

# Synthesis, structure and luminescence properties of new rare earth metal complexes with 1-phenyl-3-methyl-4-acylpyrazol-5-ones †

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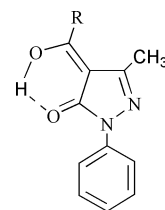
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The isolation and characterization of new lanthanide complexes of formula  $[\text{Ln}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$ , ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ;  $\text{HQ}_L = 1\text{-phenyl-3-methyl-4-phenylacetylpyrazol-5-one}$ )  $[\text{Ln}(\text{Q}_L)_3(\text{H}_2\text{O})_2]$  ( $\text{L} = \text{La}$  or  $\text{Lu}$ ),  $[\text{Ln}(\text{Q}_S)_3(\text{EtOH})(\text{H}_2\text{O})]$  ( $\text{Ln} = \text{Tb}$  or  $\text{Eu}$ ;  $\text{HQ}_S = 1\text{-phenyl-3-methyl-4-thienoylpyrazol-5-one}$ ,  $[\text{Tb}(\text{Q}_O)_3(\text{EtOH})(\text{H}_2\text{O})]$  ( $\text{HQ}_O = 1\text{-phenyl-3-methyl-4-furanoylpyrazol-5-one}$ )  $[\text{Tb}(\text{Q}_F)_3(\text{H}_2\text{O})_2]$  ( $\text{HQ}_F = 1\text{-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one}$ ) and  $[\text{NBu}_4][\text{Ln}(\text{Q})_4]$  ( $\text{Ln} = \text{Eu}$  or  $\text{Tb}$ ,  $\text{Q} = \text{Q}_F$  or  $\text{Q}_L$ ) is reported. The crystal structure of the tris( $\beta$ -diketonate) complexes  $[\text{Nd}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$ ,  $[\text{Dy}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})](\text{EtOH})$ , and  $[\text{Eu}(\text{Q}_S)_3(\text{H}_2\text{O})(\text{EtOH})]$  containing eight-coordinate lanthanide ions in a square antiprismatic environment has been determined. The coordination environment in the tetrakis complex  $[\text{NBu}_4][\text{Eu}(\text{Q}_F)_4]$  is also close to the square antiprismatic one. Photoluminescence (PL) and phosphorescence studies of selected derivatives are reported.

## Introduction

In recent years the luminescence properties of rare earth metal complexes with different  $\beta$ -diketonates have been widely studied due to their use in fabrication of polymer light-emitting diodes to enable low-cost, full-colour, flat-panel displays.<sup>1</sup> In contrast to conjugated polymers or small organic molecules, lanthanide ions linked to organic molecules provide very sharp emission spectra which make it possible to obtain pure red, green, and blue emission due to the energy transfer from the conjugated polymer in the matrix or from the ligand to the lanthanide ion. For this purpose the triplet level of the ligand must be higher in energy than the emissive level of the rare earth cation<sup>2</sup> which is the case for most europium and other lanthanide  $\beta$ -diketonate complexes.<sup>1</sup>

Several efforts in this field have been devoted to the study of lanthanide complexes with  $\beta$ -diketonates such as acetylacetonate and its derivatives.<sup>3</sup> Only recently some researchers started to investigate the emitting properties of rare earth metal derivatives of 4-acyl-5-pyrazolones (HQ), a class of heterocyclic ligand analogues of  $\beta$ -diketonates (Fig. 1). These ligands are mainly known as extractants for a wide number of metals including transition and 4f-elements.<sup>4</sup> In 1987 Bombieri and coworkers reported the synthesis and X-ray structure of tris-(1,3-diphenyl-4-acetylpyrazol-5-onate)di(aqua)ytterbium(III)<sup>5</sup> whereas more recently Langmuir film-forming and second harmonic generation properties of  $[\text{Ln}(\text{Q})_4]$  (where  $\text{A} = (\text{E})\text{-N-alkyl-4-(2-(4-(dimethylamino)phenyl)ethenyl)pyridinium}$  and  $\text{Ln} = \text{La}, \text{Nd}, \text{Dy}$  and  $\text{Yb}$ ) have been investigated.<sup>6</sup> Several efforts to correlate the structure of the 4-acyl moiety in acyl-



$\text{HQ}_L$ :  $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$   
 $\text{HQ}_F$ :  $\text{R} = \text{CF}_3$   
 $\text{HQ}_S$ :  $\text{R} = 2\text{-thienyl}$   
 $\text{HQ}_O$ :  $\text{R} = 2\text{-furyl}$

Fig. 1 Structure of the ligands employed in this work.

pyrazolones with excited state properties and intramolecular energy transfer of corresponding La, Gd and Tb derivatives with formula  $[\text{Ln}(\text{Q})_3(\text{H}_2\text{O})_2]$  were reported in 1996 by Ying *et al.*<sup>7</sup> whereas in 1997 the fluorescence, phosphorescence and molecular structure of a  $[\text{Tb}(\text{Q})_3(\text{H}_2\text{O})_2]$  derivative were described by Zhou *et al.*<sup>8</sup> The efficiency of an electroluminescent terbium complex  $[\text{Tb}(\text{Q})_3(\text{TPPO})_2]$ , which has overtaken aluminium 8-hydroxyquinolate, the commonly used green light emitter,<sup>9</sup> has provoked further studies on analogous derivatives mainly devoted to the comprehension of the role and influence of the neutral ancillary ligand L in the luminescence of  $[\text{Tb}(\text{Q})_3(\text{L})_2]$  complexes.<sup>10</sup> It has been shown that an electron-releasing alkyl group in the acyl fragment greatly enhances the luminescence of the derivative with respect to electron-withdrawing groups such as phenyl or  $\text{C}_3\text{F}_7$ .

