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A new rare-earth metal acylpyrazolonate containing the Zundel ion H_5O_2^+ stabilized by strong hydrogen bonding

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Abstract

A new luminescent europium derivative $[\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4]$ (**1**) ($\text{HQ}^{\text{Cy}} = 1\text{-phenyl-3-methyl-4-cyclohexanecarbonylpyrazole-5-one}$), achievable in high yield, characterized by high thermal stability, ionic in acetone and ethanol solution, contains the Zundel cations H_5O_2^+ stabilized by strong hydrogen bonding with the N atoms of the anionic heterocyclic ligand (Q^{Cy}).

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The design of new lanthanide complexes with luminescent and magnetic properties remains of great interest not only because of their wide application as luminescent probes, but also for their use as NMR shift and magnetic resonance imaging agents [1]. Complexes containing acylpyrazolonate ligands have been recently approved as luminescent materials for organic light emitting diodes (OLEDs) due to their saturated red-emissions [2], β -diketonate ligands being one of the most important “antenna” that allows transfer of energy to Eu and Tb ions for high harvest emissions [3].

Due to their relatively large atomic radii, lanthanide ions form ionic complexes $[\text{LnL}_4][\text{NR}_4]^+$, where L is a β -diketonate ligand and $[\text{NR}_4]^+$ bulky organic cations such as tetrabutylammonium [4]. We have recently reported and established general rational procedure for obtaining of acid complexes such as $[\text{H}_3\text{O}^+][\text{Ln}(\text{Q}^{\text{s}})_4]$ (HQ^{s} is 1-phenyl-3-methyl-4-thenoylpyrazole-5-one) [5], containing a hydroxonium cation stabilized by hydrogen bonding with a

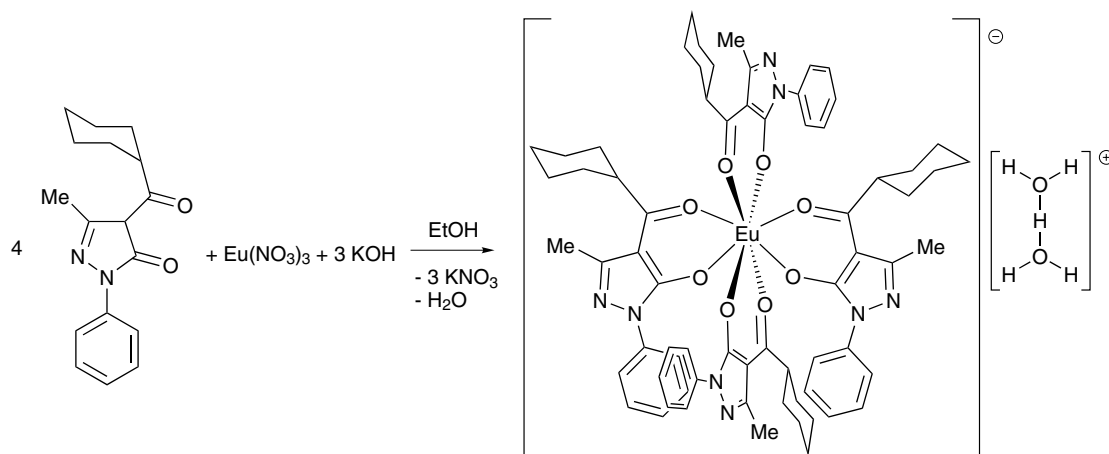
nitrogen of the pyrazole moiety in the Q^{s} ligand. These complexes are interesting in view of the fact that they can combine both luminescent properties and proton conductivity [6].

We report here an example of a luminescent and stable acid complex containing the Zundel H_5O_2^+ cation [7].

