

**PREPARATION, SPECTROSCOPIC STUDIES AND X-RAY STRUCTURE OF
HOMOBINUCLEAR LANTHANIDE(III) COMPLEXES DERIVED FROM 2,6-
DIFORMYL-4-CHLOROPHÉNOL-BIS-(2'-HYDROXY-BENZOYLHYDRAZONE)**

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ABSTRACT. Reaction of the 2,6-diformyl-4-chlorophenol-bis-(2'-hydroxy-benzoylhydrazone) with $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($n = 5$ or 6 and $\text{Ln} = \text{Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er}$ and Yb) produces homobinuclear complexes. These complexes have been characterized by analysis, molar conductance, magnetic measurements, infrared spectral studies and X-ray diffraction. The analytical data showed 1:3 (metal:ligand) stoichiometry. Molar conductance measurements in dmf indicate 1:3 electrolytes in all cases. Magnetic moment values are close proximity of the Van Vleck values. IR studies suggest the coordination of the ligand is through the azomethine, the phenolic oxygen atom and the carbonyl oxygen of the hydrazonic moiety. The nitrate ion is also found to be ionic in all the complexes. An X-ray structure determination of $[\text{C}_{66}\text{H}_{48}\text{N}_{12}\text{O}_{15}\text{Cl}_3\text{Er}_2]\text{Cl}_2\text{NO}_3 \cdot 5\text{H}_2\text{O}$ confirms the conclusion from the spectroscopic studies and show that the erbium is at the centre of a tricapped trigonal prism with coordination number nine. In all the complexes the lanthanide ions have substantially similar coordination.

KEY WORDS: Hydrazones, Binuclear complexes, Lanthanide complexes, X-ray diffraction; Crystal structure

INTRODUCTION

The chemistry of the lanthanide ions has been expanded rapidly in the past three decades. The interest in this chemistry is stimulated by their low toxicity, their potential uses as diagnostic tools in biology and their paramagnetic and luminescent properties [1-5]. A few years ago we initiated a project concerning rare earth metal chemistry [6] in a search for unusual molecular materials [7]. By use of an acyclic or cyclic Schiff's base containing large coordination cavities it is possible to introduce two identical or different lanthanide ions and to study their physico-chemical properties [8, 9]. Attention has been devoted to the study of spectroscopic properties and crystal structures. The formation of acyclic complexes depends on the dimension of the cavities, on the flexibility of the arms, on the nature of the donor atoms and on the complexing properties of the anions acting as counter ions [10].

This paper is devoted to the homobinuclear species derived from 2,6-diformyl-4-chlorophenol-bis-(2'-hydroxy-benzoylhydrazone) (H_5L). H_5L is an acyclic ligand bearing both nitrogen and oxygen donors which exhibit both hard and soft base character. This ligand contains two adjacent coordination cavities which can encapsulate large ions such as lanthanides. The hydrazonic moieties show two coordination modes (enol and keto) [11] and can form stable lanthanide(III) complexes. In order to understand the coordination chemistry we synthesized a series of binuclear complexes and investigated the spectroscopic properties. The

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structure of $[\text{Er}_2(\text{H}_4\text{L})_3]\text{Cl}_2(\text{NO}_3)\cdot 5\text{H}_2\text{O}$ has been elucidated by X-ray diffraction. The results of spectroscopic studies and crystal structure show that the ligand acts as a pentadentate in its keto coordination form.

EXPERIMENTAL

Reagents and materials

All chemicals and solvents used were of reagent grade. All metal(III) salts were used as nitrates. The NMR spectrum was recorded on a Bruker 400 spectrometer, infrared spectra were recorded on a Nicolet 55XC FT-IR spectrophotometer using KBr pellets or Nujol mulls. Elemental analysis of C, H, N and Cl was performed by the analytical laboratory of the Department of Inorganic Chemistry (University of Padua, Italy). Molar conductance measurements were made using a WTW LF-330 conductivity meter with a WTW conductivity cell on about 1 mmol dm^{-3} dimethylformamide solution at room temperature. Room temperature magnetic susceptibility measurements were made on solid complexes using a Johnson-Mathey balance with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrator.

