



# Dinuclear lanthanide(III) complexes with large-bite Schiff bases derived from 2,6-diformyl-4-chlorophenol and hydrazides: Synthesis, structural characterization and spectroscopic studies

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## ABSTRACT

Two Schiff bases ( $H_3L^1$  and  $H_5L^2$ ), derived from 2,6-diformyl-4-chlorophenol and hydrazides, and their complexes with some lanthanides (Y, La, Nd, Sm, Dy and Er) have been synthesized. These compounds have been characterized by means of elemental analysis, UV–Vis spectroscopy, IR spectroscopy,  $^1H$  and  $^{13}C$  NMR (for the organic ligands), molar conductance and room temperature magnetic measurements. Single crystal X-ray analysis of the two complexes  $[La_2(H_2L^1)_3(C_2H_5OH)_2] \cdot (Cl) \cdot (NO_3)_2 \cdot ((CH_3)_2CO)_2 \cdot (H_2O)_2$  (**1**) and  $[Er_2(H_4L^2)_3] \cdot (SCN)_3 \cdot (H_2O)$  (**8**) has revealed the nature of the structures; the lanthanide(III) ions are intramolecularly bridged by three phenolic oxygen atoms, forming a dinuclear complex. The lanthanum atom is ten-coordinated, while the erbium atom is nine-coordinated. The coordination polyhedron of the erbium complex is best described as a tricapped trigonal prism.

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## 1. Introduction

Studies involving the chelation and coordination of ligands derived from hydrazone to lanthanide centers containing flexible multidentate ligands have been an ongoing area of active research. In recent years, much attention has been given to the syntheses of acyclic ligands that can give rise to mononuclear or dinuclear lanthanide complexes with interactions between the metal centers. It is known that a considerable amount of work has been done on complexes with hydrazones because of their ability to chelate with lanthanide ions [1–10]. Hydrazone lanthanide complexes can be used as electroluminescent devices [11,12], structural probes [13] and in immunobiological assays [14]. As well as their paramagnetic and luminescent properties [15–17], the bioactivities of lanthanides, such as antimicrobial or antitumor, have been explored over the past decades [18–21]. In addition, some hydrazone lanthanide chelates have represented good antioxidant activities [19,20]. In the course of our studies on the chemistry of lanthanide compounds, we have prepared and characterized a number of chelates containing hydrazones as ligands. Herein we report a series of new lanthanide(III) complexes derived from phenol-based macro-acyclic ligands which each have two similar metal-binding sites sharing a phenolic oxygen atom. Due to the flexibility of the arms, the cavity size could be adjusted to match

the size of the metal ions, producing complexes of the type  $[Ln_2(H_2L^1)_3(C_2H_5OH)_m] \cdot (Cl) \cdot (NO_3)_2 \cdot ((CH_3)_2CO)_n \cdot (H_2O)_p$  ( $m = n = p = 2$  for (**1**) and  $m = n = 0$  and  $p = 1$  or  $2$  for the other complexes) and  $[Ln(H_4L^2)_2 \cdot (H_2O)_z] \cdot (SCN)_3 \cdot (H_2O)_t$  ( $t = 2$  and  $z = 1$  for (**6**);  $t = 0$  and  $z = 1$  or  $3$  for the other complexes). The crystal structures of the lanthanum and erbium complexes have been elucidated.

## 2. Experimental

### 2.1. Materials and procedures

2,6-Diformyl-4-chlorophenol was synthesized according to the literature [21] and recrystallized from *n*-hexane/chloroform; benzoyl hydrazide, 2-hydroxybenzoyl hydrazide and the lanthanide nitrate salts were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. The analyses for carbon, hydrogen and nitrogen were carried out using a LECO CHNS-932 instrument. The IR spectra were recorded as KBr discs on a Bruker IFS-66 V spectrophotometer ( $4000\text{--}400\text{ cm}^{-1}$ ). The molar conductances of  $10^{-3}$  M solutions of the metal complexes in DMF were measured at  $25^\circ\text{C}$  using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples {calibrant  $Hg[Co(SCN)_4]$ } were measured using a Johnson Matthey scientific magnetic susceptibility balance. Melting points were recorded on a Büchi apparatus and are uncorrected. The  $^1H$  and  $^{13}C$  NMR spectra of the

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**Table 1**  
Crystallographic data and refinement parameters for **1** and **8**.

