

# Metal-promoted synthesis and characterization of Pr(III), Nd(III) and Eu(III) Schiff base complexes derived from salicylaldehyde and 4,9-dioxa-1,12-diaminododecane

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## Abstract

*The one-step metal template reaction of salicylaldehyde with 4,9-dioxa-1,12-diaminododecane in the presence of praseodymium(III), neodymium(III) or europium(III) nitrates gives complexes containing N,N'-bis(salicylidene)-1,12-diamino-4,9-dioxadodecane ligand with N<sub>2</sub>O<sub>4</sub> set of donor atoms as a result of the [2+1] Schiff base condensation. The template reaction products were characterized by spectroscopic (IR, UV-Vis, ESI-MS) and analytical (elemental and thermogravimetric analysis) methods. All data indicate 1:1 ligand to metal stoichiometry.*

## 1. Introduction

The design and synthesis of Schiff base lanthanide complexes is currently attracting considerable attention since that can be used as supramolecular devices, contrast agents in magnetic resonance imaging, potential radiopharmaceuticals, as possible bioinorganic models for the active sites in metalloproteins and as synthetic nucleases.[1] A few years ago, the catalytic activity of complexes containing lanthanide ions for hydrolysis of nucleic acids was discovered.[2] Lanthanide Schiff base complexes not covalently bound or bound to a 5' end of DNA can be used successfully for the cleavage of RNA. These properties are of interest for gene therapy, e.g. in Machado-Joseph disease. Machado-Joseph disease (MJD) is an autosomal dominant neurodegenerative disorder that is characterized clinically by cerebellar ataxia, pyramidal and extrapyramidal signs, peripheral neuropathy and ophthalmoplegia.[3] In view of possible future applications and continuing our investigation on the lanthanide Schiff base

complexes derived from dicarbonyl compounds and primary diamines, including biogenic amines and their analogues [1,4-6] we wish to report the synthesis and characterization of Schiff base lanthanide complexes derived from salicylaldehyde and 4,9-dioxa-1,12-diaminododecane.

## 2. Experimental

The hexahydrated praseodymium(III), neodymium(III) and europium(III) nitrates were prepared by dissolving the appropriate oxide (99,99% Fluka) in excess of nitric acid. The solution were evaporated and precipitate recrystallized from methanol. Salicylaldehyde (99%) (Aldrich Chemical Company) and 4,9-dioxa-1,12-diaminododecane (97%) (Aldrich Chemical Company) were used as received.

### 2.1 Preparation of the complexes (general procedure)

All the complexes were prepared under similar conditions. To a solution of salicylaldehyde (0,02 mmol) in methanol (10 ml), an appropriate metal nitrate salt (Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) (0,01 mmol) in methanol (10 ml) and 4,9-dioxa-1,12-diaminododecane (0,01 mmol) in methanol (10 ml) were added dropwise with stirring. The reaction was carried out for 24h in ambient temperature. The solution volume was then reduced to 8-10 ml by rotatory evaporation and a yellow precipitate formed on addition

of small amount of diethyl ether (~3 ml). This was filtered off, washed with ether and dried on air. Yields: 39-58%.

## 2.2 Measurements

IR spectra were recorded using KBr pellets in the range 4000-400  $\text{cm}^{-1}$  on Perkin-Elmer 580 spectrophotometer. Electronic absorption spectra were measured on a JASCO V-550 spectrophotometer in methanol. Low resolution mass spectra were recorded on a Jeol-JMS D100 mass spectrometer operating on electron impact (EI, 70eV, 300 $\mu$ A, ion source temperature 200°C) conditions. Thermogravimetric measurements were performed using Shimadzu TGA-50 derivatograph (up to 1000°C, heating rate 10°C  $\text{min}^{-1}$ ,  $\text{N}_2$  atmosphere). Microanalyses were obtained using a Perkin-Elmer 2400 CHN microanalyzer.

