



Syntheses, spectroscopic characterization and X-ray structural studies of lanthanide complexes with adamantyl substituted 4-acylpyrazol-5-one

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Abstract

Synthesis and spectroscopic characterization of new lanthanide complexes $[\text{Ln}(\text{Q}_{\text{AD}})_3(\text{EtOH})(\text{H}_2\text{O})]$, ($\text{Ln} = \text{Tb}, \text{Eu}$; $\text{HQ}_{\text{AD}} = 1$ -phenyl-3-methyl-4-adamantylcarbonyl-pyrazol-5-one), $[\text{H}_3\text{O}][\text{Tb}(\text{Q}_{\text{AD}})_4]$, $[\text{Ln}(\text{Q}_{\text{AD}})_3(N-N)]$ ($\text{Ln} = \text{Tb}, \text{Eu}$; $N-N = 1,10$ -phenanthroline (Phen), 2,2'-bipyridyl (Bipy), 4,4'-dimethyl-2,2'-bipyridyl (4,4'-Me₂Bipy)) are reported. The crystal structures of the proligand HQ_{AD} and of complexes $[\text{H}_3\text{O}][\text{Tb}(\text{Q}_{\text{AD}})_4]$ and $[\text{Tb}(\text{Q}_{\text{AD}})_3(4,4'\text{-Me}_2\text{Bipy})]$ have been determined. In both complexes the lanthanide ions are in a square antiprismatic environment, the H_3O^+ cation in the former acid complex being stabilized by H-bonding. Luminescence studies have been performed on selected derivatives.

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1. Introduction

Terbium and europium derivatives of 4-acylpyrazol-5-ones show promising luminescent properties and therefore receive increasing attention as materials for organic light-emitting diodes (OLEDs). The first electroluminescent device based on analogous complexes containing ligands with trimethylacetyl substituents emitted green light [1]. The emission is caused by the transfer of the excitation energy from the triplet level of the ligand to the lanthanide ion preceded by initial singlet-to-triplet inter-system crossing [2]. Previous investigations have demonstrated that the redistribution of electronic density upon introduction of donor or acceptor groups in the substituents tunes the triplet energy levels of acylpyrazolones and improves the energy transfer efficiency from antenna to rare-earth ele-

ment, therefore enhancing the intensity of emission [3]. It has also been found a correlation between the luminescence intensity and the rigidity of the acyclic substituent of acylpyrazolone [4], and it has been reported by us that groups such as cyclopentyl and ethylcyclopentyl, have comparatively low quenching influence on luminescence. In this work, we present the synthesis, structure and luminescent properties of the rare-earth metal derivatives of acylpyrazolones with a rigid adamantyl substituent. Owing to bulkiness, rigidity and hydrophobicity of the adamantyl group, adamantyl substituted β -diketones have been suggested for medical uses [5], and their complexes with transition metals as catalysts for olefin oxidation [6]. The proligand 1-phenyl-3-methyl-4-adamantylcarbonylpyrazole-5-one (HQ_{AD}) has been previously prepared and used in fabrication of polymeric membrane electrodes [7], but its lanthanide derivatives have not been described. Here we report an efficient synthesis of the proligand HQ_{AD} and of its terbium and europium complexes and also a detailed structural and spectroscopic characterization.

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2. Experimental

2.1. Materials and methods

All chemicals and reagents were of reagent grade quality and were used as received without further purification. All solvents were distilled prior to use. Methanol was dried over CaO. Dichloromethane was freshly distilled from CaH₂. Other solvents were dried and purified by standard procedures. Elemental analyses (C, H, N) were performed with a Fisons Instruments 1108 CHNSO-elemental analyser. IR spectra in the range 4000–100 cm^{−1} were recorded with a Perkin–Elmer System 2000 FT-IR instrument. ¹H NMR spectra were recorded on a VXR-300 Varian Spectrometer (300 MHz). H chemical shifts are reported in ppm *vs.* SiMe₄. Melting points were determined on a Stuart SMP3 instrument. Luminescence spectra of the polycrystalline samples were recorded using a modified LOMO DFS-12 spectrometer (double monochromator with 1200 grvs/mm gratings) at 77 and 300 K. The Hg 365 nm line of spectrum of standard high pressure mercury lamp was used for luminescence excitation (spectral resolution = 0.1 nm). The spectra were recorded in digital form in the regions of 575–715 nm (Eu³⁺ spectra) and 475–700 nm (Tb³⁺ spectra).

2.2. Syntheses

2.2.1. Synthesis of the proligand (HQ_{AD}) (1)

To a hot dioxane solution of 3-methyl-1-phenylpyrazole-5-one (15 g, 0.088 mol), Ca(OH)₂ (12 g, 0.162 mol) was added. The resulting mixture was stirred under reflux for 30 min. Then 2-adamantylcarbonyl chloride (18.45 g, 0.086 mol) was added dropwise to the suspension and the reaction mixture stirred under reflux for 24 h. The brown precipitate formed was treated with 350 ml of 2 N HCl and then filtered off and re-crystallized from octane (45% yield), m.p. 135–145 °C. *Anal.* Calc. for C₂₁H₂₃N₂O₂: C, 74.23; H, 7.12; N, 8.52. Found: C, 74.57; H, 7.19; N, 8.33%. IR (Nujol, cm^{−1}): 3400br (O–H), 1698m, 1596s, 1542s ν(C=O, C=C), 1030m, 750m, 688m, 604w, 508w. ¹H NMR (CDCl₃, 300 MHz): δ 1.8 (s, 6H, 6-C₁₀H₁₅), 2.06 (d, 6H, 6-C₁₀H₁₅), 2.14 (s, 3H, 3-C₁₀H₁₅), 2.71 (s, 3H, CH₃), 3.74 (s, 1H, CH), 7.27 (t, 1H, C₆H₅), 7.43 (t, 2H, C₆H₅), 7.82 (d, 2H, C₆H₅).

