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Synthesis and characterization of new lanthanide complexes with hexadentate hydrazonic ligands

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Abstract

In this paper, we report the synthesis and the characterization of a novel series of lanthanide (III) complexes with two potentially hexadentate ligands. The ligands contain a rigid phenanthroline moiety and two flexible hydrazonic arms with different donor atom sets (NNN'N'OO and NNN'N'N"N", respectively for H_2L^1 (2,9-difformylphenanthroline)bis(benzoyl)hydrazone and H_2L^2 (2,9-difformylphenanthroline)bis(2-pyridyl)hydrazone). Both nitrate and acetate complexes of H_2L^1 with La, Eu, Gd, and Tb were prepared and fully characterized, and the X-ray crystal structure of the complex [Eu(HL¹)(CH₃ COO)₂] · 5H₂O is presented. The stability constants of the equilibria $Ln^{3+} + H_2L^1 = [Ln(H_2L^1)]^{3+}$ and $Ln^{3+} + (L^1)^{2-} = [Ln(L_1)]^+$ (Ln = La(III), Eu(III), Gd(III), and Tb(III)) are determined by UV spectrophotometric titrations in DMSO at t = 25 °C. The nitrate complexes of H_2L^2 with La, Eu, Gd and Tb were also synthesized, and the X-ray crystal structures of $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Eu(H_2L^2)(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)(NO_3)_2](NO_3)$ are discussed.

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Keywords: Lanthanide ions; Hydrazones; Hexadentate ligands, crystal structure; Phenantroline derivatives

1. Introduction

Lanthanide complexes have an increasingly important role in medicine, where they are employed as diagnostic as well as therapeutic agents [1]. The peculiar electronic properties of lanthanide ions, in fact, are exploited for the development of powerful NMR probes for medical application [2]; gadolinium(III) complexes are in current clinical use for magnetic resonance imaging [3,4] and lutetium compounds have shown a great potential as radio sensitizer for the treatment of certain types of cancers [5]. The study of the remarkable catalytic activity of the rare earth metals for the hydrolysis of nucleic acids is another active field of research, mainly because it is essential for further developments in biotechnology, molecular biology, therapy and related fields [6-9]. The numerous applications of lanthanide complexes motivate the significant efforts that have been made in recent years to design polydentate ligands for their complexation [10,11]. In particular, many studies have been done on lanthanide complexes with Schiff base macrocycles, due to their high stability [12–14]. Acyclic Schiff bases have not been extensively studied, but they offer the advantage of a flexible cavity size, as some studies regarding pentadentate bis acylhydrazones of 2,6-diacetylpyridine suggest [15–17]. As a part of our ongoing research on the coordination properties of hydrazonic ligands, we recently reported about the chelating abilities of the potentially hexadentate

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(2,9-diformylphenanthroline)bis(benzoyl)hydrazone $(H_2L^1, Scheme 1)$ towards dibutyltin diacetate and diphenyllead dichloride [18]. 2,9-Diformylphenanthroline has been widely employed as a metal-binding component in all aspects of coordination chemistry, but there are few reports about its derivatives, especially as far as hexadentate ligands are concerned [19,20]. This type of ligand mixes the rigidity imposed by the central phenanthroline ring with the flexibility of the hydrazonic arms and presents a cavity large enough to accommodate rare-earth metal ions. The variable and versatile co-ordination behavior of these ions limits their selective introduction into rigid preorganized molecular architectures, and the development of flexible, predisposed receptor with pendant arms that can adapt to the varying size of the lanthanide(III) ions is highly desirable [21].

In this paper, we report the synthesis and characterization of both nitrate and acetate complexes of (2,9-diformylphenanthroline)bis(benzoyl)hydrazone with La, Eu, Gd, and Tb and the crystal structure of the complex $[Eu(HL^{1})(CH_{3}COO)_{2}] \cdot 5H_{2}O$ is presented. The interactions between trivalent lanthanide ions and polydentate nitrogen ligands have attracted great interest in recent years, mainly because of the task of actinide/lanthanide separation in radioactive wastes coming from spent nuclear fuel processing [22]. Rare earth ions of the 4f series are known to be hard acids in the Pearson classification of acids and bases [23]. As a consequence, hard donor ligands such as oxygen donors are expected to be preferred to soft S or N donor ligands. Nevertheless, numerous studies have shown that lanthanide ions form significantly stable complexes when a multidentate nitrogen ligand is appropriately chosen [24-26]. Therefore, the hexadentate $N_2N'_2N''_2$ ligand (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone (H_2L^2 , Scheme 1) was also synthesized and characterized, together with the nitrate series of its Ln(III) (Ln = La, Eu, Gd, Tb) complexes; in particular, the X-ray structures of the complexes $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Eu(H_2L^2)-(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)(NO_3)_2](NO_3)$ are also discussed.