Synthesis of 2,6-diformyl-4-chlorophénol-bis-(2'-hydroxy-benzoylhydrazone): H_5L

To a solution of 2,6-diformyl-4-chlorophénol (2 g; 10.8 mmol) in 30 cm^3 of ethanol was added a solution of salicylaldehyde hydrazide (3.3 g; 21.7 mmol) in 10 cm^3 of the same solvent. Two drops of glacial acetic acid were added and the resulting mixture was refluxed under stirring for 2 hours. On cooling the yellow precipitate was filtered off, washed with $2 \times 10 \text{ cm}^3$ of ethanol then $2 \times 20 \text{ cm}^3$ of ether and dried under vacuum. The yield was 83%. Anal. calcd for $\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}_5\text{Cl}\cdot\text{H}_2\text{O}$. C, 56.24; H, 3.86; N, 11.92; Cl, 7.54%. Found: C, 56.36; H, 3.58; N, 11.95; Cl, 7.51%. Mass spectrum (EI): $m/z = 453$ ($[\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}_5\text{Cl}]^+$). IR (cm^{-1} , Nujol mulls) $\nu_{\text{O-H}}$ 3450; $\nu_{\text{N-H}}$ 3205; $\nu_{\text{C=O}}$ 1635; $\nu_{\text{C=N}}$ 1614; $\nu_{\text{N-N}}$ 1018. UV (λ_{max} nm, dmf solution): 270, 320, 345, 365, 420, 440, 475. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 400 MHz) δ : 7.47 (m, 3H), 7.60 (s, 2H), 7.73 (m, 4H) ppm, 8.60 (s, 2H), 12.20 (s, 2H), 12.70 (m, 2H) ppm. ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 75 MHz) δ : 122.1, 123.6, 127.84, 128.6, 132.2, 132.8, 144.9, 155.4, 163.3, 196.5.

Synthesis of the complexes of H_5L

To a solution of H_5L (6 mmol) in absolute ethanol (20 cm^3) was added LiOH (6 mmol) and $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ ($n = 5$ or 6 and Ln is Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er or Yb) (4 mmol) in 10 cm^3 of absolute ethanol. The resulting mixture was heated for one hour. On cooling the precipitate which had formed was filtered off, washed with diethyl ether and dried under vacuum. The yields are 50-70%. The solid was dissolved in dimethylsulfoxide in the presence of excess of lithium chloride. On standing for two weeks the solutions gave microcrystalline powders for all the lanthanide ions complexes except erbium for which we obtained crystals suitable for X-ray analyses. The complexes are formulated as $[\text{Ln}_2(\text{H}_4\text{L})_3]\text{Cl}_2(\text{NO}_3)\cdot x\text{H}_2\text{O}$.

Crystallographic data collection

Yellow multifaceted blocks ($\sim 0.10 \times 0.15 \times 0.20 \text{ mm}^3$) were crystallized from dimethylsulfoxide at room temperature. The chosen crystal was mounted on a nylon CryoLoop™ (Hampton Research) with Krytox® Oil (DuPont) and centered on the goniometer of a Oxford Diffraction XCalibur2™ diffractometer equipped with a Sapphire 2™ CCD detector. The data collection routine, unit cell refinement, and data processing (Table 1) were carried out with the program CrysAlis [12]. The Laue symmetry and systematic absences were consistent with the monoclinic

space group $P2_1/c$. The structure was solved by direct methods and refined using the SHELXTL NT program package [13]. The asymmetric unit of the structure comprises one crystallographically independent erbium salt and five water molecules. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. Five residual electron density peaks located 2.5-3.2 Å from other polar groups were each modelled as the oxygen atoms of water molecules. The hydrogen atoms of the water molecules were not included in the model. The program package SHELXTL NT was used for molecular graphics generation [13].

Table 1. Crystal data and structure refinement for $[\text{Er}_2(\text{LH}_4)_3]\text{Cl}_2\text{NO}_3 \cdot 5\text{H}_2\text{O}$.