2.2.2. Synthesis of [Tb(Q_{AD})₃(H₂O)(EtOH)] (2)

To an ethanol solution (5 ml) of the proligand HQ_{AD} (0.168 g, 0.5 mmol) in the presence of an equimolar amount of KOH (0.028 g, 0.5 mmol), a water:ethanol 1:1 solution (5 ml) of Tb(NO₃)₃ · 6H₂O (0.0757 g, 0.167 mmol) was added. The resulting mixture was kept under stirring for 2 h. A colorless precipitate formed which was separated by filtration, then washed with water in order to remove potassium nitrate and recrystallized from ethanol to give 0.17 g of pure compound **2**. Yield 86%. M.p. 161 °C. *Anal.* Calc. for C₆₅H₇₇TbN₆O₈: C, 63.51; H, 6.31; N, 6.84. Found: C, 63.12; H, 5.92; N, 6.96%. IR (Nujol, cm^{−1}):

3300–2800 ν(O–H), 1649br δ(H₂O), 1606s, 1592s, 1500s, 1424s ν(C=O, C=C), 1054m, 756m, 612w.

2.2.3. Synthesis of [Eu(Q_{AD})₃(H₂O)(EtOH)] (3)

Derivative **3** was obtained by an analogous procedure to that reported for **2**. Yield 84%. M.p. 165 °C. *Anal.* Calc. for C₆₅H₇₇EuN₆O₈: C, 63.87; H, 6.35; N, 6.88. Found: C, 63.47; H, 6.13; N, 6.82%. IR (Nujol, cm^{−1}): 3300–2800 ν(O–H), 1606m, 1578m, 1500s, 1424m ν(C=O, C=C), 1054w, 756w, 612w. ¹H NMR (CDCl₃, 300 MHz): δ 1.24 (s, 3H, CH₃), 1.77–2.61 (m, 17H, C₁₀H₁₅), 7.16–7.35 (m, 5H, C₆H₅).

2.2.4. Synthesis of [H₃O][Tb(Q_{AD})₄] (4)

To an ethanol solution (10 ml) of the proligand HQ_{AD} (0.168 g, 0.5 mmol) in the presence of an equimolar amount of KOH (0.028 g, 0.5 mmol), an ethanol solution (10 ml) of Tb(NO₃)₃ · 6H₂O (0.076 g, 0.167 mmol) was added under violent stirring. The resulting mixture was kept under stirring for 20 min. The complex was then extracted with CHCl₃. Slow evaporation of the chloroform solution resulted in the formation of lamellar crystals of **4** · 4H₂O. Yield 74%. M.p. 132 °C. *Anal.* Calc. for C₆₅H₇₇TbN₆O₈: C, 66.40; H, 6.26; N, 7.38. Found: C, 66.82; H, 5.97; N, 7.51%. IR (Nujol, cm^{−1}): 3300–2900 ν(O–H), 1649 δ(H₂O), 1606m, 1593s, 1500s, 1424s ν(C=O, C=C), 1054m, 756w, 612w.

2.2.5. Synthesis of [Tb(Q_{AD})₃(Bipy)] (5)

A solution of Tb(NO₃)₃ · 6H₂O (45 mg) in 1 ml of ethanol was added dropwise to an ethanol solution of HQ_{AD} (100 mg), KOH (17 mg), and Bipy (16 mg). Then 4 ml of CHCl₃ was added under stirring, potassium nitrate immediately precipitated and it was separated by filtration. Slow evaporation of the chloroform solution resulted in the formation of lamellar crystals of **5**. Yield 82%. M.p. 187 °C. *Anal.* Calc. for C₇₃H₇₇TbN₈O₆: C, 66.35; H, 5.87; N, 8.48. Found: C, 65.96; H, 5.51; N, 8.49%. IR (Nujol, cm^{−1}): 1626m, 1606s, 1578s, 1424s ν(C=O, C=C), 1054m, 756m, 612m.

Compounds **6–9** were obtained by a procedure analogous to that reported for **5**.

2.2.6. [Eu(Q_{AD})₃(Bipy)] (6)

This compound has been obtained following a procedure analogous to that reported for **5**. Yield 66%. M.p. 184 °C. *Anal.* Calc. for C₆₅H₇₇EuN₆O₈: C, 66.71; H, 5.90; N, 8.53. Found: C, 66.27; H, 6.05; N, 8.72%. IR (Nujol, cm^{−1}): 1624m, 1606s, 1592s, 1500m, 1424s ν(C=O, C=C), 1054w, 756m, 612w. ¹H NMR (CDCl₃, 300 MHz): δ 1.26 (s, 3H, CH₃), 2.36 (d, 13H, C₁₀H₁₅), 2.54 (d, 9H, C₁₀H₁₅), 2.82 (br, 10H, C₁₀H₁₅), 3.76 (s, 14H, C₁₀H₁₅), 5.26 (br, 5H, C₆H₅), 7.18 (m, 9H, C₆H₅), 10.08 (br, 2H, H4_{Bipy}), 11.29 (br, 2H, H5_{Bipy}), 15.36 (br, 2H, H2_{Bipy}).

