

Dinuclear lanthanide(III) complexes from the use of di-2-pyridyl ketone: Preparation, structural characterization and spectroscopic studies

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Abstract

The use of di-2-pyridyl ketone ((py)₂CO) in lanthanide(III) chemistry has yielded neutral dinuclear complexes. The 1:1:1 Ln(NO₃)₃ · xH₂O/(py)₂CO/LiOH · H₂O reaction mixtures in MeOH–EtOH afford the complexes [Ln₂(NO₃)₃{(py)₂C(OMe)O}₂{(py)₂C(OH)O}] (Ln = Pr, **1**; Ln = Eu, **2**; Ln = Tb, **3**; Ln = Er, **4**). The monoanionic derivatives of the hemiacetal and the *gem*-diol forms of di-2-pyridyl ketone have been derived from the Ln(III)-mediated addition of solvent (MeOH, H₂O involved in the alcohols and in the starting materials) on the carbonyl group of (py)₂CO. The crystal structure of the representative complex **4** · 0.8EtOH · 0.4MeOH has been solved by single-crystal X-ray crystallography. The two Er^{III} atoms are doubly bridged by the deprotonated oxygen atoms of the η¹:η²:η¹:μ₂ (py)₂C(OH)O[−] ligand and one η¹:η²:η¹:μ₂ (py)₂C(OMe)O[−] ion. One Er^{III} atom is in a nine-coordinate tricapped trigonal prismatic ligand environment comprising the two bridging hydroxyl oxygen atoms, four oxygen atoms from two chelating nitrate ligands and three 2-pyridyl nitrogen atoms, while dodecahedral, eight-coordination at the other Er^{III} atom is completed by two oxygen atoms of the third chelating nitrate ligand, one nitrogen atom of the bridging (py)₂C(OMe)O[−] ligand and the N,N,O_{deprotonated} triad from one tridentate chelating (py)₂C(Me)O[−] ion. The complexes were characterized by room-temperature effective magnetic moments and spectroscopic (IR, solid-state f–f) techniques. All data are discussed in terms of the nature of bonding and known (**4**) or assigned (**1–3**) structures. The Eu(III) and Tb(III) complexes **2** and **3** display in the solid state and at room temperature an intense red and green emission, respectively; this photoluminescence is achieved by an indirect process (antenna effect).

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1. Introduction

The intense, long-lived emission from the lanthanide ions Eu^{III} and Tb^{III} has made their complexes of intense interest for a wide range of applications such as display devices, luminescent sensors and probes for clinical use

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(e.g., fluoroimmunoassay) [1]. Therefore, the photophysical properties of Eu(III) and Tb(III) complexes have received a huge amount of attention [2]. Luminescence from trivalent lanthanides (Ln^{III}) arises from electronic transitions between the 4f orbitals. These transitions are forbidden on symmetry grounds, leading to poor absorption cross-sections and relatively long-lived excited states [3]. Consequently, population of the emitting levels of the Ln^{III} ion is best achieved by employing light-harvesting ligands (antenna chromophores) that normally absorb strongly UV light and can sensitize the metal ion by intramolecular

energy transfer from the resulting ligand-based triplet state [2i,3]. This is the usual basis for achieving sensitized emission from Eu(III) and Tb(III) [2]. Recently there have been intense efforts directed at attaching chromophores with relatively long wavelength absorption maxima (in the visible region), e.g., suitably functionalized organic dyes that have particularly low-energy π - π transitions [4] or d-metal complexes that have very strong charge-transfer absorptions at a range of wavelengths that span the visible region [5], to near-IR-emissive Ln^{III} ions, such as Yb(III), Nd(III), Pr(III) and Er(III).

The chances of identifying new 4f-metal complexes with interesting photophysical properties will benefit from the development of new reaction systems with suitable organic ligands. With this in mind we have started a systematic study of the coordination properties of complexing agents capable of efficiently sensitizing Eu(III) and Tb(III) emission. Our ligand design will employ simple units, based on strong binding sites for Ln^{III} coordination and bulky aromatic groups, to play the dual role of antenna and solvent shield, and to thus form – if possible – a hydrophobic shell around the metal ion. It should be mentioned at this point that species containing high-energy oscillators, such as C–H and O–H bonds (typically found in the ligand, coordinated solvent and moisture), are able to quench the metal excited states non-radiatively, leading to decreased luminescence intensities and shorter excited-state lifetimes [6]. In the ligands we plan to use, the binding and antenna domains may be or may not be independent of each other; in the former case this will allow the sensitizing group to be energetically optimized for a particular Ln^{III} ion without changing the binding characteristics of the ligand [2a].

In this paper, we describe our initial studies in this area based on the ligand di-2-pyridyl ketone, (py)₂CO (Fig. 1). Our groups [7,8] and others [9] have been explor-

ing reaction systems involving Mn, Fe, Co, Ni, Cu and Zn ions, and either (i) the monoanion, (py)₂C(OH)O[−], or the dianion, (py)₂CO₂^{2−}, of the *gem*-diol form (derivative), (py)₂C(OH)₂, of di-2-pyridyl ketone, (py)₂CO, or (ii) the monoanion, (py)₂C(OR)O[−] (R = Me, Et, etc.) of the hemiacetal form (derivative), (py)₂C(OR)(OH), of di-2-pyridyl ketone. The formulae of these ligands and their abbreviations are shown in Fig. 1. The general goal of these efforts is the isolation of polynuclear complexes with interesting magnetic and optical properties. There is a chemical characteristic of (py)₂CO that makes this molecule special as ligand; this is its carbonyl group. Water and alcohols (ROH) have been shown to add to the carbonyl group upon coordination of the carbonyl oxygen and/or the 2-pyridyl rings forming the ligands (py)₂C(OH)₂ (the *gem*-diol form of (py)₂CO) and (py)₂C(OR)(OH) (the hemiacetal form of (py)₂CO), respectively [7]. Interesting coordination modes are seen when the ligands (py)₂C(OH)₂ and (py)₂C(OR)(OH) are deprotonated. The presence of deprotonated hydroxyl group(s) leads to a great coordinative flexibility, due to the well known ability of the negatively charged oxygen atom to bridge two or three (μ_3) metal ions, while the dianionic form can bridge as many as five metal sites (μ_5). The immense structural diversity displayed by the 3d-metal complexes reported stems in part from the ability of (py)₂C(OH)O[−], (py)₂CO₂^{2−} and (py)₂C(OR)O[−] to exhibit no less than ten distinct bridging coordination modes [7]. Employment of carboxylates, β -diketonates or inorganic anions (NO₃[−], SO₄^{2−}, N₃[−], N(CN)₂[−], etc.) as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the preparation of a variety of 3d-metal clusters with nuclearities ranging from 3 to 26 [7], and with interesting physical properties including single-molecule magnetism [8d].