Due to our interest in the coordination chemistry of this family of ligands toward main group and transition metal elements,<sup>11</sup> we decided to extend our research to the study of structural and emitting features of neutral and anionic lanthanide complexes with the acylpyrazolones shown in Fig. 1. The proligand 1-phenyl-3-methyl-4-phenylacetylpyrazol-5-one

† Electronic supplementary information (ESI) available: experimental details, absorption spectra of  $\text{Eu}(\text{Q}_L)_3$  and  $\text{Tb}(\text{Q}_L)_3$ , luminescence spectra of  $\text{Ln}(\text{Q}_L)_3$  complexes and electronic transitions of luminescence of lanthanide pyrazolonates. See <http://www.rsc.org/suppdata/dt/b1/b108058j/>

(HQ<sub>L</sub>) has been previously synthesised and used only toward copper(II) acceptors,<sup>12</sup> whereas for 1-phenyl-3-methyl-4-trifluoromethylpyrazol-5-one (HQ<sub>F</sub>) some neutral 4f-element derivatives [Ln(Q<sub>F</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] have been recently reported.<sup>13</sup> To date no metal derivatives containing 1-phenyl-3-methyl-4-thienoylpyrazol-5-one (HQ<sub>S</sub>) and 1-phenyl-3-methyl-4-furanoylpyrazol-5-one (HQ<sub>O</sub>) have been described, nevertheless the thienoyl and furanoyl substituents are known to modify the luminescent properties of rare earth β-diketonates.

## Experimental

### (a) Reagents and physical methods

EtOH was used as supplied. MeCN was distilled over P<sub>2</sub>O<sub>5</sub> and DMSO was vacuum-distilled over KOH. The reagents were purchased from Aldrich or Fluka. All chemicals were standard reagent grade and used as received. The proligands 1-phenyl-3-methyl-4-phenylacetylpyrazol-5-one HQ<sub>L</sub>, 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one HQ<sub>F</sub>, 1-phenyl-3-methyl-4-(2-thienoyl)pyrazol-5-one HQ<sub>S</sub>, 1-phenyl-3-methyl-4-(2-furanoyl)pyrazol-5-one HQ<sub>O</sub>, were prepared by reported procedures.<sup>14</sup>

The samples for microanalyses were dried under vacuum to constant weight (20 °C, *ca.* 0.1 Torr). Elemental analyses (C, H, N, S) were performed in house with Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. IR spectra were recorded from 4000 to 100 cm<sup>-1</sup> using a Perkin Elmer System 2000 FT-IR instrument. <sup>1</sup>H NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for <sup>1</sup>H). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. Proton chemical shifts are reported in ppm *vs.* Me<sub>4</sub>Si. The electrical conductivity measurements (*A*<sub>m</sub>, reported as Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of acetone solutions of complexes **1–22** were taken with a Crison CDTM 522 conductimeter at room temperature. The absorption spectra were recorded on a spectrophotometer “Specord-M40”.

### (b) Syntheses

[La(Q<sub>L</sub>)<sub>3</sub>(H<sub>2</sub>O)(EtOH)] **1**. To an ethanol solution (20 ml) of the proligand HQ<sub>L</sub> (0.877 g, 3.0 mmol) in presence of an equimolar amount of KOH (0.168 g, 3.0 mmol) a water–ethanol 1 : 1 solution (20 ml) of La(NO<sub>3</sub>)<sub>3</sub>·7H<sub>2</sub>O (0.451 g, 1 mmol) was added under violent stirring. The resulting mixture was kept under stirring for 2 hours. A colorless precipitate formed which was separated by filtration, then washed with water in order to remove the traces of potassium nitrate and recrystallized from ethanol to give 0.80 g of pure compound **1** (76% yield). mp 145 °C dec. Calc. for C<sub>56</sub>H<sub>53</sub>LaN<sub>6</sub>O<sub>8</sub>: C, 62.45; H, 4.96; N, 7.80. Found: C, 62.32; H, 4.92; N, 7.96%. IR (Nujol, cm<sup>-1</sup>): 3350–3100br ν(O–H···O), 1630sh δ(O–H···O), 1615vs ν(C=O), 1592vs, 1581s, 1531m, 418s, 395m, 380m, 362m, 333s, 273m. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ, 1.24 (t, 3H, CH<sub>3EtOH</sub>), 2.51 (s, 9H, CH<sub>3</sub>), 3.2 (br, 2H, H<sub>2</sub>O), 3.70 (q, 2H, CH<sub>2EtOH</sub>), 4.0 (br, 6H, CH<sub>2</sub>), 7.0–7.2 (m, 24H, C<sub>6</sub>H<sub>5</sub>), 8.24 (d, 6H, C<sub>6</sub>H<sub>5</sub>). *A*<sub>m</sub> (acetone, 1 × 10<sup>-3</sup> M): 1.4 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>.

Complexes [M(Q<sub>L</sub>)<sub>3</sub>(H<sub>2</sub>O)(EtOH)] (**2**: M = Pr, **3**: M = Nd; **4**: M = Sm; **5**: M = Eu; **6**: M = Gd; **7**: M = Tb; **8**: M = Dy; **9**: M = Ho; **10**: M = Er; **11**: M = Tm; **12**: M = Yb) [Lu(Q<sub>L</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (**13**), [M(Q<sub>S</sub>)<sub>3</sub>(H<sub>2</sub>O)(EtOH)] (**16**: M = Eu; **17**: M = Tb) and [Tb(Q<sub>O</sub>)<sub>3</sub>(H<sub>2</sub>O)(EtOH)] (**18**) were prepared by the same procedure.

