Di-2-pyridyl ketone in lanthanide(III) chemistry: Mononuclear and dinuclear erbium(III) complexes

Katerina A. Thiakou [a], Vassilios Nastopoulos [a], Aris Terzis [b],
Catherine P. Raptopoulou [b,*], Spyros P. Perlepes [a,*]

[a] *Department of Chemistry, University of Patras, 265 04 Patras, Greece*
[b] *Institute of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Athens, Greece*

Dedicated to Malcolm Chisholm, one of the giants in inorganic chemistry, on the occasion of his 60th birthday.

Abstract

The use of di-2-pyridyl ketone ($(py)_2CO$)/SCN^- "blend" in erbium(III) chemistry has yielded mononuclear and dinuclear complexes. The Er^{III}/SCN^-/$(py)_2CO$ reaction mixture in alcohols (MeOH, EtOH) gives complexes $[Er(NCS)_3\{(py)_2C(OR)(OH)\}_3]$ (R = Me (**1**), Et (**2**)), where $(py)_2C(OR)(OH)$ is the neutral hemiacetal derivative of $(py)_2CO$. Incorporation of hydroxides in the methanolic reaction system leads to the isolation of $[Er_2(NCS)_3\{(py)_2C(OMe)O\}_3(MeOH)]$ (**3**). Complex **3** can also be isolated by the reaction of **1** with three equivalents of NMe_4OH in MeOH. The crystal structures of $2 \cdot 0.3EtOH \cdot 0.4H_2O$ and $3 \cdot MeOH$ have been solved by single-crystal X-ray crystallography. The Er^{III} atom in the former is in a nine-coordinate, tricapped trigonal prismatic ligand environment. The $(py)_2C(OEt)(OH)$ molecules adopt the novel N(2-pyridyl), O(hydroxyl)-bidentate chelating mode, while three isothiocyanate ligands complete the coordination sphere of Er^{III}. In complex $3 \cdot MeOH$ the two Er^{III} atoms are triply bridged by the deprotonated hydroxyl oxygen atoms of the $\eta^1:\eta^2:\eta^1:\mu_2(py)_2C(OMe)O^-$ ligands; three 2-pyridyl nitrogen atoms belonging to three different ligands and two isothiocyanate anions complete eight-coordination at one Er^{III} atom, while eight-coordination at the other Er^{III} atom is completed by three 2-pyridyl nitrogen atoms, one isothiocyanate ligand and one MeOH molecule. The coordination polyhedra of the eight donor atoms about both Er^{III} atoms are best described as distorted dodecahedra. The complexes were studied by room-temperature effective magnetic moments and spectroscopic (IR, solid-state f–f) methods. All data are discussed in terms of the nature of bonding and known (**2**, **3**) or assigned (**1**) structures.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Di-2-pyridyl ketone-based ligands; Dodecahedral coordination geometry; Er(III) isothiocyanate complexes; f–f spectra; Tricapped trigonal prismatic geometry

1. Introduction

Lanthanide elements (Ln), bearing special electronic and spectroscopic properties mainly associated with their 4f electronic configuration, represent a unique series of metals in the periodic table [1]. The paramagnetic and optical properties of trivalent lanthanides, their hard acid character and their high coordination numbers make lanthanide(III) complexes attractive for applications such as magnetic resonance imaging (MRI) contrast agents [2], mild reagents and catalysts in organic synthesis [3], molecular magnetic materials [4], in luminescence studies [1] and in solvent extraction of actinides(III) [5]. For example, due to the impressive luminescence characteristics of several Ln^{3+} ions, they

* Corresponding authors. Tel.: +30 2610 997146; fax: +30 2610 997118.
E-mail addresses: craptop@ims.demokritos.gr (C.P. Raptopoulou), perlepes@patreas.upatras.gr (S.P. Perlepes).

are increasingly used as highly efficient electroluminescent components for light emitting diodes [6], luminescence probes for analytes [7], labels for proteins and amino acids [8], and for molecular recognition and chirality sensing of biological substrates [9]. Moreover, by incorporating Ln^{3+} ions into liquid crystals, it is possible to obtain mesogenic complexes that are useful for the design of emissive liquid crystal displays and magnetically addressable liquid crystals [10]. Consequently, lanthanide coordination chemistry has been thoroughly investigated over the last twenty years [11–20], and the position of Ln(III) complexes, primarily mononuclear ones, in various technologically and medically important areas, has now been firmly established.

Despite the great progress in the synthesis and physical (mainly magnetic) properties of polynuclear complexes (clusters) of the d-block metals at intermediate oxidation states [21–25], the number of Ln(III) clusters is still rather limited [26–34]. Dinuclear and polynuclear Ln(III) complexes exhibit a fascinating variety of unusual symmetries and structural patterns, and are expected to find such important applications as precursors for metalloorganic chemical vapour deposition (MOCVD) [35] and sol–gel technology [36], synthetic nucleases [37], new biomedical imaging contrast agents [38] and single-molecule magnets [39], the last potential application being currently confined to 3d-4f mixed-metal clusters.

Almost all clusters are made from complex reaction mixtures, which provide metal ions, ligand or ligands,

solvent molecules, counter-ions and, perhaps, traces of absorbed oxygen. Each component may influence the final product. Other variables include the pH and ionic strength of the solution, and the temperature of the reaction. One route to polynuclear complexes – a route perhaps best termed ''designed assembly'' – controls the reaction pathway by making a specific metal–ligand interaction the most significant in the system [40]. This approach finds limited application in Ln(III) chemistry. A complementary approach is ''serendipitous assembly'' [41], where the variables in the complex system are modified following certain rationales to influence the product found, rather than to control or design the target molecule [42].

The future of the field of 4f-metal clusters and the chances of identifying new complexes with interesting properties will both benefit from the development of new reaction systems with suitable organic ligands. Our group [43–49] and others [50–52] have been exploring reaction systems involving (i) the monoanion $(py)_2C(OH)O^-$, or the dianion, $(py)_2CO_2^{2-}$, 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 in Mn, Fe, Co, Ni, Cu, Zn, and Cd chemistries. The formulae of these ligands and their abbreviations are shown in Fig. 1. The reactions of $(py)_2CO$ with 3d-metal ions have been well-studied over the last ten years or so [43]. There

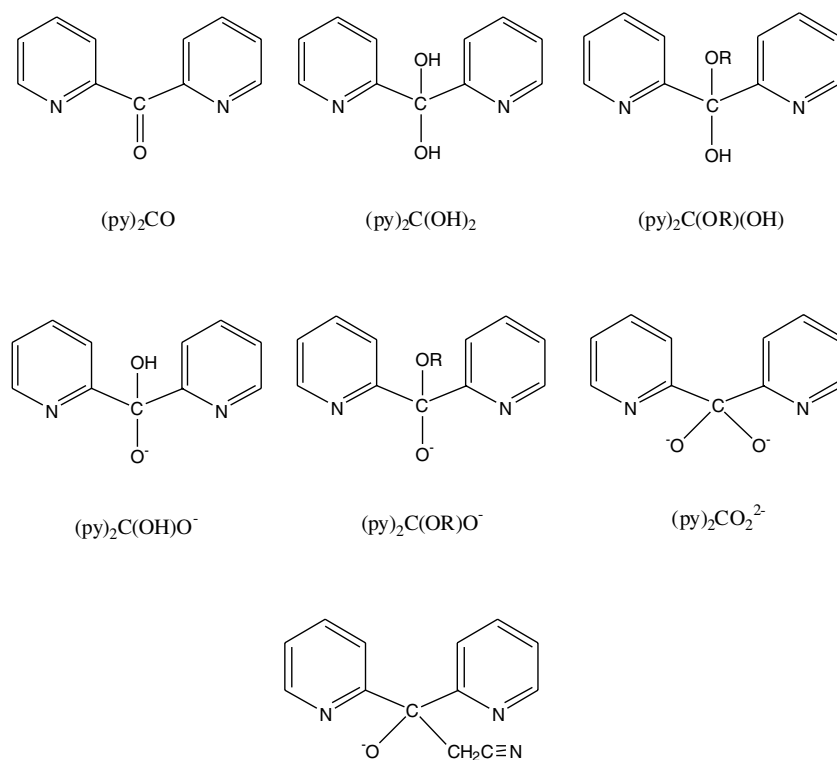Fig. 1. The derivatives of di-2-pyridyl ketone, $(py)_2CO$, discussed in the text; note that $(py)_2C(OH)_2$, $(py)_2C(OR)(OH)$ and all four anions do not exist as free species – they exist only as ligands in their metal complexes.