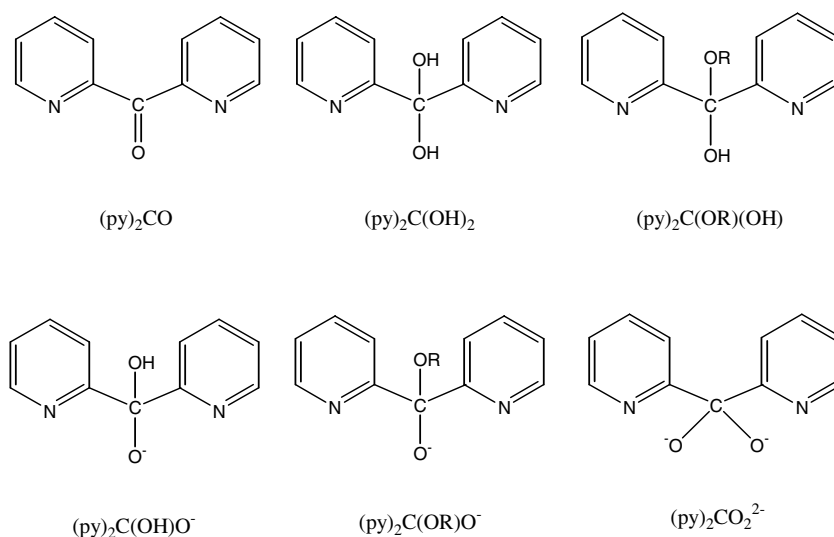


Fig. 1. The formulae of the ligands discussed in the text; note that (py)₂C(OH)₂, (py)₂C(OR)(OH) and all four anions do not exist as free species but exist only in their respective metal complexes (R = Me, Et, etc.).

Surprisingly, however, (py)₂CO-based ligands have been practically ignored in 4f-metal chemistry. We have recently extended the reactions of (py)₂CO in lanthanide(III) chemistry and investigated the Er^{III}/SCN⁻/(py)₂CO reaction mixtures in alcohols (MeOH, EtOH). Depending on the OH⁻ concentration in the reaction system, we were able to isolate and structurally characterize complexes [Er(NCS)₃{(py)₂C(OR)(OH)}₃] and [Er₂(NCS)₃{(py)₂C(OMe)O}₃(MeOH)] [10a]. We suspected that there might be a number of other Ln^{III} species accessible and have therefore been investigating the reactions of (py)₂CO with lanthanide(III) nitrates under a variety of conditions; the products of these reactions are the subject of this report. It should be mentioned at this point that lanthanide(III) nitrate complexes of the somewhat similar ligand methyl-2-pyridyl ketone benzoyl hydrazone have been recently prepared [10b]; tentative structures for the complexes were proposed based on spectroscopic techniques.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. Hydrated lanthanide(III) nitrates were purchased from Alfa Aesar.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. The metal content was determined volumetrically with ethylenediamine-tetra-acetate using Xylenol Orange as indicator. IR spectra (4000–400 cm⁻¹) were recorded on a Perkin–Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets; the spectra were also recorded as Nujol and hexachlorobutadiene mulls between CsI discs. Magnetic susceptibilities were measured at room temperature using the Faraday method with a Cahn–Ventron RM-2 balance standardized with HgCo(NCS)₄; diamagnetic corrections were estimated from Pascal's constants. Solid-state (diffuse reflectance, DRS) spectra in the 200–800 nm range were recorded on a Varian Cary 3 spectrometer equipped with an integration sphere under high-resolution detection conditions. Powders of the samples were used. Luminescence was recorded using an Ocean Optics S-2000 diode array spectrophotometer. The excitation source was a pulsed N₂ laser (336 nm). Luminescence was collected with an optical fiber. The excitation spectra were recorded using a Cary Eclipse fluorescence spectrophotometer.

2.2. Compound preparation

2.2.1. [Pr₂(NO₃)₃{(py)₂C(OMe)O}₂{(py)₂C(OH)O}] (1)

Solids (py)₂CO (0.037 g, 0.20 mmol) and LiOH · H₂O (0.0084 g, 0.20 mmol) were dissolved in MeOH (3 ml)

resulting in a colourless solution. This was added to a pale green solution of Pr(NO₃)₃ · 6H₂O (0.086 g, 0.20 mmol) in EtOH (5 ml). The resulting new pale green solution was stirred for about 1 h during which time a precipitate formed. The solid was collected by filtration, washed with cold MeOH (2 × 2 ml) and Et₂O (2 × 5 ml), and dried in vacuo over silica gel. Yield: 21% (based on the ligand). *Anal. Calc.* for C₃₅H₃₁Pr₂N₉O₁₅: C, 38.23; H, 2.85; N, 11.47; Pr, 25.63. *Found:* C, 37.99; H, 2.90; N, 11.62; Pr, 26.13%. IR (KBr pellet, cm⁻¹): 3410 mb, 2975 w, 2912 w, 1599 m, 1569 w, 1476 s, 1464 s, 1438 s, 1384 s, 1304 m, 1284 m, 1233 w, 1224 w, 1154 w, 1112 sh, 1104 m, 1075 s, 1049 m, 1035 sh, 1012 m, 815 m, 766 m, 748 sh, 683 m, 661 w, 633 m, 541 w, 432 sh, 417 m. μ_{eff} (BM) per Pr^{III}: 3.44 (22 °C). DRS (nm): 268, 280, 340, 449, 474, 485, 599.

2.2.2. [Eu₂(NO₃)₃{(py)₂C(OMe)O}₂{(py)₂C(OH)O}] (2)

Using Eu(NO₃)₃ · 6H₂O, slightly different solvent volumes (MeOH: 7 ml, EtOH: 2 ml) and following exactly the same procedure as that described for the corresponding praseodymium(III) complex, a white microcrystalline material was isolated. Yield: 25% (based on the ligand). *Anal. Calc.* for C₃₅H₃₁Eu₂N₉O₁₅: C, 37.48; H, 2.79; N, 11.24; Eu, 27.10. *Found:* C, 37.62; H, 2.69; N, 11.38; Eu, 26.31%. IR (KBr pellet, cm⁻¹): 3399 mb, 2980 w, 2942 w, 1600 m, 1568 w, 1482 s, 1465 s, 1439 m, 1384 s, 1308 m, 1266 sh, 1232 w, 1222 w, 1154 w, 1111 sh, 1105 m, 1078 s, 1051 m, 1036 sh, 1015 m, 815 m, 767 m, 749 sh, 684 m, 662 w, 634 m, 542 w, 433 w, 417 m. μ_{eff} (BM) per Eu^{III}: 3.40 (20 °C). DRS (nm): 265, 281, 338, 363, 397.

2.2.3. [Tb₂(NO₃)₃{(py)₂C(OMe)O}₂{(py)₂C(OH)O}] (3)

Solids (py)₂CO (0.037 g, 0.20 mmol) and LiOH · H₂O (0.0084 g, 0.20 mmol) were dissolved in MeOH (6 ml) resulting in a colourless solution. This was added to a pale pink solution of Tb(NO₃)₃ · 6H₂O (0.087 g, 0.19 mmol) in a solvent mixture comprising MeOH (3 ml) and EtOH (3 ml). No noticeable colour change occurred. The resulting solution was stirred for about 1 h and layered with a mixture of Et₂O and *n*-hexane (20 ml, 1:1 v/v). Slow mixing gave a white microcrystalline solid, which was collected by filtration, washed with cold MeOH (2 × 3 ml) and Et₂O (2 × 5 ml), and dried in vacuo over silica gel. Yield: 19% (based on the ligand). *Anal. Calc.* for C₃₅H₃₁Tb₂N₉O₁₅: C, 37.02; H, 2.76; N, 11.10; Tb, 27.99. *Found:* C, 37.18; H, 2.80; N, 11.01; Tb, 28.63%. IR (KBr pellet, cm⁻¹): 3400 mb, 2985 w, 2930 w, 1601 m, 1568 w, 1480 s, 1467 s, 1439 m, 1384 s, 1309 m, 1285 m, 1267 sh, 1233 sh, 1224 w, 1155 w, 1112 sh, 1106 m, 1079 s, 1051 m, 815 m, 1035 sh, 1015 m, 815 m, 767 m, 750 sh, 684 m, 665 w, 634 m, 543 w, 437 w, 420 m. μ_{eff} (BM) per Tb^{III}: 9.59 (25 °C). DRS (nm): 266, 282, ~330, 373, 492.