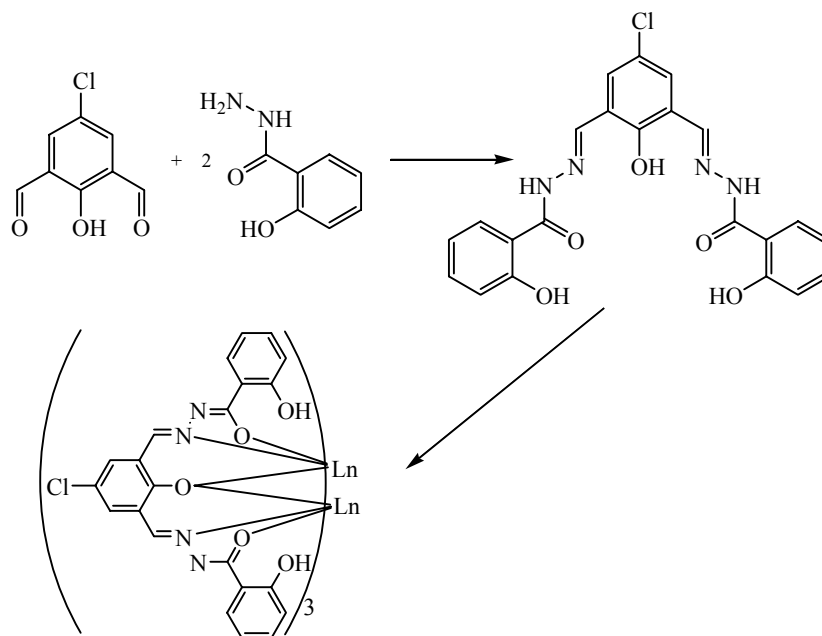
Empirical formula	$[\text{C}_{66}\text{H}_{48}\text{N}_{12}\text{O}_{15}\text{Cl}_3\text{Er}_2]\text{Cl}_2\text{NO}_3 \cdot 5\text{H}_2\text{O}$
Formula weight	1912.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	
a (Å)	13.3467(11)
b (Å)	23.187(2)
c (Å)	24.550(2)
β (°)	102.136(7)
Volume (Å ³)	7427.7(11)
Z	4
μ (mm ⁻¹)	2.500
N_{collect}	45017
N_{indep}	17143 [R (int) = 0.0439]
Completeness to $\theta = 27.59^\circ$	99.7 %
Absorption correction	Numerical
Max. and min. transmission	0.82396 and 0.58352
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$^aR_1 = 0.0793$, $^b wR_2 = 0.1583$
R indices (all data)	$^a R_1 = 0.1000$, $^b wR_2 = 0.1690$

$$^a R = \sum \|F_o\| - \|F_c\| / \|F_o\| \quad \text{and} \quad ^b wR = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w F_o^2} \right]^{1/2}$$

RESULTS AND DISCUSSION

Formation of the Schiff base

H₅L (2,6-diformyl-4-chlorophenol-bis-(2'-hydroxy-benzoylhydrazone)) was prepared from the condensation of 2,6-diformyl-4-chloro-phenol with benzoyl hydrazide (Scheme 1). The resulting compound is insoluble in ethanol and methanol. The ¹H and ¹³C NMR and IR data are consistent with the proposed structure. Bands in the region 1650-1600 cm⁻¹ are characteristic of amide (N-C=O) and imine (C=N) bonds and a band at 1018 cm⁻¹ is characteristic of N-N vibrations. In the range 3500-3200 cm⁻¹ we note bands characteristic of HO and NH vibrations. The ¹H NMR data show the appearance of two type of phenol hydroxyl at 12.20 and 12.70 ppm which suggested the non transformation of the amide groups in iminol groups in solution (Scheme 1) as observed in the case of bis-(2,6-diacetylpyridine-bis-(phenylhydrazone)) [11]. This is confirmed by the ¹³C NMR data. The signal at 196.5 ppm is attributed to the C=O group. Mass spectrum (EI) show a molecular ion at $m/z = 453$ ($[\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}_5\text{Cl}]^+$).



Scheme 1. Formation of the ligand H₅L and the related lanthanide complexes.

