO obtained from Lupin Laboratory having m.f. $C_{16}H_{17}N_3O_5S{\cdot}H_2O$ and used as received (Fig. 1). Reagents were used of AR grade. Chemicals used were purified by standard techniques.

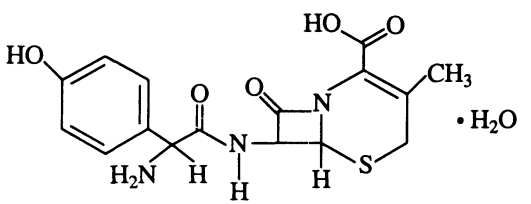

Fig. 1. 7-[(amino (4-hydroxyphenyl) acetyl) amino]-3-methyl-8-oxo, monohydrate (AHAAMO).

Synthesis of Complexes

The metal complexes were prepared by refluxing the alcoholic solution of AHAAMO with lanthanide(III) chloride for 4 h (M : L ratio 1 : 2). The pH is maintained (pH = 6–6.5). The solid coloured complexes obtained were filtered, washed with ethanol and dried in an oven. The analytical data were determined on HOSLI analyser, from Pune University, Pune. The lanthanide metal ions were estimated by standard method[1]. Chlorides were estimated by Mohr's method. The IR spectral data were recorded on Perkin-Elmer 1615 FTIR spectrophotometer using KBr disc in the 4500–450 cm^{-1} region at WRIC, Mumbai. UV-visible spectra were recorded on a UV-visible spectrophotometer Cary-50. Conductance measurement of complex solution in DMSO was carried out on Elico digital conductivity bridge at room temperature (26°C). Magnetic susceptibility of complexes was measured at room temperature on Gouy balance at Marathwada University, Aurangabad, using $Hg[Co(SCN)_4]$ as calibrant. It is observed that all the lanthanide(III) AHAAMO complexes are paramagnetic except lanthanum(III) AHAAMO which is diamagnetic.[2] ^1H NMR spectra in DMSO-d_6 were recorded on 300 MHz NMR spectrometer. Thermal analyses were carried out on a Mettler-Toledo 851 TGA-DTA instrument with a linear heating rate of 10°C min^{-1} in static air. XRD spectra were recorded on Philips XRD Model No. PW 1710 by using CuK_α as source of radiation (λ = 1.54056 Å) at room temperature in the range of 2θ from 10–70°.

RESULTS AND DISCUSSION

The analytical data of complexes (Table-1) indicate that all the eight complexes show 1 : 2 (metal : ligand) ratio. The analytical data, percentage of metal, molar conductance, magnetic moment of the Ln(III) AHAAMO complexes are represented in Table-1. Magnetic moments of complexes are in good agreement with the theorotical values calculated by Van Vleck[2]. All these complexes are soluble in DMSO, insoluble in water, and nonhygroscopic in nature.

The electronic spectra of the Pr(III), Nd(III) and Sm(III) complexes have been attributed to the transitions from ground levels $^3H_4$, $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J-levels of $4f^n$ configuration[3]. The electronic spectra of *f-f* transitions for Pr(III), Nd(III) and Sm(III) complexes and their assignments are given in Table-2. The nephelauxetic ratio β ($\nu_{complex}/\nu_{aquo}$), covalency factor ($b^{1/2}$) and Sinha's parameter δ% have been calculated. The values of β, $b^{1/2}$ and δ% suggest covalency in the metal-ligand bonding[4].

In IR spectra of ligand (AHAAMO), the band appearing at 3509 cm^{-1} indicates the presence of phenolic —OH group and it shifts at 3201 cm^{-1} in lanthanum complex. From cerium to dysprosium(III) AHAAMO complexes, the band shifts in the region 3415–3201 cm^{-1}. Carboxylic acid stretching frequency in ligand is at 1757 cm^{-1}, but it disappears in the spectra of the complexes. COO^- group of lanthanide complexes appears in the region 1748–1690 cm^{-1}. Primary amine (—NH_2) stretching frequency in the AHAAMO ligand is at 3492 cm^{-1}; it shifts to 3350 cm^{-1} in lanthanum complex. From cerium to dysprosium complexes the

