Polyhedron 43 (2012) 97–103

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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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ARTICLE INFO

Article history:
Received 22 April 2012
Accepted 5 June 2012
Available online 23 June 2012

Keywords:
Lanthanide
Hydrazone
Schiff bases

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, ^{1}H 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.

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 $[Ln(H_4L^2)_2\cdot(H_2O)_t]\cdot(SCN)_3\cdot(H_2O)_z$ ($t = 2$ 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 (4000–400 cm^{-1}). The molar conductances of 10^{-3} M solutions of the metal complexes in DMF were measured at 25 °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 ^{1}H and ^{13}C NMR spectra of the

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http://dx.doi.org/10.1016/j.poly.2012.06.025

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

Formula	$C_{76}H_{76}La_2Cl_4N_{14}O_{21}$ (**1**)	$C_{69}H_{50}Er_2Cl_3N_{15}O_{16}S_3$ (**8**)
Molecular weight	1941.12	1882.29
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	$P2_1/n$
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^3)	8243.5 (5)	7691.49 (13)
Z	4	4
D_{calc} (g cm^{-3})	1.564	1.625
μ (Mo Kα) (mm^{-1})	1.23	2.43
λ (Å)	0.71073	0.71073
F(000)	892	3728
R	0.054	0.053
w*R*	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^{-3})	1.17	2.54
Minimum residual hole(e Å^{-3})	−0.91	−1.57

$R = \sum||F_0| - |F_c||)/\Sigma|F_0|$, $wR = [\Sigma w^2(|F_0|^2 - |F_c|^2)^2/\Sigma w^2(|F_0|^2)^2]^{1/2}$.

Schiff bases were recorded in $CDCl_3$ 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 Autospec 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 $[La_2(H_2L^1)_3(C_2H_5OH)_2]\cdot(Cl)\cdot(NO_3)_2\cdot((CH_3)_2CO)_2\cdot(H_2O)_2$ (**1**) and $[Er_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)$ (**8**). 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^2 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_4O_{10}. The yield of the Schiff bases was quantitative.

H_3L^1: Yield 96%. M.P. 221–225 °C. *Anal.* Calc. for $C_{22}H_{17}ClN_4O_3$: 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. ^1H NMR dmso-d$_6$ δ (ppm): 7.47 (m, 6H, H_{Ar}), 7.60 (m, 1H, –N*H*), 7.73 (m, 6H, H_{Ar}), 8.60 (s, 2H, –N=C*H*), 12.20 (s (broad), 1H, –O*H*), 12.70 (s (broad), 1H, –O*H*). ^{13}C NMR dmso-d$_6$ δ (ppm): 196.52 (–*C*=O), 163.28 (–*C*=N), 155.45 (HO–C_{Ar}), 144.87, 132.78, 132.19, 128.65, 127.84, 123.56, 122.08 (C_{Ar}).

H_5L^2: Yield 83%. M.P. >230 °C. *Anal.* Calc. for $C_{22}H_{17}ClN_4O_5$: 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. ^1H NMR dmso-d$_6$ δ (ppm): 7.47 (m, 6H, H_{Ar}), 7.60 (m, 2H, –N*H*), 7.73 (m, 4H, H_{Ar}), 8.60 (s, 2H, –N=C*H*), 12.20 (s (broad), 2H, –O*H*), 12.70 (s (broad), 1H, –O*H*). ^{13}C NMR dmso-d$_6$ δ (ppm): 196.52 (–*C*=O), 163.28 (–*C*=N), 155.45 (HO–C_{Ar}), 144.87, 132.20, 132.78, 128.65, 127.84, 123.55, 122.08 (C_{Ar}).

2.4. Preparation of the complexes

2.4.1. Complexes of H_3L^1

Lanthanide (III) nitrate heptahydrate (1 mmol) in methanol (20 mL) was added to a suspension of 5-chloro-1,3-diformyl-2-hydroxybenzene-bis(benzoylhydrazone) (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.

$[La_2(H_2L^1)_3(C_2H_5OH)_2]\cdot(Cl)\cdot(NO_3)_2\cdot((CH_3)_2CO)_2\cdot(H_2O)_2$ (**1**). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone/ethanol solution of the complex. Yield 55%. *Anal.* calc. for $[C_{76}H_{76}Cl_4N_{14}O_{21}La_2]$: C, 47.03; H, 3.95; N, 10.10. Found: C, 46.99; H, 3.93; N, 10.12%. Diamagnetic. Λ_M (S cm^2 mol^{-1}): 205.

$[Nd_2(H_2L^1)_3]\cdot(Cl)\cdot(NO_3)_2\cdot(H_2O)_2$ (**2**). Yield 65%. *Anal.* calc. for $[C_{66}H_{52}Cl_4Nd_2N_{14}O_{17}]$: C, 45.47; H, 3.01; N, 11.25. Found: C, 45.58; H, 3.09; N, 11.19%. μ_{eff} (μ_B): 7.18. Λ_M (S cm^2 mol^{-1}): 222.