2.2.7. [Tb(Q_{AD})₃(Phen)] (7)

This compound has been obtained following a procedure analogous to that reported for **5**. Yield 73%. M.p.

194 °C. *Anal.* Calc. for $C_{75}H_{77}TbN_8O_6$: C, 66.95; H, 5.77; N, 8.33. Found: C, 67.40; H, 5.87; N, 8.11%. IR (Nujol, cm^{-1}): 1608s, 1578s, 1500m, 1424s $\nu(C=O, C=C)$, 1054m, 756m, 612w.

2.2.8. $[Eu(Q_{AD})_3(Phen)]$ (**8**)

This compound has been obtained following a procedure analogous to that reported for **5**. Yield 76%. M.p. 186 °C. *Anal.* Calc. for $C_{75}H_{77}EuN_8O_8$: C, 67.30; H, 6.05; N, 8.37. Found: C, 66.95; H, 5.96; N, 8.51%. IR (Nujol, cm^{-1}): 1624s, 1604s, 1595s, 1500s, 1424s $\nu(C=O, C=C)$, 1310m, 1054m, 756m, 612m. 1H NMR ($CDCl_3$, 300 MHz): δ 0.79 (s, 9H, CH_3), 2.26 (d, 10H, $C_{10}H_{15}$), 2.37 (d, 7H, $C_{10}H_{15}$), 2.66 (br, 8H, $C_{10}H_{15}$), 3.33 (s, 20H, $C_{10}H_{15}$), 3.74 (br, 2H, $C_{10}H_{15}$), 5.30 (br, 6H, C_6H_5), 7.10 (m, 8H, C_6H_5), 8.54 (br, 2H, H_{4phen}), 10.56 (br, 2H, H_{5phen}), 10.95 (br, 2H, H_{2phen}).

2.2.9. $[Tb(Q_{AD})_3(4,4'-Me_2-Bipy)]$ (**9**)

This compound has been obtained following a procedure analogous to that reported for **5**. Yield 88%. M.p. 177 °C. *Anal.* Calc. for $C_{75}H_{81}TbN_8O_6$: C, 66.75; H, 6.05; N, 8.30. Found: C, 67.12; H, 6.11; N, 8.19%. IR (Nujol, cm^{-1}): 1606m, 1578s, 1422s $\nu(C=O, C=C)$, 1310m $\delta(C-H)$ 1054m, 756w, 612m.

2.3. Single-crystal X-ray structure determination

Single crystals of **1**, **4**, **9** were obtained by slow evaporation of heptane (**1**) and ethanol– $CHCl_3$ solution (**4**, **9**). Data collection for crystals of **1**, **4**, **9** was carried out at low temperature (140–160 K) on an IPDS (Stoe) diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Details of data collection and refinement are given in Table 1. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 . Hydrogen atoms were placed at the calculated positions and were included in the final refinements in a riding mode. Selected bond lengths and angles for **1**, **4**, **9** are listed in Table 2.

3. Results and discussion

3.1. Syntheses

The proligand HQ_{AD} was synthesized by a classical route, i.e. acylation of 1-phenyl-3-methyl-pyrazole-5-one with 2-adamantylcarbonyl chloride (Chart 1) [8]. The proligand HQ_{AD} can be conveniently separated and purified by extraction and re-crystallization from heptane.

The tris-(4-acylpyrazolonate) derivatives $[M(Q_{AD})_3 \cdot (H_2O)(EtOH)]$ (**2**) ($M = Tb$) and **3** ($M = Eu$) were obtained by interaction of the ligand HQ_{AD} with terbium and europium nitrates in the presence of equimolar amounts of KOH (Chart 2).

When the reaction of $Tb(NO_3)_3 \cdot 6H_2O$ with HQ_{AD} is carried out in ethanol solution (95%) and the residue

Table 1

Crystallographic data and details of structure refinements for compounds **1**, **4**, **9**

Compound	1	4	9
Formula	$C_{21}H_{24}N_2O_2$	$C_{84}H_{103}N_8O_{13}Tb$	$C_{84}H_{95}N_8O_9Tb$
Formula weight	336.42	1591.66	1373.42
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$
<i>a</i> (Å)	14.342(3)	22.284(4)	28.006(6)
<i>b</i> (Å)	9.191(2)	14.960(3)	9.6710(10)
<i>c</i> (Å)	12.839(3)	24.851(5)	49.694(10)
β (°)	94.73(3)	93.63(3)	96.66(2)
<i>V</i> (Å ³)	1686.6(6)	8268(3)	13 369(4)
<i>Z</i>	4	4	8
<i>D</i> _{calc} (Mg/m ³)	1.325	1.279	1.365
<i>T</i> (K)	140	150	160
<i>R</i> (000)	720	3328	5696
Crystal dimensions (mm)	0.60 × 0.50 × 0.40	0.35 × 0.08 × 0.08	0.60 × 0.13 × 0.02
θ_{max} (°)	26.7	24.4	27.1
Reflections collected	3062	24439	19836
Independent reflections	3062	11 262	11 820
Parameters	231	952	834
Goodness-of-fit	1.094	0.809	0.692
<i>R</i> ₁ ($I > 2\sigma(I)$)	0.0576	0.0835	0.0648
<i>wR</i> ₂ (F^2)	0.1162	0.1922	0.0899
ΔQ (e Å ⁻³)	0.245/−0.205	1.854/−0.887	0.873/−0.996