Characterization and spectroscopic studies

The binuclear Ln(III) complexes were prepared by heating at reflux two equivalents of hydrated lanthanide nitrate salts and three equivalents of 2,6-diformyl-4-chlorophenol-bis-(benzoylhydrazone) (H₅L) treated with lithium hydroxide in absolute ethanol. The immediate colour change indicated formation of the complex. The yields are quite high for the lanthanide complexes (50-70%). Crystallization of the resulting complexes in dimethylsulfoxide in the presence of excess of lithium chloride results a microcrystalline solid. The elemental analyses of the complexes were consistent with the composition of [Ln₂(H₄L)₃]Cl₂(NO₃).xH₂O, where H₄L denotes a monodeprotonated ligand molecule. Crystals suitable for X-ray analysis were isolated when the erbium nitrate complex was treated with an excess of lithium chloride to obtain [(Er₂(H₄L)₃]Cl₂(NO₃).5H₂O] in dimethylsulfoxide. The complexes were characterized by elemental analyses, molar conductance, magnetic measurements, IR and UV-Visible spectroscopy and, in the case of [Er₂(LH₄)₃]Cl₂NO₃.5H₂O, by an X-ray crystallography study. All the results are summarized in Table 2 and 3.

Table 2. Elemental analysis, effective magnetic moments and conductance of the complexes.

Compounds	Calc. (found)				μ_{eff} (μ_{B})	Λ_{M} ($\text{S cm}^2 \text{ mol}^{-1}$)
	% C	% H	% N	% Cl		
[Y ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).2H ₂ O	46.65 (46.02)	2.90 (2.88)	10.71 (10.42)	10.43 (10.39)	Diam.	199
[La ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).6H ₂ O	42.36 (42.31)	3.07 (3.11)	9.73 (9.90)	9.47 (9.45)	Diam	205
[Ce ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).7H ₂ O	41.91 (41.56)	3.14 (3.12)	9.63 (9.61)	9.37 (9.31)	2.51	208
[Pr ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	42.68 (42.33)	2.98 (2.88)	9.80 (9.67)	9.54 (9.43)	3.19	216
[Nd ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	42.53 (42.50)	2.97 (2.99)	9.77 (9.69)	9.51 (9.46)	3.18	222
[Sm ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).4H ₂ O	42.66 (42.42)	2.87 (2.81)	9.80 (9.86)	9.54 (9.47)	1.42	199
[Gd ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).6H ₂ O	41.54 (41.49)	3.01 (3.09)	9.54 (9.36)	9.29 (9.24)	7.68	217
[Dy ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	41.71 (41.67)	2.92 (3.01)	9.58 (9.55)	9.33 (9.27)	10.53	220
[Er ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	41.50 (41.46)	2.90 (2.88)	9.53 (9.49)	9.28 (9.22)	9.56	200
[Yb ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).4H ₂ O	41.65 (41.59)	2.81 (2.77)	9.57 (9.53)	9.31 (9.28)	4.57	198

Table 3. Main IR and UV bands of the complexes.