The acid complex $[\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4]$ (**1**) has been obtained in accordance with Scheme 1 [8]. Recrystallization from 96% ethanol in a sealed ampoule always gives the same product containing the H_5O_2^+ cation. Synthesis of **1** is reproducible always in high yields, but only using the stoichiometry indicated. It is worthy to note that the obtainment of acid complexes containing the Zundel cation seems possible only by using the Q^{Cy} ligand. The IR spectrum of **1** is analogous to those reported for other Ln derivatives of 4-acylpyrazole-5-ones [9], the values for $\nu(\text{C}=\text{C}, \text{C}=\text{O})$ frequencies in the diketonate chelate rings being the same as in the tris-complexes $\text{Ln}(\text{Q})_3$ [9]. A broad adsorption band (with maximum at 3300 cm^{-1}) and narrow peaks at 1674 and 1050 cm^{-1} found in the spectrum of **1** are characteristic of the H_5O_2^+ moiety [10]. It is interesting to note that $\delta(\text{O}=\text{H}\cdots\text{O})$ vibration in the spectrum of **1** falls in the highest part of the limit given in Ref. [9]. This

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Scheme 1.

correlates with the occurrence of a short O \cdots O distance (see below), when O—H \cdots O bond are strong.

Compound **1** crystallizes in the monoclinic space group (C2/c) with four molecules in the unit cell, different [Eu(Q^{Cy})₄][−] (Fig. 1) anions being connected by [H₅O₂]⁺ bridges. In the anion of **1**, the Eu is 8-coordinate by four bidentate acylpyrazolonate moieties, the metal center geometry being well described as a square antiprism with square planes [O(1)O(2)O(3)O(4)] and [O(1A)O(2A)O(3A)O(4A)]. They are connected by a twofold axis, and, hence, are equivalent. The length of Eu—O bonds falls in the interval 2.361–2.448 Å with average distance of 2.40(2) Å virtually the same as in [H₃O][Eu(Q^s)₄] (2.39 Å) [5].

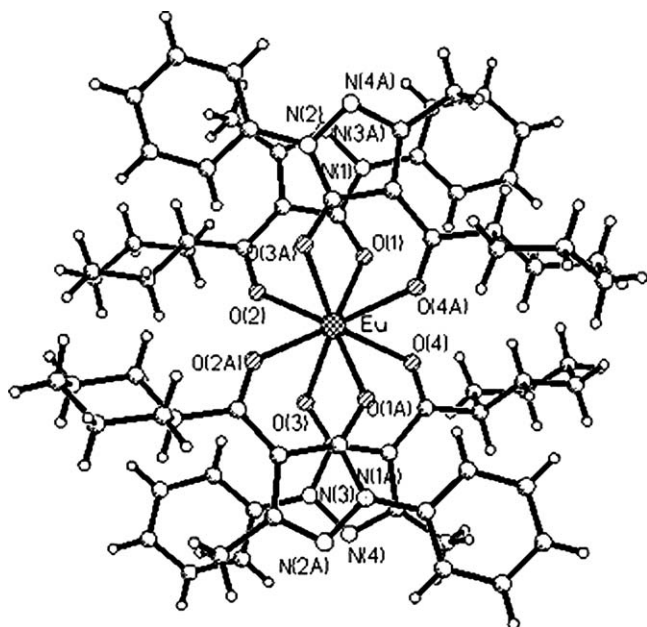
The O \cdots O distance in the cation (2.345(5) Å) is the shortest described in the literature for hydronium acids,

being the reason for the stability of **1**. In bis (benzo-15-crown-5)tetrachloro-aurate(III) oxonium monohydrate [11] and in [H₅O₂][V(H₂O)₆][(CF₃SO₃)₄] studied by neutron diffraction [12], the analogous distance is nearly 2.4 Å. In our complex, the [H₅O₂]⁺ cation is stabilized by four hydrogen bonds with nitrogen atoms of pyrazole rings (Fig. 2) two from each oxygen (O(5) \cdots N(2) 2.637 Å, O(5) \cdots N(4) 2.821 Å). The positive charge is delocalized between two oxygen atoms that results in the weakening of the hydrogen bonding, the shortest bond being in fact longer than in the [H₃O⁺][Ln(Q^s)₄] (2.593(3) Å).