## 3. Results and discussion

The template reactions of salicylaldehyde with 4,9-dioxa-1,12-diaminododecane in the presence of praseodymium(III), neodymium(III) or europium(III) nitrates produce the complexes containing *N,N'*-bis(salicylidene)-1,12-diamino-4,9-dioxadodecane ligand ( $\text{H}_2\text{L}$ ) (Figure 1) with an  $\text{N}_2\text{O}_4$  set of donor atoms as result of [2+1] Schiff base condensation. These complexes are formulated as  $[\text{Pr}(\text{HL})(\text{NO}_3)(\text{H}_2\text{O})]\text{NO}_3$  (**1**),  $\text{Nd}(\text{HL})(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**2**), and  $[\text{Eu}(\text{HL})(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**3**) and

characterized on the basis of elemental analysis (Table 1), IR, UV-Vis (Table 2) spectroscopy, thermogravimetric analysis (Table 3) and ESI (Table 4) mass spectral data. The complexes are yellow air-stable solids, soluble in methanol, water and insoluble in chloroform and acetonitrile.

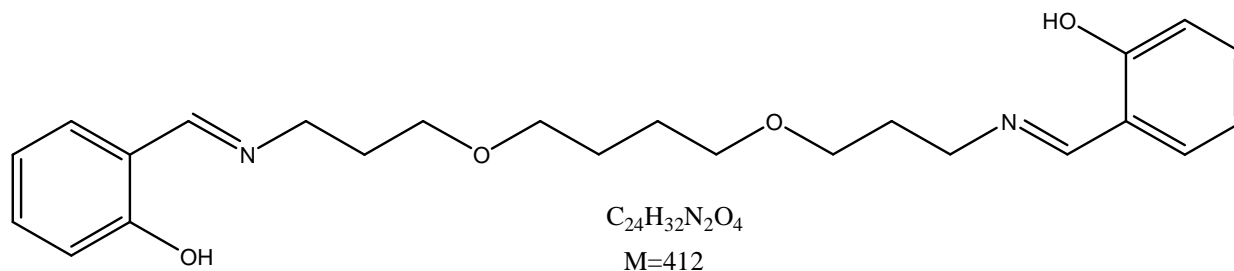
**Table 1**

Analytical data

Complex	Found (calc.) %		
	C	H	N
<b>1</b>	41.04 (41.51)	4.60 (4.79)	8.45 (8.07)
<b>2</b>	38.49 (41.31)	5.03 (4.77)	8.20 (8.03)
<b>3</b>	38.64 (40.86)	4.94 (4.71)	7.95 (7.94)

### 3.1 Infrared spectra

All the complexes give very similar infrared spectra indicating the presence of the same ligand throughout the series. The IR spectra (Table 2) of the complexes show a strong band at 1653  $\text{cm}^{-1}$  attributable to C=N stretching modes confirming the Schiff base condensation. The complexes exhibit the broad diffuse band centered at 3415  $\text{cm}^{-1}$  for **1**, 3404  $\text{cm}^{-1}$  for **2** and 3404  $\text{cm}^{-1}$  for **3**, due to the stretching and bending modes of water molecule. In addition, weak band in Pr(III) complex **1** is detectable at 883  $\text{cm}^{-1}$  region which may be assigned to rocking or wagging modes of water molecule interacting with the metal ion. The nitrate vibrations in the complexes are seen as split bands at 1767-1732  $\text{cm}^{-1}$ , 1767-1733  $\text{cm}^{-1}$ , and 1768-1730  $\text{cm}^{-1}$  region as well as at 1482-1285  $\text{cm}^{-1}$ , 1481-1288  $\text{cm}^{-1}$  and 1482-1288  $\text{cm}^{-1}$  region for **1**, **2** and **3** complexes,