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 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 (Fig. 1). Recently [53] it has also been reported that the ligand (py)₂C(OH)-(CH₂CN)⁻, see Fig. 1, can be generated in situ during the preparation of a heterometallic Ni₁₂K₄ cluster by the reaction of CH₃CN and (py)₂CO at room temperature under aerobic conditions. The neutral ligands coordinate to the metal ion as tridentate *N,N,O* chelates, with the M–O bond often being weak; therefore, both neutral ligands do not present interest from the cluster formation viewpoint [43]. Completely different and much more interesting (for cluster chemistry) coordination modes are seen when the ligands (py)₂C(OH)₂ and (py)₂C(OR)(OH) are deprotonated. Upon deprotonation, the latter becomes monoanionic, whereas the former can function either as mono- or dianionic. The presence of deprotonated hydroxyl group(s) leads to a great coordinative flexibility, due to the well known ability of the negatively charged oxygen to bridge two or three 3d-metal ions. The immense structural diversity displayed by the complexes reported stems in part from the ability of (py)₂C(OH)O⁻, (py)₂CO₂²⁻ and (py)₂C(OR)O⁻ to exhibit no less than nine distinct bridging coordination modes ranging from μ_2 to μ_5 [43]. Employment of carboxylates, β-diketonates or organic oxo anions (NO₃⁻, SO₄²⁻, etc.) as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the isolation of a variety of 3d-metal clusters with nuclearities ranging from 3 to 14 [43] and with interesting physical properties including single-molecule magnetism [46].

Surprisingly, however, (py)₂CO-based ligands have been completely ignored in Ln(III) chemistry. Here, we report some experiments that lead to the first members of the new and diverse family of Ln(III) complexes with (py)₂CO-based ligands.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. For the preparation of the complexes, a methanolic solution of "Er(NCS)₃" (solution A) was prepared as follows: A solution (10 ml) of KSCN (6.0 mmol) in MeOH was treated with ErCl₃ · 6H₂O (2.0 mmol). The solid erbium(III) chloride soon dissolved, the mixture was stirred for 30 min and the white crystals of KCl were

removed by filtration. The resulting filtrate (∼11 ml) has a known concentration of "Er(NCS)₃". An ethanolic solution (∼25 ml) of "Er(NCS)₃" (solution B) was prepared by an analogous manner using a solution (23 ml) of KSCN (6.0 mmol) in warm EtOH and ErCl₃ · 6H₂O (2.0 mmol). Solutions A and B contain less than 10% of the original Cl⁻ ions (in the form of KCl) as deduced by the potentiometric determination of chlorides. It seems that the chloride concentration in solutions A and B does not affect the reactions.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. The metal content was determined volumetrically with ethylenediaminetetra-acetate using xylenol orange as indicator. IR spectra (4000–450 cm⁻¹) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. 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) spectra in the 200–800 nm range were recorded on a Varian Cary 3 spectrometer equipped with an integration sphere.

2.2. Compound preparation

2.2.1. [Er(NCS)₃{(py)₂C(OMe)(OH)₃}] (1)

To a pale pink solution A (1.1 ml, 0.2 mmol "Er(NCS)₃") was slowly added a solution of (py)₂CO (0.074 g, 0.40 mmol) in MeOH (8 ml). The resulting almost colourless solution was kept under stirring at room temperature for about 5 min, and then layered with Et₂O (15 ml). Slow mixing gave a pink polycrystalline solid, which was collected by filtration, washed with ice-cold MeOH (1 ml) and Et₂O (2 × 5 ml), and dried in vacuo over silica gel. Yield: 62% (based on the ligand). *Anal.* Calc. for C₃₉H₃₆ErN₉O₆S₃: C, 47.30; H, 3.67; N, 12.73; Er, 16.89. Found: C, 47.45; H, 3.50; N, 12.81; Er, 17.44%. IR (KBr, cm⁻¹): 3420 (mb), 3057 (w), 3044 (w), 2966 (w), 2902 (w), 2062 (s), 1598 (s), 1570 (m), 1472 (m), 1434 (s), 1294 (w), 1258 (m), 1234 (m), 1152 (sh), 1124 (m), 1104 (sh), 1050 (s), 1016 (m), 984 (m), 778 (s), 756 (sh), 684 (s), 636 (s), 530 (w), 501 (w), 454 (m). Effective magnetic moment (μ_{eff}): 9.56 BM (23 °C). Diffuse reflectance spectrum (DRS, nm): 261, 368, 378, 406, 447, 450, 488, 523, 530 (sh), 542, 552 (sh), 652, 657.

2.2.2. [Er(NCS)₃{(py)₂C(OEt)(OH)}₃] · 0.3EtOH · 0.4H₂O (2 · 0.3EtOH · 0.4H₂O)

To a pale pink solution B (2.5 ml, 0.2 mmol "Er(NCS)₃") was slowly added a solution of (py)₂CO (0.074 g, 0.40 mmol) in EtOH (7 ml). The resulting

homogeneous, almost colourless solution was allowed to stand undisturbed for one day at 5 °C, during which time X-ray quality pink crystals of the product were precipitated. The crystals were collected by filtration, washed with ice-cold EtOH (2×1 ml) and Et_2O (2×5 ml), and dried in vacuo over silica gel. Yield: 49% (based on the ligand). A sample for crystallography was covered with epoxy glou to prevent collapse. The vacuum-dried sample analysed as unsolvated. *Anal.* Calc. for $C_{42}H_{42}ErN_9O_6S_3$: C, 48.86; H, 4.11; N, 12.21; Er, 16.20. Found: C, 48.67; H, 4.20; N, 12.07; Er, 16.99%. IR (KBr, cm^{-1}): 3446 (mb), 3058 (w), 3045 (w), 2976 (w), 2930 (w), 2894 (w), 2062 (s), 1598 (s), 1572 (sh), 1468 (w), 1438 (m), 1336 (w), 1268 (w), 1236 (s), 1156 (w), 1118 (m), 1065 (sh), 1050 (s), 1018(m), 962 (w), 886 (w), 806 (w), 762 (s), 670 (sh), 642 (m), 628 (m), 572 (m), 532 (w), 486 (w), 464 (w). μ_{eff} (BM): 9.51 (20 °C). DRS (nm): 262, 365, 374 (sh), 380, 405, 448, 451, 489, 523, 529 (sh), 543, 553 (sh), 653, 659.