[La(Q<sub>L</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] **14**. This compound was obtained as for **1** in a water : ethanol 2 : 1 solution (73% yield) mp 151 °C dec. Calc. For C<sub>54</sub>H<sub>49</sub>LaN<sub>6</sub>O<sub>8</sub>: C, 61.83; H, 4.71; N, 8.01. Found: C, 61.70; H, 4.94; N 8.06%. IR (Nujol, cm<sup>-1</sup>): 3300–3100br s ν(O–H···O), 1651m δ(O–H···O), 1615vs ν(C=O), 1592vs,

1581s, 1531m, 1490m, 418s, 380m, 326s, 273m. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ, 2.50 (s, 9H, CH<sub>3</sub>), 3.3 (br, 4H, H<sub>2</sub>O), 4.0 (br, 6H, CH<sub>2</sub>), 7.0–7.2 (m, 24H, C<sub>6</sub>H<sub>5</sub>), 8.24 (d, 6H, C<sub>6</sub>H<sub>5</sub>). *A*<sub>m</sub> (acetone, 0.9 × 10<sup>-3</sup> M): 0.5 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>.

[Tb(Q<sub>F</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] **15**. This compound was obtained as for **1** in a water : ethanol 3 : 1 solution (93% yield). mp 290–293 °C. Calc. for C<sub>36</sub>H<sub>28</sub>F<sub>9</sub>N<sub>6</sub>O<sub>8</sub>Tb: C, 43.13; H, 2.82; N, 8.38. Found: C, 43.36; H, 2.75; N, 8.34. IR (Nujol, cm<sup>-1</sup>): 3300–3100br s ν(O–H···O), 1678sh δ(O–H···O), 1635vs ν(C=O), 1596s, 1586s, 1543m, 1520vs, 1499vs, 446vs, 410m, 388m, 368s, 301w, 265m, 238m. *A*<sub>m</sub> (acetone, 1.0 × 10<sup>-3</sup> M): 0.9 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>.

[NBu<sub>4</sub>][Tb(Q<sub>L</sub>)<sub>4</sub>] **19**. To a solution of HQ<sub>L</sub> (0.438 g, 1.5 mmol) in ethanol (20 ml), NBu<sub>4</sub>I (0.11 g, 0.3 mmol) and KOH (0.0842 g, 1.5 mmol) were added. The solution was stirred vigorously. After 10 minutes a solution of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.13 g, 0.3 mmol) in ethanol (30 ml) was added dropwise. The reaction mixture was boiled for 3 hours, then filtered and slowly cooled to room temperature. Yellowish crystals formed which were washed with a small amount of water and recrystallized from ethanol (0.47 g, 79% yield). mp 164–168 °C. Calc. for C<sub>88</sub>H<sub>96</sub>N<sub>9</sub>O<sub>8</sub>Tb: C, 67.46; H, 6.18; N, 8.05. (Found: C, 67.35; H, 6.04; N, 8.20. IR (Nujol, cm<sup>-1</sup>): 1620vs ν(C=O), 1592s, 1580s, 1544m, 1500s, 595s, 564w, 553w, 513m, 502m, 469w, 410s, 387s, 379s, 338w, 317w, 302w, 278m, 266m. *A*<sub>m</sub> (acetone, 0.4 × 10<sup>-4</sup> M): 135 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>.

Complexes [NBu<sub>4</sub>][Eu(Q<sub>L</sub>)<sub>4</sub>] (**20**), [NBu<sub>4</sub>][Tb(Q<sub>F</sub>)<sub>4</sub>] (**21**), and [NBu<sub>4</sub>][Eu(Q<sub>F</sub>)<sub>4</sub>] (**22**) were prepared by the same procedure.

The synthesis and spectroscopic characterization of compounds **2–13**, **16–18**, and **20–22** is available as ESI. †

### (c) Photoluminescence, phosphorescence and luminescence lifetimes measurements

The visible photoluminescence (PL) and phosphorescence spectra were taken on a spectrofluorimeter MPF-4 “Hitachi”. The infrared luminescence spectra were registered on home-built equipment with emission collected at 180 degrees to the excitation beam.

The luminescence lifetimes of lanthanides were measured with an impulse laser fluorimeter LIF-200 utilizing excitation by a nitrogen laser with λ = 337 nm and impulse duration = 20 ns.

The luminescence quantum yields of the chelates in solutions at excitation into the ligand absorption band for Sm<sup>3+</sup> and Eu<sup>3+</sup> chelates were measured relative to Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (λ<sub>ex</sub> = 400 nm, φ = 2.8% in water<sup>15</sup>), for Tb<sup>3+</sup> and Dy<sup>3+</sup> relative to Tb(AA)<sub>3</sub>·H<sub>2</sub>O (λ<sub>ex</sub> = 313 nm, φ = 19% in ethanol<sup>16</sup>), for Pr<sup>3+</sup> relative to Yb(TTA)<sub>3</sub>.<sup>17</sup>

The solutions of the chelates (5 × 10<sup>-4</sup> mol l<sup>-1</sup>) in MeCN or DMSO (for Pr<sup>3+</sup>) were used in photophysical experiments.

### (d) X-Ray crystal structure determination

The data for complex **3** were collected on a Smart-1000 CCD diffractometer (Bruker) and those for complexes **8**, **16** and **22** on an image plate diffractometer (IPDS, Stoe) using graphite monochromated Mo Kα radiation. Numerical absorption correction was only applied for the Eu complex **16**. The structures were solved by direct methods (SHELXS-97)<sup>18</sup> and refined anisotropically for all non-hydrogen atoms using SHELXL-93.<sup>19</sup> Due to the poor quality of the crystals of **16** the final *wR*<sub>2</sub> and *R*<sub>1</sub> values are much higher for this compound as well as the residual electron density, which, however, had no chemical meaning. In the structure **8** and **16** it was necessary to use the ISOR instruction for a few atoms. The hydrogen atoms of neutral ligands bonded to oxygen could be localized from the Δ*F* syntheses and refined isotropically (with some restraints for structure **8**). All other H atoms were included in the calculated positions and refined in a riding mode.