Table 2

Selected bond lengths (Å)

Compound	1	4	9
Tb–O(1)		2.322(11)	2.331(7)
Tb–O(2)		2.321(12)	2.292(5)
Tb–O(3)		2.408(12)	2.320(9)
Tb–O(4)		2.434(10)	2.346(5)
Tb–O(5)		2.317(9)	2.302(6)
Tb–O(6)		2.337(12)	2.331(5)
Tb–O(7)		2.365(12)	
Tb–O(8)		2.418(12)	
Tb–N(7)			2.558(8)
Tb–N(8)			2.582(7)
O(1)–C(1)	1.325(3)	1.308(18)	1.283(9)
O(2)–C(3)	1.256(3)	1.223(17)	1.276(11)

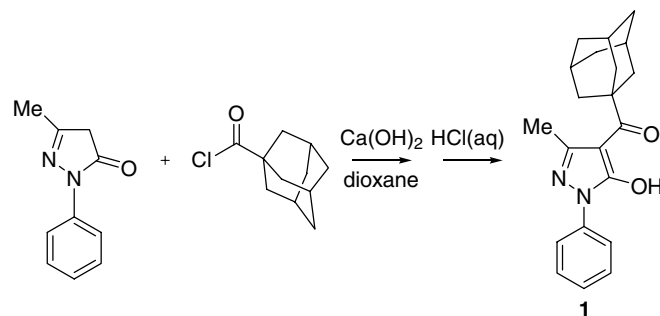


Chart 1.

obtained is extracted with chloroform, the ionic acid complex $[H_3O][Tb(Q_{AD})_4]$ (**4**) formed (Chart 3). This further confirms the high stability and easy formation of

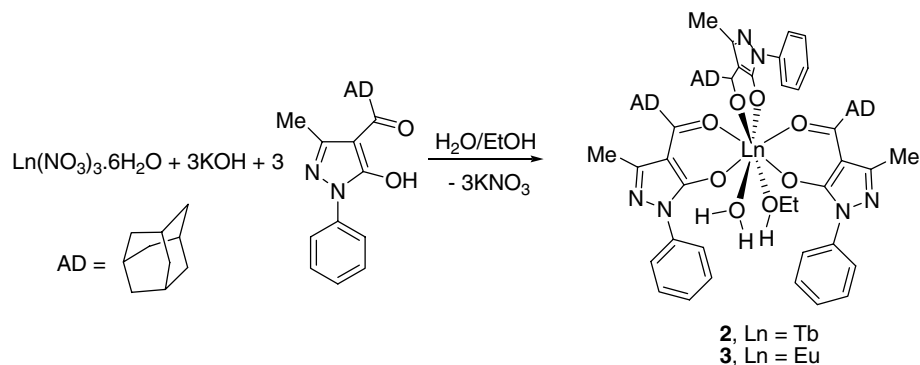


Chart 2.

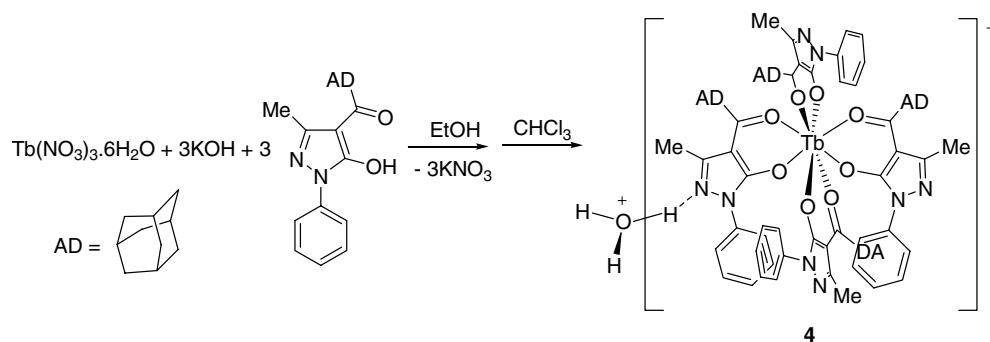


Chart 3.

tetrakis(diketonate) acid complexes when Ln salts and acylpyrazolones ligands were employed [9]. When the reaction between HQ_{AD} , KOH and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was carried out in the presence of chelating N_2 -donors such as Bipy, Phen and 4,4'- Me_2 -Bipy, derivatives $[\text{M}(\text{Q}_{\text{AD}})_3(\text{N}_2\text{-donor})]$ (**5**: M = Tb, N_2 -donor = Bipy; **6**: M = Eu, N_2 -donor = Bipy; **7**: M = Tb, N_2 -donor = Phen; **8**: M = Eu, N_2 -donor = Phen; **9**: M = Tb, N_2 -donor = 4,4'- Me_2 -Bipy) were obtained, the solvent molecules present in **2**, **3** being fully replaced by the N_2 -donor chelating ligand (Chart 4). Complexes **5–9** are soluble in slightly polar solvents such as chloroform and benzene and poorly soluble in ethanol.