$[Sm_2(H_2L^1)_3]\cdot(Cl)\cdot(NO_3)_2\cdot(H_2O)$ (**3**). Yield 71%. *Anal.* calc. for $[C_{66}H_{50}Cl_4Sm_2N_{14}O_{16}]$: C, 45.62; H, 2.90; N, 11.28. Found: C, 45.69; H, 3.11; N, 11.37%. μ_{eff} (μ_B): 3.32. Λ_M (S cm^2 mol^{-1}): 200.

$[Dy_2(H_2L^1)_3]\cdot(Cl)\cdot(NO_3)_2\cdot(H_2O)$ (**4**). Yield 59%. *Anal.* calc. for $[C_{66}H_{50}Cl_4Dy_2N_{14}O_{16}]$: C, 44.99; H, 2.86; N, 11.13. Found: C, 45.06; H, 2.79; N, 11.23%. μ_{eff} (μ_B): 18.08. Λ_M (S cm^2 mol^{-1}): 220.

2.4.2. Complexes of H_5L^2

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 hydrazone) (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.

$[Y_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)_3$ (**5**). Yield 62%. *Anal.* calc. for $[C_{69}H_{54}Cl_3N_{15}O_{18}S_3Y_2]$: C, 47.04; H, 3.09; N, 11.93. Found: C, 46.85; H, 3.15; N, 11.83%. Diamagnetic. Λ_M (S cm^2 mol^{-1}): 204.

$[La_2(H_4L^2)_3\cdot(H_2O)_2]\cdot(SCN)_3\cdot(H_2O)$ (**6**). Yield 65%. *Anal.* calc. for $[C_{69}H_{54}Cl_3N_{15}O_{18}S_3La_2]$: C, 44.52; H, 2.92; N, 11.29. Found: C, 44.47; H, 3.05; N, 11.25%. Diamagnetic. Λ_M (S cm^2 mol^{-1}): 198.

$[Sm_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)_3$ (**7**). Yield 61%. *Anal.* calc. for $[C_{69}H_{54}Cl_3N_{15}O_{18}S_3Sm_2]$: C, 43.98; H, 2.89; N, 11.15. Found: C, 44.05; H, 2.79; N, 11.37%. μ_{eff} (μ_B): 2.22. Λ_M (S cm^2 mol^{-1}): 240.

$[Er_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)$ (**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 $[C_{69}H_{50}Cl_3N_{15}O_{16}S_3Er_2]$: C, 44.03; H, 2.68; N, 11.16. Found: C, 44.10; H, 2.60; N, 11.27. μ_{eff} (μ_B): 16.42. Λ_M (S cm^2 mol^{-1}): 230.

3. Result and discussion

3.1. Synthesis and spectroscopic studies

Here we have prepared the acyclic Schiff bases H_3L^1 and H_5L^2 (Chart 1) following a method well known in the literature. The

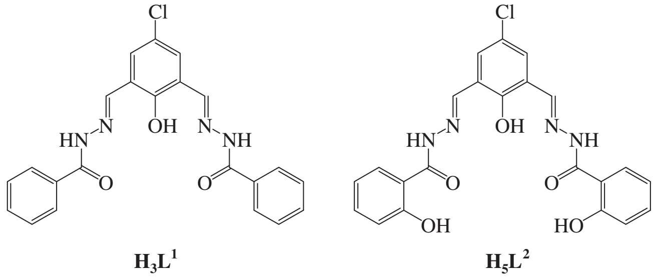

Chart 1. Scheme of H_3L and H_5L

Table 3
The UV–Vis data λ (nm) and ε (L mol^{-1} cm^{-1}) for the ligands and the complexes.

Compounds	λ(nm)
H_3L^1	227 (5.36), 271 (3.04) [pH 7], 287 (3.04) [pH 13], 319 (3.19), 345 (1.07), 363 (3.39), 418 (1.30), 438 (1.45)
H_5L^2	225 (5.36), 270 (3.08) [pH 7], 285(3.13) [pH 13], 320 (3.15), 345 (1.01), 365 (3.48), 420 (1.25), 440 (1.56)
1	287 (3.06), 330 (5.2), 370(15,52), 410 (5.3), 530 (5.83)
2	286 (3.02), 330 (4.2), 370(5,78), 410 (6.5), 530 (0.39)
3	289 (3.00), 335 (2.50), 365 (1.28), 405 (3.89), 460 (3.35)
4	285 (2.98), 330 (3.15), 370(12.50), 405 (12.50), 460 (12.50)
5	287 (3.66), 330 (1.55), 345 (1.20), 360 (1.38), 463 (2.45)
6	284 (3.54), 335 (2.58), 344 (0.55), 366 (0.98), 461 (1.33)
7	286 (3.55), 325 (2.50), 340 (0.66), 365 (1.83), 465 (2.30)
8	285 (3.27), 325 (5.50), 340 (3.89), 360 (3.83), 440 (1.17), 465 (5.83)

