Asian Journal of Chemistry Vol. 20, No. 4 (2008), 2774-2780

Synthesis, Characterization and Antibacterial Activities of Lanthanide Complexes with Schiff Base N-Salicylidene-1-aminoadamantane

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Fourteen solid complexes of the lanthanide(III) complexes of the type[$Ln(NO_3)_3(HL)_2$] (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, HL = $C_{17}H_{21}NO$, a Schiff base ligand derived from 1-aminoadamantane and salicylaldelyde have been synthesized and characterized by elemental analyses, molar electrical conductivities, spectra (Infrared, ^{1}H NMR) and thermal studies. The elemental analyses indicate 1:2 (metal:ligand) stoichiometry for the complexes. The spectral studies show that the ligand acts as a monodentate ligand with the phenolic-CO as coordinating site. The nitrate group is coordinated in a bidentate fashion. The ligand and the complexes were screened for antibacterial. It was found that activity against *Escherichia coli* and *Bacillus subtilis* has significantly enhanced on complexation.

Key Words: Synthesis, Lanthanide(III), Complexes, Schiff base, Antibacterial activities.

INTRODUCTION

Schiff bases form an important class of compounds and find varied applications. Various studies have shown that the Schiff bases derived from salicylaldehyde and its derivants have considerable biological importance because such ligands have many donor atoms (N, O) and biological environment. They are widely used in the fields of biology, pharmacology, catalysis, organic synthesis, chemical, analysis, *etc.*[1-4]. More attentions have been focused on these Schiff bases because of the stability of the ligands and various properties of their metal complexes[5-10]. 1-Aminoadamantane has an obvious effect on controlling the exuviating the influenza A virus. It can also prevent virus going into host cells and influenza A_2 in Asia. In addtion it can alleviate the Parkinson symptom[11]. We report here the synthesis, characterization, antibacterial activity of lanthanide(III) complexes with Schiff base derived from 1-aminoadamantane and salicylaldehyde.

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EXPERIMENTAL

Hydrated lanthanide(III) nitrates were prepared from the respective oxides (99.9 % pure) with nitric acid. Salicylaldehyde (C.P) was distalled before use. 1-Aminoadamantane (99 % pure) was recrystallized from absolute alcohol before use. The other chemicals and solvents used were of analytical grade.

Synthesis of N-salicylidene-1-aminoadamantane (Hsaiaad): 1-Aminoadamantane 6.05 g (40 mmol) was refluxed with salicylaldehyde 5.01 g (41 mmol) in ethanol (*ca.* 50 mL) on a water bath for 1 h, the solution was cooled to room temperature.The separated ligand was washed with ethanol three times and dried. Yield 7.0 g (*ca.* 67 %), m.p. 93 ºC.

Synthesis of lanthanide(III) complexes: Lanthanide salt (1 mmol) dissolved in 10 mL of dry alcohol was stirred with 0.51 g (2 mmol) of N-salicylidene-1-aminoadamantane in 20 mL dry alcohol for 0.5 h until yellow precipitate appeared. The precipitate was separated by filtration, washed with dry alcohol. and dried over calcium chloride. Yield *ca.* 0.52 g (60 %).

IR spectra were recoreded on a Nicolet NEXUS 670 FTIR spectrometer (4000-400 cm^{-1}) using KBr discs. Carbon, hydrogen and nitrogen were determined by a Elementar Vario EL III elemental analysis instrument. After destruction of the organic matter with $HClO_4$, the lanthanides were titrated with EDTA in the presence of a buffer solution (uroropine buffer pH 5.5) using xylenol organic as indicater. Electrical conductivities of 1.0×10^{-3} mol dm^{-3} DMF solutions of the complexes were measured at 25 ºC by a DDS-11A digital conductometer (xiaoshan FELLOW Instrument COLTO). The ^{1}H NMR spectra were recorded at 400 MHz on a Bruker-400 spectrometer using d_6-DMSO solutions, chemical shifts are expressed as δ (ppm) with respect to tetramenthylsilane as an external reference. TG-DTG mensurements were carried out on a METTLEA-TOLEDO TGA/SDTA851^e thermal analyzer in air from 30 to 900 ºC with a heating rate of 10 ºC/min. Antibacterial activity were measured of concentration 1.0×10^{-1} mol L^{-1}, 1.0×10^{-2} mol L^{-1} in DMF.

RESULTS AND DISCUSSION

The elemental analysis results and physical properties of the complexes are listed in Table-1. All of the complexes are yellow solids. The elemental analyses indicate that the complexes have the general formula $LnL_2(NO_3)_3$. All the complexes are soluble in DMSO, DMF, pyridine, methanol, ethanol, $CHCl_3$ and CH_3CN, but are insoluble in water, ether and benzene. The molar conductivity of the complexes in DMF (1.0×10^{-3} mol dm^{-3}) are in the range of 22-28 S cm^2 mol^{-1}, indicating that the complexes are non-electrolytes[12].