2. Experimental

2.1. General

All reagents of commercial quality were used without further purification. ¹H NMR spectra were recorded at 27 °C on a Bruker 300 FT spectrophotometer by using SiMe₄ as internal standard, while IR spectra were obtained with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm⁻¹ range, using KBr disks. Elemental analyses were performed by using a Carlo Erba Model EA 1108 apparatus. 2,9-Diformyl-1,10-phenanthroline (DFF) and H₂L¹ were made according to the literature methods [18,27].

2.2. Synthesis

2.2.1. H_2L^2

A solution of 2-pyridylhydrazine (0.23 g, 2.1 mmol) in methanol (20 ml) was added to a refluxing solution of DFF (0.25 g, 1.05 mmol) in the same solvent (75 ml). After few minutes, a brown precipitate appeared. The solution was refluxed for additional 2 h. After cooling, the precipitate was filtered off and washed with methanol. Yield: 64%; m.p. = 211–213 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): δ = 6.86 (t, $J_{H,H}$ = 7 Hz; 2H, H₇); 7.43 (d, $J_{H,H}$ = 8 Hz, 2H, H₅); 7.72 (d, $J_{H,H}$ = 7 Hz; 2H, H₆); 7.95 (s, 2H, H₁); 8.19 (d,



Scheme 1. The potentially hexadentate ligands (2,9-diformylphenanthroline)bis(benzoyl)hydrazone (H_2L^1) and (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone (H_2L^2).

 $J_{\text{H,H}} = 5$ Hz, 2H, H₈); 8.35 (d, $J_{\text{H,H}} = 8$ Hz; 2H, H₃); 8.45 (m, 4H, H₂ + H₄); 10.41 (s, 2H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{\text{NH}} = 3268$; $v_{\text{C}=\text{N}} = 1573$. MS– CI (pos. ions): m/z 420 [MH⁺, 100]. Anal. Calc. for $C_{28}H_{20}N_6O_2 \cdot 3H_2O$: C, 63.90; H, 4.93; N, 15.95. Found: C, 64.04; H, 4.69; N, 15.62%.

2.2.2. $[La(HL^{1})(CH_{3}COO)_{2}] \cdot 2H_{2}O$

The ligand (0.08 g, 0.16 mmol) was dissolved in warm ethanol (50 ml). After addition of the metal salt (0.053 g, 0.16 mmol), the solution turned from brown to intense yellow. After refluxing for 4 h, the solution was concentrated and diethyl ether added: a yellow powder precipitated, which was filtered off and washed with ether. Yield: 61%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): $\delta = 1.56$ (s, 6H, CH₃COO); 7.49 (m, 6H, H₆ + H₇); 8.03 (s, 2H, H₁); 8.08 (d, $J_{\rm H, H} = 8$ Hz; 2H, H₃); 8.30 (m, 4H, H₅); 8.65 (s, 2H, H₄); 8.70 (d, $J_{\rm H, H} = 8$ Hz; 2H, H₂). IR (cm⁻¹): $v_{\rm OH} = 3414$; $v_{\rm NH} \approx 3200$ br; $v_{\rm C-O} = 1545$; $v_{\rm C=O(acet)} = 1437$, 1355. *Anal.* Calc. for C₃₂H₂₅LaN₆O₆ · 2H₂O: C, 50.26; H, 3.92; N, 10.99. Found: C, 50.39; H, 3.66; N, 10.73%.

The other complexes are synthesized by using the same procedure, with the appropriate metal salt.

2.2.3. $[Eu(HL^{1})(CH_{3}COO)_{2}] \cdot 3H_{2}O$

Yield: 52%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): δ = 2.69 (s, br); 5.46–5.55 (m, br); 5.80 (s, br); 6.19 (s, br). IR (cm⁻¹): v_{OH} = 3425; $v_{NH} \approx$ 3200, br; v_{C-O} = 1548; $v_{C=O(acet)}$ = 1438, 1360. *Anal.* Calc. for C₃₂H₂₅EuN₆O₆ · 3H₂O: C, 48.31; H, 3.72; N, 10.55. Found: C, 48.14; H, 3.46; N 10.30%.

2.2.4. $[Gd(HL^{1})(CH_{3}COO)_{2}] \cdot 2H_{2}O$

Yield: 54%; m.p. >300 °C. IR (cm⁻¹): v_{OH} = 3380; $v_{NH} \approx 3200$, br; v_{C-O} = 1550; $v_{C-O(acet)}$ = 1437, 1380. *Anal.* Calc. for C₃₂H₂₅GdN₆O₆ · 2H₂O: C, 49.09; H, 3.73; N, 10.74. Found: C, 49.23; H, 3.47; N 10.80%.

2.2.5. $[Tb(HL^1)(CH_3COO)_2] \cdot 5H_2O$

Yield: 66%; m.p. >300 °C. IR (cm⁻¹): v_{OH} = 3401; v_{NH} = 3218, br; v_{C-O} = 1552; $v_{C=O(acet)}$ = 1455, 1369. *Anal.* Calc. for C₃₂H₂₅N₆O₆Tb · 5H₂O: C, 45.94; H, 3.97; N, 10.04. Found: C, 46.07; H, 3.71; N, 10.13%.