Compounds	IR (cm ⁻¹ , Nujol mulls)	UV (nm, dmf solution)
[Y ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).2H ₂ O	$\nu_{\text{O-H}}$ 3450, $\nu_{\text{N-H}}$ 3205, $\nu_{\text{C=O}}$ 1615, $\nu_{\text{C=N}}$ 1575, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 475, $\nu_{\text{Ln-N}}$ 272	266, 318, 356, 373 (sh)
[La ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).6H ₂ O	$\nu_{\text{O-H}}$ 3462, $\nu_{\text{N-H}}$ 3202, $\nu_{\text{C=O}}$ 1613, $\nu_{\text{C=N}}$ 1572, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 463, $\nu_{\text{Ln-N}}$ 276	270, 320, 350(sh), 360, 375 (sh)
[Ce ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).7H ₂ O	$\nu_{\text{O-H}}$ 3487, $\nu_{\text{N-H}}$ 3198, $\nu_{\text{C=O}}$ 1618, $\nu_{\text{C=N}}$ 1583, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 478, $\nu_{\text{Ln-N}}$ 277	267, 305(sh), 320, 405
[Pr ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	$\nu_{\text{O-H}}$ 3455, $\nu_{\text{N-H}}$ 3200, $\nu_{\text{C=O}}$ 1616, $\nu_{\text{C=N}}$ 1567, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 479, $\nu_{\text{Ln-N}}$ 268	265, 305(sh), 335, 353, 405, 425(sh)
[Nd ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	$\nu_{\text{O-H}}$ 3498, $\nu_{\text{N-H}}$ 3207, $\nu_{\text{C=O}}$ 1617, $\nu_{\text{C=N}}$ 1592, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 480, $\nu_{\text{Ln-N}}$ 282	265, 335, 407, 417(sh)
[Sm ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).4H ₂ O	$\nu_{\text{O-H}}$ 3475, $\nu_{\text{N-H}}$ 3196, $\nu_{\text{C=O}}$ 1611, $\nu_{\text{C=N}}$ 1588, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 475, $\nu_{\text{Ln-N}}$ 278	265, 323(sh), 335, 407, 418(sh)
[Gd ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).6H ₂ O	$\nu_{\text{O-H}}$ 3485, $\nu_{\text{N-H}}$ 3202, $\nu_{\text{C=O}}$ 1614, $\nu_{\text{C=N}}$ 1572, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 465, $\nu_{\text{Ln-N}}$ 256;	265, 333, 345(sh), 410, 430(sh)
[Dy ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	$\nu_{\text{O-H}}$ 3489, $\nu_{\text{N-H}}$ 3212, $\nu_{\text{C=O}}$ 1609, $\nu_{\text{C=N}}$ 1565, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 457, $\nu_{\text{Ln-N}}$ 265	265, 330, 340, 353, 405, 418(sh)
[Er ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).5H ₂ O	$\nu_{\text{O-H}}$ 3453, $\nu_{\text{N-H}}$ 3202, $\nu_{\text{C=O}}$ 1607, $\nu_{\text{C=N}}$ 1569, $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 459, $\nu_{\text{Ln-N}}$ 268	265, 323(sh), 340, 352, 407, 425(sh)
[Yb ₂ (H ₄ L) ₃]Cl ₂ (NO ₃).4H ₂ O	$\nu_{\text{N-H}}$ 3208, $\nu_{\text{C=O}}$ 1608, $\nu_{\text{C=N}}$ 1564; $\nu_{\text{N-N}}$ 1018, $\nu_{\text{Ln-O}}$ 455, $\nu_{\text{Ln-N}}$ 262	265, 323(sh), 342, 350, 407, 425(sh).

A considerable lowering of the $\nu(\text{C}=\text{O})$ frequency is observed in the spectra of all the complexes, indicating a decrease in the stretching force constant of the C=O bond as a consequence of the coordination of the oxygen atom to the metal ion. This band appears at *ca.* 1615 cm^{-1} . The important band at 1614 cm^{-1} in the free ligand attributed to $\nu(\text{C}=\text{N})$, is shifted to lower frequencies and appears in $1595\text{--}1560\text{ cm}^{-1}$ range in the spectra of all the complexes. This fact suggests the involvement of the nitrogen atom of the azomethine moieties in the coordination of the ligand to the metal ion. The bands at 3200 cm^{-1} characteristic of the H-N vibration are indicative of the non-iminolisation of the amide groups. The broad band of medium intensity occurring in the range $3500\text{--}3400\text{ cm}^{-1}$ not affected by metal coordination is due to the O-H stretching vibration of the phenolic groups and the non-coordinated water molecules [14]. No characteristic band of coordinated water molecules was observed. The weak band of moderate intensity at 1018 cm^{-1} is due to the N-N vibrations [15].

The strong and sharp band at 1380 cm^{-1} is characteristic of ionic nitrate [16]. No characteristic band of bidentate or monodentate nitrate was observed. In the region $450\text{--}480\text{ cm}^{-1}$ a medium-intensity band characteristic of a $\nu(\text{Ln-O})$ vibration of the phenolic oxygen was observed [17]. Bands in the far infrared spectra, in the region $280\text{--}250\text{ cm}^{-1}$ can be assigned to $\nu(\text{Ln-N})$ vibration in the new complexes [17].