3.2. Spectroscopic characterization

The IR spectra of complexes **2–9** exhibit absorptions typical of lanthanide derivatives containing 4-acylpyrazol-5-onates [10]. A number of peaks of medium intensity due to the C–H bending and torsion vibrations (~ 1400 – 400 cm^{-1}) (Fig. 1) can be easily detected. The strong bands at 1606 , 1578 , and 1500 cm^{-1} have been assigned to the stretching $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{C})$, and $\nu(\text{C}=\text{N})$ vibration modes of the acylpyrazolonate ring coordinated to the metal center. In the IR spectrum of the proligand HQ_{AD} , the same absorptions occurred at 1698 , 1596 and 1542 cm^{-1} [5]. Therefore, the separation between these bands increases

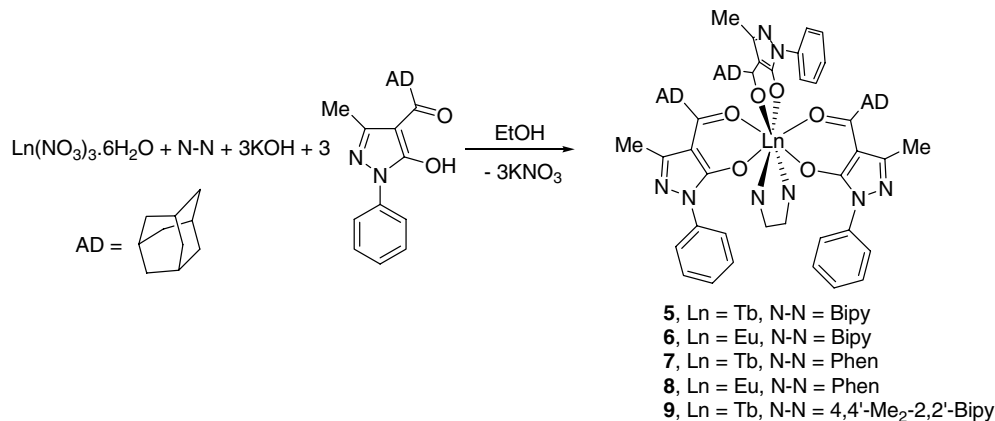


Chart 4.

upon coordination, as a consequence of delocalization of electrons of the β -diketone system. In **2–4**, broad bands in the region $3000\text{--}3500\text{ cm}^{-1}$ are observed due to the presence of water and ethanol (**2** and **3**) [11,12] and of H_3O^+ (**4**) [9]. Absorption bands due to Phen in **7** and **8** appear at 1626 , 842 , and 730 cm^{-1} [13].

The ^1H NMR spectra of the ligand and its complexes have been recorded in chloroform solution. The ^1H NMR spectrum of **HQ_{AD}** shows three signals due to the protons in the adamantylic group in accordance with the presence of three equivalent groups of protons (H1 + H2 at 2.06 ppm , H3 at 2.14 ppm , H4 + H5 at 1.80 ppm) (Fig. 2). In deuterated chloroform, the keto–enol equilibrium is also observed. The signal at 3.74 ppm , corresponding to the proton of the enol form [14], has an integral equal to 0.33 H , suggesting that keto and enol forms are present in $1:2$ ratio in accordance with the slight polarity of CDCl_3 [15]. Very broad signals are found in the spectrum of hydrate **3**, always highfield shifted with respect to the analogous signals in the spectrum of the free ligand. This fact can be related to the dissociation of the complex in solution and to rapid ligand exchange. On the contrary, in the proton spectra of adducts **6** and **8** sharp signals with fine structures are observed. It could be caused by the greater inertness of mixed-ligand complexes with respect to the hydrates. In fact, all the ligands in the coordination sphere of our lanthanide complexes are chelating and can-

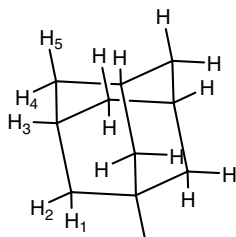


Fig. 2. Types of non-equivalent protons in adamantyl substituent.

not be quickly replaced. Adamantyl protons give four resonances in the proton spectra of **6** and **8** and these signals are downfield shifted, as previously reported for similar derivatives [4]. These signals can be assigned using positions of signals in free ligand and ratio $\Delta H/H = k(3\cos^2\theta - 1)/r^3$ [16] (k is the constant, related with the nature of the central ion; θ is the angle about the metal ion between the bond defining the C_∞ axis and the i th protons; r is the distance from central ion to proton). In the spectrum of **8**, there are H1 + H2 (broad resonances at 3.32 ppm), H3 (2.66 ppm), H4 (2.37 ppm), and H5 (at ca. 2.26 ppm).