2.2.6. $[La(H_2L^1)(NO_3)_2](NO_3)(C_2H_6O)$

Yield: 47%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): δ = 7.56–7.65 (m, 6H, H₆ + H₇); 7.97 (d, $J_{\rm H, H}$ = 8 Hz, 4H, H₅); 8.28 (m, 4H, H₁ + H₃); 8.58 (d, $J_{\rm H, H}$ = 8 Hz; 2H, H₂); 9.01 (s, 2H, H₄); 9.70 (s, 2 H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{\rm OH}$ = 3420; $v_{\rm NH}$ = 3201; $v_{\rm C=O}$ = 1639; $v_{\rm NO2(sym)}$ = 1465; $v_{\rm NO3(ionic)}$ = 1383; $v_{\rm NO2(asym)}$ = 1297. *Anal.* Calc. for C₂₈H₂₀La-N₉O₁₁ · C₂H₆O: C, 42.72; H, 3.10; N, 14.93. Found: C, 42.78; H, 2.65; N, 15.24%.

2.2.7. $[Eu(H_2L^1)(NO_3)_2](NO_3) \cdot 2H_2O$

Yield: 65%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): δ = 7.56–7.65 (m, 6H, H₆ + H₇); 7.97 (d, $J_{\rm H, H}$ = 7 Hz, 4H, H₅); 8.08 (s, 2H, H₁); 8.39 (d, br; 2H, H₃); 8.58 (d, $J_{\rm H, H}$ = 8 Hz; 2H, H₂); 8.84 (s, 2H, H₄); 9.71 (s, 2H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{\rm OH}$ = 3419; $v_{\rm NH}$ = 3162; $v_{\rm C=O}$ = 1623; $v_{\rm NO2}(_{\rm sym})$ = 1497; $v_{\rm NO3}({\rm ionic})$ = 1377; $v_{\rm NO2}(_{\rm asym})$ = 1301. *Anal.* Calc. for $C_{28}H_{20}EuN_9O_{11} \cdot 2H_2O$: C, 39.74; H, 2.83; N, 14.88. Found: C, 39.50; H, 2.55; N, 14.45%.

2.2.8. $[Gd(H_2L^1)(NO_3)_2](NO_3) \cdot 2H_2O$

Yield: 71%; m.p. >300 °C. IR (cm⁻¹): v_{OH} = 3417; v_{NH} = 3134; $v_{C=O}$ = 1615; NO2(sym) = 1498; $v_{NO3(ionic)}$ = 1384; $v_{NO2(asym)}$ = 1302. *Anal.* Calc. for $C_{28}H_{20}GdN_9O_{11} \cdot 2H_2O$: C, 39.49; H, 2.81; N, 14.79. Found: C, 39.50; H, 2.46; N, 14.29%.

2.2.9. $[Tb(H_2L^1)(NO_3)_2](NO_3) \cdot H_2O$

Yield: 63%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): δ = 7.57–7.66 (m, 6H, H₆ + H₇); 7.98 (d, $J_{\rm H, H}$ = 6 Hz, 4H, H₅); 8.09 (s, 2H, H₁); 8.38 (d, $J_{\rm H, H}$ = 8 Hz; 2H, H₃); 8.60 (d, $J_{\rm H, H}$ = 8 Hz; 2H, H₂); 8.84 (s, 2H, H₄); 12.28 (s, 2 H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{\rm OH}$ = 3419; $v_{\rm NH}$ = 3175; $v_{\rm C=O}$ = 1614; $v_{\rm NO2(sym)}$ = 1493; $v_{\rm NO3(ionic)}$ = 1384; $v_{\rm NO2(asym)}$ = 1302. *Anal.* Calc. for C₂₈ H₂₀N₉O₁₁Tb · H₂O: C, 40.28; H, 2.65; N, 15.09. Found: C, 40.43; H, 2.40; N, 15.11%.

2.2.10. $[La(H_2L^2)(NO_3)_2](NO_3)$

The ligand (0.08 g, 0.19 mmol) was dissolved in warm THF (50 ml). After addition of the metal salt (La(- NO_3 ₃ · 6H₂O, 0.060 g, 0.19 mmol), the solution turned from brown to intense yellow and a precipitate occurred within few minutes. The reaction mixture was stirred at reflux for additional 2 h, the yellow-brown powder was filtered off and washed with ether. Yield: 67%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆]DMSO, 25 °C): $\delta = 6.88$ (t, $J_{H, H} = 6$ Hz, 2H, H₇); 7.43 (d, $J_{H, H} = 8$ Hz, 2H, H₅); 7.75 (t, $J_{H,H} = 8$ Hz, 2H, H₆); 7.97 (s, 2H, H₁); 8.20 (d, $J_{H, H} = 6$ Hz, 2H, H₈); 8.38 (d, 2H, $J_{\rm H, H} = 8$ Hz, H₃); 8.44–8.49 (s + d, 4H, H₄ + H₂); 10.38 (s, 2H, N–H, exchange with D_2O). IR (cm⁻¹): $v_{\text{OH}} = 3456; v_{\text{NH}} = 3233; v_{\text{NO2(sym)}} = 1485; v_{\text{NO3(ionic)}} =$ 1384; $v_{NO2(asym)} = 1292$. Anal. Calc. for $C_{24}H_{18}La$ -N₁₁O₉: C, 38.78; H, 2.44; N, 20.71. Found: C, 38.65; H, 2.35; N, 20.46%.