**Table 1** Crystallographic data and some details of data collection and refinement for [LnQ<sub>3</sub>L<sub>2</sub>] and [(NBu<sub>4</sub>)(EuQ<sub>4</sub>)] complexes

	<b>3</b>	<b>8</b> ·EtOH	<b>16</b>	<b>22</b>
Molecular formula	C <sub>56</sub> H <sub>53</sub> N <sub>6</sub> O <sub>8</sub> Nd	C <sub>58</sub> H <sub>59</sub> N <sub>6</sub> O <sub>9</sub> Dy	C <sub>47</sub> H <sub>46</sub> N <sub>6</sub> O <sub>8</sub> Eu	C <sub>64</sub> H <sub>66</sub> N <sub>9</sub> O <sub>8</sub> F <sub>12</sub> Eu
<i>M</i>	1082.28	1146.61	1066.00	1469.22
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	13.187(1)	13.526(3)	8.853(2)	24.759(3)
<i>b</i> /Å	14.912(1)	15.219(3)	34.270(6)	21.455(3)
<i>c</i> /Å	15.199(1)	16.225(3)	15.100(4)	26.353(3)
<i>a</i> <sup>o</sup>	87.84(1)	63.31(3)	90	90
<i>β</i> <sup>o</sup>	66.55(1)	85.20(3)	90.34(3)	112.54(1)
<i>γ</i> <sup>o</sup>	64.16(1)	63.76(3)	90	90
<i>V</i> /Å <sup>3</sup>	2434.1(3)	2648.9(9)	4581(2)	13451(3)
<i>Z</i>	2	2	4	8
<i>D</i> /Mg m <sup>-3</sup>	1.477	1.438	1.546	1.451
<i>μ</i> /mm <sup>-1</sup>	1.130	1.473	1.566	1.025
Crystal size/mm	0.5 × 0.3 × 0.2	0.5 × 0.4 × 0.2	0.5 × 0.1 × 0.1	0.5 × 0.3 × 0.06
<i>T</i> /K	100	180	180	160
Data collection range, <i>θ</i> /deg	1.5–28.9	2.5–27.0	2.6–26.9	2.4–26.1
Reflections collected	21126	22019	22331	35698
Independent reflections ( <i>R</i> <sub>int</sub> )	11366 (0.040)	10572 (0.071)	9698 (0.091)	13097(0.078)
Data/parameters	8736/653	6823/684	6785/551	10536/877
Goodness of fit on <i>F</i> <sup>2</sup>	1.032	1.010	1.150	0.868
<i>wR</i> <sub>2</sub>	0.1047	0.1251	0.3151	0.0758
<i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0442	0.0587	0.1244	0.0351
Largest diff. peak and hole/e Å <sup>-3</sup>	1.049; -0.750	0.510; -0.447	2.698; -2.131	0.516; -0.821

**Table 2** Ln–O and hydrogen bond distances (Å) in the crystal structures **3**, **8**, **16**, and **22**

Distance	<b>3</b> (Ln = Nd)	<b>8</b> (Ln = Dy)	<b>16</b> (Ln = Eu)	<b>22</b> (Ln = Eu)
Ln–O(1)	2.387(3)	2.271(3)	2.40(2)	2.363(3)
Ln–O(2)	2.449(3)	2.349(3)	2.36(2)	2.441(3)
Ln–O(3)	2.386(3)	2.342(3)	2.41(2)	2.331(3)
Ln–O(4)	2.458(2)	2.356(3)	2.35(2)	2.462(3)
Ln–O(5)	2.428(2)	2.268(4)	2.39(2)	2.366(3)
Ln–O(6)	2.419(3)	2.410(3)	2.38(2)	2.436(3)
Ln–O(7)	2.490(3)	2.368(4)	2.51(2)	2.315(3)
Ln–O(8)	2.475(3)	2.411(3)	2.50(2)	2.474(3)
Ln–O <sub>Pz</sub> (av.)	2.421	2.333	2.377	2.398
O(8) ⋯ N(2)	2.781(4)	2.934(6)	2.98(3)	—
O(8) ⋯ N(4)	2.851(4)	2.885(5)	2.99(3) <sup>b</sup>	—
O(7) ⋯ N(6)	2.782(4)	2.666(6) <sup>a</sup>	—	—
O(9) ⋯ N(6)	—	2.816(7)	—	—

<sup>a</sup> The O(7) ⋯ O(9) distance. <sup>b</sup> The O(8) ⋯ N(2') distance.

Crystallographic data and some details of data collection and structures refinement are found in Table 1. Interatomic bond lengths and angles for the Ln environments and data on the hydrogen bonds are listed in Table 2.

CCDC reference numbers 170585–170588.

See <http://www.rsc.org/suppdata/dt/b1/b108058j/> for crystallographic data in CIF or other electronic format.

## Results and discussion

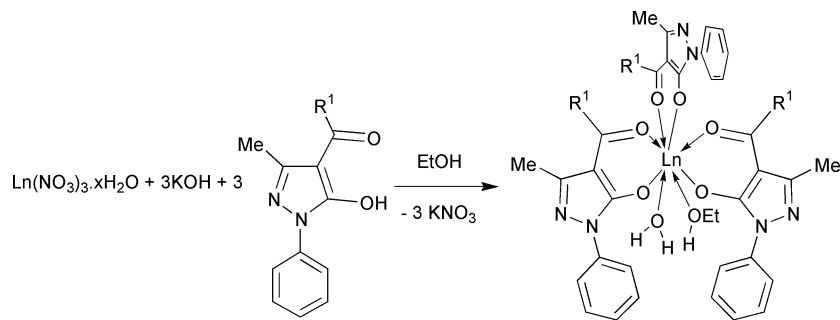
### Syntheses

The reaction of Ln(NO<sub>3</sub>)<sub>3</sub>·*x*H<sub>2</sub>O with 1-phenyl-3-methyl-4-acylpyrazol-5-one proligands HQ and KOH in water : ethanol 1 : 1 mixture yielded the air stable eight-coordinate complexes [M(Q)<sub>3</sub>(H<sub>2</sub>O)(EtOH)] **1–12** and **16–18** (Scheme 1) which were investigated by combined IR, UV, conductivity measurements and in the case of La, Nd and Eu complexes also by <sup>1</sup>H NMR spectroscopy. No difference was observed in the stoichiometry of the complexes of Ce and Y subgroups within all the lanthanide family.