Formula	C <sub>76</sub> H <sub>76</sub> La <sub>2</sub> Cl <sub>4</sub> N <sub>14</sub> O <sub>21</sub> ( <b>1</b> )	C <sub>69</sub> H <sub>50</sub> Er <sub>2</sub> Cl <sub>3</sub> N <sub>15</sub> O <sub>16</sub> S <sub>3</sub> ( <b>8</b> )
Molecular weight	1941.12	1882.29
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 <sub>1</sub> /n
T (K)	173(2)	173(2)
a (Å)	21.1020 (6)	13.14300 (10)
b (Å)	18.5070 (7)	23.0550 (2)
c (Å)	23.1880 (9)	25.5410 (3)
α (°)	90	90
β (°)	114.4520 (10)	96.367 (3)
γ (°)	90	90
V (Å <sup>3</sup> )	8243.5 (5)	7691.49 (13)
Z	4	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.564	1.625
μ (Mo Kα) (mm <sup>-1</sup> )	1.23	2.43
λ (Å)	0.71073	0.71073
F(000)	892	3728
R	0.054	0.053
wR	0.126	0.121
Parameters refined	552	966
No. of measured reflections	13469	22521
No. of independent reflections	8574	22521
Goodness-of-fit	0.91	0.87
Maximum residual peak (e Å <sup>-3</sup> )	1.17	2.54
Minimum residual hole(e Å <sup>-3</sup> )	-0.91	-1.57

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR = [\sum w^2(|F_o|^2 - |F_c|^2)^2 / \sum w^2(|F_o|^2)]^{1/2}.$$

Schiff bases were recorded in CDCl<sub>3</sub> on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The L-SIMS mass spectra were recorded using a Micromass Auto-spec spectrometer using 3-nitrobenzyl alcohol as the matrix.

## 2.2. X-ray crystal structure determination

Slow evaporation of an ethanol/acetone solution gave X-ray quality crystals of the two compounds [La<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](Cl)(NO<sub>3</sub>)<sub>2</sub>·((CH<sub>3</sub>)<sub>2</sub>CO)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> (**1**) and [Er<sub>2</sub>(H<sub>4</sub>L<sup>2</sup>)<sub>3</sub>](SCN)<sub>3</sub>·(H<sub>2</sub>O) (**8**). Details of the X-ray crystal structure solution and refinement are given in Table 1. Measurements were made on a Bruker SMART CCD Area Detector. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [22]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters for all non hydrogen atoms [23]. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using ORTEP-3 [24].

## 2.3. Preparation of the ligands

The ligands were obtained from the condensation of 2,6-diformyl-4-chlorophenol and the corresponding hydrazide in a 1:2 M ratio, in an ethanol medium; two drops of glacial acetic acid was used as a catalyst. The yellow precipitates obtained were filtered, washed with ethanol and dried in vacuum over P<sub>4</sub>O<sub>10</sub>. The yield of the Schiff bases was quantitative.