2.2.11. $[Eu(H_2L^2)(NO_3)_2](NO_3)$

Yield: 72%; m.p. >300 °C. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): $\delta = 6.90$ (t, $J_{H, H} = 6$ Hz, 2H, H_7); 7.44 (d, $J_{H, H} = 8$ Hz, 2H, H_5); 7.77 (t, $J_{H, H} = 8$ Hz, 2H, H_6); 7.98 (s, 2H, H_1); 8.20 (d, $J_{H, H} = 6$ Hz, 2H, H_8); 8.39 (d, 2H, $J_{H, H} = 8$ Hz, H_3); 8.46–8.50 (s + d, 4H, $H_4 + H_2$); 10.32 (s, 2H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{OH} = 3410$; $v_{NH} = 3265$; $v_{NO2(sym)} = 1486$; $v_{\text{NO3(ionic)}} = 1383; v_{\text{NO2(asym)}} = 1292.$ Anal. Calc. for $C_{24}H_{18}\text{EuN}_{11}O_9$: C, 38.11; H, 2.39; N, 20.36. Found: C, 37.95; H, 2.63;, N, 20.15%.

2.2.12. $[Gd(H_2L^2)(NO_3)_2](NO_3)$

Yield: 76%; m.p. >300 °C. IR (cm⁻¹): v_{OH} = 3404; v_{NH} = 3274; $v_{NO2(sym)}$ = 1486; $v_{NO3(ionic)}$ = 1383; $v_{NO2(asym)}$ = 1291. *Anal.* Calc. for C₂₄H₁₈GdN₁₁O₉: C, 37.84; H, 2.38; N, 20.21. Found: C, 37.86; H, 2.22; N, 20.67%.

2.2.13. $[Tb(H_2L^2)(NO_3)_2](NO_3) \cdot 3/2H_2O$

Yield: 68%. ¹H NMR (300 MHz, [D₆] DMSO, 25 °C): $\delta = 6.86$ (t, br, 2H, H₇); 7.44 (d, br, 2H, H₅); 7.73 (t, br, 2H, H₆); 7.97 (s, 2H, H₁); 8.18 (d, br, 2H, H₈); 8.38 (d, 2H, J_{H, H} = 8 Hz, H₃); 8.46 (m, 4H, H₄ + H₂); 10.44 (s, 2H, N–H, exchange with D₂O). IR (cm⁻¹): $v_{OH} = 3426$; $v_{NH} = 3274$; $v_{NO2(sym)} = 1486$; $v_{NO3(ionic)} = 1384$; $v_{NO2(asym)} = 1286$. *Anal.* Calc. for C₂₄H₁₈N₁₁O₉Tb · 1.5H₂O: C, 36.47; H, 2.67; N, 19.48. Found: C, 36.51; H, 2.33; N 19.32%.

2.3. X-ray Crystallography

Single crystals of $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Ln(H_2L^2)(NO_3)_2](NO_3)$ (Ln = Eu, Tb) and $[Eu(HL^1)$ $(CH_{3}COO)_{2}] \cdot 5H_{2}O$ suitable for X-ray structure analysis were obtained by slow evaporation of the mother liqueur. For $[Ln(H_2L^2)(NO_3)_2](NO_3)$ (Ln = Eu, Tb), cell dimensions and diffraction intensities were measured at room temperature on a Philips PW 1100 diffractometer, using graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Both the crystal structures are described by the triclinic system and the systematic absences allowed to identify the correct space group as $P\overline{1}$. The unit-cell dimensions were obtained from the setting angles of 24 reflections with $\theta > 8^{\circ}$ for Tb and $\theta > 10^{\circ}$ for Eu complex. Crystal decay resulted negligible in both cases. The intensity data were corrected for Lorentz, polarization and absorption effects using psiscan technique. X-ray diffraction data for $[La(H_2L^2) (NO_3)_2(H_2O)](NO_3)$ and $[Eu(HL^1)(CH_3COO)_2] \cdot 5H_2O$ were collected at room temperature on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated Mo Ka radiation. Data were corrected for absorption effects by the SADABS [28] procedure. The phase problem was solved by direct methods [29] and refined by full matrix least squares on all F^2 [30] by using the WinGX package [31]. Anisotropic displacement parameters were refined for all non hydrogen atoms, except for O4w and O5w in the Eu acetate complex and for the uncoordinated nitrate ions in all the nitrate complexes, since they show very high thermal motions and were therefore refined isotropically. In $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, only the metal, the nitrogens, the oxygens and the carbons involved in the chelation rings were refined anisotropically. Hydrogen atoms were partly located from difference Fourier maps and refined isotropically and were partly introduced in idealized positions. Details of data collection and structure refinement are summarized in Table 1.