TABLE-1
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF LIGAND AND COMPLEXES

Compound / (Colour)	m.p. (ºC)	Elemental analysis %: Found (Calcd.)				Λ_M (S cm^2 mol^{-1})
		C	H	N	Ln	
HL	93	80.05	5.47	8.31	–	2.7
(Yellow)		(79.96)	(5.49)	(8.29)		
La(HL)$_2$(NO$_3$)$_3$	272	48.66	5.01	8.32	16.70	28.1
(Yellow)		(48.87)	(5.07)	(8.38)	(16.62)	
Ce(HL)$_2$(NO$_3$)$_3$	234	48.70	5.04	8.31	16.80	24.3
(Yellow)		(48.80)	(5.06)	(8.37)	(16.74)	
Pr(HL)$_2$(NO$_3$)$_3$	209	48.38	5.17	8.31	16.75	23.1
(Yellow)		(48.75)	(5.05)	(8.36)	(16.82)	
Nd(HL)$_2$(NO$_3$)$_3$	212	48.34	5.09	8.19	17.20	22.1
(Yellow)		(48.56)	(5.03)	(8.33)	(17.15)	
Sm(HL)$_2$(NO$_3$)$_3$	213	48.08	5.12	8.13	17.61	26.2
(Yellow)		(48.20)	(5.00)	(8.27)	(17.75)	
Eu(HL)$_2$(NO$_3$)$_3$	217	47.80	5.04	8.15	17.88	25.2
(Yellow)		(48.11)	(4.99)	(8.25)	(17.91)	
Gd(HL)$_2$(NO$_3$)$_3$	234	47.65	5.04	8.16	18.30	25.1
(Yellow)		(47.81)	(4.96)	(8.20)	(18.42)	
Tb(HL)$_2$(NO$_3$)$_3$	216	47.55	5.02	8.11	18.50	24.2
(Yellow)		(47.79)	(4.95)	(8.19)	(18.57)	
Dy(HL)$_2$(NO$_3$)$_3$	258	47.35	5.05	8.12	18.61	24.3
(Yellow)		(47.52)	(4.93)	(8.15)	(18.75)	
Ho(HL)$_2$(NO$_3$)$_3$	267	47.26	5.01	8.02	19.20	23.1
(Yellow)		(47.39)	(4.91)	(8.13)	(19.14)	
Er(HL)$_2$(NO$_3$)$_3$	261	47.06	4.98	8.08	19.48	26.2
(Yellow)		(47.26)	(4.90)	(8.11)	(19.36)	
Tm(HL)$_2$(NO$_3$)$_3$	253	46.98	5.00	8.01	19.60	22.8
(Yellow)		(47.17)	(4.89)	(8.09)	(19.51)	
Yb(HL)$_2$(NO$_3$)$_3$	242	46.92	4.96	8.00	19.77	24.6
(Yellow)		(46.95)	(4.87)	(8.05)	(19.89)	
Lu(HL)$_2$(NO$_3$)$_3$	258	46.77	4.98	7.89	20.22	27.3
(Yellow)		(46.84)	(4.86)	(8.04)	(20.08)	

IR spectral date of the compounds and their relative assignments are shown in Table-2. A broad weak band in the infrared spectrum of the ligand in ~3460 cm^{-1} is assigned to the phenolic hydroxyl (Ph-OH) vibration. It appears at lower frequency in 3430-3420 cm^{-1} corresponding complexes, showing coordination of oxygen atom of phenolic hydroxy with the central Ln(III) ion. The shift of the C-O stretching vibration of the phenolic part of salicylaldehyde from 1280 cm^{-1} to 1235-1224 cm^{-1} also supports the coordination of oxygen atom. A strong band occurring at 1630 cm^{-1} due to (C=N)

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) FOR LIGAND AND ITS Ln(III) COMPLEXES