2.2.3. [Er₂(NCS)₃{(py)₂C(OMe)O}₃(MeOH)] · MeOH (3 · MeOH)

2.2.3.1. Method A. Solids (py)₂CO (0.037 g, 0.20 mmol), LiOH · H₂O (0.0084 g, 0.20 mmol) and LiClO₄ · 3H₂O (0.064 g, 0.40 mmol) were dissolved in MeOH (15 ml), resulting in a colourless solution. This was added to a pale pink solution A (1.1 ml, 0.2 mmol). The resulting new pinkish solution was stirred for about 1 h and filtered to remove a very small quantity of insoluble material. The filtrate was allowed to stand undisturbed for 4 days during which time the product slowly crystallized. The pink crystals were collected by filtration, washed with cold MeOH (1 ml) and Et_2O (2×5 ml), and dried in vacuo. Yield: 79% (based on the ligand). A sample for crystallography was kept in contact with the mother liquor to prevent interstitial MeOH loss. The air-dried sample analysed as unsolvated. *Anal.* Calc. for $C_{40}H_{37}Er_2N_9O_7S_3$: C, 40.49; H, 3.15; N, 10.63; Er, 28.19. Found: C, 40.61; H, 3.20; N, 10.99; Er, 27.71%. IR (KBr, cm^{-1}): 3430 (mb), 3072 (w), 2962 (w), 2930 (w), 2066 (s), 1600 (s), 1570 (m), 1472 (m), 1436 (s), 1340 (w), 1294 (m), 1258 (s), 1230 (s), 1124 (s), 1108 (sh), 1054 (s), 1038 (sh), 1010 (m), 984 (m), 968 (sh), 952 (sh), 778 (s), 752 (sh), 686 (s), 634 (s), 576 (w), 534 (w), 492 (w), 456 (m). μ_{eff} (BM): 9.54 (21 °C). DRS (nm): 269, 366, 379, 408, 442, 451, 488, 522, 525 (sh), 533 (sh), 543, 655, 670 (sh).

2.2.3.2. Method B. Treatment of a slurry of complex **1** (0.099 g, 0.10 mmol) in MeOH (20 ml) with NMe₄OH (0.054 g, 0.30 mmol) resulted in a pink solution. The solution was heated at 40 °C for 5 min, during which time no noticeable colour change was observed. The solution was filtered through celite and allowed to slowly evaporate at room temperature. The resulting microcrystalline solid was collected by filtration, washed

with Et_2O (2×3 ml), and dried in vacuo over silica gel. Yield 30% (based on **1**). The dried solid analysed satisfactorily as **3**. The identity of the product was further confirmed by IR spectroscopic comparison with the authentic sample prepared by Method A.

2.3. Single-crystal X-ray crystallography

Crystals of **2** · 0.3EtOH · 0.4H₂O and **3** · MeOH were mounted in air and covered with epoxy glou, and in capillary, respectively. 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 $11 < 2\vartheta < 23°$. 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.

Table 1
Crystallographic data for complexes **2** · 0.3EtOH · 0.4H₂O and **3** · MeOH

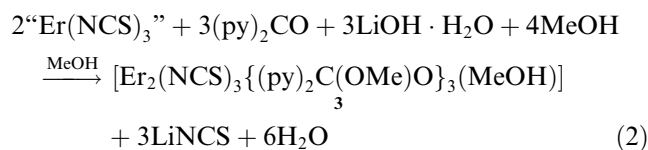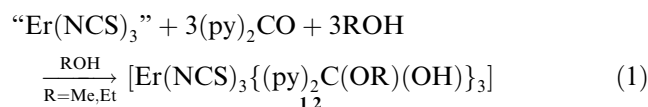| Parameter	**2** · 0.3EtOH · 0.4H₂O	**3** · MeOH
Formula	$C_{42.6}H_{44.6}ErN_9O_{6.7}S_3$	$C_{41}H_{41}Er_2N_9O_8S_3$
Formula weight	1053.31	1218.53
Crystal colour, habit	pale pink, prism	pale pink, prism
Crystal dimensions (mm)	$0.50 \times 0.50 \times 0.60$	$0.08 \times 0.18 \times 0.40$
Crystal system	hexagonal	triclinic
Space group	$P3_1$	$P\bar{1}$
Unit cell dimensions		
α (Å)	12.218(6)	10.458(6)
b (Å)	12.218(6)	14.128(8)
c (Å)	30.30(2)	16.747(9)
α (°)	90	84.14(2)
β (°)	90	75.52(2)
γ (°)	120	85.68(2)
V (Å³)	3917(4)	2380(2)
Z	3	2
ρ_{calc} (g cm⁻³)	1.339	1.700
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Temperature (K)	298	298
Scan mode/speed (° min⁻¹)	ϑ–2ϑ/4.0	ϑ–2ϑ/5.0
$2\theta_{max}$ (°)	50.0	50.04
μ (mm⁻¹)	1.777	3.691
Reflections collected/ unique (R_{int})	8201/7672(0.1096)	8504/8035(0.0221)
Data with $I > 2\sigma(I)$	7299	6340
Parameters refined	563	580
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å⁻³)	0.915, −0.963	0.675, −0.535
Goodness-of-fit (on F^2)	0.0690, 0.01797	1.137
R_1,[a] wR_2[b] (all data)	0.0729, 0.1880	0.0481, 0.0953
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0690, 0.1797	0.0312, 0.0868

[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 structures were solved by direct methods using SHELXS-86 [54] and refined by full-matrix least squares techniques on F^2 with SHELXL-97 [55]. For both structures, all hydrogen atoms were introduced at calculated positions as riding on bonded atoms. For $3 \cdot MeOH$, all non-hydrogen atoms were refined using anisotropic thermal parameters. For $2 \cdot 0.3EtOH \cdot 0.4H_2O$, all non-hydrogen atoms – except those of the solvate molecules – were refined anisotropically.

3. Results and discussion

3.1. Synthetic comments

The chemical and structural identities of the products from the "Er(NCS)$_3$"/(py)$_2$CO reaction system in alcohols depend on the OH$^-$ concentration. The mononuclear complexes **1** and **2** were isolated from the direct reaction between "Er(NCS)$_3$" and (py)$_2$CO, whereas employment of hydroxides leads to the dinuclear complex **3**. The formation of these Er(III) complexes can be summarized in balanced Eqs. (1) and (2).

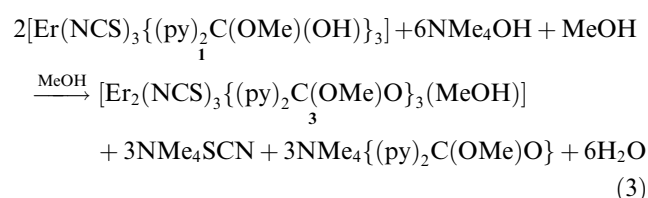$$\text{"Er(NCS)}_3\text{"} + 3(py)_2CO + 3ROH$$
$$\xrightarrow[\text{R=Me,Et}]{ROH} [Er(NCS)_3\{(py)_2\underset{\mathbf{1,2}}{C}(OR)(OH)\}_3] \qquad (1)$$

$$2\text{"Er(NCS)}_3\text{"} + 3(py)_2CO + 3LiOH \cdot H_2O + 4MeOH$$
$$\xrightarrow{MeOH} [Er_2(NCS)_3\{(py)_2\underset{\mathbf{3}}{C}(OMe)O\}_3(MeOH)]$$
$$+ 3LiNCS + 6H_2O \qquad (2)$$

The Er(III)-mediated addition of solvent (MeOH, EtOH) to (py)$_2$CO to give the neutral hemiacetal derivative of di-2-pyridyl ketone, (py)$_2$C(OR)(OH) (Fig. 1), in **1** and **2**, and the monoanion of this derivative, (py)$_2$C(OR)O$^-$ (Fig. 1), in **3** involves a nucleophilic attack of the ROH molecule on the carbonyl group [43]. The electrophilic character of the carbonyl group of (py)$_2$CO 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) [43].

Two features of the reactions represented by Eqs. (1) and (2) deserve comments. First, the "wrong" stoichiometries employed for the preparation of **1**–**3** (see Section 2.2), compared to those required by Eqs. (1) and (2), obviously did not prove detrimental to the formation of the complexes. With the identities of **1**–**3** established, the "correct" stoichiometries, i.e., Er(III):(py)$_2$CO = 1:3, were employed and led to pure compounds in high yields. Second, the presence of LiClO$_4 \cdot$ 3H$_2$O in the reaction mixture that leads to **3** might imply that cationic complexes are capable of existing; we did *not* have such an evidence during our synthetic efforts.