**Fig. 1.** *N,N'*-bis(salicylidene)-1,12-diamino-4,9-dioxadodecane ( $\text{H}_2\text{L}$ )

**Table 2**  
Infrared ( $\text{cm}^{-1}$ ) and UV-Vis (nm) spectral data for the complexes

Complex	O-H	C-H	C=N	C=C	C-O-C	M-O	M-N	$\text{NO}_3^-$	$\lambda$
1	3415	2942, 2866	1653	1608	1111	540	489	1767, 1732, 1482, 1384, 1285, 817	221, 253, 315, 387
2	3404	2942, 2866	1653	1608	1111	541	490	1767, 1733, 1481, 1384, 1288, 817	210, 254, 315, 391
3	3411	2942, 2866	1653	1608	1112	541	489	1768, 1730, 1482, 1384, 1288, 817	214, 253, 315, 398

respectively. The separation of these modes has been used as a criterion to distinguish between mono- and bidentate chelating nitrates. The magnitude of the separation at range  $1280\text{-}1490\text{ cm}^{-1}$  which is equal to  $197\text{ cm}^{-1}$  for **1**,  $193\text{ cm}^{-1}$  for **2** and  $194\text{ cm}^{-1}$  for **3** (Figure 2), indicates the bidentate interaction of the nitrate anions with the lanthanide ions.[7-9]

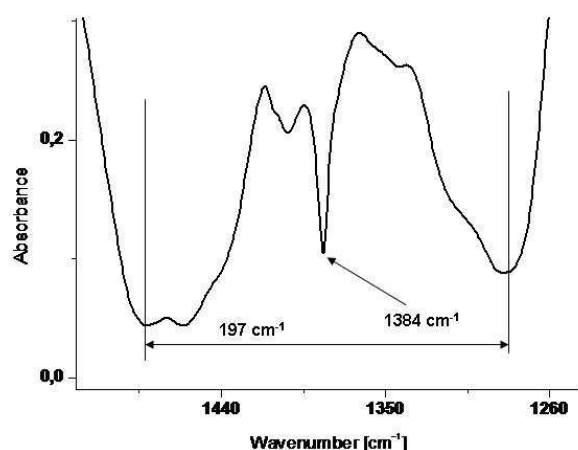


Fig. 2. Separation of IR nitrate modes for complex **1** at range *ca*  $1280\text{-}1490\text{ cm}^{-1}$

This is confirmed by the magnitude of the separation at region *ca.*  $1730\text{-}1780\text{ cm}^{-1}$ :  $35\text{ cm}^{-1}$  for **1**,  $35\text{ cm}^{-1}$  for **2** and  $38\text{ cm}^{-1}$  for **3**, which is typical of bidentate chelating behavior of the nitrate groups (Figure 3). The occurrence of a strong absorption at  $1384\text{ cm}^{-1}$  for all the complexes indicates that the uncoordinated nitrate anions are also present in the complexes.[10]

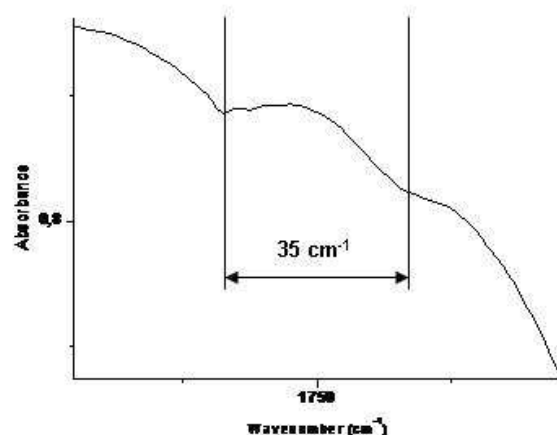


Fig. 3. Separation of IR nitrate modes for complex **1** at range *ca*  $1730\text{-}1780\text{ cm}^{-1}$

The bands at  $540\text{ cm}^{-1}$  and  $488\text{ cm}^{-1}$  for **1**,  $541\text{ cm}^{-1}$  and  $490\text{ cm}^{-1}$  for **2** and  $541\text{ cm}^{-1}$  and  $490\text{ cm}^{-1}$  for **3**, attributable to the Ln-O and Ln-N interaction, respectively, give the evidence for metal-ligand coordination.