The position of the resonance due to the phenyl groups is similar to that in europium complexes of 1-phenyl-3-methyl-4-cyclopentylcarbonylpyrazole-5-one [4]. The chemical shift ratios of H(2) and H(4) are 1.22 for $\text{Eu}(\text{fod})_3(\text{Phen})$, 1.68 for $\text{Eu}(\text{fod})_3(\text{Bipy})$ ($\text{fod} = 6,6,7,7,8,8,8\text{-heptafluoro-2,2-dimethyl-3,5-octanedionate}$) [17], 1.25 for $\text{Eu}(\text{thd})_3(\text{Phen})$, 1.56 for $\text{Eu}(\text{thd})_3(\text{Bipy})$ ($\text{thd} = 2,2,6,6\text{-tetramethylheptane-3,5-dionate}$) [16], 1.28 and 1.52 for **6** and **8**, respectively. These results suggest similar geometry of complexes in solution.

3.3. X-ray discussion

The structures of the adamantyl substituted β -diketone **HQ_{AD}** and its complexes are firstly characterized in this work. Brown crystals of **1** have a space group $P2_1/c$.

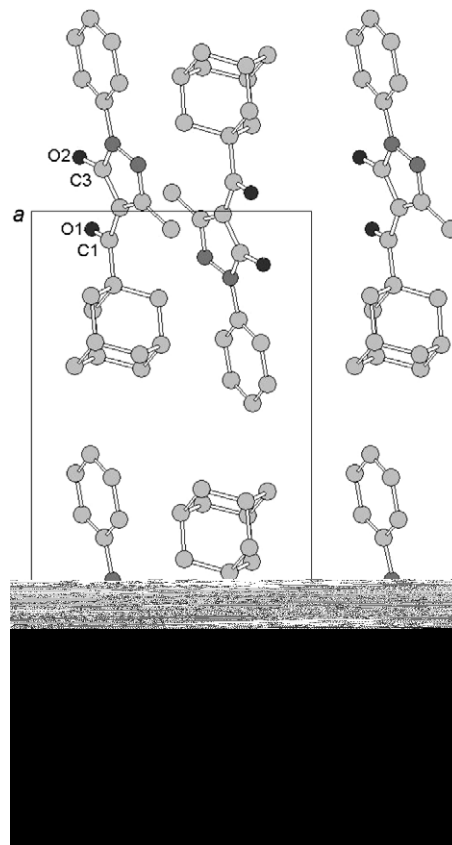


Fig. 3. The molecular packing in **HQ_{AD}**.

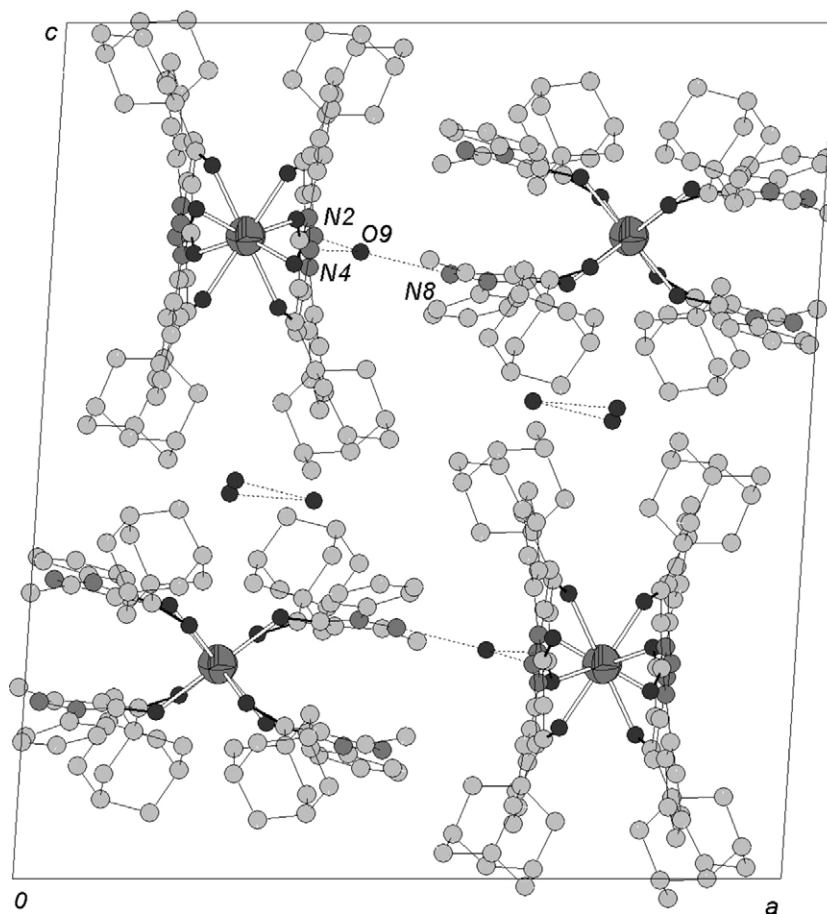


Fig. 4. The molecular packing in the acid complex 4.

Hydrogen atom in diketone system is involved in H-bonding with the oxygen atom of the azole ring. That is, the molecule is in enol-form in the crystal state. Presence of the enolic form is usual for β -diketones due to the formation of intramolecular hydrogen bond. In HQ_{AD} , the O–O distance (2.515(3) Å) confirms the presence of a H-bond. The length of the C–O bond in the acyclic group is 1.256(2) Å, that is typical for C–O distance in ketones (1.23 Å) [18]. The HQ_{AD} molecules form layer in plane bc (Fig. 3). The adamantyl groups are directed out of the layer and together with phenyl groups form its hydrophobic cover.