2.4. UV–Vis measurements and calculations

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer by using match cells of 1 cm pathlength. Stock solution of H_2L^1 and Na_2L^1 (ca. 2.5×10^{-3} M) and of the metal nitrates (ca. 1.0×10^{-2} M) in DMSO was prepared and used within 2 days. Absorption spectra of H_2L^1 and Na_2L^1 were registered using a ca. 1.5×10^{-5} M solution that is prepared by dilution of the stock solution; the same solution was employed for the complexation studies. Each metal/ligand system was studied by titrating a 10 ml sample of the ligand solution with the metal stock solution; 8–12 spectra of samples with M:L molar ratio ranging from 0 to 1.5 are measured. The stability constants were calculated by means of the PSEQUAD program [32]. All titrations were performed twice in order to ensure the reproducibility of the data.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

The hydrazonic ligand H_2L^1 (Scheme 1) was synthesized, following a strategy previously described [18]. H_2L^2 was analogously prepared by condensation of 2,9-diformylphenanthroline and 2-pyridylhydrazine. In both cases, the spectroscopic characterization does not show any remarkable aspects: in solution, the ligands show C_{2v} symmetry and, accordingly, only one set of signals is present in their ¹H NMR spectrum.

The acetate complexes of H_2L^1 were obtained by adding the metal salts (Ln(III) = La, Eu, Gd, Tb) to a refluxing solution of the ligand in methanol: the complexes were isolated as air stable solids after partial removal of the solvent. In all cases, the IR spectrum shows a weak absorption around 3200 cm^{-1} , attributable to the presence of the NH group, suggesting that the ligand is not completely deprotonated. A partial deprotonation of the ligand is supported by a peak around 1550 cm⁻¹, which is characteristic of the phenolic C-O stretching mode [33], while a shoulder at 1635 cm^{-1} is assignable to the coordinated C=O of the still protonated hydrazonic arm (1682, 1653 cm⁻¹ in the free ligand). The coordinated acetate groups are confirmed by two bands at around 1435 and 1360 cm^{-1} ($\Delta \cong 75 \text{ cm}^{-1}$), which are diagnostic for a bidentate chelating acetate [34,25]. Eu and Tb complexes show Table 1

Crystal data and structure refinement for $[Ln(H_2L^2)(NO_3)_2](NO_3)$ (Ln = Eu, Tb), $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, and $[Eu(HL^1)(CH_3 COO)_2] \cdot 5H_2O$

Identification code	$[Tb(H_2L^2)(NO_3)_2](NO_3)$	$[Eu(H_2L^2)(NO_3)_2](NO_3)$	$[La(H_2L^2)(H_2O)(NO_3)_2](NO_3)$	$\begin{bmatrix} Eu(HL^1)(CH_3COO)_2 \end{bmatrix} \cdot 5H_2O$
Empirical formula	C ₂₄ H ₁₈ N ₁₁ O ₉ Tb	C24H18EuN11O9	C ₂₄ H ₂₀ LaN ₁₁ O ₁₀	C ₃₂ H ₂₅ EuN ₆ O ₁₁
Formula weight	762.41	756.45	761.31	821.54
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	$P2_1/c$
Unit cell dimensions				
a (Å)	11.317(5)	11.310(3)	20.133(2)	8.574(1)
b (Å)	13.000(7)	12.994(10)	27.187(3)	27.362(4)
<i>c</i> (Å)	9.796(3)	9.802(5)	12.010(1)	17.204(2)
α (°)	100.98(3)	101.01(5)		
β (°)	100.88(4)	100.63(8)	121.72(1)	93.66(1)
γ (°)	93.57(3)	93.89(8)		
Volume (Å ³)	1382(1)	1382(2)	5592(1)	4028(1)
Ζ	2	2	8	4
Density (calculated) (Mg/m ³)	1.835	1.818	1.804	1.335
Absolute coefficient (mm ⁻¹)	2.634	0.710	1.606	1.615
<i>F</i> (000)	752	532	3008	1640
θ Range (°)	3.11-28.10	3.11-30.02	1.86-30.63	1.90-26.59
Index ranges	$-14 \leqslant h \leqslant 14$,	$-15 \leqslant h \leqslant 15$,	$-26 \leqslant h \leqslant 26$,	$0 \leq h \leq 10,$
	$-16 \leq k \leq 16$,	$-17 \leqslant k \leqslant 11,$	$-37 \leqslant k \leqslant 37$,	$0 \leqslant k \leqslant 34$,
	$-12 \leq l \leq 12$	$-13 \leq l \leq 13$	$-17 \leq l \leq 17$	$-21 \leqslant l \leqslant 21$
Reflection collected/unique	6652/6652	8042/5158	21,368/7769	4814/4727
Data/restraints/parameters	6652/0/464	8042/0/464	7769/6/282	4727/0/442
Goodness-of-fit on F^2	1051	0.867	0.742	1.295
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0697, wR_2 = 0.1157$	$R_1 = 0.0441, wR_2 = 0.0934$	$R_1 = 0.0675, wR_2 = 0.1410$	$R_1 = 0.0686, wR_2 = 0.1692$
R indices (all data)	$R_1 = 0.1348, wR_2 = 0.1370$	$R_1 = 0.0811, wR_2 = 0.1042$	$R_1 = 0.2502, wR_2 = 0.1912$	$R_1 = 0.0686, wR_2 = 0.1692$
Largest difference peak and hole (e $Å^{-3}$)	0.968; -0.967	1.826; -2.215	1.645; 0.757	1.874; 1.072