syntheses of the ligands were achieved in a one step procedure using the direct condensation of 2,6-diformyl-4-chlorophenol with the appropriate hydrazide in quantitative yields. The mass spectra of the two ligands present an intense peak at 421 and 453 uma, corresponding to the molecular ions of $[H_3L^1 + H]^+$ and $[H_5L^2 + H]^+$, respectively. The ^1H NMR spectra of the ligands were recorded in deuterated dimethylsulfoxide. The NMR spectra of the compounds are comparable and show an added signal for H_5L^2. Indeed, the spectrum of H_3L^1 revealed peaks at 12.2 (*H*O–Ar) and 12.7 ppm (*H*O–C=N), which is indicative of the iminolisation of one of the two amide groups. This fact is not observable in the spectrum of H_5L^2. In this case only signals attributable to *H*O–Ar are observable; the amide groups remain stable. The ^{13}C NMR spectra of the ligands show a signal at δ 196.52 ppm which represent the carbon atom of the carbonyl *C*=O group. The peaks at δ 155.45 represent the aromatic C_{ipso} of the OH of the phenol in the spectra of H_3L^1 and H_5L^2. The main IR bands are summarized in Table 2. The IR spectra of the two compounds show moderate-intensity absorptions at *ca.* 1620 cm^{-1} which are attributable to *ν*(C=N). No bands are observed for the free 2,6-diformyl-4-chlorophenol or hydrazides indicating that complete condensation has occurred. The phenol and/or iminol moieties reveal a band at *ca.* 3400 cm^{-1}. The amide function exhibits strong absorptions, *ν*(N–C=O), at *ca.* 1660 cm^{-1}.

The reactions of H_3L^1 and H_5L^2 with nitrate or thiocyanate lanthanide salts in 3:2 M ratios were investigated, and the complexation was performed by mixing ethanol or methanol solutions of both the ligand and metal salt. The products isolated were dinuclear complexes. In all cases the complexes appear to be air stable and are soluble in common organic solvents. Crystals suitable for X-ray analysis were obtained by slow evaporation of solutions of $[La_2(H_2L^1)_3(C_2H_5OH)_2]\cdot(Cl)\cdot(NO_3)_2\cdot((CH_3)_2CO)_2\cdot(H_2O)_2$ (**1**) and $[Er_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)$ (**8**). All the compounds are characterized by elemental analysis (C, H, N), IR spectroscopy, molar conductivity, magnetic measurements and X-ray diffraction for **1** and **8**.

Upon complexation of H_3L^1 or H_5L^2 with lanthanide ions, the C=N bands shift toward lower frequency, appearing in the range 1512–1555 cm^{-1} in the IR spectra of the complexes, suggesting an interaction between the metal ion and the imino nitrogen atom. The hydroxyl groups of water lattice molecules and coordinated ethanol in the case of **1** appear near 3490 cm^{-1} [25]. In the complexes from H_3L^1 information regarding the possible bonding modes of the nitrate group was obtained. The presence of a band near 1380 cm^{-1} indicates that ionic nitrate groups are present [26]. In the infrared spectra of the complexes from H_5L^2, a strong band near 2050 cm^{-1} appears and confirms the presence of SCN^- as counter-ions in these compounds. Additional bands at *ca.* 1615 and 3220 cm^{-1} were observed in the spectra of both complexes and are assignable respectively to coordinated N–C=O and N–H stretching vibrations, respectively. The water present in all the complexes is probably lattice and/or coordinated according to the broad band at 3460 cm^{-1}.

The electronic spectral data of the ligands H_3L^1 and H_5L^2 and the complexes are recorded in methanol and the main bands are listed in Table 3. The assignments are made by a comparison with literature data [27–29]. The ligands H_3L^1 and H_5L^2 show an intense absorption band respectively at 271 and 270 nm which shift to a higher wavelength at 287 and 285 nm, respectively, when increasing the pH. This fact is diagnostic of the presence of a phenol group in the ligands molecules. An intense band is also observed in the spectra of the ligands near 227 nm and this is assigned to a $\pi \rightarrow \pi^*$ transition of the aromatic rings. A $\pi \rightarrow \pi^*$ transition attributed to the C=N chromophore is observed in the spectra of the ligands at 320 nm [29]. In the region 340–440 nm intense bands are observed and these are assigned to the $n \rightarrow \pi^*$ transition in the carbonyl group. Upon coordination to lanthanide(III) ions these bands are shifted to lower wavelengths, supporting the coordination of the hydrazonic moieties via the imino nitrogen and the carbonyl oxygen atoms to the metal center. In the spectra of the complexes a new band around 286 nm was observed. This is indic-

Table 2
Vibration frequencies in the infrared spectra of the compounds and their assignments.