LiClO$_4 \cdot$ 3H$_2$O is beneficial only for the isolation of single crystals of **3**; in other words, its presence does not affect the identity of the product, but only its crystallization, most probably through the alteration of the ionic strength of the reaction solution. We have not performed experiments to see how different ratios of LiClO$_4$ affect the yield of **3**. If no LiClO$_4$ is added, the same product is isolated (elemental analyses and IR confirmation) in ∼70% yield, but in the form of microcrystalline powder.

The fact that complexes **1** and **3** contain basically the same ligand set (the only difference being in the protonation state of the ligand), led us to suspect that **1** would be transformed to **3**; this has, indeed, turned out to be the case. This Brönsted acidity of **1** is summarized in Eq. (3).

$$2[Er(NCS)_3\{(py)_2\underset{\mathbf{1}}{C}(OMe)(OH)\}_3] + 6NMe_4OH + MeOH$$
$$\xrightarrow{MeOH} [Er_2(NCS)_3\{(py)_2\underset{\mathbf{3}}{C}(OMe)O\}_3(MeOH)]$$
$$+ 3NMe_4SCN + 3NMe_4\{(py)_2C(OMe)O\} + 6H_2O$$
$$(3)$$

3.2. Description of structures

Partially labelled plots of the mononuclear and dinuclear molecules present in complexes $2 \cdot 0.3EtOH \cdot 0.4H_2O$ and $3 \cdot MeOH$ are shown in Figs. 2 and 4, respectively. The coordination polyhedra of the Er^{III} atoms are shown in Figs. 3 and 5. Selected interatomic distances and angles are listed in Tables 2 and 3.

The crystal structure of $2 \cdot 0.3EtOH \cdot 0.4H_2O$ consists of discrete [Er(NCS)$_3$\{(py)$_2$C(OEt)(OH)\}$_3$] molecules and solvate molecules; the latter will not be further discussed.
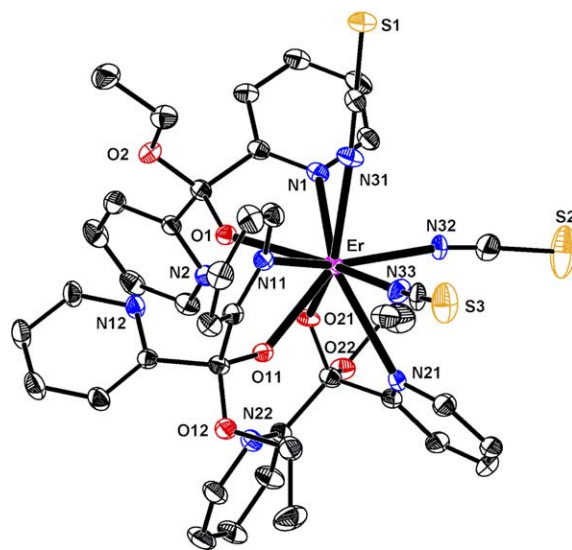

Fig. 2. The structure of the mononuclear complex molecule present in complex $2 \cdot 0.3EtOH \cdot 0.4H_2O$.

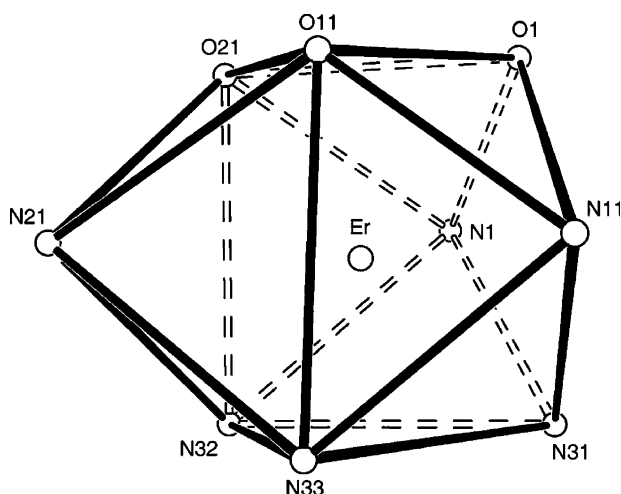Fig. 3. A view of the inner coordination polyhedron of **2** · 0.3EtOH · 0.4H$_2$O showing the tricapped trigonal prismatic coordination of the Er^{III} atom.
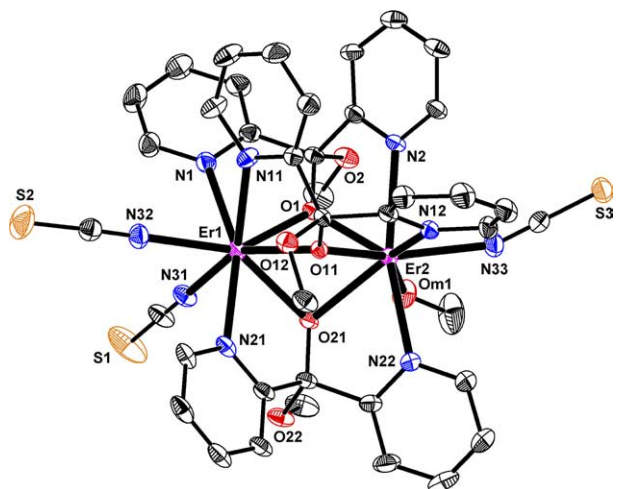
Fig. 4. The structure of the dinuclear molecule present in complex **3** · MeOH.

Fig. 5. The dodecahedral stereochemistry about the Er^{III} atoms in complex **3** · MeOH.

The Er^{III} atom is in a nine-coordinate ligand environment comprising three hydroxyl oxygen atoms and three 2-pyridyl nitrogen atoms from the three (py)$_2$C(OEt)(OH) ligands, and the three nitrogen atoms from the isothiocyanate anions. The Er–N bond lengths fall into two distinct categories; those involving the organic ligands (2.707(10)–2.755(11) Å) and those involving the isothiocyanate ligands (2.356(11)–2.376(11) Å). The Er–N(isothiocyanate) distances have an average value of 2.364(11) Å which is slightly longer, as expected, than that of an eight-coordinated Er(III) complex containing terminal isothiocyanate ligands (2.327(6) Å) [56]. The SCN$^-$ ions are not perfectly linear, the N–C–S bond angles being in the range 175.9(18)–179.0(12)°. The terminal isothiocyanate anions involving N(31) and N(33) as donor atoms are coordinated in a slightly bent fash-
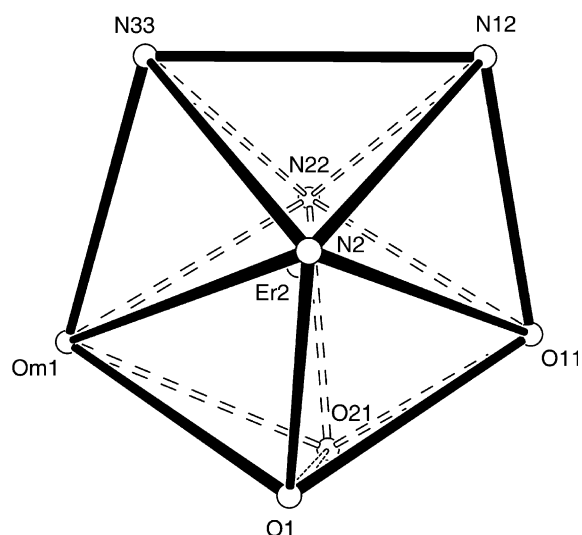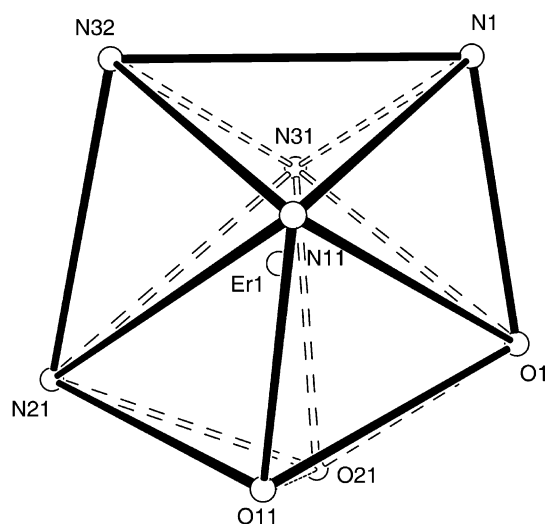
ion, as indicated by the Er–NC angles (160.7(11)°, 161.5(11)°); the third SCN$^-$ion is coordinated in a more linear fashion (Er–N(32)–C(62) = 170.5(14)°). No hydrogen bonds are involved in the crystal lattice.