2.2.4. $[Er_2(NO_3)_3\{(py)_2C(OMe)O\}_2\{(py)_2C(OH)O\}] \cdot 0.8EtOH \cdot 0.4MeOH$ ($4 \cdot 0.8EtOH \cdot 0.4MeOH$)

Solids $(py)_2CO$ (0.037 g, 0.20 mmol) and $LiOH \cdot H_2O$ (0.0084 g, 0.20 mmol) were dissolved in MeOH (5 ml) resulting in a colourless solution. This was added to a pale pink solution of $Er(NO_3)_3 \cdot 5H_2O$ (0.090 g, 0.20 mmol) in a solvent mixture comprising MeOH (2 ml) and EtOH (3 ml). The resulting new pinkish solution was stirred for about 90 min and stored at 5 °C. After 8 days, pale pink (almost colourless), X-ray quality prisms formed; they were collected by filtration, washed with cold MeOH (2×2 ml) and Et_2O (2×5 ml) and dried in vacuo over silica gel. Yield: 39% (based on the ligand). A sample for crystallography was kept in contact with the mother liquor to prevent interstitial solvent loss. The dried sample analysed as solvent-free. *Anal. Calc.* for $C_{35}H_{31}Er_2N_9O_{15}$: C, 36.48; H, 2.72; N, 10.94; Er, 29.03. *Found*: C, 36.70, H, 2.65; N, 11.13; Er, 30.00%. IR (KBr pellet, cm^{-1}): 3380 mb, 2983 w, 2935 w, 1602 m, 1570 m, 1506 s, 1475 sh, 1438 m, 1384 m, 1298 m, 1284 m, 1260 sh, 1226 m, 1156 m, 1116 m, 1084 m, 1050 m, 1016 sh, 814 m, 786 sh, 762 m, 684 m, 666 w, 636 m, 532 w, 454 m, 425 m. μ_{eff} (BM) per Er^{III} : 9.54 (20 °C). DRS (nm): 262, 277, ~ 330 , 370 sh, 380, 492, 520, 524, 530 sh, 542, 652, 657.

2.3. Single-crystal X-ray crystallography

A crystal of $4 \cdot 0.8EtOH \cdot 0.4MeOH$ was mounted in capillary. Diffraction measurements were made on a Crystal

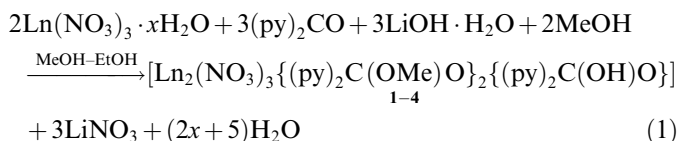
Logic Dual Goniometer diffractometer using graphite-monochromated Mo radiation. Complete crystal data and parameters for data collection and processing are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23^\circ$. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and Ψ -scan absorption corrections were applied using Crystal Logic software.

The structure was solved by direct methods using SHELXS-86 [11a] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [11b]. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms and were refined isotropically. All non-hydrogen atoms were refined using anisotropic thermal parameters, except of the solvent molecules, which were refined isotropically.

3. Results and discussion

3.1. Synthetic comments

The 1:1:1 reactions between $Ln(NO_3)_3 \cdot xH_2O$ ($Ln = Pr, Eu, Tb, Er; x = 5$ or 6), OH^- and $(py)_2CO$ in MeOH–EtOH gave the dinuclear complexes $[Ln_2(NO_3)_3\{(py)_2C(OMe)O\}_2\{(py)_2C(OH)O\}]$ (**1–4**); the erbium(III) compound was crystallographically identified as $4 \cdot 0.8EtOH \cdot 0.4MeOH$. The formation of these lanthanide(III) complexes can be summarized in the general balanced Eq. (1).



The Ln^{III} -mediated addition of solvent (MeOH, H_2O) from the solvents and the starting materials) to $(py)_2CO$ to give the monoanion of the hemiacetal form of di-2-pyridyl ketone, $(py)_2C(OMe)O^-$ (Fig. 1), and the monoanion of the *gem*-diol form of this ligand, $(py)_2C(OH)O^-$ (Fig. 1), in **1–4** involves a nucleophilic attack of the MeOH and H_2O molecules on the carbonyl group [7]. The electrophilic character of the carbonyl group of $(py)_2CO$ is increased by coordination of the carbonyl oxygen to the metal ion (direct polarization) and/or coordination of the more remote 2-pyridyl sites (induced polarization) [7].

Several features of the general reaction represented by Eq. (1) deserve comments. First, the “wrong” reaction ratio employed for the preparation of **1–4** (see Section 2.2), compared to the stoichiometric ratio required by Eq. (1), obviously did not prove detrimental to the formation of the complexes. With the identities of **1–4** established, the “correct” stoichiometric ratio, i.e., $Ln(III): OH^-:(py)_2CO = 2:3:3$, was employed and led to pure compounds in satisfactory yields. Second, use of bases other than $LiOH \cdot H_2O$ leads again to the same complexes. Thus,

Table 1
Crystallographic data for complex $4 \cdot 0.8EtOH \cdot 0.4MeOH$

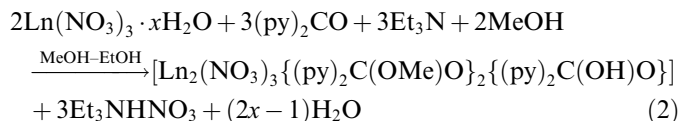
Formula	$C_{37}H_{37.4}Er_2N_9O_{16.2}$
Formula weight	1201.88
Crystal colour, habit	colourless, prism
Crystal dimensions (mm)	$0.04 \times 0.12 \times 0.40$
Crystal system	monoclinic
Space group	$P2_1/c$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	11.261(5)
<i>b</i> (Å)	21.560(10)
<i>c</i> (Å)	18.669(8)
β (°)	101.46(1)
<i>V</i> (Å ³)	4442(3)
<i>Z</i>	<i>Z</i>
ρ_{calc} (g cm ⁻³)	1.797
Radiation, λ (Å)	Mo K α , 0.71073
Temperature (K)	298
Scan mode/speed (° min ⁻¹)	θ - $2\theta/1.5$
$2\theta_{max}$ (°)	50.0
μ (mm ⁻¹)	3.832
Reflections collected/unique (R_{int})	8073/7817 (0.0338)
Data with $I > 2\sigma(I)$	5150
Parameters refined	584
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ (e Å ⁻³)	0.908, -0.679
Goodness-of-fit (on F^2)	1.072
R_1, wR_2^b (all data)	0.1106, 0.1262
R_1, wR_2^b ($I > 2\sigma(I)$)	0.0569, 0.1067

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$.