In the structure of the tetrakis-complex $[\text{H}_3\text{O}][\text{Tb}(\text{Q}_{\text{AD}})_4] \cdot 4\text{H}_2\text{O}$ ($4 \cdot 4\text{H}_2\text{O}$), there are two crystallographically independent Tb atoms both lying on the twofold axis. The coordination environment of both Tb atoms is close to the square antiprismatic. Two pairs of ligands (O1O2 and O3O4 for Tb1, and O5O6 and O7O8 for Tb2) occupy the slightly distorted square faces of the antiprisms (Fig. 6). The Tb–O distances are in the range of 3.32–3.42 Å (average 2.37 Å). They are very similar to the Tb–O distances in $[\text{H}_3\text{O}][\text{Tb}(\text{Q}_S)_4]$ ($\text{HQ}_S = 1\text{-phenyl-3-methyl-4-thenoylpyrazole-5-one}$) [9]. An analogous coordination environment has been found in other anionic tetrakis-(β -diketonate)Ln complexes [19,20]. The H_3O^+ ions are involved in H-bond-

ing with nitrogen atoms of pyrazole moiety of the ligand. Each hydroxonium ion forms three H-bonds with three different ligands of three different complex molecules ($\text{O}(9) \cdots \text{N}(2)$ 2.859(8), $\text{O}(9) \cdots \text{N}(4)$ 2.850(8), $\text{O}(9) \cdots \text{N}(8)$ 2.781(8) Å). All the nitrogen atoms coordinated to Tb1 participate in such interaction, but among the ligands linked with Tb2 only N2 is involved in H-bonding. Hydrogen bonds connect anions in plane ab (Fig. 4).

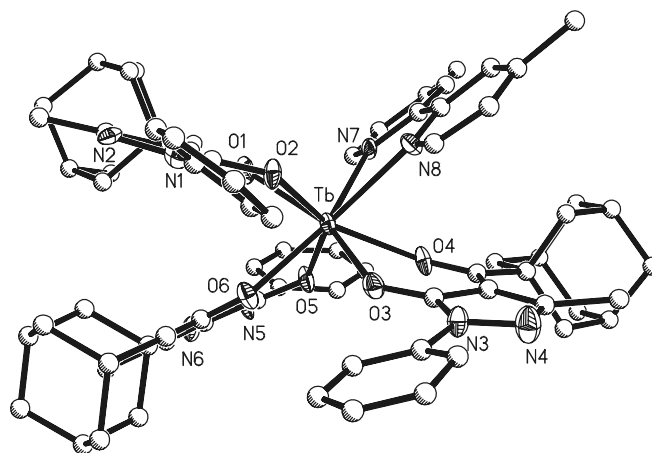


Fig. 5. A single molecule of complex 9.

The complex $[\text{Tb}(\text{Q}_{\text{AD}})_3(4,4'\text{-Me}_2\text{Bipy})]$ (**9**) has a molecular structure with Tb atom situated in a square-antiprismatic environment of nitrogen atoms from 4,4'-Me₂Bipy and oxygen atoms from three chelating bidentate acylpyrazolonates (Fig. 5). A similar arrangement has been reported for other lanthanide acylpyrazolonates [21] and for the adducts of lanthanides β -diketones with Bipy and 4,4'-Me₂Bipy [22,23]. According to our classification of coordination patterns in diketonate complexes of lanthanides [11], compound **9** belongs to the type *e*. Distortion from the square antiprism (angles O–Tb–O from 70° to 77°) may be caused by differences in lanthanide affinity to O and N donor ligands and by steric difficulties in adamantyl-group of acylpyrazolonate and methyl group of 4,4'-dimethyl-2,2'-Bipy. The Tb–O(Q_{AD}) distances fall in the range 2.293–2.346 Å, with average value 2.320 Å. This is a little smaller than in $\text{Tb}(\text{Q}_{\text{CP}})_3(4,4'\text{-Me}_2\text{Bipy})$ (where $\text{HQ}_{\text{CP}} = 1\text{-phenyl-3-methyl-4-cyclopentyl carbonylpyrazole-5-one}$) [4]. Distances Tb–N are not equivalent, their lengths being 2.558(5) and 2.583(5) Å due to the interaction of 4,4'-Me₂Bipy with adamantyl group of a neighbour molecule. Whereas in the analogous Bipy and 4,4'-Me₂Bipy Ln complexes containing Q_{CP} ligand, the Tb–N bonds are equal [4]. These molecules form a hexagonal layer in plane *ac*. The layers are packed along axes *b*, so their molecules settled one after the other.

3.4. Luminescence studies

Complexes **2–9** possess the intensive red (in the case of europium) and green, (in the case of terbium derivatives) luminescence upon irradiation by UV light in the interval 250–360 nm at 77 and 300 K accordingly. Quantum yields of the luminescence of Tb–Q_{AD} chelates are higher than those of Eu ones. The Eu–Q_{AD} species do not exhibit luminescence at 300 K. It could be explained by the multiphonon mechanism of the quenching of the excitation energy of metastable ⁵D₄ and ⁵D₀ levels of the Tb³⁺ and Eu³⁺ ions by high-frequency stretching vibrations, $\nu(\text{C–H})$, of the ligands. The luminescence quantum yield of the terbium complexes is low with respect to analogous Q_{CP} derivatives likely due to a great number of C–H bonds whose vibrations are quenching the luminescence.