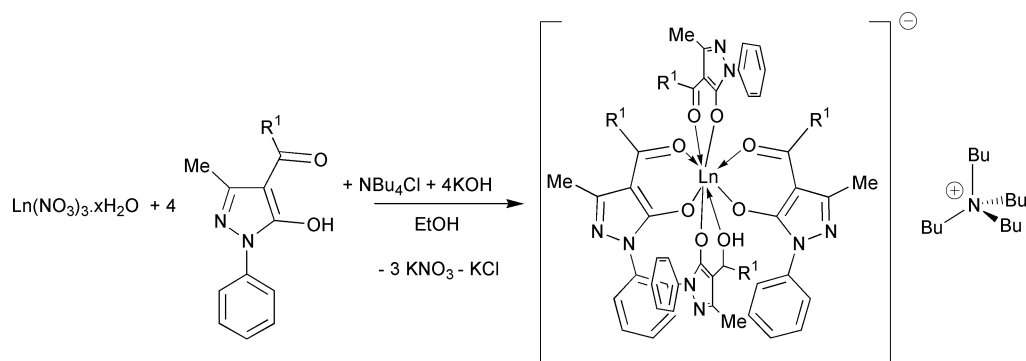
The dihydrate derivatives [M(Q)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] **14** and **15** were obtained by recrystallising the compound from a water : ethanol mixture in a ratio greater than 2 : 1. When Lu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was employed only the dihydrate compound [Lu(Q)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] **13** was isolated, likely due to the smaller ionic radius of Lu<sup>3+</sup> with

respect to other lanthanide ions. Complexes **1–18** are soluble in DMSO and acetone in which they are non-electrolytes. Their IR spectra in the 1600–1500 cm<sup>-1</sup> region exhibit bands due to C=O, C=C stretching vibrations, typical of metal chelates containing deprotonated acylpyrazolones.<sup>11</sup> The presence of water and ethanol molecules is confirmed from the presence of a strong broad absorption between 3500 and 2800 cm<sup>-1</sup>, due to O–H ⋯ O strongly hydrogen bonded.<sup>5,20</sup> In the far-infrared region several new absorptions not present in the free ligands appeared upon coordination in the complexes due to M–O stretching vibrations.<sup>5,20</sup> The <sup>1</sup>H NMR spectra of **1**, **3**, **5**, **13** and **14** confirm the structure proposed. Negligible shift has been found for the proton signals in the case of diamagnetic lanthanum and lutetium complexes with respect to the unbound ligand signals.<sup>12</sup> A larger shift has been observed for the Nd(III) and Eu(III) derivatives **3** and **5** as expected.<sup>21</sup> The presence of two or three signals for each equivalent group of protons in the spectrum of **3** can be due to the formation of different species in solution as a consequence of displacement by deuterated acetone of water or ethanol molecules from the coordination sphere of the Ln<sup>3+</sup> or existence of different isomers not fluxional in solution.<sup>22</sup>

From the reaction of one equiv. of terbium(III) and europium(III) nitrates with 4 equiv. of HQ<sub>L</sub> or HQ<sub>F</sub>, 4 equiv. of KOH in ethanol in presence of 1 equiv. of tetrabutylammonium iodide, the tetrakis complexes [NBu<sub>4</sub>][M(Q)<sub>4</sub>] **19–22** (Scheme 2)



Scheme 1



Scheme 2

were isolated. Complexes **19–22** are air-stable, soluble in water, DMSO and sparingly in acetone in which the conductivity measurements show them to be 1 : 1 electrolytes.

The IR spectra of **19–22** and  $^1\text{H}$  NMR spectra of **20** and **22** confirm the ionic structure of these tetrakis complexes, the presence of  $[\text{NBu}_4]^+$  cation being easily detected. The C=O, C=C and M–O vibrations fall in the same region as in the tris-(diketonate) complexes **1–18**. Larger shifts have been found for the *ortho* aromatic protons in complex **22** likely due to the interaction of the  $\text{CF}_3$  groups with the shielding cone of the phenyl of a neighbouring ligand.

### Absorption spectra

The absorption spectra of lanthanide pyrazolonates show intense broad band in UV with  $\epsilon \approx 10^4\text{--}10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The absorption spectra for the complexes formed by one ligand do not differ much for different lanthanide ions and thus this band is ascribed to the ligand singlet–singlet  $n\text{--}\pi^*$  transition, which involves non-bonding electron pairs of the oxygen atoms. Introduction of electron-withdrawing  $\text{CF}_3$ -groups to the ligand results in the red-shifting of this band. The absorption at 300–350 nm for the  $[\text{Eu}(\text{Q}_L)_3(\text{H}_2\text{O})(\text{EtOH})]$  complex **5** probably belongs to a ligand  $\rightarrow \text{Eu}^{3+}$  charge transfer transition since the europium ion is easily reducible to the divalent state.

### Photoluminescence studies of lanthanide pyrazolonates

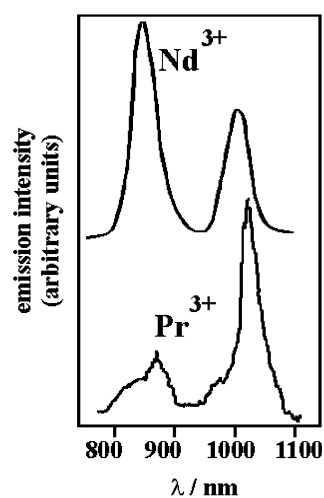
The luminescence of lanthanide pyrazolonates upon excitation into the ligand absorption band arises from the  $f\text{--}f$  transitions from the radiative level of  $\text{Ln}^{3+}$  to its lower-lying states. Some selected luminescence spectra of studied complexes are shown in Fig. 2 and the ESI†.