Compound	Vibration frequencies (cm^{-1})							
	ν (O–H)	ν (N–H)	ν (C=O)	ν (C=N)	ν (Ln–O)	ν (Ln–N)	ν (SCN)	ν (NO_3)
H_3L^1	3447	32 52	1660	1620	–	–	–	–
H_5L^2	3489	3212	1660	1620	–	–	–	–
1	3462	3207	1610	1555	465	276	–	1387
2	3498	3205	1613	1572	480	282	–	1383
3	3475	3198	1610	1560	475	278	–	1385
4	3489	3212	1608	1565	457	265	–	1388
5	3450	3205	1615	1575	475	272	2054	–
6	3462	3150	1616	1560	525	475	2050	–
7	3475	3100	1616	1559	530	482	2052	–
8	3453	3202	1607	1569	459	268	2054	–

ative of the transformation of the phenol in the phenolate groups upon reaction with lanthanide(III) ions. No absorption bands due to f–f transitions could be observed in the visible region of the spectra. This may be attributed to intense charge-transfer transitions that obscure the f–f bands. The electronic spectral data of the complexes further support the coordination of the ligand to the lanthanide through the imino nitrogen, carbonyl oxygen and phenolate oxygen atoms.

Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The conductivities increased very slightly with time in dmf for all the complexes. The conductance values lie in the range observed for 3:1 electrolytes (200–240 $cm^2\ \Omega^{-1}\ mol^{-1}$) [30]. The μ_{eff} value of the lanthanide complexes show that these are paramagnetic except for complexes **1**, **5** and **6**, which are diamagnetic in nature. This paramagnetic behavior is consistent with the presence of unpaired 4f electrons. The observed μ_{eff} values are in close proximity to the values for the free metal ions reported by Van Vleck and Frank [31]. This shows that the magnetic moments of the Ln^{3+} ions are not affected by the ligand field. The 4f-electrons are not involved in the coordination.

The formulations obtained from the infrared spectra for these complexes are in accordance with the measured molar conductivities. The overall observations on the geometrical features found for all complexes by conductivity and spectroscopic studies are in complete agreement as that elucidated by X-ray crystallography for complexes **1** and **8**.

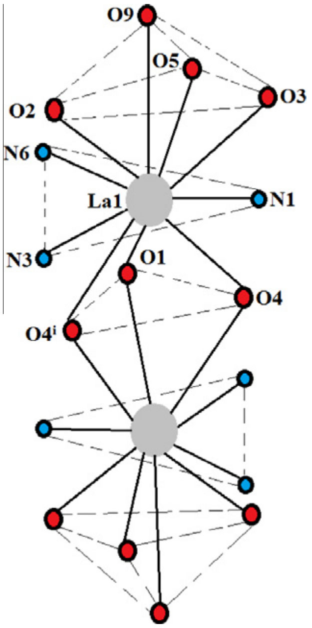

Fig. 2. A view of the coordination environment around each La^{III} ion in complex **1**.

3.2. Description of the structures

Partially labelled plots of the dinuclear structures of complexes **1** and **8** are shown in Fig. 1 and Fig. 3, respectively. The coordination polyhedra of the La^{III} and Er^{III} ions are shown in Figs. 2 and 4. Selected interatomic distances and angles are listed in Tables 4 and 5.

The structure of complex **1** consists of $[La_2(H_2L^1)_3(C_2H_5OH)_2]^{3+}$ discrete entities, nitrate and chloride anions in a NO_3^-/Cl^- ratio of 2. Two non-coordinated water and acetone molecules per two La-containing units, intervene as lattice solvent. As is evident from the structure, the coordination to the lanthanide ion occurs via the phenolate oxygen rather than the nitrogen atom. In the titled complex, both lanthanide(III) ions have a coordination number of ten, binding the three imine nitrogen atoms, three neutral oxygen atoms of the hydrazone, the three phenolate oxygen atoms of the three ligand molecules and one neutral oxygen atom of the coordinated ethanol molecule. The complex crystallizes in the monoclinic space group C2/c. The coordination of the hydrazone to La results in the formation of five and six membered (LaOCNN and LaOCCCN)