The coordination polyhedron of the Er^{III} atom is best described as a distorted tricapped trigonal prism with the three 2-pyridyl nitrogen donor atoms, N(1), N(11) and N(21), forming the three rectangular face caps. The angle sum subtended by the three capping atoms at Er is 358.3°.

The (py)$_2$C(OEt)(OH) molecules behave as η^1:η^1 ligands in **2**, see Fig. 6. The ethoxy oxygen atom remains unbound to the Er^{III} atom. The ligand forms one five-membered ErNCCO chelating ring. 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 [43], but the particular bidentate chelating coordination mode (Fig. 6) observed for (py)$_2$C(OEt)-

Table 2
Selected bond distances (Å) and angles (°) for the mononuclear erbium(III) complex **2** · 0.3EtOH · 0.4H$_2$O

Bond distances	
Er–O(1)	2.378(7)
Er–O(11)	2.358(7)
Er–O(21)	2.388(8)
Er–N(1)	2.717(10)
Er–N(11)	2.707(10)
Er–N(21)	2.755(11)
Er–N(31)	2.376(11)
Er–N(32)	2.361(10)
Er–N(33)	2.356(11)
C(61)[a]–N(31)	1.156(17)
C(61)[a]–S(1)	1.615(13)
C(62)[a]–N(32)	1.10(2)
C(62)[a]–S(2)	1.657(19)
C(63)[a]–N(33)	1.193(19)
C(63)[a]–S(3)	1.613(15)
Bond angles	
O(1)–Er–O(11)	71.9(3)
O(1)–Er–N(11)	74.6(3)
O(1)–Er–N(32)	134.7(4)
O(11)–Er–O(21)	73.5(2)
O(11)–Er–N(1)	127.8(3)
O(11)–Er–N(33)	90.0(4)
O(21)–Er–N(11)	129.4(3)
O(21)–Er–N(21)	62.0(3)
O(21)–Er–N(32)	86.9(4)
N(1)–Er–N(11)	120.8(3)
N(1)–Er–N(31)	67.3(4)
N(1)–Er–N(32)	74.6(4)
N(11)–Er–O(11)	61.0(3)
N(11)–Er–N(21)	117.8(3)
N(11)–Er–N(32)	142.7(4)
N(21)–Er–O(11)	72.1(3)
N(21)–Er–N(31)	143.1(4)
N(21)–Er–N(33)	73.1(4)
N(31)–Er–O(11)	135.6(4)
N(31)–Er–N(11)	75.5(4)
N(31)–Er–N(32)	81.6(4)
N(32)–Er–O(11)	139.6(4)
N(32)–Er–N(21)	86.9(4)
N(32)–Er–N(33)	79.1(5)
N(33)–Er–O(21)	134.9(3)
N(33)–Er–N(11)	68.8(4)
N(33)–Er–N(31)	81.9(4)
N(31)–C(61)[a]–S(1)	179.0(12)
N(32)–C(62)[a]–S(2)	175.9(18)
N(33)–C(63)[a]–S(3)	178.3(12)

[a] These carbon atoms, which have not been labelled in Fig. 2, belong to the isothiocyanate ligands.

Table 3
Selected interatomic distances (Å) and bond angles (°) for the dinuclear erbium(III) complex **3** · MeOH

Interatomic distances	
Er(1)···Er(2)	3.380(2)
Er(1)–O(1)	2.253(4)
Er(1)–O(11)	2.331(4)
Er(1)–O(21)	2.317(4)
Er(1)–N(1)	2.528(5)
Er(1)–N(11)	2.589(6)
Er(1)–N(21)	2.483(5)
Er(1)–N(31)	2.346(6)
Er(1)–N(32)	2.364(6)
Er(2)–O(1)	2.269(4)
Er(2)–O(11)	2.231(4)
Er(2)–O(21)	2.327(4)
Er(2)–N(2)	2.529(5)
Er(2)–N(12)	2.549(5)
Er(2)–N(22)	2.472(5)
Er(2)–Om(1)	2.380(5)
Er(2)–N(33)	2.367(6)
Bond angles	
O(1)–Er(1)–O(21)	67.3(1)
O(1)–Er(1)–N(31)	96.5(2)
O(11)–Er(1)–N(21)	76.8(2)
O(11)–Er(1)–N(31)	149.4(2)
O(21)–Er(1)–N(21)	67.3(2)
O(21)–Er(1)–N(31)	81.6(2)
N(1)–Er(1)–O(11)	123.9(2)
N(1)–Er(1)–N(21)	158.0(2)
N(11)–Er(1)–O(21)	129.0(1)
N(11)–Er(1)–N(32)	76.2(2)
N(21)–Er(1)–O(1)	133.1(2)
N(21)–Er(1)–N(31)	87.9(2)
N(31)–Er(1)–N(1)	76.6(2)
N(31)–Er(1)–N(11)	147.0(2)
N(32)–Er(1)–O(21)	145.1(2)
N(32)–Er(1)–N(21)	81.0(2)
O(1)–Er(2)–O(11)	77.9(1)
O(1)–Er(2)–Om(1)	79.6(2)
O(11)–Er(2)–N(22)	91.2(2)
O(11)–Er(2)–N(33)	142.0(2)
O(21)–Er(2)–N(22)	67.1(2)
O(21)–Er(2)–N(33)	141.8(2)
N(2)–Er(2)–O(11)	89.9(2)
N(2)–Er(2)–Om(1)	107.7(2)
N(12)–Er(2)–O(21)	126.0(2)
N(12)–Er(2)–N(33)	76.8(2)
N(22)–Er(2)–N(12)	85.7(2)
N(22)–Er(2)–Om(1)	82.7(2)
Om(1)–Er(2)–N(12)	150.3(2)
Om(1)–Er(2)–N(33)	75.4(2)
N(33)–Er(2)–N(2)	80.0(2)
N(33)–Er(2)–N(22)	87.4(2)

(OH) in **2** is unprecedented. In all the up-to-now structurally characterized d-metal complexes containing O-bound (py)$_2$C(OR)(OH) ligands (R = Me, Et), the alkylated oxygen is the ligated atom [43,57,58].