### 3.2. Thermal analysis

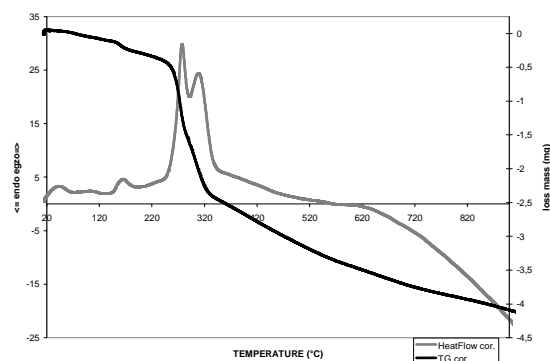
The thermal stability of complexes **1**, **2** and **3** was examined by thermogravimetry in  $\text{N}_2$  atmosphere in the temperature range  $20\text{-}1000^\circ\text{C}$ . As shown in Table 3, Figure 3 and 4, the thermal decomposition process of complexes can be divided into three stages. There is difference between the thermogravimetric diagram of Pr(III) (**1**) complex and the thermogravimetric diagrams of Nd(III) (**2**) and Eu(III) (**3**) complexes which are similar one to another. In thermogravimetric diagram of Pr(III) complex (Figure 4) the dehydration step is observed at  $122\text{-}197^\circ\text{C}$  corresponding to the loss of one water molecule and supporting

the presence of water bound to the metal ion.

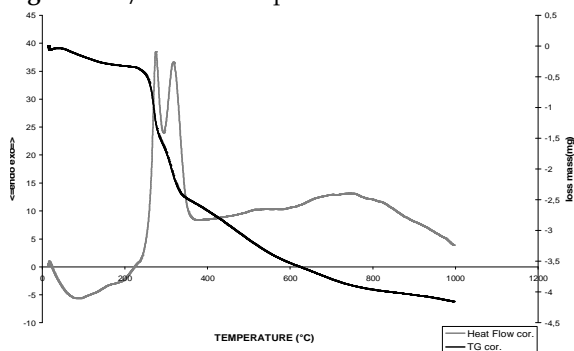
**Table 3**  
Thermogravimetric data

Complex	Temp. range (TG/°C)		Mass loss (%)	
			Found	Calc.
1	122-197	H <sub>2</sub> O	2.59	2.58
	246-281	NO <sub>3</sub>	8.93	9.44
	286-330	NO <sub>3</sub>	8.93	9.62
2	38-124	H <sub>2</sub> O	2.51	2.51
	250-278	NO <sub>3</sub>	8.88	9.54
	288-336	NO <sub>3</sub>	8.88	9.29
3	36-141	H <sub>2</sub> O	2.55	2.39
	242-267	NO <sub>3</sub>	8.79	9.24
	274-319	NO <sub>3</sub>	8.79	8.80

TGA of Nd(III) and Eu(III) complexes shows a first step at 36-140°C associated with the loss of one molecule of lattice water (Figure 5).[11, 12]



**Fig. 4.** TGA/DTA of complex 1



**Fig. 5.** TGA/DTA of complex 2

Additionally, in the temperature range of *ca* 286-336°C the further loss of mass is observed. It corresponds to the removal of second nitrate ion coordinating to the metal ions. These results are in good accordance with the composition of the complexes.

### 3.2. Mass spectroscopy

Mass spectrometry was used to investigate molecular species in methanol solution. The ESI-MS spectra give the successive degradation of target compound with the series of peaks corresponding to the various fragments (Table 4). In the mass spectrum of praseodymium(III) and neodymium(III) complex fragmentation pattern is similar. The [LLn(NO<sub>3</sub>)<sub>2</sub>]<sup>-</sup> fragment (H<sub>2</sub>L - ligand in neutral form) was found in mass spectrum at appropriate value of *m/z* 675 for **1** and *m/z* 678 for **2**. In the mass spectrum of europium(III) complex **3**, [LEu]<sup>+</sup> fragment (H<sub>2</sub>L - ligand in neutral form) was found at position *m/z* 562. The peak at *m/z* 413 found in the mass spectra of all the complexes is related to the free protonated ligand.