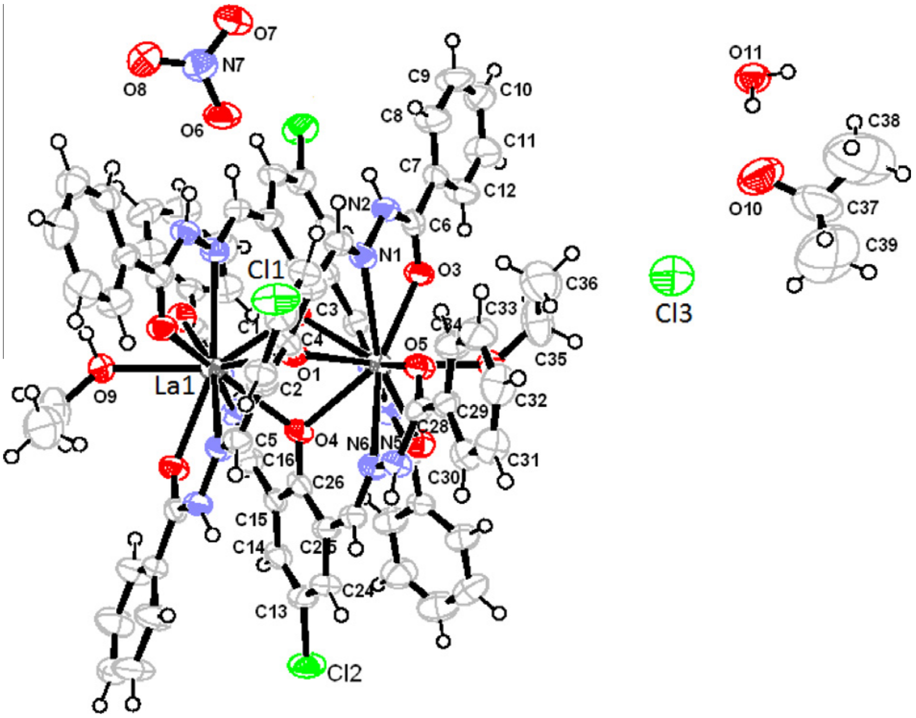

Fig. 1. Crystal structure of the dinuclear complex $[La_2(H_2L^1)_3(C_2H_5OH)_2]\cdot(Cl)\cdot(NO_3)_2\cdot((CH_3)_2CO)_2\cdot(H_2O)_2$ (**1**), showing partially the atom numbering scheme.

Table 4
Selected bond lengths (Å) and bond angles (°) of complex **1**.

La1—O1	2.493(3)	La1—O9	2.627(4)
La1—O4	2.498(4)	La1—N1	2.819(5)
La1—O4^{i}	2.507(4)	La1—N3	2.787(5)
La1—O2	2.566(4)	La1—N6	2.787(5)
La1—O3	2.499(4)	La1—La1^{i}	3.8540(8)
La1—O5	2.528(4)		
O1—La1—O4	66.20(11)	N6—La1—N3	123.36(15)
O1—La1—O4^{i}	66.06(11)	N3—La1—N1	116.70(15)
O4—La1—O4^{i}	68.50(15)	O5—La1—N6	58.93(13)
La1—O1—La1^{i}	101.24(18)	O3—La1—N1	58.05(13)
La1—O4—La1^{i}	100.72(13)	O4—La1—N3	61.28(11)
N6—La1—N1	118.05(14)	O1—La1—N1	62.02(11)

Symmetry codes: (i) $-x + 1, y, -z + 3/2$.

Table 5
Selected bond lengths (Å) and bond angles (°) of complex **8**.

Er1—O1	2.257(3)	Er2—O1	2.353(3)
Er1—O6	2.319(4)	Er2—O6	2.290(4)
Er1—O11	2.377(3)	Er2—O11	2.274(4)
Er1—O4	2.317(4)	Er2—O2	2.337(4)
Er1—O9	2.295(4)	Er2—O7	2.348 (4)
Er1—O14	2.316(4)	Er2—O12	2.369(4)
Er1—N3	2.558(5)	Er2—N1	2.594(4)
Er1—N7	2.553(4)	Er2—N5	2.577(4)
Er1—N11	2.584(4)	Er2—N9	2.605(4)
Er1—Er2	3.4871(4)		
O1—Er1—O6	69.93(12)	O1—Er2—O6	68.80(12)
O1—Er1—O11	68.65(12)	O1—Er2—O11	68.81(12)
O6—Er1—O11	68.69(12)	O11—Er2—O6	71.00(12)
N3—Er1—N7	126.96(14)	O2—Er2—N1	63.17(13)
N3—Er1—N11	111.12(14)	N1—Er2—N5	125.70(14)
N7—Er1—N11	121.52(14)	N1—Er2—N9	112.06(14)
O4—Er1—N3	62.56(14)	N5—Er2—N9	121.82(14)
O9—Er1—N7	63.35(13)	O7—Er2—N5	63.81(13)
O14—Er1—N11	62.74(13)	O12—Er2—N9	62.72(13
O1—Er1—N3	68.87(13)	O1—Er2—N1	64.64(13)
O6—Er1—N7	66.71(13)	O11—Er2—N9	67.98(13)
O11—Er1—N11	64.43(13)	O6—Er2—N5	67.99(13)
Er1—O1—Er2	98.28(13)	Er2—O6—Er1	98.32(13)
Er1—O11—Er2	97.13(13)		