Complex **3** · MeOH crystallizes in monoclinic space group P1̄. Its structure consists of dinuclear [Er$_2$(NCS)$_3${(py)$_2$C(OMe)O}$_3$(MeOH)] molecules and solvate MeOH molecules; the latter will not be further discussed. In the dinuclear molecule, the monoanionic hemiacetal

form of the organic ligand bridges the metal centers through the deprotonated hydroxyl group and the –OMe group points away from the metals. The two Er^{III} atoms are triply bridged by the deprotonated hydroxyl oxygen atoms (O(1), O(11), O(21)) of the (py)$_2$C(OMe)O$^-$ ligands. Three 2-pyridyl nitrogen atoms (N(1), N(11), N(21)) and two isothiocyanate ligands complete eight-coordination at Er(1), while eight-coordination at Er(2)
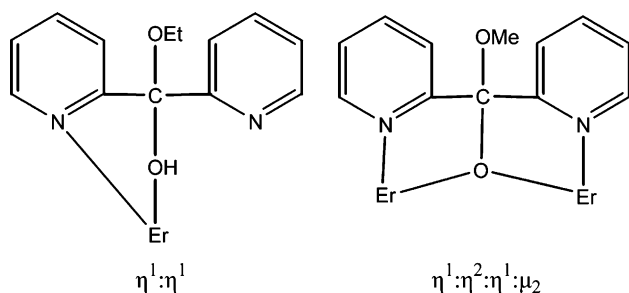
Fig. 6. The crystallographically established coordination modes of $(py)_2C(OEt)(OH)$ and $(py)_2C(OMe)O^-$ in complexes $\mathbf{2} \cdot 0.3EtOH \cdot 0.4H_2O$ and $\mathbf{3} \cdot MeOH$, respectively.

is completed by three 2-pyridyl nitrogen atoms (N(2), N(12), N(22)), one isothiocyanate ligand and one methanol molecule.

The Er–O distances are in the relatively narrow range 2.231(4)–2.380(5) Å; this range is typical for eight-coordinate Er(III) complexes [59–61]. The Er–N bond lengths again fall into two distinct categories; those involving the organic ligands (2.472(5)–2.589(6) Å) and those involving the isothiocyanate ligands (2.346(6)–2.367(6) Å). The Er–N(2-pyridyl) distances in $\mathbf{3} \cdot MeOH$ have an average value of 2.525(6) Å, which is shorter than the corresponding value in $\mathbf{2} \cdot 0.3EtOH \cdot 0.4H_2O$ (2.726(11) Å); the decreased Er–N(2-pyridyl) distances in the former are a consequence of the lower coordination number of the Er^{III} atoms compared to that in the latter (eight versus nine). However, an analogous trend does not hold true for the Er–N(isothiocyanate) distances. These bond distances have similar average values in $\mathbf{2} \cdot 0.3EtOH \cdot 0.4H_2O$ (2.364(11) Å) and $\mathbf{3} \cdot MeOH$ (2.359(6) Å). This discrepancy emphasizes the fact that in lanthanide complexes, where the bonding is regarded as being substantially ionic, the coordination number is determined by packing considerations, this in turn determining the bond lengths between the central metal ion and the atoms surrounding it [62]. The bridging Er–O distances involving O(11) are asymmetric (Er(1)–O(11) = 2.331(4) Å, Er(2)–O(11) = 2.231(4) Å). The terminal isothiocyanate ligands bind to Er(1) in an almost linear fashion, as indicated by the Er–N≡C angles (175.6(6)°, 177.5(6)°); the third isothiocyanate ligand binds to Er(2) in a slightly bent fashion (Er(2)–N(33)–C(63) = 159.5(6)°). The Er(1)···Er(2) distance is 3.380(2) Å.

The coordination polyhedra of the eight donor atoms about the Er^{III} atoms are best described as distorted dodecahedra [63], see Fig. 5. For example, if we consider the polyhedron of Er(2), atoms N(33), N(12), O(1), O(21) 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(22), O(11), Om(1) 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 [63] as two interpenetrating planar trapezoids N(12)N(33)O(11)Om(1) and N(2)N(22)O(1)O(21).

The $(py)_2C(OMe)O^-$ anions behave as $\eta^1:\eta^2:\eta^1:\mu_2$ ligands in $\mathbf{3}$, see Fig. 6. The methoxy oxygen atom remains unbound to the metals. The monoanionic ligand forms two five-membered ErNCCO chelating rings with two different Er^{III} atoms; these rings share a common C–O edge. This ligation mode is common in the coordination chemistry of the hemiacetal forms of di-2-pyridyl ketone [43,44].

No hydrogen bonds are involved in the crystal structure of $\mathbf{3} \cdot MeOH$. The crystal structure is stabilized by two intermolecular π–π stacking interactions. The first involves the two 2-pyridyl rings that involve N(21) and is shown in Fig. 7; the centroid···centroid distance is 3.505 Å (the symmetry code is $-x$, $-y$, $-z + 1$). The two rings are strictly parallel due to the presence of a crystallographically imposed inversion center at $c/2$. The second type of the π–π stacking interactions involves the two 2-pyridyl rings that involve N(2) and are in the symmetry relationship x, y, z and $-x + 1$, $-y + 1$, $-z$; the centroid···centroid distance is 3.653 Å. There also appears to be a weak intramolecular stacking interaction between the two 2-pyridyl rings involving N(2) and N(11), the centroid···centroid distance being 3.934 Å.

3.3. Magnetic moments, electronic and IR spectra

The experimental, room-temperature μ_{eff} values per Er^{III} for complexes 1–3 (see Section 2.2) show very little deviation from the theoretical value of 9.6 BM predicted by Eq. (4), suggesting that the 4f electrons in the com-
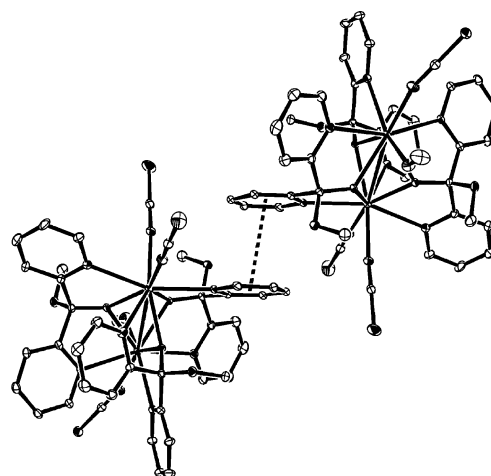

Fig. 7. A view of the intermolecular π–π stacking interaction between the parallel 2-pyridyl rings that involve N(21) in complex $\mathbf{3} \cdot MeOH$. The symmetry codes of the two rings are x, y, z and $-x$, $-y$, $-z + 1$. Only two neighbouring dinuclear molecules have been drawn; the centroid···centroid distance is 3.505 Å.

plexed Er^{III} atoms are well-shielded by the outermost 5s and 5p electrons [64]

$$\mu_{eff} = g[J(J+1)]^{1/2}. \tag{4}$$

The solid-state (diffuse reflectance) electronic spectra of the prepared complexes involve mainly intraligand and f–f transitions. Detailed assignments of the main f–f-bands for complex **2** (considered as a representative example) are given in Table 4. The values of the bonding parameters $\bar{\beta}$ (nephelauxetic ratio), δ (Sinha's parameter) and $b^{1/2}$ (covalent factor), calculated [65–67] from the solid-state f–f spectra by Eqs. (5)–(7), are listed in Table 5. The values indicate that the interaction between Er^{III} and the ligands is essentially electrostatic and that there is a minor participation of the 4f orbitals in bonding [65–67]

$$\bar{\beta} = \frac{1}{2} \sum_{n=1}^{n} \frac{\bar{V}_{complex}}{\bar{V}_{aquo}}, \tag{5}$$

$$\delta \; (\%) = \frac{1 - \bar{\beta}}{\bar{\beta}} \times 100, \tag{6}$$

$$b^{1/2} = \left[\frac{1}{2} \left(1 - \bar{\beta} \right) \right]^{1/2}. \tag{7}$$

The shape and fine structure of the f–f band assigned to the "hypersensitive" transition $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (Er–I) are sensitive to coordination number [68]. By comparing the spectra of **1**–**3** with the spectra of Er(III) complexes of known structures [59,68,69] in the region of the above-mentioned transition, it is confirmed (complex **2**) or concluded (complex **1**) that the metal ion is nine-coordinate; similarly, this comparison confirms that

the Er^{III} atoms in **3** are eight-coordinate (the bands/shoulders due to this transition appear at 522, 525 and 533 in the spectrum of **3**).