The excited  $f\text{--}f$  levels of  $\text{Ln}^{3+}$  are populated as a result of energy transfer from the triplet level of the ligand, which is formed by rapid ( $k_{\text{ST}} \approx 10^{10} \text{ s}^{-1}$ ) intersystem conversion  $\text{L}_S^* \rightarrow \text{L}_T^*$ . The excitation energy of the resonant level of lanthanide ion is further deactivated either with emission of luminescence, or nonradiatively by energy exchange to the vibrations of surrounding molecular groups. The dissipation of excitation energy occurs at all stages of the energy transfer steps and the ratio of the rates of radiative and non-radiative pro-

**Table 3** Quantum yields and lifetimes of luminescence of lanthanide complexes as  $5 \times 10^{-4} \text{ mol l}^{-1}$  solutions in MeCN

No.	Compound	$\nu_T/\text{cm}^{-1}$	$\phi^a$ (%)	$\tau/\mu\text{s}$
<b>21</b>	$[\text{NBu}_4][\text{Tb}(\text{Q}_F)_4]$		0.4	
<b>7</b>	$[\text{Tb}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$	23500	1.3	520
<b>17</b>	$[\text{Tb}(\text{Q}_S)_3(\text{EtOH})(\text{H}_2\text{O})]$	22400	0.8	420
<b>18</b>	$[\text{Tb}(\text{Q}_O)_3(\text{EtOH})(\text{H}_2\text{O})]$	22700	0.9	360
<b>5</b>	$[\text{Eu}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$		0.02	95
<b>4</b>	$[\text{Sm}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$		0.12	—
<b>8</b>	$[\text{Dy}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$		0.008	—
<b>2</b>	$[\text{Pr}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$		0.006 [30]	
	$[\text{Pr}(\text{Q}_S)_3(\text{EtOH})(\text{H}_2\text{O})]$		[12]	
<b>3</b>	$[\text{Nd}(\text{Q}_L)_3(\text{EtOH})(\text{H}_2\text{O})]$		[100]	

<sup>a</sup> The relative luminescence intensities in arbitrary units are shown in the square brackets.



**Fig. 2** The luminescence spectra of  $\text{Nd}(\text{Q}_L)_3$  and  $\text{Pr}(\text{Q}_L)_3$  in MeCN and DMSO at 20 °C (emission slit = 10 nm).

cesses determines the efficiency of the lanthanide luminescence. The quantum yields of the luminescence of lanthanide pyrazolonates are given in Table 3. It can be seen from Table 3 that

for the  $[\text{Tb}(\text{Q})_3(\text{H}_2\text{O})(\text{EtOH})]$  species the quantum yield is decreased when the energy position of the triplet level of the ligand is lowered. This is a result of back energy transfer from the  $^5\text{D}_4$  level of  $\text{Tb}^{3+}$  to the triplet level of the ligand followed by nonradiative energy dissipation.<sup>23</sup> The energy transfer processes and energy levels of  $\text{Ln}^{3+}$  ions are shown in Fig. 3.

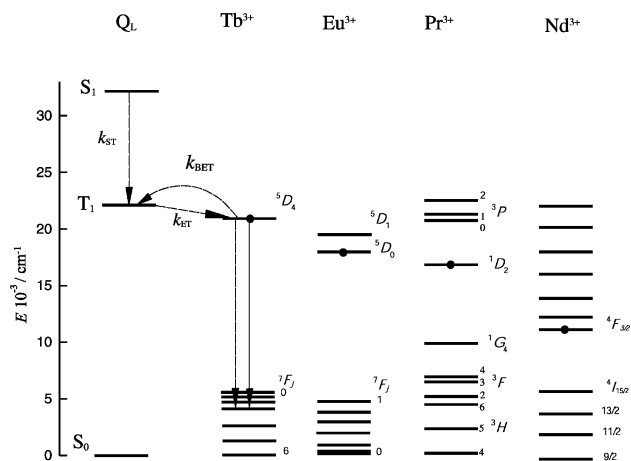


Fig. 3 The energy levels and intramolecular energy transfer processes in the lanthanide pyrazolonates.

The luminescence of  $[\text{Pr}(\text{Q}_\text{S})_3(\text{H}_2\text{O})(\text{EtOH})]$ ,  $[\text{Pr}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})]$  **2** and  $[\text{Nd}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})]$  **3** in the solvents containing O–H/C–H bonds is inefficient due to a low energy gap  $<7000\text{ cm}^{-1}$  between the radiative and lower-lying states of these ions. The estimation of the quantum yield of **2** was performed in DMSO, a solvent which is known to effectively displace water and alcohol molecules from the inner coordination sphere of the lanthanide ion. However even in DMSO the  $\text{Pr}^{3+}$  chelates studied show extremely low luminescence efficiency. Moreover the luminescence of  $\text{Pr}^{3+}$  was observed from the  $^1\text{D}_2$  level only, since the population of  $^3\text{P}_0$  level is inefficient due to the low energy of the ligand triplet level.<sup>24</sup>

### Crystal structures

The crystal and molecular structures of derivatives  $[\text{Nd}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})]$  (**3**),  $[\text{Dy}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})]\cdot\text{EtOH}$  (**8·EtOH**),  $[\text{Eu}(\text{Q}_\text{S})_3(\text{H}_2\text{O})(\text{EtOH})]$  (**16**) and  $[\text{NBu}_4][\text{Eu}(\text{Q}_\text{F}_4)]$  (**22**) have been determined with different precision levels. In particular, for the Eu complex (**16**) the results are not very precise, but representative enough. Up to now only two other crystal structures of lanthanide acylpyrazolonates have been reported in the literature:  $[\text{Yb}(\text{DPAP})_3(\text{H}_2\text{O})_2]\cdot 3\text{EtOH}$  (HDPAP = 1,3-diphenyl-4-acetylpyrazol-5-one)<sup>5</sup> and  $[\text{Tb}(\text{PMPP})_3(\text{H}_2\text{O})_2]\cdot\text{EtOH}$  (HPMPP = 1-phenyl-3-methyl-4-propionylpyrazol-5-one).<sup>8</sup> For the Yb structure the precision level is high,<sup>5</sup> but it is not for the Tb structure.<sup>8</sup>