chelating rings. In the complex the La–N bonds involving the hydrazone nitrogen atoms show the largest metal–ligand distances (La1–N6 = 2.786(5) Å, La1–N3 = 2.787(5) Å and La1–N1 = 2.819(5) Å). The La–O bonds involving the hydrazonic oxygen atoms are in the range 2.499(4)–2.566(4) Å and are comparable to those found in hydrazonic complexes [32]. The phenolate oxygen atoms acting as bridges have bonds distances in the range 2.493(3)–2.507(4) Å and are comparable to the values in the complex $[La_2(2,6\text{-DNP})_6(H_2O)_4]\cdot 4H_2O$ (where 2,6-DNP is 2,6-dinitrophenol) [33]. The largest metal–oxygen bond distance in the complex is found in the bond of La with the oxygen atom of the ethanol solvent molecule (La1–O9 = 2.627(4) Å). The La···La distance is 3.8540(8) Å. The C14–N18 distance and its related symmetry are consistent with a single bond while the C22–N19 and C14–O3 distances and their related symmetries are consistent with double bond character. The bond angles of the ligands, which involve the La(III) ion and the bridged oxygen atoms of the ligand, are in the range 66.09(11)–68.50(15)°. The three sets of donor atoms [(O1, O4, O4^{i}); (N1, N3, N6) and (O2, O3, O5)] form three planes to lie upon, medium and under the sheets of the lanthanum^{III} centers, respectively. The oxygen atom of the coordinated ethanol molecule, O9, is over the plane formed by O2, O3 and O5. The La^{III} ion is positioned on a plane formed by three nitrogen atoms, N1, N3 and N6. The angle sum subtended by these three nitrogen atoms at La1 is 358.11°. In this complex, the planes [O2, O3, O5], [N1, N3, N6] and [O1, O4, O4^{i}] are nearly parallel to each other, with small dihedral angles of 1.37–2.67°. These planes are perpendicular to the plane [La1, O9, O2], with a dihedral angle of 89.72°. As reported by Bu et al. [4] for $[Ho_2(L)_3(H_2O)](NO_3)_2\cdot(OH)\cdot 3.5H_2O$ (where HL is *N,N′*-diisonicotinoyl-2-hydroxy-5-methylisophthalaldehyde dihydrazone), the coordination polyhedron around each lanthanum atom can be regarded as a 1333 stacking pattern (Fig. 2).

In this compound, there is extensive hydrogen bonding leading to a very complex motif. The uncoordinated water molecules [corresponding to O11] are hydrogen bonded to either uncoordinated acetone molecules [O10] or nitrate [O6, O7] oxygen atoms, while the coordinated ethanol molecule [O9] is hydrogen bonded only to the nitrate oxygen and nitrogen atoms [O8, N7]. The NH of the hydrazonic moieties of the ligand molecule [N2, N4 and N5] are hydrogen bonded respectively to the uncoordinated water molecules [O11], to the chlorine atom of the ligand [Cl3] and to the oxygen atom of the nitrate ion [O8].

The structure of complex **8** consists of $[Er_2(H_4L^2)_3]^{3+}$ discrete entities, thiocyanate anions and one non-coordinated water molecule per two Er-containing units, intervening as lattice solvent. The coordination of the hydrazones to Er results in the formation of five OCNNEr and six NCCCOEr membered chelating rings which share one Er–N bond. In the two rings, the Er–N bonds have the largest metal–ligand distances [Er1–N3 = 2.555(4) Å, Er1–O4 = 2.322(4) Å, Er1–N7 = 2.555(4) Å]. The Er–O bonds involving the hydrazonic oxygen have metal–ligand distances comparable in the three ligand molecules [Er1–O4 = 2.322(4) Å, Er1–O9 = 2.296(3) Å, Er1–O14 = 2.318(4) Å]. The phenolic oxygen atoms, acting as bridges between the two Er atoms, have metal–ligand distances in the range 2.256(3)–2.374(3) Å. The Er1···Er2 distance is 3.4871(4) Å. These are consistent with those found in other nine-coordinated erbium(III) complexes [34].