very broad ¹H NMR signals and a significant shift to higher fields of the aromatic protons with respect to the diamagnetic La complex. The spectrum of the La compound shows that the symmetry of the ligand is maintained in the complex. As a consequence of the coordination, the protons in position (5) (Scheme 1) are deshielded versus the free ligand and an analogous shift to lower fields can be observed for the phenanthroline protons in position (2). From the spectroscopic data, it is possible to conclude that H_2L^1 is monodeprotonated and $N_2N'_2O_2$ hexadentate; the coordination sphere of the metal ions is completed by two bidentate acetate anions. The stoichiometries of the complexes are confirmed by the elemental analysis. Finally, crystals of [Eu(HL¹)(CH₃COO)₂] · 5H₂O suitable for X-ray analysis were obtained by slow evaporation of the mother liqueur (see Section 3.2).

The corresponding nitrate complexes were obtained by an analogous procedure. In this case, the deprotonation of H₂L¹ does not occur (in the IR spectra, v(N-H) 3200 cm⁻¹; in the ¹H NMR spectra, $\delta(N-H)$ in the 10–12 ppm range); the absorptions of the asymmetric and symmetric stretching modes of the bidentate covalent nitrates are visible around 1490 and 1300 cm⁻¹, respectively, while the anionic nitrates are near 1384 cm⁻¹. Upon coordination, the carbonyl group absorption shifts to 1615–1630 cm⁻¹ (1682–1653 cm⁻¹ in the free ligand). In conclusion, also H_2L^1 still behaves as hexadentate, the coordination of the metal being completed by two bidentate nitrate groups; an ionic nitrate assures the neutrality of the system.

In order to investigate the coordination properties of a similar hexadentate ligand, the nitrate complexes of La, Eu, Gd and Tb with the ligand H_2L^2 were prepared. Attempts to isolate the acetate analogs were unsuccessful, probably because of the presence of side reactions and the formation of different chemical species. On the contrary, the reaction between the metal nitrate and a refluxing solution of H₂L² in THF leads to the corresponding compounds with general formula $[Ln(H_2L^2)(NO_3)](NO_3)$. Elemental analysis and spectroscopic data (see Section 2) led us to conclude that the ligand is neutral and coordinates the metal by means of the phenanthroline, imine and pyridine nitrogen atoms; as in the H_2L^1 nitrate complexes, the coordination sphere of the metal ion is completed by two bidentate nitrates, while an ionic nitrate assures the neutrality of the system. Crystals of $[La(H_2L^2)(NO_3)_2 (H_2O)](NO_3)$, $[Eu(H_2L^2)(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)-$

 $(NO_3)_2](NO_3)$ suitable for X-ray analysis were obtained by slow evaporation of the mother liqueur and their crystal structure is discussed below (see Section 3.2).

stability constants for the complexes The $[Ln(H_2L^1)]^{3+}$ and $[Ln(L^1)]^+$ (Ln = La(III), Eu(III), Gd(III), Tb(III)) are determined by UV spectrophotometric titrations in DMSO and their values are reported in Table 2. DMSO is required because of the poor solubility of the ligands. The speciation model that gives the best fitting of the experimental data involves only one complex species with 1:1 metal:ligand molar ratio; this is supported also by the presence of an isosbestic point in each studied system. It is known [16] that the pentadentate ligand 2,6-diacetylpyridine bis(p-nitrobenzoylhydrazone) gives with gadolinium(III) a 1:2 M:L complex, so, alternative models with additional species (i.e., $[Ln_2(L^1)]$, $[Ln(L^1)_2]$, etc.) were considered, but they gave worse fitting of the experimental data. The exclusive presence of species with a 1:1 metal:ligand molar ratio can be correlated to the rigidity of the ligand, to the dimensions of its cavity and to its capability of chelating the metal ions with six donor atoms. In both series of spectra (Ln(III)/H₂L¹ and Ln(III)/L₁²⁻), the absorption in the region 400-500 nm increases as the metal concentration increases. The opposite trend is observed in the range 300-370 nm, where an isosbestic point is present close to 375 nm. The spectroscopic behavior is very similar for all four lanthanide cations. In Figs. 1 and 2, the experimental spectra for the titration of $Tb(III)/H_2L^1$ and $Tb(III)/(L^{1})^{2-}$ are reported. The values of the stability constants show that all the complexes have almost the same stability, starting from the neutral ligand; on the contrary, with the deprotonated ligand $(L^1)^{2-}$, very different values were obtained for the different cations. The log β trend (Eu³⁺ < Gd³⁺ < Tb³⁺) could be explained in terms of an increased charge/radius ratio, but the La³⁺ value is not easily interpreted just taking into account this parameter.