**H<sub>3</sub>L<sup>1</sup>**: Yield 96%. M.P. 221–225 °C. *Anal. Calc.* for C<sub>22</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>5</sub>: C, 62.77; H, 4.08; N, 13.33; Cl, 8.46. Found: C, 62.79; H, 4.07; N, 13.31; Cl, 8.42%. MS (FAB), *m/z*: 421. <sup>1</sup>H NMR dms<sub>o</sub>-d<sub>6</sub> δ (ppm): 7.47 (m, 6H, H<sub>Ar</sub>), 7.60 (m, 1H, -NH), 7.73 (m, 6H, H<sub>Ar</sub>), 8.60 (s, 2H, -N=CH), 12.20 (s (broad), 1H, -OH), 12.70 (s (broad), 1H, -OH). <sup>13</sup>C NMR dms<sub>o</sub>-d<sub>6</sub> δ (ppm): 196.52 (-C=O), 163.28 (-C=N), 155.45 (HO-C<sub>Ar</sub>), 144.87, 132.78, 132.19, 128.65, 127.84, 123.56, 122.08 (C<sub>Ar</sub>).

**H<sub>5</sub>L<sup>2</sup>**: Yield 83%. M.P. >230 °C. *Anal. Calc.* for C<sub>22</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>5</sub>: C, 58.36; H, 3.77; N, 12.34; Cl, 7.85. Found: C, 58.35; H, 3.78; N, 12.37; Cl, 7.83%. MS (FAB), *m/z*: 453. <sup>1</sup>H NMR dms<sub>o</sub>-d<sub>6</sub> δ (ppm): 7.47 (m, 6H, H<sub>Ar</sub>), 7.60 (m, 2H, -NH), 7.73 (m, 4H, H<sub>Ar</sub>), 8.60 (s, 2H, -N=CH), 12.20 (s (broad), 2H, -OH), 12.70 (s (broad), 1H, -OH). <sup>13</sup>C NMR dms<sub>o</sub>-d<sub>6</sub> δ (ppm): 196.52 (-C=O), 163.28 (-C=N), 155.45 (HO-C<sub>Ar</sub>), 144.87, 132.20, 132.78, 128.65, 127.84, 123.55, 122.08 (C<sub>Ar</sub>).

## 2.4. Preparation of the complexes

### 2.4.1. Complexes of H<sub>3</sub>L<sup>1</sup>

Lanthanide (III) nitrate heptahydrate (1 mmol) in methanol (20 mL) was added to a suspension of 5-chloro-1,3-diformyl-2-hydroxybenzene-bis(benzoylhydrazide) (1.5 mmol) in methanol (80 mL). The mixture was refluxed for 1 h. LiCl (0.1272 g, 3 mmol) was added. The resulting yellow solution was filtered-off and the filtrate was kept at 298 K. Yellow crystals began to appear after three days and were collected by filtration.

[La<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](Cl)(NO<sub>3</sub>)<sub>2</sub>·((CH<sub>3</sub>)<sub>2</sub>CO)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> (**1**). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone/ethanol solution of the complex. Yield 55%. *Anal. calc.* for [C<sub>76</sub>H<sub>76</sub>Cl<sub>4</sub>N<sub>14</sub>O<sub>21</sub>La<sub>2</sub>]: C, 47.03; H, 3.95; N, 10.10. Found: C, 46.99; H, 3.93; N, 10.12%. Diamagnetic. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 205.

[Nd<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>3</sub>](Cl)(NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> (**2**). Yield 65%. *Anal. calc.* for [C<sub>66</sub>H<sub>52</sub>Cl<sub>4</sub>Nd<sub>2</sub>N<sub>14</sub>O<sub>17</sub>]: C, 45.47; H, 3.01; N, 11.25. Found: C, 45.58; H, 3.09; N, 11.19%. μ<sub>eff</sub> (μ<sub>B</sub>): 7.18. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 222.

[Sm<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>3</sub>](Cl)(NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O) (**3**). Yield 71%. *Anal. calc.* for [C<sub>66</sub>H<sub>50</sub>Cl<sub>4</sub>Sm<sub>2</sub>N<sub>14</sub>O<sub>16</sub>]: C, 45.62; H, 2.90; N, 11.28. Found: C, 45.69; H, 3.11; N, 11.37%. μ<sub>eff</sub> (μ<sub>B</sub>): 3.32. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 200.