The following bonds are not altered in the complex: C8–O2, C16–O4, C30–O7, C38–O9, C52–O12 and C60–O14 are short, consistent with a double bond, and C8–N2, C16–NO4, C30–O6, C38–N8, C52–N10 and C60–N12 are long, consistent with a single bond. The remaining bond distances of the hydrazone molecule, as well as C26–O6, C37–N7 and C29–N5 are slightly different in the three ligand molecules. The bond angles of the ligands, which involve the Er(III) ion, and the bridging oxygen atoms of the ligand are very similar for the two erbium(III) metal centers [O1–Er1–O6 = 69.99(12)°; O6–Er2–O1 = 68.73(12)°; O1–Er1–O11 = 68.63 (12)°; O11–Er2–O1 = 68.68(12)°; O6–Er1–O11 = 68.75(12)°; O11–Er2–O6 = 70.94 (12)°]. The three sets of donor atoms [(O1, O6, O11); (N3, N7, N11) and (O4, O9, O14)] (Er1) and [(O1, O6, O11) and (N1, N5, N9) and (O2, O7, O12)] (Er2) form three planes to lie upon, medium and under the sheets of each erbium^{III} center, respectively. Each erbium^{III} ion is positioned on a plane formed by three nitrogen atoms, [N3, N7, N11] (Er1) and [N1, N5, N9] (Er2). The angle sum subtended by the three capping atoms is 359.60° at Er1 and 359.58° at Er2. In this complex the planes around the erbium centers are nearly parallel; e.g. [O1, O6, O11], [N11, N3, N7] and [O4, O9, O14] are nearly parallel to each other with dihedral angles of 1.48–8.66°. Both erbium(III) atoms in the complex are nine-coordinated, being bound to three oxygen atoms of carbonyl groups, three nitrogen atoms of the azomethine groups and three phenolate oxygen atoms. The three thiocyanate moieties act as counter ions. The water molecule remains uncoordinated. Two possible coordination polyhedra with nine vertexes are known. The coordination polyhedra around each erbium atoms are better described as a distorted tricapped trigonal prisms with three hydrazones nitrogen atoms forming the three face caps: N3, N7, and N11 for Er1 and N1, N5 and N9 for Er2 (Fig. 3).

In this compound, there is extensive intramolecular hydrogen bonding. Indeed each ligand molecule possesses two free hydroxyl

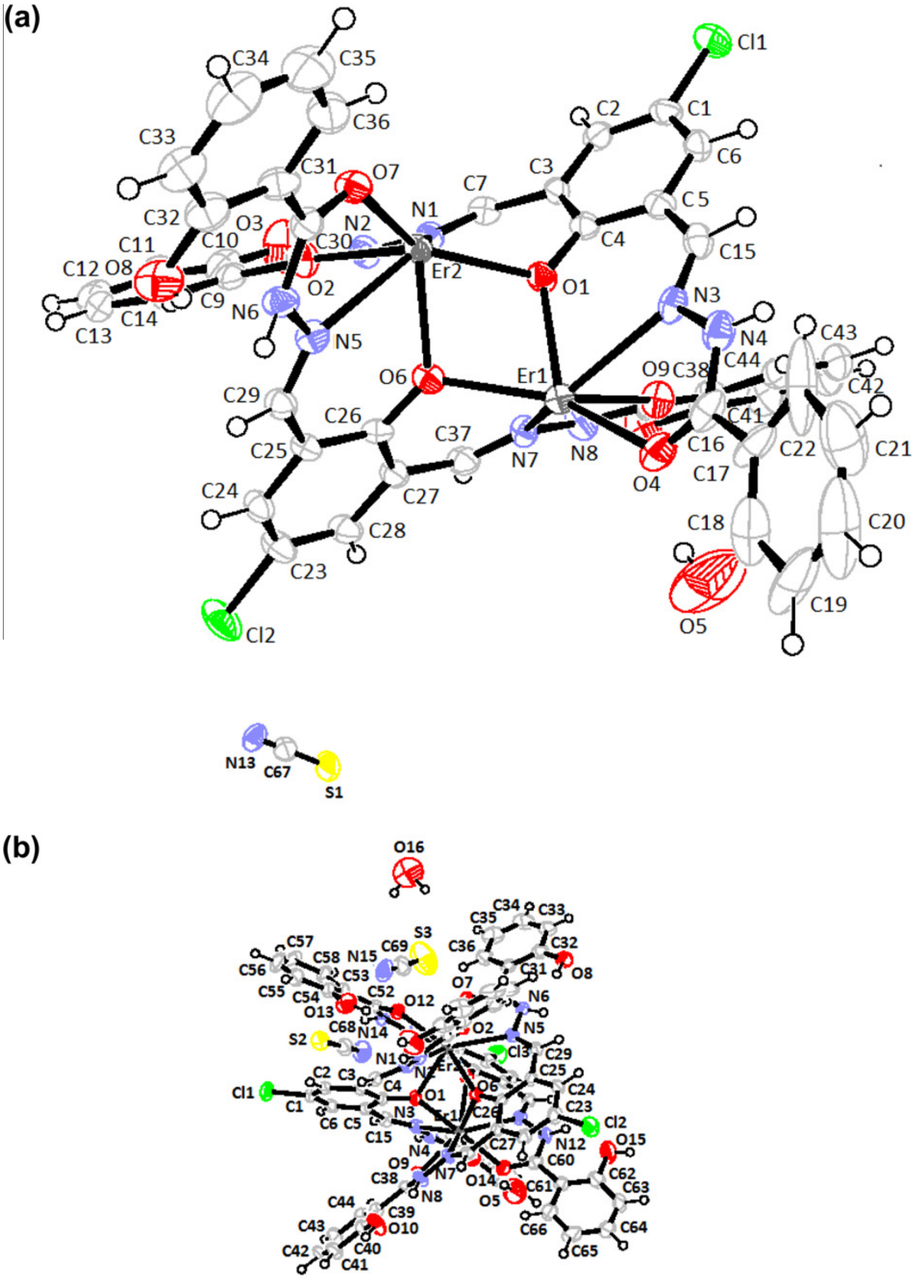

Fig. 3. (a) Crystal structure of the dinuclear complex $[Er_2(H_4L^2)_3]\cdot(SCN)_3\cdot(H_2O)$ (**8**) where one ligand molecule, a water molecule and thiocyanate counter-ions are omitted for clarity.(b) Crystal structure of the dinuclear complex showing partially the atom numbering scheme.