All compounds **3**, **8·EtOH**, **16**, and **22** are built up of molecules containing eight-coordinate lanthanide atoms in a square antiprismatic environment (Fig. 4–6), however **3**, **8·EtOH**, and **16** represent different compositions and different coordination patterns, with respect to the lanthanide acylpyrazolonates reported previously.<sup>5,8</sup> In **3**, **8·EtOH**, and **16** the lanthanide atom is coordinated by six oxygen atoms (O1–O6) from three chelating Q ligands, by one ethanol molecule (O7) and by one water molecule (O8). Moreover, in the structure **8·EtOH** there is an additional EtOH solvate molecule. In contrast, two  $\text{H}_2\text{O}$  molecules are present in the coordination sphere of both  $\text{Yb}^{3+}$  and  $\text{Tb}^{3+}$  derivatives with an additional three and one EtOH solvated molecules, respectively.

Several geometrical isomers are theoretically possible for this kind of square antiprismatic geometry. Lanthanide acylpyrazolonates have been shown to adopt basically the three isomers given in Scheme 3 (a–c). It can be noticed that the Yb and Tb

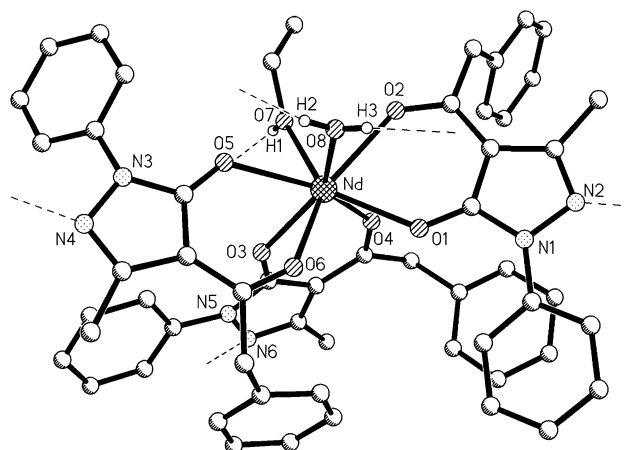


Fig. 4 Molecular structure of  $[\text{Nd}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})]$  (**3**) with the H-bonding connections shown as dashed lines.

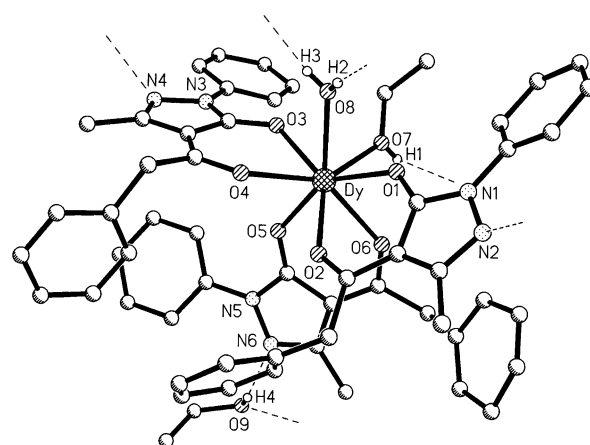


Fig. 5 Molecular structure of  $[\text{Dy}(\text{Q}_\text{L})_3(\text{H}_2\text{O})(\text{EtOH})](\text{EtOH})$  (**8·EtOH**) with the H-bonding connections shown as dashed lines.

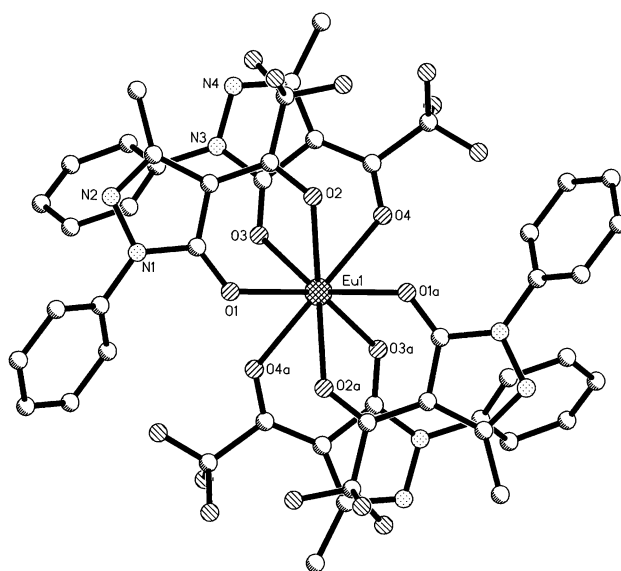
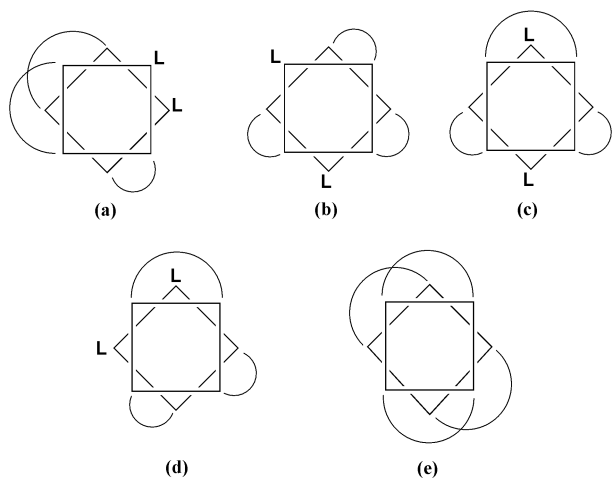