The electronic spectra of the complexes were recorded in freshly prepared dmf solutions. The spectra are virtually identical for all the complexes. A fairly symmetrical new band is observed for each complex at *ca.* 407 nm . This band disappears when the complex is treated with NaBH_4 so it must be associated with the C=N chromophore coordinated to the metal ion through the nitrogen atom. The UV spectra of the complexes provided also further information. An intense band at *ca.* 335 nm , absent in the free ligand and the nitrates is assigned to charge transfer between the coordinated ligand and the metal ion.

The magnetic moments of the lanthanide(III) complexes are consistent the presence of unpaired 4f electrons and close to the values for the free metal ions reported by Van Vleck [18]. These observations suggest that the 4f electrons of the lanthanide(III) do not take part in bond formation in these species.

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 coordination moieties present cannot be replaced by the solvent molecules. The values of these conductances are in the range $198\text{--}222\text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in dmf and are in accordance with those reported for 1:3 electrolytes in this solvent [19]. This is indicative that these complexes dissociate very slightly in this solvent. As observed in the infrared spectra where the compounds were formulated as 1:3 electrolytes with two chloride and one nitrate as counterions, the molar conductivities show that the counterions are not present in the coordination sphere.

Description of the structures

The structure consists of $[\text{Er}_2(\text{H}_4\text{L})_3]^{3+}$ discrete entities, chloride and nitrate anions in the ratio $\text{Cl}/\text{NO}_3=2$. Five non-coordinated water molecule per two Er-containing unit were found. A view of the complete structure is presented in Figure 1 along with the atomic labelling. Each Er atom is nine-coordinated. The ligand is pentadentate with the phenolato oxygen in the central ring acting as a bridge between the two Er(III) ions. The molecules of the ligand are linked to each of Er(III) atoms via one N atom and two O atoms. Thus each Er atom is nine coordinate (Figure 2). The two phenolic oxygen atoms in the benzoyl fragments are not coordinated. In the triple phenolate oxygen bridge holding the two erbium atoms together the mean dihedral angle between the planes defined by O-Er1-O1 and O-Er2-O is 47° . The Er \cdots Er distances is $3.4738(7)\text{ \AA}$. The Er-O bond lengths are in the range $2.289(6)\text{--}2.376(6)\text{ \AA}$ but those to bridging

phenolic O atoms are significantly shorter than the other bond from the metal to the O atom of the hydrazoneic moieties.