TABLE-1
ANALYTICAL, MAGNETIC AND CONDUCTIVITY DATA OF LANTHANIDE(III) COMPLEXES OF AHAAMO

Complexes	Colour	Decomposition point (°C)	% Analysis: Found (Calcd.)						μ_{eff} (B.M.)	Mol. cond. (ohm^{-1} cm^2 mol^{-1})
			Ln	C	H	N	S	Cl		
$[La(AHAAMO)_2(H_2O)_2]Cl$	Light yellow	335	14.27	39.45	4.31	8.63	6.57	3.64	diamag.	10.4
			(14.11)	(39.38)	(4.28)	(8.55)	(6.48)	(3.61)		
$[Ce(AHAAMO)_2(H_2O)_2]Cl$	Brown	341	14.38	39.41	4.31	8.62	6.56	3.63	3.22	12.2
			(14.24)	(39.35)	(4.27)	(8.58)	(6.45)	(3.56)		
$[Pr(AHAAMO)_2(H_2O)_2]Cl$	Yellow	372	14.44	39.37	4.30	8.61	6.56	3.63	5.72	14.4
			(14.18)	(39.29)	(4.22)	(8.60)	(6.46)	(3.60)		
$[Nd(AHAAMO)_2(H_2O)_2]Cl$	Light yellow	322	14.74	39.24	4.29	8.58	6.54	3.62	2.68	12.6
			(14.68)	(39.14)	(4.25)	(8.52)	(6.51)	(3.52)		
$[Sm(AHAAMO)_2(H_2O)_2]Cl$	Yellowish white	314	15.27	38.99	4.26	8.53	6.49	3.60	4.12	16.4
			(15.08)	(38.85)	(4.18)	(8.48)	(6.41)	(3.54)		
$[Gd(AHAAMO)_2(H_2O)_2]Cl$	Light yellow	365	15.85	38.72	4.23	8.47	6.45	3.57	4.62	14.8
			(15.79)	(38.68)	(4.20)	(8.35)	(6.38)	(3.58)		
$[Tb(AHAAMO)_2(H_2O)_2]Cl$	Yellow	348	16.00	38.66	4.22	8.45	6.44	3.56	3.88	16.6
			(15.95)	(38.49)	(4.17)	(8.38)	(6.32)	(3.48)		
$[Dy(AHAAMO)_2(H_2O)_2]Cl$	Light yellow	352	16.30	38.52	4.21	8.42	6.42	3.55	6.54	18.8
			(16.24)	(38.46)	(4.14)	(8.32)	(6.34)	(3.46)		

band shifts in the region 3465–3382 cm^{-1}. The secondary amine (>NH—) stretching in case of ligand is at 1562 cm^{-1}; it is shifted in all Ln(III) AHAAMO complexes in the region 1548–1515 cm^{-1}. The broad band appearing in the spectra of all the complexes at 3550–3500 cm^{-1} is attributed to the presence of coordinate water molecule[5].

TABLE-2
ELECTRONIC SPECTRAL DATA OF Ln(III) (AHAAMO) COMPLEXES

Complex	Band (cm^{-1})	Assignments	Calculated parameter			
			(1–β)	β	$b^{1/2}$	δ%
$[Pr(AHAAMO)_2(H_2O)_2]Cl$	22214	$^3H_4 \rightarrow {}^3P_1$	0.0024	0.9976	0.0346	0.2405
	21218	$\rightarrow {}^3P_1$	0.0036	0.9964	0.0424	0.3613
	20312	$\rightarrow {}^3P_0$	0.0102	0.9898	0.0714	1.0305
	16716	$\rightarrow {}^1D_2$	0.0120	0.9880	0.0774	1.2145
$[Nd(AHAAMO)_2(H_2O)_2]Cl$	19792	$^4I_{9/2} \rightarrow {}^4G_{9/2}$	0.0020	0.9980	0.0316	0.2004
	17202	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.0029	0.9971	0.0380	0.2908
	14574	$\rightarrow {}^4F_{9/2}$	0.0036	0.9964	0.0424	0.3613
	13502	$\rightarrow {}^2S_{3/2}{}^4F_{7/2}$	0.0112	0.9888	0.0748	1.1326
	12442	$\rightarrow {}^4F_{5/2}$	0.0118	0.9882	0.0768	1.1940
$[Sm(AHAAMO)_2(H_2O)_2]Cl$	33422	$^6H_{5/2} \rightarrow {}^7F_{5/2}$	0.0032	0.9968	0.0400	0.3210
	28252	$\rightarrow {}^4H_{7/2}$	0.0038	0.9962	0.0435	0.3814
	26158	$\rightarrow {}^4I_{17/2}$	0.0046	0.9954	0.0479	0.4621
	22694	$\rightarrow {}^4I_{15/2}$	0.0056	0.9944	0.5290	0.5631

^1H NMR spectrum of ligand in DMSO-d_6 indicates signals at δ 11.55 ppm for —OH, δ 10.2 ppm for —NH proton while multiplet signals appearing in δ 7.66–8.00 ppm region are due to aromatic ring protons[6]. The signal at δ 2.2 ppm region is for —COOH proton. In the spectra of Ln(III) AHAAMO complexes, the signals due to —OH, >NH— and —COOH group protons show downfield shift appearing in the regions δ 10.15–10.80 ppm, δ 9.42–9.78 ppm and δ 2.0–2.1 ppm respectively. COOH proton signal disappears in the complex indicating that the proton of —COOH is replaced during the complex formation.

The paramagnetic behaviour of the lanthanide complexes is consistent with the presence of unpaired electrons. The La(III) AHAAMO complex is diamagnetic, while all the remaining complexes except those of Nd(III) AHAAMO and Dy(III) AHAAMO show a very little deviation from the Van Vleck values[2] indicating a little participation of 4f-electrons in bonding. The relatively high values obtained in case of Nd(III) and Dy(III) complexes are due to J-J separation, which leads to thermal population of high energy levels and shows susceptibilities due to a first order Zeeman effect[7].