In the spectra of **3**, **6**, **8**, signals corresponding to the transition from ⁵D₀ level of Eu³⁺ to ⁷F_{0–4} have been detected. The intensity distribution in the luminescence spectra of the tris-chelates $\text{Eu}(\text{Q}_{\text{AD}})_3(\text{N}_2\text{-donor})$ confirms low symmetry (*C_s*) of the Ln coordination environment. A typical spectrum for analogous complexes of formula $\text{Eu}(\text{Q}_{\text{CP}})_3(\text{N}_2\text{-donor})$ has been published earlier [4]. The main difference between that and our adamantyl derivatives is in the broadening of the lines in the spectra of the latter due to smaller crystallinity of the samples (Fig. 7, curves 1 and 2). Transition from ⁵D₄ level of Tb³⁺ to ⁷F_{1–6} is observed in the terbium complexes. The intensity distribution found in the spectra of $\text{Tb}(\text{Q}_{\text{AD}})_3(\text{N}_2\text{-donor})$ species is evident in Fig. 6 where the spectrum of $\text{Tb}(\text{Q}_{\text{AD}})_3(4,4'\text{-Me}_2\text{Bipy})$ is reported. Eu and

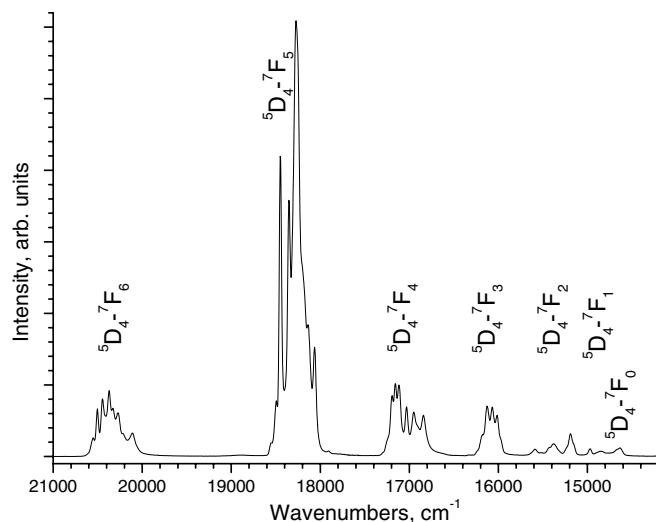


Fig. 6. Luminescence spectrum of $\text{Tb}(\text{Q}_{\text{AD}})_3(4,4'\text{-Me}_2\text{Bipy})$ at 77 K.

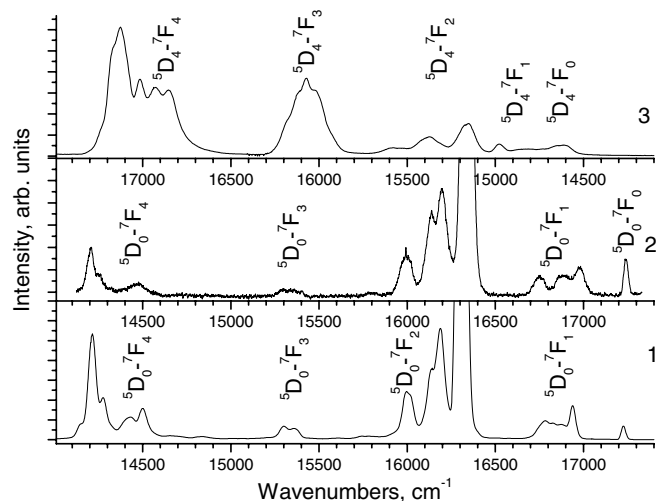


Fig. 7. Luminescence spectra of $\text{Eu}(\text{Q}_{\text{CP}})_3(\text{Phen})$ (**1**), $\text{Eu}(\text{Q}_{\text{AD}})_3(\text{Phen})$ (**2**), $\text{Tb}(\text{Q}_{\text{AD}})_3(\text{Phen})$ (**3**) at 77 K.

Tb pyrazolonate derivatives possess analogous structures as demonstrated by the likeness of their spectra in the regions of the ⁵D₀–⁷F_{1,2,3,4} transition for europium compounds and ⁵D₄–⁷F_{1,2,3,4} transitions for the terbium ones [24], as illustrated in Fig. 7 (curves 2 and 3).

4. Conclusion

We have described synthesis, structure and luminescence properties of new tris and tetrakis-acylpyrazolonates of Tb and Eu with 4-adamantyl substituted acylpyrazolone. The complexes with this ligand have been structurally characterized for the first time. The crystal structures of ligand **1**, of the complex acid **4** and of the mixed-ligand complex **9** have been determined. High stability of tetrakis acids in the Ln – acylpyrazolone systems is confirmed. Terbium complexes of HQ_{AD} can be used as luminescent materials when other properties such as hydrophobicity, solubility in non-polar solvents, and large size of the molecules are required.

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Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 610158–610160 for derivatives **1**, **4** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2006.04.045](https://doi.org/10.1016/j.ica.2006.04.045).

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