Fig. 6 Structure of the anion (Eu1) in  $(\text{NBu}_4)[\text{Eu}(\text{Q}_\text{L})_4]$  (**22**) shown in the direction of the pseudo-tetragonal axis of the  $\text{EuO}_8$  antiprism.

derivatives, both with two  $\text{H}_2\text{O}$  molecules in the coordination sphere, adopt different isomeric structures due to the nature of the substituent in the acylpyrazolonate ligand. However, different structural isomers are also found in the Nd and Dy compounds **3** and **8·EtOH**, both with one  $\text{H}_2\text{O}$ , one EtOH and the same Q ligand. The complex **16** adopts a new pattern of square antiprismatic co-ordination with two L ligands ( $\text{H}_2\text{O}$  and



**Scheme 3** Coordination patterns within a square antiprismatic  $\text{LnO}_8$  environment for  $[\text{Dy}(\text{Q}_1)_3(\text{H}_2\text{O})(\text{EtOH})(\text{EtOH})](\text{EtOH})$  and  $[\text{Yb}(\text{DPAP})_3 \cdot (\text{H}_2\text{O})_2] \cdot 3\text{EtOH}$  (a),  $[\text{Tb}(\text{PMPP})_3(\text{H}_2\text{O})_2] \cdot \text{EtOH}$  (b),  $[\text{Nd}(\text{Q}_1)_3(\text{H}_2\text{O})(\text{EtOH})]$  (c),  $[\text{Eu}(\text{Q}_S)_3(\text{H}_2\text{O})(\text{EtOH})]$  (d), and the  $[\text{Eu}(\text{Q}_F)_4]$  anion (e).

$\text{EtOH}$  in the *cis*-position and in the same square plane (Scheme 3(d)). The different coordination patterns in the five lanthanide complexes mentioned above could be influenced by such factors as the size of the metal atom, the  $\text{EtOH} : \text{H}_2\text{O}$  ratio in the solution during crystallisation and packing effects in the crystal structures.

An almost regular variation in mean values of  $\text{Ln}-\text{O}(\beta\text{-diketonate})$  bond lengths can be noticed: 2.428 Å for Nd, 2.38 Å (Eu), 2.338 Å (Tb), 2.333 Å (Dy) and 2.305 Å (Yb), with differences determined mainly by the size of the metal atom. In the  $\text{Yb}^5$  and  $\text{Tb}^8$  structures, there are two sets of  $\text{Ln}-\text{O}(\beta\text{-diketonate})$  distances, with all three acylpyrazolonate ligands asymmetrically coordinated (shorter  $\text{Ln}-\text{O}$  distances for the pyrazole arm of the bidentate ligand). However, in Nd, Eu, and Dy complexes **3**, **16** and **8**· $\text{EtOH}$ , only two Q ligands are asymmetrically coordinated, the third being nearly symmetrically bonded. In the case of Dy, this fact can be more easily correlated to its geometrical structure with two chelating ligands each with both carbonyls in the same square plane of the antiprism and the third ligand connecting both planes. However, for the Nd compound, which adopts the isomeric structure *c* shown in Scheme 3, this correlation is not valid. The  $\text{Ln}-\text{O}$  distances for neutral ligands ( $\text{H}_2\text{O}$ ,  $\text{EtOH}$ ) are in all cases longer than those for  $\beta\text{-diketonate}$  ligands.

In contrast to the structures reported previously,<sup>5,8</sup> we were able to analyse all hydrogen bonds present in **3** and **8**· $\text{EtOH}$ . Hydrogen atoms of coordinated  $\text{H}_2\text{O}$  and  $\text{EtOH}$ , and also of the solvated ethanol molecule in **8**· $\text{EtOH}$  are involved in intermolecular H-bonding, as shown in Fig. 4 and 5. In the structure of **16**, the coordinated water molecule participates in two H bonds to two different N2 atoms from two neighbouring complexes, giving rise to the formation of the H bonded chains. These interactions are of intermediate strength, as can be deduced from  $\text{O} \cdots \text{N}$  and  $\text{O} \cdots \text{O}$  distances in Table 2.

In the structure of the tetrakis-complex  $[\text{NBu}_4][\text{Eu}(\text{Q}_F)_4]$  **22**, there are two crystallographically independent Eu atoms both lying on the 2-fold axis. The coordination environment of both Eu atoms is also close to the square antiprismatic one (Scheme 3e). Two pairs of ligands (O1O2 and O3O4 for Eu1, and O5O6 and O7O8 for Eu2) occupy the slightly distorted square faces of the antiprisms (Fig. 6). The  $\text{Eu}-\text{O}$  distances are in the range of 2.32–2.47 Å (average 2.398 Å) with the longer arm lying on the trifluoromethyl side due to the strong electron-withdrawing effect (Table 2). Very similar coordination has been found for other anionic tetrakis-( $\beta\text{-diketonate}$ )Ln complexes, mainly with the trifluorothienylbutanedione as the ligand.<sup>3h,25–27</sup> The average  $\text{Eu}-\text{O}$  distance slightly varies from 2.381 to 2.391 Å in the complexes with different cations such as 3,6-di(dimethylamine)-

diphenyliodonium,<sup>25</sup> 1,4-dimethylpyridinium,<sup>3h</sup> 4-methylpyridinium,<sup>26</sup> and *N*-ethylpyridinium.<sup>27</sup>

## Conclusion

We have described synthesis, structure and luminescence properties of new tris- and tetrakis-acylpyrazolonates of rare earth elements with different 4-acyl substituents. We have shown that the nature of the substituent does not influence the stoichiometry and the antiprismatic structure of the molecule but has a large effect on the luminescence properties. The presence of a thiophenyl group in the ligand does not provide a sufficient increase in the quantum yield as it was for thienyltrifluoroacetone.

Further investigations on the effect of ancillary ligands such as N and P-donors able to replace the water molecule on the luminescence properties are in progress.

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