3.2. X-ray Crystallography

The molecular structures of the complexes $[Eu(HL^1)(CH_3 COO)_2] \cdot 5H_2O$ and $[La(H_2L^2)(NO_3)_2-(H_2O)](NO_3)$ are shown in Figs. 3 and 4, respectively. The nitrate complexes $[Eu(H_2L^2)(NO_3)_2](NO_3)$ and

Table 2 Logarithm of the stability constants for the equilibria $Ln^{3+} + H_2L^1 = [Ln(H_2L^1)]^{3+}$ and $Ln^{3+} + (L^1)^{2-} = [Ln(L_1)]^+$ (Ln = La(III), Eu(III), Gd(III), Tb(III)), in DMSO at t = 25 °C

	$[Ln(H_2L^1)]^{3+}$	$[Ln(L^1)]^+$	
La ³⁺	5.85(11)	6.56(4)	
Eu ³⁺	6.03(12)	4.53(4)	
Gd ³⁺	6.48(9)	5.08(9)	
Tb ³⁺	6.00(6)	7.24(11)	

Standard deviations are given in parentheses.



Fig. 1. Experimental spectra of the titration of H_2L^1 $(1.48 \times 10^{-5} \text{ mol dm}^{-3})$ with a solution of Tb(NO₃)₃ · 5H₂O (Tb³⁺: H₂L¹ ratio from 1:10 to 15:10).



Fig. 2. Experimental spectra of the titration of L_1^{2-} $(1.47 \times 10^{-5} \text{ mol dm}^{-3})$ with a solution of Tb(NO₃)₃ · 5H₂O (Tb³⁺: L_1^{2-} ratio from 1:10 to 15:10).

 $[Tb(H_2 L^2)(NO_3)_2](NO_3)$ are isostructural; the crystal structure of the former is presented in Fig. 5. The most relevant bond distances and angles are shown in Table 3.

The crystal structure of the acetate complex [Eu-(HL¹)(CH₃COO)₂] \cdot 5H₂O (Fig. 3) confirms that only one arm of the ligand is deprotonated, a situation already found in some bis-acylhydrazonic complexes of 2,6-diacetylpyridine [35]. The ligand acts as hexadentate through the phenanthroline and imine nitrogen atoms and the acylhydrazonic oxygens. The coordination of the metal center is completed by two bidentate acetate ions. The complex crystallizes with five water molecules in the asymmetric unit and one of these forms an hydrogen bond with N1 (N1...O2w 2.832(16) Å; H1...O2w 2.014(13) Å; and N1–H1^{...}O2w 158.7(7)°). As it will be found also in the complexes of H₂L², the two flexible arms of H₂L¹ are folded in order to embrace the cation. The hydrazonic chains form with the planar phenanthr-



Fig. 3. ORTEP drawing of the complex $[Eu(HL^1)(CH_3COO)_2] \cdot 5H_2O$ with the atom-labeling scheme. Hydrogens, with the exception of the hydrazone one, and water molecules are omitted for clarity.



Fig. 4. ORTEP drawing of the complex $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$ with the atom-labeling scheme. Hydrogens, with the exception of the hydrazone ones, are omitted for clarity.

oline moiety a dihedral angle of 12.3(3) and 9.0(3)°, respectively; the deviations from the mean plane of the six donor atoms are maximum for O1 (0.591(9) Å) and O2 (-0.445(8) Å). Table 3 shows the most important bond lengths and angles for the complex: the Eu– O distances (2.454(8) and 2.476(7) Å) are shorter than the Eu–N ones (ranging from 2.652(10) to 2.701(10) Å), as can be expected for a hard oxygen donor bounded to a f-lanthanide ion. In the previously reported [18] dibutyltin and diphenyllead complexes of H₂L¹, the metal– N(imino) bond distances are remarkably shorter than the metal–N(phenanthroline) ones (2.696(2) and 2.678(4) versus 2.936(5) and 2.905(3) Å for Pb and Sn,



Fig. 5. ORTEP drawing of the complex $[Eu(H_2L^2)(NO_3)_2](NO_3)$. Hydrogens, with the exception of the hydrazone ones, are omitted for clarity.

respectively), while in $[Eu(HL^1)(CH_3COO)_2] \cdot 5H_2$ O the four metal-nitrogen distances are similar.