The IR spectra of **1** and vacuum-dried (solvent free) **2** exhibit a medium intensity band at 3420 (**1**) and 3446 (**2**) cm^{-1}, assignable to $v(OH)$ vibration of the $(py)_2C$-$(OR)(OH)$ ligands [57]. The presence of coordinated MeOH in vacuum-dried **3** is manifested by the medium intensity band at 3430 cm^{-1} assigned to $v(OH)$ [70]. The spectra of the three complexes do not exhibit bands in the region expected for $v(C=O)$ vibration (1684 cm^{-1} for free $(py)_2CO$) with the nearest IR absorptions at 1598 (**1**, **2**) and 1600 (**3**) cm^{-1} assigned as a 2-pyridyl stretching mode raised from 1582 cm^{-1} on coordination, as observed earlier on complex formation involving alcoholysis or hydration of $(py)_2CO$ [44,71]. The bands at $\sim$1050, $\sim$770 and $\sim$640 cm^{-1} can be assigned [58] to pyridyl ring breathing, pyridyl C–H out-of-plane bending and in-plane pyridyl ring deformation vibrations, respectively. The IR spectra of **1**–**3** exhibit the $v(CN)$ mode of the SCN^- ligands at $\sim$2065 cm^{-1}; this wavenumber is typical of terminal isothiocyanate groups [72,73]. The expected $v(CS)$ and $\delta(NCS)$ bands could not be located and unambiguously assigned because they are obscured by $(py)_2C(OR)(OH)/(py)_2$-$C(OMe)O^-$ absorptions.

4. Conclusions and perspectives

Complexes $[Er(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ (**2**) and $[Er_2(NCS)_3\{(py)_2C(OMe)O\}_3(MeOH)]$ (**3**) cover a gap in the literature, because these are the first structurally characterized lanthanide(III) complexes with $(py)_2CO$-based ligands. Thus, the principal objective of our studies has been realized. Based on analytical and spectroscopic data, it seems that complex **1** has a similar molecular structure with that of **2**. It is also of interest that complex **2** (and presumably **1**) exhibits a novel coordination mode for the ligand $(py)_2C(OEt)(OH)$.

Although only mononuclear and dinuclear complexes have been discovered from our work, clearly the $Ln^{III}/(py)_2CO$ chemistry warrants further study and expansion to other solvents (e.g., H_2O, MeCN, DMF, etc.) that favour the formation of the *gem*-diol form of di-2-pyridyl ketone, $(py)_2C(OH)_2$ (Fig. 1). For example, the ability of this form to act as a dianionic ligand and to bridge 3, 4 or 5 metal ions [43] gives hopes for the isolation of high-nuclearity Ln(III) clusters. A ligand "blend" that might prove highly successful for this synthetic purpose is $(py)_2CO_2^{2-}/RCO_2^-$ [43]. The isothiocyanate terminal ligands present in **1**–**3** could have future utility as sites for facile incorporation of other monodentate ligands by metathesis, or as a means to access higher-nuclearity neutral or cationic clusters using bis(monodentate) and/or bis(bidentate) bridging

Table 4
Main, solid-state f–f bands of the representative complex **2**

λ (nm)	Assignment
659, 653	$^4I_{15/2} \rightarrow {}^4F_{9/2}$
543	$^4I_{15/2} \rightarrow {}^4S_{3/2}$
529 (sh), 523	$^4I_{15/2} \rightarrow {}^2H_{11/2}$ (Er–I)[a]
489	$^4I_{15/2} \rightarrow {}^4F_{7/2}$
380, 374 (sh)	$^4I_{15/2} \rightarrow {}^4G_{11/2}$ (Er–II)[a]

[a] These transitions are "hypersensitive".

Table 5
Bonding parameters[a,b] for the Er(III) complexes **1**–**3**

Complex	$\bar{\beta}$	δ (%)	$b^{1/2}$
1	0.996	+0.40	0.045
2	0.995	+0.50	0.050
3	0.994	+0.60	0.055

[a] Calculated from solid-state f–f spectra taking into account the wavenumbers of the $^4I_{15/2} \rightarrow {}^4F_{9/2}, {}^4S_{3/2}, {}^2H_{11/2}, {}^4F_{7/2}, {}^4F_{5/2}, {}^4F_{3/2}, ({}^2G, {}^4F, {}^2H)_{9/2}$ and $^4G_{11/2}$ transitions.
[b] For the definition of the bonding parameters $\bar{\beta}$, δ (%) and $b^{1/2}$, see text.

ligands, including aromatic heterocycles and dicar-boxylates.

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 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 numbers 274911 ($\mathbf{2} \cdot 0.3EtOH \cdot 0.4H_2O$) and 274912 ($\mathbf{3} \cdot MeOH$).