^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

the 2:3:3 $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/(\text{py})_2\text{CO}/\text{Et}_3\text{N}$ reaction mixtures in MeOH–EtOH (the detailed procedures are not given in Section 2.2) lead to the isolation of **1–4** in yields higher than 30% according to Eq. (2). Third, the incorporation of the monoanions of *both* the hemiacetal and the *gem*-diol forms of $(\text{py})_2\text{CO}$ as ligands in **1–4** was rather unexpected, given the fact that the complexes were isolated from alcohols. For example, the products isolated from the $\text{Er}^{\text{III}}/\text{SCN}^-/(\text{py})_2\text{CO}$ reaction mixtures in MeOH contain *only* $(\text{py})_2\text{C}(\text{OMe})(\text{OH})$ or $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ species as ligands [10a]. With hindsight this can be explained by the presence of H_2O (from the starting materials and from the moisture of the organic solvents) in the reaction mixtures. One possible reason for the presence of both $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ is the satisfaction of the crystal lattice. It is likely that the reaction solution contains a complicated mixture of several species in equilibrium, with factors such as relative solubility, lattice energy and crystallization kinetics – amongst others – determining the identity of the isolated product. It should be mentioned at this point that the presence of both $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OR})\text{O}^-$ in the same complex is rare in d-metal chemistry [9c,9f,12]. Forth, complexes **1–4** seem to be the only isolable products from the $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{OH}^-/(\text{py})_2\text{CO}$ reaction systems in MeOH or MeOH–EtOH. The Ln^{III} to ligand reaction ratio, the presence/absence of counter-cations or – anions (e.g., NBU_4^+ or ClO_4^-), and the precipitation/crystallization method have no influence on the identity of the products. With the identity of compounds **1–4** established we also tried similar reactions but employing a large excess of OH^- as a means of obtaining complexes containing the doubly deprotonated ligand $(\text{py})_2\text{CO}_2^{2-}$ (Fig. 1) [7]. However, these yielded the same complexes $[\text{Ln}_2(\text{NO}_3)_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}]$ and/or amorphous hydroxo materials with poor analytical results. Fifth, the full synthetic investigation of the $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{LiOH} \cdot \text{H}_2\text{O}$ or $\text{Et}_3\text{N}/(\text{py})_2\text{CO}$ reaction systems in H_2O , MeCN or MeCN/ H_2O led to non-crystalline solids with non-reproducible analytical results. Sixth, the employment of EtOH as co-solvent is beneficial only for the isolation of crystalline solids in the case of **1–3** and single crystals of **4** · 0.8EtOH · 0.4MeOH; in other words, its presence does not affect the identity of the product, but only its crystallization. The employment of EtOH might imply the presence of the monoanion $(\text{py})_2\text{C}(\text{OEt})\text{O}^-$ in the complexes. Although this is possible *in solution*, only the $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligands are present in the *solid* complexes **1–4**. This result is difficult to be rationalized; suffice it to say that complexes **1–4** are the thermodynamically stable products from the $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{OH}^-/(\text{py})_2\text{CO}$ reaction system in a solvent mixture comprising non-absolute MeOH and EtOH. And seventh, despite our efforts, we could not isolate mononuclear complexes containing the neutral or anionic ligand, e.g., $\text{Ln}(\text{NO}_3)_3\{(\text{py})_2\text{C}(\text{OR})(\text{OH})\}_x$ ($x = 1$ or 2) and $\text{Ln}(\text{NO}_3)_2\{(\text{py})_2\text{C}(\text{OR})\text{O}\}$. In the absence of external base, the

$\text{Er}^{\text{III}}/\text{SCN}^-/(\text{py})_2\text{CO}$ reaction mixture in alcohols (MeOH, EtOH) yielded [10a] the mononuclear complexes $[\text{Er}(\text{NCS})_3\{(\text{py})_2\text{C}(\text{OR})(\text{OH})\}_3]$ ($\text{R} = \text{Me}, \text{Et}$).



3.2. Description of structure

A partially labelled plot of the dinuclear molecule present in complex **4** · 0.8EtOH · 0.4MeOH is shown in Fig. 2. A graphical representation of this complex appears in Fig. 3. The coordination polyhedra of the two Er^{III} atoms are shown in Fig. 5. Selected interatomic distances and angles are listed in Table 2.

The crystal structure of **4** · 0.8EtOH · 0.4MeOH consists of discrete dinuclear $[\text{Er}_2(\text{NO}_3)_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}]$ molecules and solvate molecules; the latter will not be further discussed. In the dinuclear molecule, the

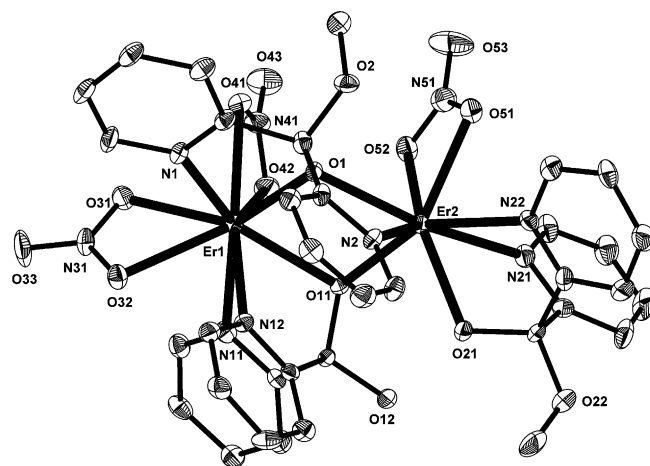


Fig. 2. The structure of the dinuclear molecule present in complex **4** · 0.8EtOH · 0.4MeOH.

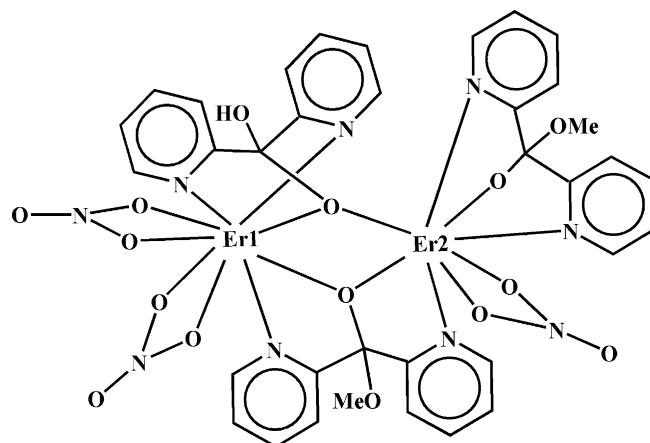


Fig. 3. An informative graphical representation of **4**.