In $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Eu(H_2L^2)(NO_3)_2]$ (NO_3) and $[Tb(H_2L^2)(NO_3)_2](NO_3)$, the ligand H_2L^2 is neutral and hexadentate, through the phenanthroline, imine and pyridine nitrogens. In the coordination sphere of the Eu and Tb ions, there are two bidentate nitrate groups (Fig. 5); in the case of the lanthanum ion, there are one water molecule, one bidentate nitrate and one nitrate that is intermediate between unidentate and bidentate (La–O4N = 2.833(7), La–O5N = 2.647(7) Å) (Fig. 4). The lengthening of the La-O4N distance can be due to a significant steric crowding of the coordinated water molecule that shows the shortest bond length (2.531(6) Å) [36]. The coordination number is 10 for europium and terbium and 11 for lanthanum. In all cases, another nitrate, disordered on two positions, is out of the coordination sphere of the metal. In [Eu- $(H_2L^2)(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)(NO_3)_2](NO_3)$, the mean distance between the metal and the six nitrogen donors is 2.627(11) and 2.610(14) Å, respectively, while the mean distance between the metal and the four oxygen atoms of the bidentate nitrate groups is 2.470(7)and 2.450(10) Å. These values are consistent with the ones found in $[Tb(tpen)(NO_3)_2](NO_3) \cdot 3H_2O$ (tpen, hexadentate ligand, tetrakis(2-pyridyl-methyl)-1,2-ethylenediamine), where the Tb–N and Tb–O bond lengths are 2.624(29) and 2.492(33) Å, respectively [37]. In [La $(\text{tpen})(\text{NO}_3)_2$ (NO₃) · 3H₂O [37], the mean distance La-N (2.720(21) Å) is similar to the one we found in $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3) \cdot (2.712(12) A)$, while the La-O mean distance is slightly shorter (2.587(13) versus 2.665(30) Å). The bond distances between the metal center and the nitrogen donors increase in the order

Table 3

Most relevant bond distances (Å) and angles (°) for the complexes $[Tb(H_2L^2)(NO_3)_2](NO_3)$, $[Eu(H_2L^2)(NO_3)_2](NO_3)$, $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, and $[Eu(HL^1)(CH_3COO)_2] \cdot 5H_2O$

	[Tb(H ₂ L ²)(NO ₃) ₂](NO ₃)	$[Eu(H_2L^2)(NO_3)_2](NO_3)$	[La(H ₂ L ²)(NO ₃) ₂ (H ₂ O)](NO ₃)	$[Eu(HL^1)(CH_3COO)_2] \cdot 5H_2O$
Me–N1	2.668(7)	2.683(5)	2.727(8)	
Me-N3	2.632(7)	2.636(4)	2.697(8)	2.619(9)
Me-N4	2.579(6)	2.607(4)	2.673(8)	2.659(9)
Me-N5	2.580(7)	2.599(4)	2.714(8)	2.697(9)
Me-N6	2.593(6)	2.617(4)	2.705(9)	2.661(9)
Me–N8	2.625(7)	2.651(5)	2.767(9)	
Me-Oln	2.447(7)	2.472(4)	2.724(7)	
Me-O2n	2.431(6)	2.455(4)	2.625(7)	
Me-O4n	2.446(7)	2.466(4)	2.833(7)	
Me-O5n	2.475(6)	2.488(4)	2.647(7)	
Me-O1w			2.531(7)	
Me-O1				2.454(8)
Me-O2				2.476(7)
Me–O1a				2.505(8)
Me-O2a				2.461(8)
Me-O3a				2.486(8)
Me–O4a				2.486(8)
N1-Me-N3	59.4(2)	59.5(1)	58.7(3)	
N3-Me-N4	61.1(2)	61.1(1)	60.2(3)	60.3(3)
N4–Me–N5	62.9(2)	62.2(1)	60.7(3)	61.0(3)
N5-Me-N6	61.5(2)	60.9(1)	59.0(3)	59.5(3)
N6-Me-N8	60.4(2)	60.3(1)	58.5(3)	
O1-Me-N3	× /	~ /	· /	60.2(3)
O2-Me-N6				60.0(3)

Tb <Eu <La and N(phenanthroline) < N(imine) < N(pyridine). The two flexible arms of the ligand are not coplanar and form an angle of 34.2(1)° for Tb and Eu complexes and 23.4(2)° for La. In all the complexes, the nitrogen atoms deviate from the planarity, with N3, N4 and N8 above, and N1, N5, and N6 below the mean plane. In all the complexes the nitrogen atoms deviate from the planarity, with N3, N4, and N8 above, and N1, N5, and N6 below the mean plane. In the Eu and Tb complexes, the two bidentate nitrates are nearly perpendicular to the ligand plane (177.9(2) av.).

4. Supplementary material

CCDC Nos. 235438-235441 contain the supplementary crystallographic data. They can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam. ac.uk.

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