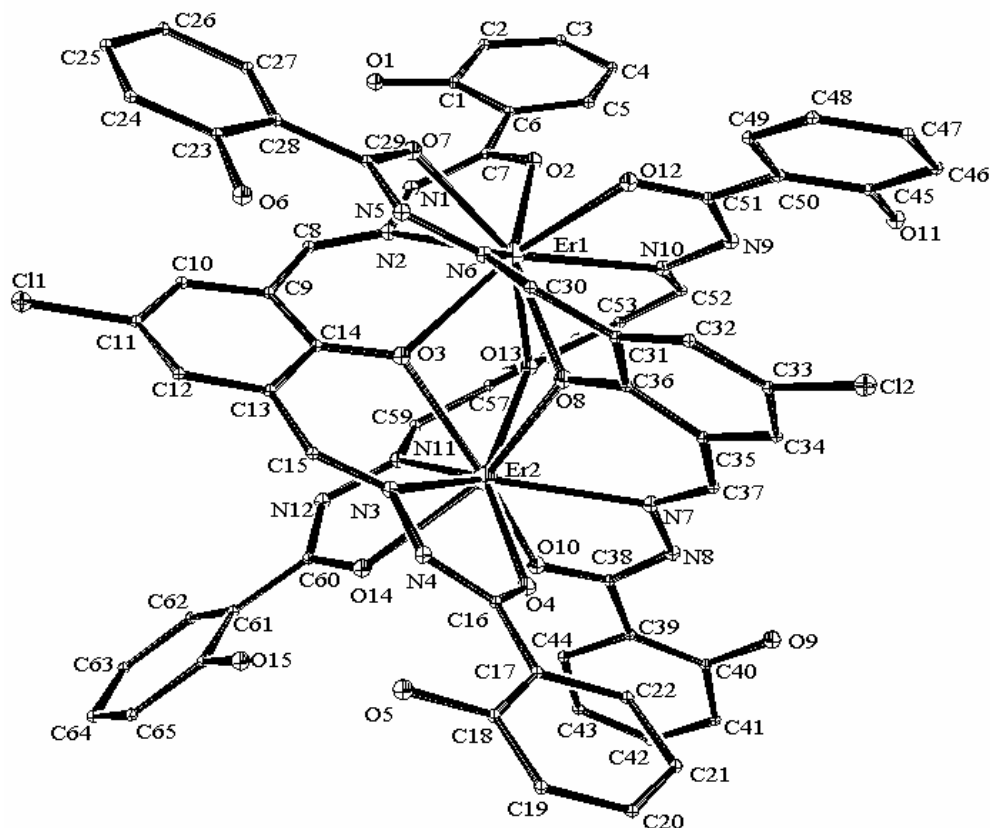


Figure 1. Ortep drawing for $[\text{Er}_2(\text{LH}_4)_3]^{3+}$ with scheme numbering.

All the Er-N bond lengths are in the range 2.564(8)-2.631(8) Å. Structurally characterized nine coordinate Erbium complexes are well known. In the structure of $[\text{Er}(\text{C}_{13}\text{H}_{11}\text{N}_3\text{O})_2(\text{NO}_3)_2]\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ [20] the Er-O distances are in the range 2.361(3)-2.465(3) Å and are similar to those found for the title complex. In the $[\text{Er}_2(\text{LH}_4)_3]\text{Cl}_2\text{NO}_3 \cdot \text{H}_2\text{O}$ complex the Er- $\text{O}_{\text{carbonyl}}$ bond lengths (average 2.342 Å) are similar to the Er- $\text{O}_{\text{phenolic}}$ bond lengths for which the average value is 2.304 Å. The coordination polyhedron around each Er atom can be described as a distorted tricapped trigonal prism formed (e.g. for Er2) by O13, O8, O3 and O4, O10, O14 with capping positions occupied by N3, N7 and N11 atoms (Figure 2). The Er1 center is in the plane formed by the N2, N6 and N10 atoms and the sum of the angles N-Er1-N is 359.9° while the Er2 is in the plane defined by N3, N7 and N11 where the sum of the angles N-Er2-N is 359.6°. Distortions from idealized geometry arise from geometrical constraints due to the rigid structure induced by the three phenolate oxygen bridges between the two Er atoms. These bridging oxygen and the two metal centers form three four-membered ring with Er...Er separation of 3.4738(7) Å and angles of oxygen bridgehead Er1-O3-Er2, Er1-O8-Er2 and Er1-O13-Er2 respectively 97.0(2), 98.0(2) and 98.7(2). The $\text{Er}(\mu\text{-O})_3\text{Er}$ core has close to three-fold symmetry.

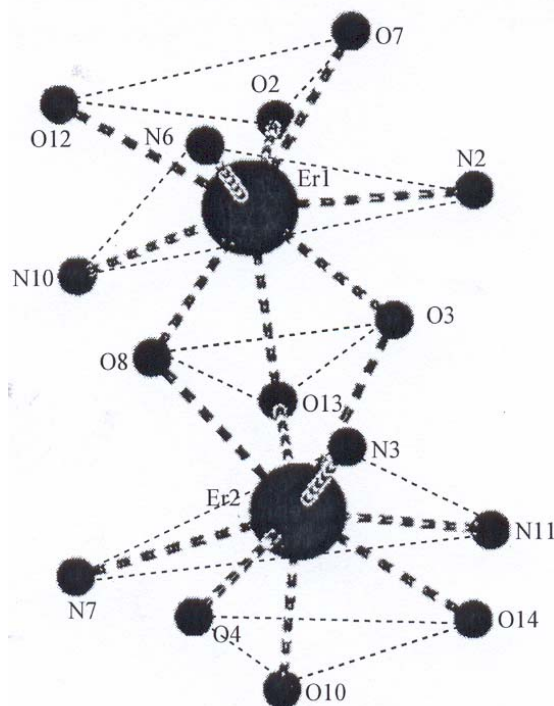


Figure 2. Coordination environment around each Er(III). Coordination polyhedron around the lanthanide ion is described as a tricapped trigonal prism.