[Dy<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)<sub>3</sub>](Cl)(NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O) (**4**). Yield 59%. *Anal. calc.* for [C<sub>66</sub>H<sub>50</sub>Cl<sub>4</sub>Dy<sub>2</sub>N<sub>14</sub>O<sub>16</sub>]: C, 44.99; H, 2.86; N, 11.13. Found: C, 45.06; H, 2.79; N, 11.23%. μ<sub>eff</sub> (μ<sub>B</sub>): 18.08. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 220.

### 2.4.2. Complexes of H<sub>5</sub>L<sup>2</sup>

To a solution of lanthanide (III) nitrate heptahydrate (1 mmol) in methanol (10 mL) was added a solution of KSCN (3 mmol) in 10 mL of methanol. The mixture was stirred at room temperature for 1 h. The white precipitate that formed was discarded by filtration. The resulting solution was added to a suspension of 5-chloro-1,3-diformyl-2-hydroxybenzene-bis(2'-hydroxybenzoyl hydrazide) (1.5 mmol) in methanol (80 mL) and then the mixture was refluxed for 1 h. The resulting yellow solution was filtered-off and the filtrate was kept at 298 K. Yellow crystals began to appear after 3 days and were collected by filtration.

[Y<sub>2</sub>(H<sub>4</sub>L<sup>2</sup>)<sub>3</sub>](SCN)<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub> (**5**). Yield 62%. *Anal. calc.* for [C<sub>69</sub>H<sub>54</sub>Cl<sub>3</sub>N<sub>15</sub>O<sub>18</sub>S<sub>3</sub>Y<sub>2</sub>]: C, 47.04; H, 3.09; N, 11.93. Found: C, 46.85; H, 3.15; N, 11.83%. Diamagnetic. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 204.

[La<sub>2</sub>(H<sub>4</sub>L<sup>2</sup>)<sub>3</sub>](SCN)<sub>3</sub>·(H<sub>2</sub>O) (**6**). Yield 65%. *Anal. calc.* for [C<sub>69</sub>H<sub>54</sub>Cl<sub>3</sub>N<sub>15</sub>O<sub>18</sub>S<sub>3</sub>La<sub>2</sub>]: C, 44.52; H, 2.92; N, 11.29. Found: C, 44.47; H, 3.05; N, 11.25%. Diamagnetic. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 198.

[Sm<sub>2</sub>(H<sub>4</sub>L<sup>2</sup>)<sub>3</sub>](SCN)<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub> (**7**). Yield 61%. *Anal. calc.* for [C<sub>69</sub>H<sub>54</sub>Cl<sub>3</sub>N<sub>15</sub>O<sub>18</sub>S<sub>3</sub>Sm<sub>2</sub>]: C, 43.98; H, 2.89; N, 11.15. Found: C, 44.05; H, 2.79; N, 11.37%. μ<sub>eff</sub> (μ<sub>B</sub>): 2.22. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 240.

[Er<sub>2</sub>(H<sub>4</sub>L<sup>2</sup>)<sub>3</sub>](SCN)<sub>3</sub>·(H<sub>2</sub>O) (**8**). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone/methanol solution of the complex. Yield 55%. *Anal. calc.* for [C<sub>69</sub>H<sub>50</sub>Cl<sub>3</sub>N<sub>15</sub>O<sub>16</sub>S<sub>3</sub>Er<sub>2</sub>]: C, 44.03; H, 2.68; N, 11.16. Found: C, 44.10; H, 2.60; N, 11.27. μ<sub>eff</sub> (μ<sub>B</sub>): 16.42. Λ<sub>M</sub> (S cm<sup>2</sup> mol<sup>-1</sup>): 230.

## 3. Result and discussion

### 3.1. Synthesis and spectroscopic studies

Here we have prepared the acyclic Schiff bases H<sub>3</sub>L<sup>1</sup> and H<sub>5</sub>L<sup>2</sup> (Chart 1) following a method well known in the literature. The

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