Compound	ν(C=N)	ν(OH)	ν(C–O)	NO_3^-					ν(Ln–O)
				ν_1	ν_4	ν_2	ν_3	ν_5	
HL	1630 s	3460 w	1280 s	–	–	–	–	–	–
$La(HL)_2(NO_3)_3$	1649 s	3425 w	1235 m	1507 s	1300 s	1037 m	817 m	729 m	491 w
$Ce(HL)_2(NO_3)_3$	1650 s	3430 w	1234 m	1506 s	1297 s	1028 m	815 m	731 m	493 w
$Pr(HL)_2(NO_3)_3$	1649 s	3430 w	1235 m	1501 s	1299 s	1030 m	816 m	729 m	489 w
$Nd(HL)_2(NO_3)_3$	1649 s	3426 w	1234 m	1506 s	1299 s	1037 m	817 m	730 m	491 w
$Sm(HL)_2(NO_3)_3$	1649 s	3437 w	1234 m	1507 s	1297 s	1028 m	815 m	731 m	493 w
$Eu(HL)_2(NO_3)_3$	1645 s	3424 w	1236 m	1501 s	1299 s	1035 m	817 m	729 m	493 w
$Gd(HL)_2(NO_3)_3$	1650 s	3422 w	1235 m	1505 s	1300 s	1036 m	817 m	729 m	490 w
$Tb(HL)_2(NO_3)_3$	1650 s	3422 w	1235 m	1506 s	1299 s	1034 m	815 m	730 m	493 w
$Dy(HL)_2(NO_3)_3$	1650 s	3422 w	1234 m	1506 s	1298 s	1030 m	815 m	729 m	490 w
$Ho(HL)_2(NO_3)_3$	1649 s	3430 w	1235 m	1505 s	1297 s	1029 m	817 m	731 m	493 w
$Er(HL)_2(NO_3)_3$	1650 s	3422 w	1235 m	1506 s	1298 s	1030 m	815 m	729 m	493 w
$Tm(HL)_2(NO_3)_3$	1650 s	3420 w	1234 m	1503 s	1300 s	1029 m	816 m	730 m	492 w
$Yb(HL)_2(NO_3)_3$	1649 s	3422 w	1234 m	1502 s	1299 s	1030 m	815 m	729 m	493 w
$Lu(HL)_2(NO_3)_3$	1650 s	3430 w	1235 m	1506 s	1297 s	1029 m	815 m	731 m	490 w

stretching is found shifted to highter frequency in 1650-1645 cm^{-1} region for its complexes, but the nitrogen atom of azomethine is regarded as non-coordinated to Ln(III) ion[13,14]. The infrared absorption bands of covalent nitrate with C_{2v} symmetry in the complexes are observed at different frequencies (Table-2). The five absorption bands appear near1500 cm^{-1} (ν_1), 1300 cm^{-1} (ν_4), 1030 cm^{-1} (ν_2), 815 cm^{-1} (ν_3), 730 cm^{-1} (ν_5), respectively. The difference between ν_1 and ν_4 is about 200 cm^{-1}, which is associated with typical of bidentate nitrate coordination[15,16]. A new band at ~490 cm^{-1} was present due to (Ln-O) stretching vibration[17], confirming the metal-ligand bond. Thus, the coordination bond were formed between Ln(III) ion and oxygen atoms of phenol-hydroxy and coordinated nitrates.

Table-3 shows the data of ^{1}H NMR for Schiff base ligand and its ytterbium complex $Yb(HL)_2(NO_3)_3$. The ^{1}H NMR spectra of the free ligand and complex are very similar. It indicated that the proton of phenolic hydroxyl of Schiff base ligand in complex was not deprotonated.

TABLE-3

^{1}H NMR DATA OF LIGAND AND $Yb((HL)_2NO_3)_3$

Compound	Chemical shift (δ ppm)			
HL	14.41 (s, 1H, Ph-OH)	8.55 (s, 1H, -CH=N-)	6.82~7.47 (m, 4H, Benzene ring)	1.65~2.51 (m, 15H, adamantane ring)
$Yb(NO_3)_3(HL)_2$	14.44 (s, 1H, Ph-OH)	8.56 (s, 1H, -CH=N-)	6.87-7.45 (m, , 4H, Benzene ring)	1.77~2.57 (m, 15H, adamantane ring)

It is suggested that the complex consists of one central metal ion Ln(III), two Schiff base ligands N-salicylidene-1-aminoadamantane and three bidentate coordinated nitrates. Their coordination number are eight. The proposed structures are showed as Fig. 1.

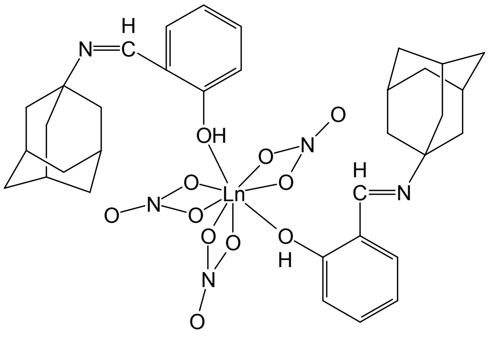

Fig. 1. Proposed structure of Ln(III) complex

The TG-DTG curves of the complex $Yb(HL)_2(NO_3)_3$ are shown in Fig. 2. The TG degradation of the compound reveals two decomposition stages predicted by the DTG curve. The first stage from 247.0 to 347.1 ºC with a mass loss of 24.90 % corresponds to the loss of 2 mol salicylidene (theoretical loss 24.37 %), the second one in the 347.1- 649.6 ºC range with a mass loss of 50.34 % corresponds to the loss of 3 mol NO_3^- and 2 mol 1-aminoadamantaneamine (theoretical value 50.81 %). The complex was finally completely degraded into Yb_2O_3. The thermal decomposition of other complexes are similar as $Yb(HL)_2(NO_3)_3$.