Table 2
Selected interatomic distances (Å) and bond angles (°) for complex $4 \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$

Er(1)··Er(2)	3.681(2)	Er(1)–N(12)	2.479(9)
Er(1)–O(1)	2.253(6)	Er(2)–O(1)	2.293(6)
Er(1)–O(11)	2.330(7)	Er(2)–O(11)	2.258(6)
Er(1)–O(31)	2.447(8)	Er(2)–O(21)	2.222(8)
Er(1)–O(32)	2.465(7)	Er(2)–O(51)	2.380(9)
Er(1)–O(41)	2.466(8)	Er(2)–O(52)	2.451(9)
Er(1)–O(42)	2.411(8)	Er(2)–N(2)	2.496(9)
Er(1)–N(1)	2.572(9)	Er(2)–N(21)	2.539(9)
Er(1)–N(11)	2.531(9)	Er(2)–N(22)	2.497(9)
O(1)–Er(1)–O(11)	71.9(2)	O(1)–Er(2)–O(11)	72.5(2)
O(1)–Er(1)–O(31)	139.9(3)	O(1)–Er(2)–O(51)	89.0(3)
O(1)–Er(1)–N(11)	138.2(3)	O(1)–Er(2)–N(22)	128.9(3)
O(11)–Er(1)–O(42)	81.7(3)	O(11)–Er(2)–O(21)	82.6(3)
O(11)–Er(1)–O(32)	125.4(3)	O(11)–Er(2)–O(51)	132.4(3)
O(11)–Er(1)–N(12)	66.6(3)	O(11)–Er(2)–N(2)	99.3(3)
O(31)–Er(1)–O(32)	52.0(3)	O(21)–Er(2)–O(52)	136.5(3)
O(31)–Er(1)–N(12)	121.3(3)	O(21)–Er(2)–N(21)	67.3(3)
O(32)–Er(1)–O(41)	118.5(3)	O(21)–Er(2)–N(22)	67.5(3)
O(32)–Er(1)–N(11)	73.2(3)	O(51)–Er(2)–O(52)	53.4(3)
O(41)–Er(1)–O(42)	52.1(3)	O(51)–Er(2)–N(21)	79.8(3)
O(41)–Er(1)–N(12)	159.6(3)	O(52)–Er(2)–N(2)	140.4(3)
O(42)–Er(1)–N(11)	73.0(3)	O(52)–Er(2)–N(22)	122.2(3)
N(1)–Er(1)–N(11)	146.8(3)	N(2)–Er(2)–N(21)	142.8(3)
N(1)–Er(1)–N(12)	86.7(3)	N(2)–Er(2)–N(22)	77.1(3)
N(11)–Er(1)–N(12)	76.7(3)	N(21)–Er(2)–N(22)	72.7(3)
Er(1)–O(1)–Er(2)	108.1(3)	Er(2)–O(11)–Er(1)	106.7(3)

monoanion of the *gem*-diol form of di-2-pyridyl ketone, $(\text{py})_2\text{C}(\text{OH})\text{O}^-$, and one monoanionic hemiacetal form of the organic ligand, $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$, bridge the metal centers through their deprotonated hydroxyl groups. Thus, the two Er^{III} atoms are doubly bridged by the deprotonated hydroxyl oxygen atoms O(1) and O(11). The Er(1) atom is in a nine-coordinate ligand environment comprising the two just mentioned hydroxyl oxygen atoms, four oxygen atoms from two chelating nitrate ligands (O(31), O(32), O(41), O(42)), the two 2-pyridyl nitrogen atoms from the $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligand (N(11), N(12)) and one 2-pyridyl nitrogen atom from the bridging $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligand (N(1)). Two oxygen atoms from the remaining chelating nitrate ligand (O(51), O(52)), the second nitrogen atom from the bridging $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligand (N(2)) and the N(21), N(22), O(21) triad of atoms from the tridentate chelating (i.e., terminal) $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligand complete eight-coordination at Er(2).

The coordination modes of the organic ligands of complex $4 \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$ are shown in Fig. 4. The $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ anion behaves as an $\eta^1:\eta^2:\eta^1:\mu_2$ ligand or in a 2.201_11_1 mode (as described using Harris notation [13]). According to the latter, the binding mode of a ligand is referred to as $X.Y_1Y_2Y_3\cdots Y_n$, where X is the overall number of metals bound by the whole ligand and each value of Y refers to the metal ions attached to the different donor atoms. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here O before N. In the case of chelating/bridging ligands, to distinguish between several alternatives, a subscript number is included

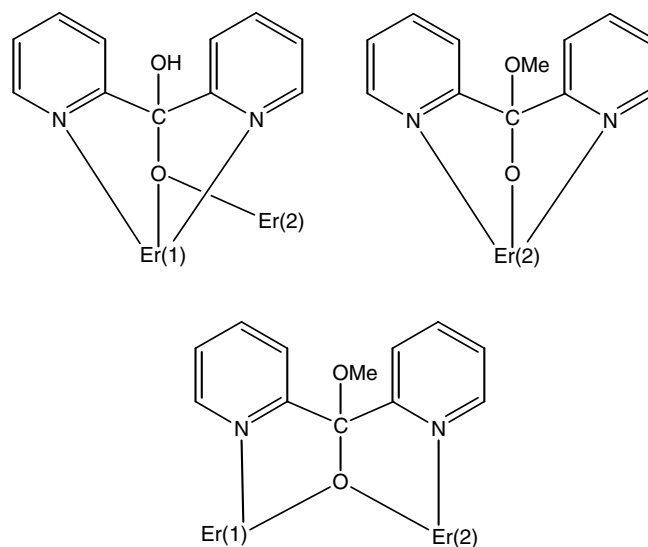


Fig. 4. The crystallographically established coordination modes of the organic ligands $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ in complex $4 \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$, and the Harris notation [13] that describes these modes.

to show to which metal ion the donor is attached. The bridging $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ anion behaves as an $\eta^1:\eta^2:\eta^1:\mu_2$ (or as 2.201_11_2 using Harris notation [13]) ligand, while the terminal $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligand is tridentate chelating ($\eta^1:\eta^1:\eta^1$ or 1.1011). The methoxy oxygen atom of both the $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligands and the hydroxyl oxygen atom of the $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligand remain unbound to the metals. Ligands based on the *gem*-diol or the hemiacetal forms of di-2-pyridyl ketone have been observed in numerous ligation modes over the years [7]. The observed terminal and bridging ligation modes of $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ are common in the coordination chemistry of the hemiacetal forms of di-2-pyridyl ketone [7]. On the contrary, the observed 2.201_11_1 coordination mode of $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ (Fig. 4) is extremely rare and has crystallographically been identified only in the dinuclear complex $[\text{Bi}_2(\text{O}_2\text{CCF}_3)_4\{(\text{py})_2\text{C}(\text{OH})\text{O}\}_2(\text{THF})_2]$ [14].

The presence of two monoatomic bridges (O(1), O(11)) causes the Er(1)··Er(2) distance to be relatively short (3.681(2) Å). The Er–N distances are in the relatively narrow range 2.478(9)–2.572(9) Å; this range is typical for eight- and nine-coordinate Er(III) complexes [2f,2k,5c,13]. The Er–O bond lengths fall into two distinct categories; those involving the organic ligands (2.222(8)–2.330(7) Å) and those involving the nitrate ligands (2.380(9)–2.466(8) Å). The bridging Er–O distances involving O(1) and O(11) are asymmetric, e.g., Er(1)–O(11) = 2.330(7) Å and Er(2)–O(11) = 2.258(6) Å. The Er(2)–O bond distance for the bridging alkoxo-type oxygen atom of $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ (Er(2)–O(1) = 2.293(6) Å) is longer than the Er(2)–O distance exhibited by the terminal oxygen atom of $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ (Er(2)–O(21) = 2.222(8) Å). The Er(2)–O(alkoxo-type) distances have an average value of 2.258(8) Å, which is shorter than the corresponding value