The thermal studies indicate the loss of two water molecules in the Ln(III) AHAAMO complexes at 110–200°C with weight loss of 52.42–55.38% due to the organic moiety and 530–800°C with weight loss 15.5–20.5% due to the chloride followed by the formation of lanthanide(III) oxides[8]. The DTA studies

indicate that both the decomposition of organic moiety and the formation of Ln(III) oxides are exothermic processes. Thermal data are represented in Table-3.

TABLE-3
THERMAL DATA OF Ln(III) AHAAMO COMPLEXES

Complex	Decomposition temp. (°C)	% Weight loss		Probable assignments
		Obs.	Calcd.	
$[La(AHAAMO)_2(H_2O)_2]Cl$	120–200	4.22	4.16	$2H_2O$
	220–520	54.50	55.38	$2H_2O + 2C_4H_9N + Cl$
	540–800	68.45	69.12	La_2O_3
$[Sm(AHAAMO)_2(H_2O)_2]Cl$	110–200	3.52	3.68	$2H_2O$
	230–490	52.42	54.60	$2H_2O + 2C_4H_9N + Cl$
	530–750	69.24	70.34	Sm_2O_3

The powder X-ray diffraction spectra of La(III) and Sm(III) AHAAMO complexes have considerable number of diffraction lines suggesting the crystalline nature of the compounds[9]. A strong peak at 32.905° and 32.940° respectively of high intensity. The d values of the complexes show that no lines are common suggesting that these complexes are new entities rather than mixtures. The lattice constant[10] a = b = c (11.54 Å) indicate that complex complex molecules are packed in *bcc* lattice. Four donor groups are present in the ligand; therefore *bcc* system is proposed for the complex.

The lattice parameters (a, b, c) of unit cell and cell volume were calculated by assuming a cubic structure for the complex[11].

In conclusion, the probable structures of these complexes have been tentatively assigned as given in Fig. 2.

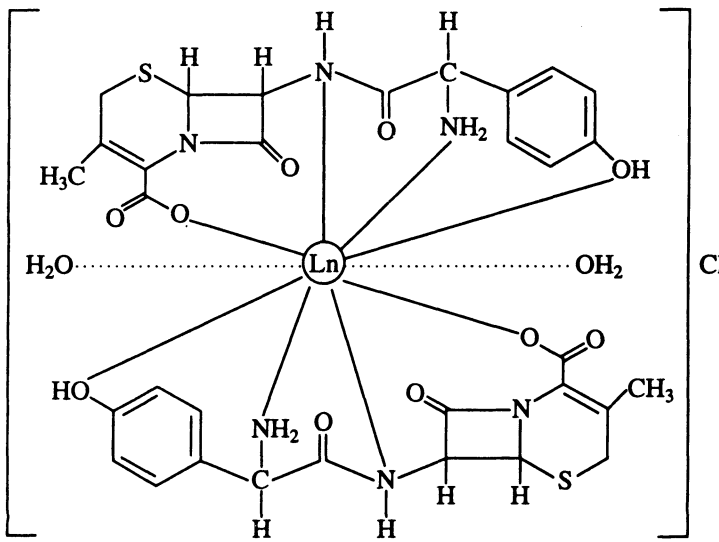

Fig. 2. Tentative structures of Ln(III) AHAAMO complexex. Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III).

REFERENCES

1. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, including Instrumental Analysis, ELBS, London (1978).
2. R.L. Dutta and A. Syamal, Elements of Magnetochemistry, 2nd Edn., Affiliated East-West Press Pvt. Ltd., New Delhi (1992).
3. R.K. Agarwal and Himanshu Agarwal, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 263 (2001).
4. B. Singh, Preeti Sahai and Praveen K. Singh, *Indian J. Chem.*, **35A**, 494 (1996).
5. M.M. Patel, H.R. Patel and K.C. Patel, *J. Indian Chem. Soc.*, **74**, 1 (1997).
6. N.K. Singh and Namita Rani Agrawal, *Indian J. Chem.*, **37A**, 276 (1998).
7. J.P. Phillips and L.L. Merritt, *J. Am. Chem. Soc.*, **71**, 3984 (1949).
8. K.P. Deepa, K.K. Aravindakshan and F. Suhara, *Asian J. Chem.*, **13**, 1549 (2001).
9. Anshu Agarwal and S.P. Singh Jadon, *Asian J. Chem.*, **13**, 1525 (2001).
10. Teresa O. Kocaba and Charales G. Young, *Inorg. Chim. Acta*, **174**, 143 (1990).
11. Joop A. Peters and Herman Van Bekkum, *Inorg. Chim. Acta*, **181**, 233 (1991).

(*Received*: 14 May 2002; *Accepted*: 27 July 2002) AJC-2803