**Table 4**  
ESI-MS spectral data

Complex	ESI-MS <i>m/z</i>	Assignment
1	389 (100%)	[Pr(NO <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>
	413 (100%)	[(C <sub>24</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> )+H] <sup>+</sup>
	675 (5.2%)	[(C <sub>24</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> )Pr(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>
2	392 (100%)	[Nd(NO <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>
	413 (100%)	[(C <sub>24</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> )+H] <sup>+</sup>
	678 (4.0%)	[(C <sub>24</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> )Nd(NO <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>
3	400 (100%)	[Eu(NO <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>
	413 (45%)	[(C <sub>24</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> )+H] <sup>+</sup>
	562 (4.0%)	[(C <sub>24</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> )Eu] <sup>+</sup>

On the basis of available analytical and spectral data it seems reasonable to propose the coordination mode in the lanthanides complexes.

In praseodymium(III) complex (**1**) the coordination sphere consists of mono-deprotonated ionic form of ligand, one bidentate nitrate ion and one molecule of water. The second nitrate group is uncoordinated (Figure 6).

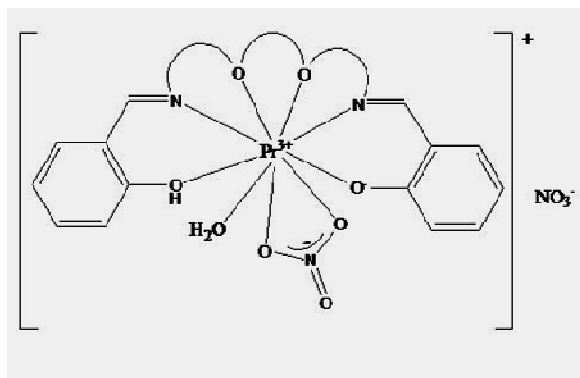


Fig. 6. The proposed coordination mode in the complex 1

In the coordination sphere of neodymium(III) (2) and europium(III) (3) complexes mono-deprotonated ionic form of ligand and one bidentate nitrate ion are likely to be present. The second nitrate ion and one molecule of water do not participate in the coordination (Figure 7).

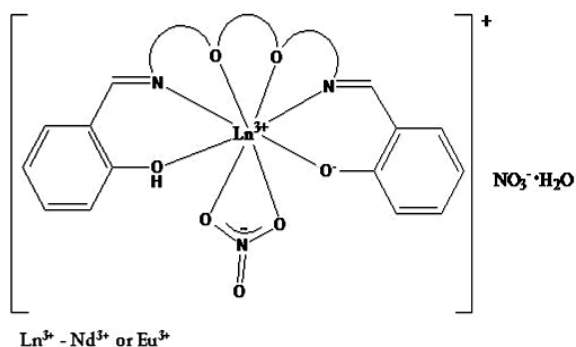


Fig. 7. The proposed coordination mode in the complexes 2 and 3

#### 4. Conclusions

The praseodymium(III), neodymium(III) and europium(III) complexes containing a hexadentate *N,N'*-bis(salicylidene)-1,12-diamino-4,9-dioxado-decane ligand with  $N_2O_4$  set of donor atoms were obtained in the one-step metal-promoted [2+1] Schiff base condensation reaction of salicylaldehyde with 4,9-dioxa-1,12-diaminododecane. All six potential donor atoms of this ligand may be regarded as coordinated to the metal ion. Thus, the tentative coordination number for praseodymium(III) complex is assumed to be nine (six donor atoms from the ligand, one oxygen atom from water molecule and

two oxygen atoms from one bidentate nitrate ion). In neodymium(III) and europium(III) complexes the coordination number is eight (six donor atoms from ligand and two oxygen atoms from one bidentate nitrate ion). Efforts to prepare free ligand in the reaction of salicylaldehyde with 4,9-dioxa-1,12-diaminododecane in absence of metal ion were unsuccessful and resulted in the mixture of [2+1] and [1+1] condensation products.

Having in mind the suggestion that lanthanide Schiff base complexes are the reactive species for the hydrolytic cleavage or transesterification of DNA and the RNA phosphate diester backbone, we are now investigating the cleavage of RNA by these complexes in the covalently and not covalently DNA binding approach.

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