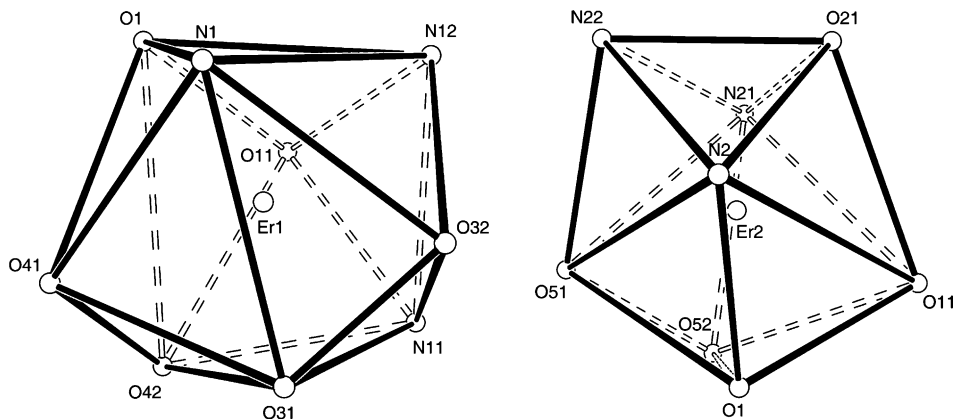


Fig. 5. Views of the inner coordination polyhedra of $4 \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$ showing the tricapped trigonal prismatic coordination of Er(1) and the dodecahedral stereochemistry about Er(2).

for the Er(1)–O (alkoxo-type) distances (2.292(7) Å); the decreased Er–O distances for Er(2) may be a consequence of the lower coordination number of this metal ion compared to that for Er(1) (eight versus nine). An analogous trend holds true for the Er–O(nitrato) bond distances; the average Er(1)–O(nitrato) and Er(2)–O(nitrato) distances are 2.447(8) and 2.416(9) Å, respectively. The nitrato ligands are planar, as indicated by the sum of O–N–O angles (359.7–360.0°), and almost symmetrically chelated. The Er–O(nitrato) bond lengths agree well with the values reported [15] for other eight- and nine-coordinate erbium(III) nitrate complexes.

The coordination polyhedron of Er(1) (Fig. 5) is best described as a distorted tricapped trigonal prism with the alkoxo-type oxygen atom, O(11), and the nitrato oxygen atoms O(32) and O(41) forming the three rectangular face caps. The angle sum subtended by the three capping atoms at Er(1) is 357.8°. It may be emphasized that in each nitrato ligand, the capping atom forms a slightly weaker bond to Er(1) than the non-capping atom, e.g., Er(1)–O(41) = 2.466(8) Å versus Er(1)–O(42) = 2.411(8) Å. The coordination polyhedron of the eight donor atoms about Er(2) (Fig. 5) is best described [10a] as a distorted dodecahedron. Atoms N(22), O(21), O(1), O(52) constitute a distorted tetrahedron that has been elongated along the fourfold inversion axis of the idealized polyhedron, whereas the set of atoms N(2), N(21), O(11), O(51) form a distorted tetrahedron that has been squashed along the same axis. An alternative way of viewing the dodecahedron about Er(2) is to consider it [16] as two interpenetrating planar trapezoids N(22)O(21)O(11)O(51) and N(2)N(21)O(1)O(52).

The distances O(12)···O(21) and O(ethanol)···O(42) ($-x + 2, y + 1/2, -z + 3/2$) are only 2.557 and 2.985 Å, respectively, raising the possibility of the presence of hydrogen bonds. However, due to the fact that the hydrogen atoms of the structure were not located, the hydrogen bonds can not be considered in detail. The crystal structure is stabilized by four, crystallographically independent π – π stacking interactions (one intramolecular, three intermolecular). The intramolecular interaction involves the two

2-pyridyl rings that possess N(2) and N(12), the intercentroid distance ($\text{Cg} \cdots \text{Cg}^*$) and the dihedral angle being 3.740 Å and 10.1°, respectively. The corresponding perpendicular distances from Cg and Cg* to the best least-squares ring planes of the other stacking moieties are 3.490 and 3.549 Å. The first type of intermolecular interaction involves the two 2-pyridyl rings that possess N(11) and N(22) (the symmetry code is $x + 1, y, z$), the intercentroid distance and the dihedral angle being 3.795° and 5.5°, respectively. The corresponding perpendicular distances from Cg and Cg* to the best least-squares ring planes of the other stacking moieties are 3.439 and 3.575 Å. The other intermolecular π – π stacking interactions involve the rings that possess N(2) and N(21) ($x, -y + 1/2, z + 1/2$), and the rings that possess N(1) and N(1) ($-x + 2, -y + 1, -z + 1$).

The structural comparison of the dinuclear complexes $[\text{Er}_2(\text{NO}_3)_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}]$ (**4**) and $[\text{Er}_2(\text{NCS})_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_3(\text{MeOH})]$ [10a] reveals the following differences: (i) The former possesses two different types of monoanionic $(\text{py})_2\text{CO}$ -based ligands, whereas the latter only one; (ii) the organic ligands in **4** exhibit three *different* coordination modes (one terminal and two bridging), whereas the three $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ ligands in the isothiocyanate complex exhibit the same coordination mode; (iii) the two Er^{III} atoms are doubly bridged by deprotonated hydroxyl oxygens in **4** but triply bridged in the isothiocyanate compound [10a], and as a result the Er···Er distance is longer in the former (3.681(2) Å) than in the latter (3.380(2) Å), and (iv) the two Er^{III} atoms in the nitrate complex **4** have different coordination numbers (eight and nine) and hence two different coordination geometries (dodecahedral and tricapped trigonal prismatic), whereas the coordination number for both Er^{III} atoms in the isothiocyanate complex is the same (eight).

Complex $4 \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$ is the third structurally characterized lanthanide(III) complex with a $(\text{py})_2\text{CO}$ -based ligand (see Section 1) and joins only a handful of complexes of any metal that contain both $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OR})\text{O}^-$ ions as ligands [9c,9f,12].

It also covers a gap in the erbium(III) literature in being the first crystallographically characterized dinuclear nitrate complex.

3.3. Magnetic moments, electronic and IR spectra

The experimental, room-temperature effective magnetic moment (μ_{eff}) values per Ln^{III} atom for complexes **1–4** (see Section 2.2) show very little deviation from the theoretical values (Pr^{III}, 3.62 BM; Eu^{III}, 3.5 BM; Tb, 9.7 BM; Er, 9.6 BM) predicted by Eq. (3), suggesting that the 4f electrons in the complexed Ln^{III} atoms are well-shielded by the outermost 5s and 5p electrons [16]

$$\mu_{\text{eff}} = g[J(J + 1)]^{1/2} \quad (3)$$

The solid-state (diffuse reflectance) electronic spectra of the prepared complexes involve intraligand and f–f transitions. Detailed assignments (based on the literature data [17]) of the observed weak f–f bands are given in Table 3. The shape and the fine structure of the f–f band assigned to the “hypersensitive” transition $^4I_{15/2} \rightarrow ^2H_{11/2}$ (Er-I) in the spectrum of **4** are sensitive to the coordination number [18]. By comparing the spectrum of **4** with the spectra of Er(III) complexes of known structures [10a,18,19] in the region of this transition (520–530 nm), it is confirmed that the metal ions are eight- or/and nine-coordinate.

The values of the bonding parameters β (nephelauxetic ratio), δ (Sinha’s parameter) and $b^{1/2}$ (covalent factor) for complexes **1** and **4**, calculated from the solid-state f–f spectra by standard equations [10a,19,20] and listed in Table 4, indicate that the interaction between Pr^{III} and Er^{III} and the ligands is essentially electrostatic and that there is a minor participation of the 4f orbitals in bonding [20].