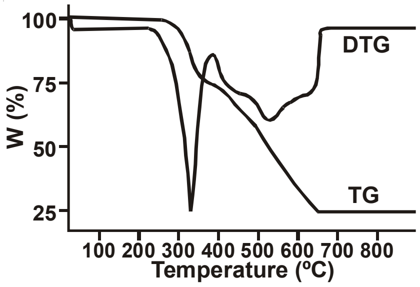

Fig. 2 TG-DTG Curve of $Yb(HL)_2NO_3)_3$

Antibacterial activity: The tests of antibacterical activity adopts a method by filter paper[18] using DMF as the solvent. Table-4 shows the zone

TABLE-4
ANTIBACTERIAL SCREENING RESULTS
(DIAMETER OF INHIBITION ZONE/mm)

Bacterial compound	*E. coli*		*B. subtilis*	
	10^{-1} mol dm^{-3}	10^{-2} mol dm^{-3}	10^{-1} mol dm^{-3}	10^{-2} mol dm^{-3}
HL	14.4 ± 1.08	10.0 ± 0.04	14.7 ± 0.61	10.0 ± 0.00
$La(NO_3)_3(HL)_2$	21.0 ± 0.90**	10.1 ± 0.10	16.7 ± 1.89	10.4 ± 0.69
$Ce(NO_3)_3(HL)_2$	18.4 ± 1.21*	10.0 ± 0.00	17.3 ± 0.58*	10.5 ± 0.87
$Pr(NO_3)_3(HL)_2$	21.3 ± 1.53**	10.0 ± 0.00	17.3 ± 1.04*	10.0 ± 0.00
$Nd(NO_3)_3(HL)_2$	22.9 ± 1.21**	10.0 ± 0.00	20.2 ± 1.26*	10.7 ± 0.58
$Sm(NO_3)_3(HL)_2$	19.6 ± 0.90**	10.2 ± 0.29	21.2 ± 0.29**	10.0 ± 0.00
$Eu(NO_3)_3(HL)_2$	24.2 ± 0.89**	10.2 ± 0.29	20.2 ± 1.26**	10.0 ± 0.00
$Gd(NO_3)_3(HL)_2$	19.4 ± 1.18**	10.0 ± 0.00	19.7 ± 1.15**	10.0 ± 0.00
$Tb(NO_3)_3(HL)_2$	20.3 ± 0.61**	10.0 ± 0.00	20.3 ± 1.04	10.0 ± 0.00
$Dy(NO_3)_3(HL)_2$	25.5 ± 1.80**	10.0 ± 0.00	19.8 ± 2.47	11.5 ± 0.71
$Ho(NO_3)_3(HL)_2$	21.7 ± 2.02**	10.2 ± 0.26	20.8 ± 1.06	10.0 ± 0.00
$Er(NO_3)_3(HL)_2$	23.1 ± 0.14**	11.4 ± 1.48	18.3 ± 0.76	10.0 ± 0.00
$Tm(NO_3)_3(HL)_2$	20.7 ± 2.48**	10.5 ± 0.35	17.7 ± 0.76*	11.0 ± 1.00
$Yb(NO_3)_3(HL)_2$	19.2 ± 0.70**	10.0 ± 0.00	20.0 ± 1.50**	13.0 ± 0.50**
$Lu(NO_3)_3(HL)_2$	19.3 ± 2.75**	10.8 ± 0.29	19.4 ± 0.57*	10.0 ± 0.00

The data in the table are average values of three experiments, the diameter of filter paper is 10 mm ; *The difference is significant; **The difference is very significant.

of inhibition for the two concentrations (1.0×10^{-1} mol dm^{-3}, 1.0×10^{-2} mol dm^{-3}) of the test solutions on two bacteria, *Escherichia coli* and *Bacillus subtilis*. From the data it can be seen that the Schiff base ligand and its complexes are almost the same for both bacteria at 1.0×10^{-1} mol dm^{-3} and have shown that metal complexes are potent bactericidal than their precursor Schiff base, hence, complexation increases the antibacterical activity. The antibacterical activity is not changed Schiff base ligand and its complexes for both bacteria at 1.0×10^{-2} mol dm^{-3}. The tests indicates that the antibacterical activity lies on its concentration of the compound.

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(*Received*: 10 May 2007; *Accepted*: 7 January 2008) AJC-6178