According to the infrared and NMR data of the 2,6-diformyl-4-chlorophenol-bis-(benzoylhydrazone) the imine group (O=C–NH) is not transformed into an iminol group in solution as observed in the case of bis-(2,6-diacetylpyridine-bis-(phenylhydrazone)) [11]. In solution the ligand acts with the lanthanide ion in his amide form. In the structure of the erbium complex the C8—N2, C15—N3, C30—N6, C37—N7, C52—N10 and C59—N11 bonds retain their double bond character. All the O–C distances are in the range [1.226(13) to 1.271(12) Å] while the mean N–C distances is 1.277 Å. Selected bond lengths and angles are given in Table 4.

Supplementary material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 237006. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1ZE, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.cam.ac.uk>).

Table 4. Bond lengths [Å] and angles [°] for [Er₂(H₄L)₃]Cl₂(NO₃)₂·5H₂O.

Er(1)-O(13)	2.291(6)	O(13)-Er(1)-O(8)	68.8(2)
Er(1)-O(8)	2.315(6)	O(13)-Er(1)-O(3)	69.6(2)
Er(1)-O(3)	2.322(6)	O(8)-Er(1)-O(3)	69.1(2)
Er(1)-O(12)	2.334(6)	O(13)-Er(1)-O(12)	124.4(2)
Er(1)-O(7)	2.349(7)	O(8)-Er(1)-O(12)	84.7(2)
Er(1)-O(2)	2.362(6)	O(3)-Er(1)-O(12)	143.8(2)
Er(1)-N(6)	2.567(7)	O(13)-Er(1)-O(7)	145.1(2)
Er(1)-N(2)	2.573(8)	O(8)-Er(1)-O(7)	125.4(2)
Er(1)-N(10)	2.586(7)	O(3)-Er(1)-O(7)	85.6(2)
Er(1)-Er(2)	3.4738(7)	N(6)-Er(1)-N(10)	122.6(2)
Er(2)-O(13)	2.289(6)	N(2)-Er(1)-N(10)	118.1(2)
Er(2)-O(8)	2.290(6)	N(6)-Er(1)-N(2)	119.2(2)
Er(2)-O(10)	2.304(7)	O(13)-Er(1)-N(6)	129.5(2)
Er(2)-O(3)	2.317(6)	O(8)-Er(1)-N(6)	65.0(2)
Er(2)-O(4)	2.325(6)	O(3)-Er(1)-N(6)	75.8(2)
Er(2)-O(14)	2.376(7)	O(13)-Er(1)-N(2)	79.0(2)
Er(2)-N(11)	2.564(8)	O(8)-Er(1)-N(2)	132.2(2)
Er(2)-N(7)	2.595(8)	O(3)-Er(1)-N(2)	66.9(2)
Er(2)-N(3)	2.631(8)	O(13)-Er(1)-N(10)	65.4(2)
O(3)-Er(1)-N(10)	131.9(2)	O(8)-Er(1)-N(10)	79.6(2)
O(8)-Er(2)-O(10)	127.2(2)	O(13)-Er(2)-O(10)	87.3(2)
O(8)-Er(2)-O(3)	69.6(2)	O(13)-Er(2)-O(3)	69.7(2)
N(11)-Er(2)-N(7)	123.2(2)	O(10)-Er(2)-O(3)	145.1(2)
N(7)-Er(2)-N(3)	122.0(2)	N(11)-Er(2)-N(3)	114.4(3)

Mean values are given. E.s.d.s. for individual values are shown in parentheses.

No value differs significantly from the mean.

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