The IR spectra of vacuum-dried samples of **1–4** exhibit a medium intensity band at 3410–3380 cm⁻¹, assignable to

Table 3
Solid-state f–f bands for complexes **1–4**

λ (nm)	Assignment
Complex 1	
449	$^3H_4 \rightarrow ^3P_2$
474	$^3H_4 \rightarrow ^3P_1$
485	$^3H_4 \rightarrow ^3P_0$
599	$^3H_4 \rightarrow ^1D_2$
Complex 2	
363	$^7F_0 \rightarrow ^5D_4$
397	$^7F_0 \rightarrow ^5L_6$
Complex 3	
373	$^7F_6 \rightarrow ^5G_6$
492	$^7F_6 \rightarrow ^5D_4$
Complex 4	
370 sh, 380	$^4I_{15/2} \rightarrow ^4G_{11/2}$ (Er-II) ^a
492	$^4I_{15/2} \rightarrow ^4F_{7/2}$
520, 524, 530 sh	$^4I_{15/2} \rightarrow ^2H_{11/2}$ (Er-I) ^a
542	$^4I_{15/2} \rightarrow ^4S_{3/2}$
652, 657	$^4I_{15/2} \rightarrow ^4F_{9/2}$

^a These transitions are “hypersensitive”.

Table 4
Bonding parameters^a for the Pr(III) and Er(III) complexes **1** and **4**

Complex	β	δ (%)	$b^{1/2}$
1	0.994	+0.60	0.055
4	0.996	+0.40	0.045

^a Calculated from the solid-state f–f spectra taking into account the wavenumbers of the transitions mentioned in Table 3.

the $\nu(\text{OH})$ vibration of the $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ ligand [8b]. The spectra of the four complexes do not exhibit bands in the region expected for the carbonyl stretching vibration ($\nu(\text{C}=\text{O})$, at 1684 cm⁻¹ for free $(\text{py})_2\text{CO}$) with the nearest IR absorption at ~ 1600 cm⁻¹ assigned as a 2-pyridyl stretching mode raised from 1582 cm⁻¹, as observed earlier on complex formation involving hydration or alcoholysis of $(\text{py})_2\text{CO}$ [8b,21]. The bands at ~ 1050 , ~ 765 and ~ 635 cm⁻¹ can be assigned [22] to pyridyl ring breathing, pyridyl C–H out-of-plane bending and in-plane pyridyl ring deformation vibrations, respectively.

Diagnostic IR bands assigned to nitrate vibrations are listed in Table 5. The cited nitrate frequencies in Table 5 arise from spectra obtained as Nujol and hexachlorobutadiene mulls (whereas those cited in Section 2.2 arise from KBr pellets), since it is well known that pressing a pellet affects the nitrate coordination [23]; the organic ligands’ frequencies are identical in both the KBr and mull spectra. The IR spectra of **1–4** in KBr are indicative of the presence of ionic nitrates (although the X-ray structure of $\mathbf{4} \cdot 0.8\text{EtOH} \cdot 0.4\text{MeOH}$ revealed no nitrate counterions); their existence in the KBr pellet is deduced from the appearance of the $\nu_3(\text{E}')(\nu_d(\text{NO}))$ mode of the D_{3h} ionic nitrate at 1384 cm⁻¹ [24], suggesting [23] that a certain amount of nitrato ligands are replaced by bromides (thus generating ionic nitrates) in the KBr matrix. In the mull spectra of **1–4**, the bands at ~ 1475 and ~ 1285 cm⁻¹ are assigned [24] to the $\nu_1(\text{A}_1)$ and $\nu_5(\text{B}_2)$ (under C_{2v} symmetry) stretching modes of the nitrato ligands, respectively. Their separation is large (~ 190 cm⁻¹) suggesting (**1–3**) or confirming (**4**) the bidentate character of the nitrato ligands [24]. The 1700–1800 cm⁻¹ region is viewed as the key to

Table 5
Diagnostic IR bands (cm⁻¹) of the NO₃⁻ ligands present in complexes **1–4**^{a,b}

Complex	$\nu_1(\text{A}'_1) + \nu_4(\text{E}')^c$	$\nu_1(\text{A}_1)^d$	$\nu_5(\text{B}_2)^e$
1	1754, 1725	1474 s	1284 m
2	1749, 1712	1480 s	1283 m
3	1753, 1715	1480 s	1287 m
4	1758, 1716	1473 m	1282 m

^a The cited wavenumbers arise from spectra recorded as Nujol and hexachlorobutadiene mulls.

^b The spectra of these complexes in KBr exhibit a medium to strong intensity band at 1384 cm⁻¹ (see text in Section 3.3).

^c These terms refer to the free NO₃⁻; $\nu_1(\text{A}'_1)$ and $\nu_4(\text{E}')$ are the $\nu_s(\text{NO})$ and $\delta_d(\text{ONO})$ vibrations, respectively.

^d $\nu(\text{N}=\text{O})$.

^e $\nu_{\text{as}}(\text{NO}_2)$.

differentiate between bidentate and monodentate nitrate coordination [15d,23–25]. Lever et al. [25] proposed the combination band $\nu_1(A'_1) + \nu_4(E')$ of free NO_3^- , which appears in the 1700–1800 cm^{-1} region, as a spectroscopic criterion for structural diagnosis. Upon coordination, ν_4 (E' , in-plane bending) near 700 cm^{-1} splits into two bands, and the magnitude of the splitting is expected to be larger for bidentate than for monodentate ligands. This is reflected in the separation of the two ($\nu_1 + \nu_4$) weak bands in the 1700–1800 cm^{-1} region. The separation of the combination bands is 29–42 cm^{-1} (see Table 5) in our complexes and these values indicate bidentate nitrate ligands [15d,23–25]. As it has been observed by Fukuda et al. [15d], the value of this splitting parameter increases with decreasing ionic size across the lanthanide series.

3.4. Photoluminescence properties of the Eu(III) and Tb(III) complexes

Excitation and luminescence spectra of complex **2** and the luminescence spectrum of complex **3**, recorded in the solid state at 295 K, are shown in Figs. 6 and 7, respectively. Excitation at 336 nm into the lowest energy ligand-centered absorption band results in the luminescence characteristic of the Ln^{3+} ion ($\text{Ln} = \text{Eu}, \text{Tb}$).

The strong red emission of **2** is assigned to the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j=0-4$) transitions or Eu^{3+} . Specific assignments [2a,2j,26] are as follows: $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (580 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (587 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (615 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (652 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (688 nm). The appearance of a slight structure in the symmetry-forbidden emission $^5\text{D}_0 \rightarrow ^7\text{F}_0$ may indicate that more than one coordination environments are present for Eu(III) [2j,26a,26b]. The Eu^{3+} ion is unique in that both the ground state $^7\text{F}_0$ and the excited emissive state $^5\text{D}_0$ are non-degenerate. Since the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition occurs between non-degenerate energy levels, neither of which can be split by a ligand field,

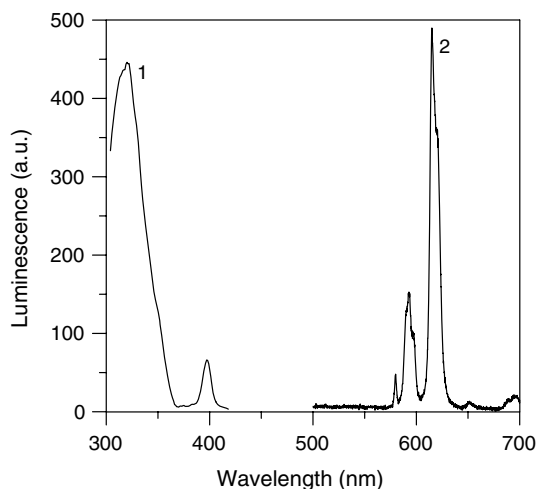


Fig. 6. Excitation (emission at 616 nm) (1) and emission (excitation at 336 nm) (2) spectra of **2** in the solid state at room temperature.