Acknowledgements

References

[1] See the various chapters in G.R. Choppin, J.-C.G. Bünzli (Eds.), Lanthanide Probes in Life, Chemical and Earth Science, Elsevier, Amsterdam, 1989.
[2] S. Aime, M. Botta, M. Fasano, E. Terreno, Chem. Soc. Rev. 27 (1998) 19.
[3] T. Imamoto, Lanthanides in Organic Synthesis, Academic Press, New York, 1994.
[4] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J. Am. Chem. Soc. 125 (2003) 8694.
[5] M.G.B. Drew, P.B. Iveson, M.J. Hudson, J.O. Liljenzin, L. Spjuth, P.-Y. Cordier, A. Enarsson, C. Hill, C. Madic, J. Chem. Soc., Dalton Trans. (2000) 821.
[6] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
[7] D. Parker, Coord. Chem. Rev. 205 (2000) 109.
[8] V.W.W. Yam, K.K.W. Lo, Coord. Chem. Rev. 184 (1999) 157.
[9] H. Tsukube, S. Shinoda, H. Tamiaki, Coord. Chem. Rev. 226 (2002) 227.
[10] K. Binnemans, C. Görller-Walrand, Chem. Rev. 102 (2002) 2303.
[11] R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut, P.-V. Cordier, C. Madic, Inorg. Chem. 37 (1998) 6690.
[12] A. Bellusci, G. Barberio, A. Crispini, M. Ghedini, M. La Deda, D. Pucci, Inorg. Chem. 44 (2005) 1818.
[13] G. Mancino, A.J. Ferguson, A. Beeby, N.J. Long, T.S. Jones, J. Am. Chem. Soc. 127 (2005) 524.
[14] C. Piguet, J.-C.G. Bünzli, Chem. Soc. Rev. 28 (1999) 347.
[15] D.R. van Staveren, G.A. van Albada, S. Gorter, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 300–302 (2004) 1104.
[16] M.K. Thompson, A.J. Lough, A.J. White, D.J. Williams, I.A. Kahwa, Inorg. Chem. 42 (2003) 4828.
[17] G. Champion, N. Lalioti, V. Tangoulis, M.-A. Arrio, P. Sainctavit, F. Villain, A. Caneschi, D. Gatteschi, C. Giorgetti, Baudelet, M. Verdaguer, C.C. dit Moulin, J. Am. Chem. Soc. 125 (2003) 8371.
[18] V. Monga, B.O. Patrick, C. Orvig, Inorg. Chem. 44 (2005) 2666.
[19] S.W. Magennis, S. Parsons, Z. Pikramenou, Chem. Eur. J. 8 (2002) 5761.
[20] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, D.P. Shum, R.L. Carlin, Inorg. Chem. 28 (1989) 272.
[21] R.E.P. Winpenny, Adv. Inorg. Chem. 52 (2001) 1.
[22] G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, MRS Bull. 25 (2000) 66.
[23] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268.
[24] A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, G. Christou, Angew. Chem., Int. Ed. 43 (2004) 2117.
[25] S. Mukhopadhyay, S.K. Mandal, S. Bhaduri, W.H. Armstrong, Chem. Rev. 104 (2004) 3981.
[26] Z. Zheng, R. Wang, Comments Inorg. Chem. 22 (2000) 1.
[27] Z. Zheng, Chem. Commun. (Feature Article) (2001) 2521.
[28] J.-C.G. Bunzli, C. Piguet, Chem. Rev. 102 (2002) 1897.
[29] L.G. Westin, M. Kritikos, A. Caneschi, Chem. Commun. (2003) 1012.
[30] I.A. Setyawati, S. Liu, S.J. Rettig, C. Orvig, Inorg. Chem. 39 (2000) 496.
[31] A.J. Blake, D.M.J. Doble, W.-S. Li, M. Schröder, J. Chem. Soc., Dalton Trans. (1997) 3655.
[32] G.B. Deacon, T. Feng, D.C.R. Hockless, P.C. Junk, B.W. Skelton, A.H. White, Chem. Commun. (1997) 341.
[33] X.-M. Chen, Y.-L. Wu, Y.-X. Tong, Z. Sun, D.N. Hendrickson, Polyhedron 16 (1997) 4265.
[34] T. Kujiwara, H. Wu, T. Ito, N. Iki, S. Miyano, Angew. Chem., Int. Ed. 43 (2004) 1832.
[35] L.G. Hubert-Pfalzgraf, New J. Chem. 19 (1995) 727.
[36] P. Chanaud, A. Julbe, P. Vaija, M. Persin, L. Cot, J. Mater. Sci. 29 (1994) 4244.
[37] N.H. Williams, B. Takasaki, M. Wall, J. Chin. Acc. Chem. Res. 32 (1999) 485.
[38] S. Yu, A. Watson, Chem. Rev. 99 (1999) 2353.
[39] A. Mishra, W. Wernsdorfer, S. Parsons, G. Christou, E.K. Brechin, Chem. Commun. (2005) 2086, and references therein.
[40] M. Ruben, J. Rojo, F.J. Romero-Salguero, L.H. Uppadine, J.-M. Lehn, Angew. Chem., Int. Ed. 43 (2004) 3644.
[41] R.E.P. Winpenny, J. Chem. Soc., Dalton Trans. (Dalton Perspective) (2002) 1.
[42] G. Aromi, A.R. Bell, M. Helliwell, J. Raftery, S.J. Teat, G.A. Timco, O. Roubeau, R.E.P. Winpenny, Chem. Eur. J. 9 (2003) 3024.
[43] G.S. Papaefstathiou, S.P. Perlepes, Comments Inorg. Chem. 23 (2002) 249, and references therein.
[44] E. Katsoulakou, V. Bekiari, C.P. Raptopoulou, A. Terzis, P. Lianos, E. Manessi-Zoupa, S.P. Perlepes, Spectrochim. Acta Part A 61 (2005) 1627.
[45] G.S. Papaefstathiou, A. Escuer, F.A. Mautner, C. Raptopoulou, A. Terzis, S.P. Perlepes, R. Vicente, Eur. J. Inorg. Chem. (2005) 879.
[46] A.K. Boudalis, B. Donnadieu, V. Nastopoulos, J. Modesto Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues, S.P. Perlepes, Angew. Chem. 116 (2004) 2316.
[47] A.K. Boudalis, F. Dahan, A. Bousseksou, J.-P. Tuchagues, S.P. Perlepes, Dalton Trans. (2003) 3411.
[48] C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, R. Vicente, N. Lalioti, A. Escuer, S.P. Perlepes, Chem. Commun. (2003) 819.
[49] G.S. Papaefstathiou, A. Escuer, M. Font-Bardia, S.P. Perlepes, X. Solans, R. Vicente, Polyhedron 21 (2002) 2027.
[50] K.N. Crowder, S.J. Garcia, R.L. Burr, J.M. North, M.H. Wilson, B.L. Conley, P.E. Fanwick, P.S. White, K.D. Sienerth, R.M. Granger II, Inorg. Chem. 43 (2004) 72.

[51] M.-L. Tong, S.-L. Zheng, J.-X. Shi, Y.-X. Tong, H.K. Leey, X.-M. Chen, J. Chem. Soc., Dalton Trans. (2002) 1727.

[52] Z.E. Serna, M.K. Urtiaga, M.G. Barandika, R. Cortes, S. Martin, L. Lezama, M.I. Arriortua, T. Rojo, Inorg. Chem. 40 (2001) 4550.

[53] M.-L. Tong, M. Monfort, J.M. Clemente Juan, X.-M. Chen, X.-H. Bu, M. Ohba, S. Kitagawa, Chem. Commun. (2005) 233.

[54] G.M. Sheldrick, SHELXS-86, Structure Solving Program, University of Göttingen, Germany, 1986.

[55] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.

[56] R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny, J. Chem. Soc., Dalton Trans. (2000) 2349.

[57] A representative reference: V. Tangoulis, C.P. Raptopoulou, S. Paschalidou, A.E. Tsohos, E.G. Bakalbassis, A. Terzis, S.P. Perlepes, Inorg. Chem. 36 (1997) 5270.

[58] A representative reference: Z.E. Serna, R. Cortés, M.K. Urtiaga, M.G. Barandika, L. Lezama, M.I. Arriortua, T. Rojo, Eur. J. Inorg. Chem. (2001) 865.

[59] A. Messimeri, V. Nastopoulos, A. Terzis, C.P. Raptopoulou, C. Papadimitriou, S.P. Perlepes, Inorg. Chem. Commun. (2005) 578.

[60] R.E. Morris, A.P. Wilkinson, A.K. Cheetham, Inorg. Chem. 31 (1992) 4774.

[61] J.A. Darr, D.M.P. Mingos, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, Polyhedron 15 (1996) 3225.

[62] J.F. Bower, S.A. Cotton, J. Fawcett, R.S. Hughes, D.R. Russell, Polyhedron 22 (2003) 347.

[63] D.L. Kepert, Inorganic Stereochemistry, Springer-Verlag, Berlin, 1982, p. 152.

[64] S. Liu, L. Gelmini, S.J. Rettig, R.C. Thompson, C. Orvig, J. Am. Chem. Soc. 114 (1992) 6081.

[65] C.K. Jorgensen, Modern Aspects of Ligand Field Theory, North-Holland, Amsterdam, 1971.

[66] S.P. Sinha, Spectrochim. Acta 22 (1966) 57.

[67] D.E. Henrie, G.R. Choppin, J. Chem. Phys. 49 (1968) 477.

[68] (a) D.G. Karraker, Inorg. Chem. 6 (1967) 1863;
(b) D.G. Karraker, Inorg. Chem. 7 (1968) 473.

[69] A. Messimeri, C.P. Raptopoulou, V. Nastopoulos, A. Terzis, S.P. Perlepes, C. Papadimitriou, Inorg. Chim. Acta 336 (2002) 8.

[70] V. Tangoulis, C.P. Raptopoulou, V. Psycharis, A. Terzis, K. Skorda, S.P. Perlepes, O. Cador, O. Kahn, E.G. Bakalbassis, Inorg. Chem. 39 (2000) 2522.

[71] P.K. Byers, A.J. Canty, L.M. Engelhardt, J.M. Patrick, A.H. White, J. Chem. Soc., Dalton Trans. (1985) 981.

[72] J.L. Burmeister, S.D. Patterson, E.A. Diardorff, Inorg. Chim. Acta 3 (1969) 105.

[73] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986, p. 283.