groups which are hydrogen bonded with the nitrogen or oxygen atoms of the hydrazonic moieties. There is also established hydrogen bonding between these hydroxyls groups with the uncoordinated water molecules and free thiocyanates anions. The NH of the hydrazonic moieties of the ligand molecules are hydrogen bonded to the uncoordinated hydroxyl groups of the ligand and to the uncoordinated thiocyanate anions through the sulfur atom.

In the literature, for a series of lanthanide complexes, the repulsion between ligand molecules in the coordination sphere increases when the size of the lanthanides ions decreases [35–38]. The averaged Ln–N and Ln–O bond distances in complex **1** (2.798(5) and 2.515(4) Å (Ln=La)) are larger than those in complex **8** (2.578(4) and 2.321(4) Å (Ln=Er)), and the averaged O–Ln–N angle in complex **1** (61.65(12)°) is smaller than that found in complex **8** (66.77(13)°). These results are consistent with the reduced size of the ionic radius on going from La^{3+} to Er^{3+}. The larger La^{III} ion ($r_{La}{}^{3+}$ = 1.16 Å) [39] forms longer coordination bond distances with the donor atoms of the Schiff base ligands and smaller chelate angles than does the Er^{III} ion which has a smaller ionic radius ($r_{Er}{}^{3+}$ = 1.00 Å) [39]. This has the result of reducing the coordination number and seeing the structure change. When comparing complexes **1** and **8** we note that the separation of La1···La1^{i}, in complex **1** is 0.3669 Å, higher than the Er1···Er2 separation in complex **8**. Bu et al. [4] report a similar observation when comparing $[Ho_2(\mathbf{L})_3(H_2O)](NO_3)_2\cdot(OH)\cdot3.5H_2O$ and $[Lu_2(\mathbf{L})_3](OH)_3$ (where HL is *N,N′*-diisonicotinoyl-2-hydroxy-5-methylisophthalaldehyde dihydrazone); the Ho···Ho separation is 0.1438 Å, higher than the Lu···Lu separation. We can note that the decrease in ionic radius is correlated to increased repulsions between the ligands in the complex.

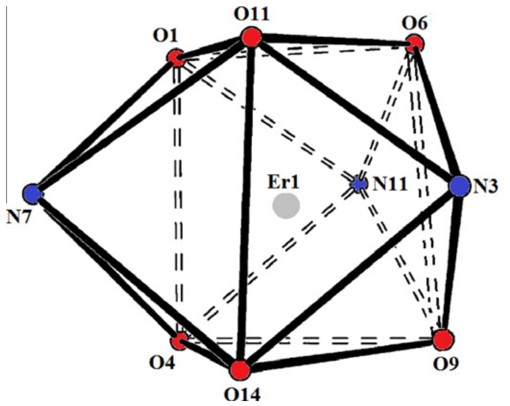

Fig. 4. A view of the inner coordination polyhedron of **8** showing the tricapped trigonal prismatic coordination of the Er^{III} ion (Er1).

4. Conclusion

The results presented in this study indicate that lanthanides (Y, La, Nd, Sm, Dy, Er) form stable complexes with Schiff basis derivates from 2,6-diformyl-4-chlorophenol and hydrazides. According to the data of elemental analysis, molar conductivity, FT-IR and UV–Vis spectra, and X-ray crystallographic structure determination, these complexes have a metal to hydrazone stoichiometry of 2:3. This coordination mode found for structures obtained for all complexes is in full accordance with the corresponding species suggested in the solution studies. As the only difference between the two ligands consists of the presence of the phenyl uncoordinated hydroxyl group in H_5L^2, no difference in coordination mode is observed between H_3L^1 and H_5L^2. Except for the lanthanum complexes, in which the metal ions are deca-coordinated, in all other complexes the lanthanide ions are nine-coordinated. The counter-ions, with a weak binding ability, are not coordinated to metal center in all the dinuclear complexes.

Appendix A. Supplementary material

Supplementary data CCDC 871848 and 871849 contains the supplementary crystallographic data for $[La_2(H_2L_1)_3(C_2H_5OH)_2]\cdot(Cl)\cdot(NO_3)_2\cdot((CH_3)_2CO)_2\cdot(H_2O)_2$ (**1**) and $[Er_2(H_4L_2)_3]\cdot(SCN)_3\cdot(H_2O)$ (**8**), respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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