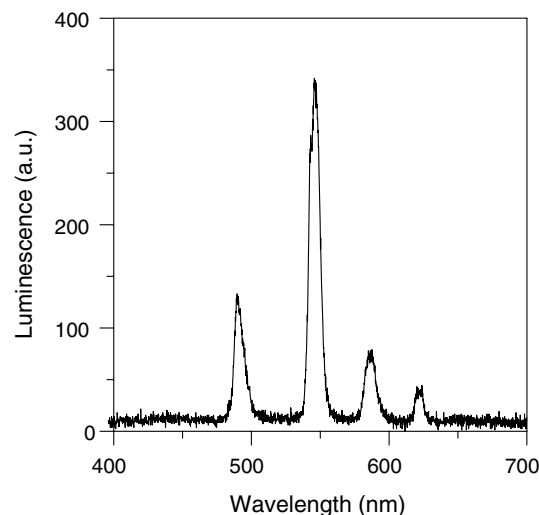


Fig. 7. The emission spectrum of **3** in the solid state at room temperature (excitation at 336 nm).

a single environment gives rise to only a single transition; if more than one Eu^{III} environments are present, each will have its own characteristic transition energy [2j]. The dominant band in the emission spectrum is the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, which shows signs of splitting. The higher intensity of this transition compared to that of the magnetic-dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition indicates that this complex has a structure with no imposed symmetry [26a]. As a matter of fact, complexes with a centrosymmetric coordination sphere have $(^5\text{D}_0 \rightarrow ^7\text{F}_2)/(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ intensity ratios lower than 0.7 [26a,26c].

The Tb(III) complex **3** gives an entirely typical Tb^{3+} emission spectrum containing the expected sequence of $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions, with the $j=3-6$ components being visible. Specific assignments [2a,26a,27] are as follows: $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (489 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (546 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (586 nm) and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (622 nm). The spectrum is dominated by the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition, which gives an intense green luminescence output for the solid sample.

Generally, it is possible to obtain detectable luminescence for Eu(III) and Tb(III) only by direct excitation at their absorption peaks (at 396 and 370 nm, respectively) [28]. The fact that, for both **2** and **3**, strong luminescence was observed by excitation at 336 nm indicates that we have succeeded to increase the absorption cross-section of both lanthanides by excitation of the ligand(s) and energy transfer to the Ln^{III} ion, i.e., by an indirect process (antenna effect).

It is well known that the antenna-to-cation sensitization process, which seems to be general in Eu(III) and Tb(III) complexes, includes a sequence of steps [1j,2a,2e,2k]: (i) Light absorption to produce an excited singlet (S) from the ground singlet state in the organic ligand(s). (ii) Intersystem crossing (ISC) to populate the lowest-lying triplet (T) state by a radiationless process; competing with this are organic fluorescence and radiationless deactivation of the excited singlet as thermal energy. (iii) Radiationless

transfer of energy from the triplet state to one (or more) lanthanide-centered excited levels; the requirement for effective transfer is that the triplet state should be close in energy to or above the 4f levels concerned, and (iv) Emission of energy if one of the 4f levels excited by the transfer has an allowed transition to a lower 4f level.

4. Concluding comments and perspectives

The present work extends the body of results that emphasize the ability of the monoanionic ligands $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ to form structurally interesting 4f-metal complexes. The use of the $(\text{py})_2\text{CO}/\text{NO}_3^-$ “blend” in erbium(III) chemistry has provided access to the new complex $[\text{Er}_2(\text{NO}_3)_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_2\{(\text{py})_2\text{C}(\text{OH})\text{O}\}]$ (**4**) which has been structurally characterized; this complex has the $\{\text{Er}_2(\mu\text{-OR})(\mu\text{-OR}')\}^{4+}$ core, where $\text{R} = (\text{py})_2\text{C}(\text{OH})^-$ and $\text{R}' = (\text{py})_2\text{C}(\text{OMe})^-$. Thus, complex **4** becomes the third structurally characterized lanthanide(III) complex with $(\text{py})_2\text{CO}$ -based ligands. Contrary to the previously characterized complexes $[\text{Er}(\text{NCS})_3\{(\text{py})_2\text{C}(\text{OEt})(\text{OH})\}_3]$ and $[\text{Er}_2(\text{NCS})_3\{(\text{py})_2\text{C}(\text{OMe})\text{O}\}_3(\text{MeOH})]$ [10], compound **4** possesses two different types of $(\text{py})_2\text{CO}$ -based ligands, i.e., $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$, that exhibit three distinct coordination modes. Thus, the principal objective of our studies, i.e., new structural types in $\text{Ln}(\text{III})/(\text{py})_2\text{CO}$ chemistry, has been realized. Based on analytical and spectroscopic studies, it seems that complexes **1–3** have a similar molecular structure with that of **4**. In this paper we have also demonstrated that the coordination of $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ and $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$ leads to complexes with efficient $\text{Ln}(\text{III})$ luminescence sensitization for Eu^{III} and Tb^{III} that emit in the visible region. This can be attributed to several factors such as the shielding of the metal ion from water and/or alcohol ligands, the lack of any strong ligand-to-metal charge-transfer bands that are usually responsible for the weak emission of the more readily reduced $\text{Eu}(\text{III})$, the lack of any energy back-transfer from the sensitizer triplet state, etc.

The nitrate terminal ligands present in **1–4** could have future utility as a means to access higher-nuclearity neutral or cationic clusters using bis(bidentate) bridging ligands, including aromatic heterocycles and dicarboxylates; such chemistry might alter the photophysical properties of the products. The ability of the *gem*-diol form of di-2-pyridyl ketone, “ $(\text{py})_2\text{C}(\text{OH})_2$ ” (Fig. 1), to act as a dianionic ligand ($(\text{py})_2\text{CO}_2^{2-}$, Fig. 1) and to bridge 3, 4 or 5 transition metal ions [7] gives also hopes for the isolation of high-nuclearity $\text{Ln}(\text{III})$ clusters if we find the right synthetic conditions for the formation of $(\text{py})_2\text{CO}_2^{2-}$. A ligand “blend” that might prove successful for this synthetic purpose is $(\text{py})_2\text{CO}/\text{RCO}_2^-$ [7]. Although only mononuclear and dinuclear complexes have been discovered from our work to date with lanthanide isothiocyanates and nitrates, clearly the $\text{Ln}^{\text{III}}/(\text{py})_2\text{CO}$ chemistry warrants further study

and also expansion to other inorganic anions with a higher charge and a higher bridging ability, e.g., SO_4^{2-} . Such synthetic efforts are in progress. In addition, we plan to try to design ligands in which the binding and antenna domains will be independent of each other; this will offer a wealth of possibilities for further derivatisation on the antenna part of the organic ligand, whilst maintaining binding properties, leading to improved photoluminescence properties of the resultant lanthanide(III) complexes.

5. Supplementary data

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax : +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) quoting the deposition number CCDC 295807 (**4** · 0.8EtOH · 0.4MeOH).

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