Hydronium cations has been already described for rare-earth metal complexes [(H₅O₂)(pydaH)₂][Gd(pydc)₃](H₂O) (pydaH – 2,6-diaminopyridinium), (pydc – 2,6-pyridinedicarboxylate), oxalate [(H₅O₂)Tb(C₂O₄)₂(H₂O)] and sulfates (H₅O₂)(H₃O)₂Nd(SO₄)₃ [13] H₅O₂⁺ forming hydrogen bonds with oxygen atoms of anion. For oxalate derivative a polymeric structure is established, that suggests the proton conductivity. According to the literature, the best way for the stabilization of hydronium H₅O₂⁺ cation is the use of crown ethers [14]; 24-crown-8 being the most suitable for this purpose. In the complexes with crown-ethers, the hydronium cation enters a cavity of crown being linked with oxygen atoms by four hydrogen bonds.

Complex **1** possesses the intensive red luminescence when irradiated by UV light in the interval 250–400 nm at 77 K. A series of signals in the spectrum of **1** corresponds to the transition from ⁵D₀ level of Eu³⁺ to ⁷F_{0–4}. The most intensive line in the spectrum at 612 nm corresponds to transition ⁵D₀–⁷F₂. Intensity of this line five times surpasses that of transition ⁵D₀–⁷F₁ at 590 nm. Owing to this the complex radiates clean red color. The absence of the band fission for the ⁵D₀–⁷F₀ transition means all the luminescence centers to be equivalent. Small half-width of lines (3 nm for ⁵D₀–⁷F₂) testifies high symmetry of the central ion environment.

Thermogravimetric studies indicate for **1** a very sharp loss water process corresponding to the simultaneous evolution of two water molecules (weight loss of ca 2.7% at

Fig. 1. The molecular structure of the anion [Eu(Q^{Cy})₄][−] of **1**.

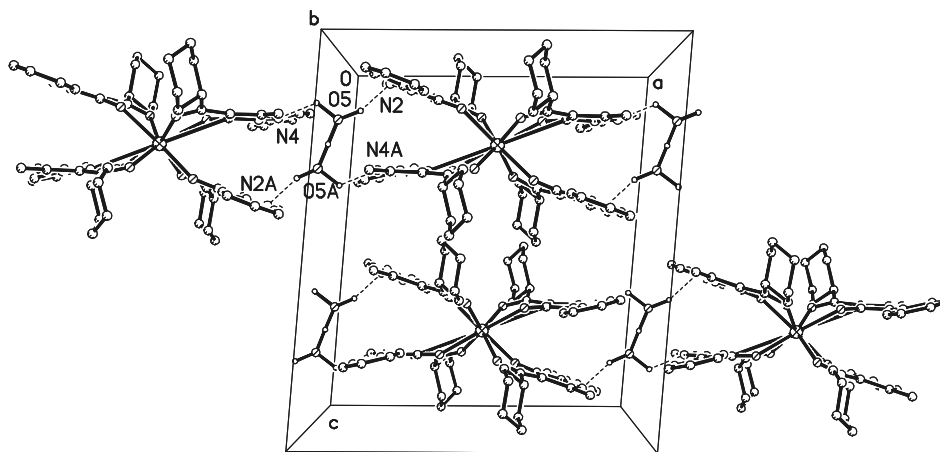


Fig. 2. The molecular packing in complex **1**. The H-bonds are shown as dashed lines.

180 °C). The decomposition temperature of **1** is rather high, that is in agreement with a high stability of the cation in the given system in comparison with $[\text{H}_5\text{O}_2][\text{Au}(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ [15] for which water loss begins at 80 °C. Then at 340 °C $[\text{HQ}^{\text{Cy}}][\text{Ln}(\text{Q}^{\text{Cy}})_3]$ decomposes to the neutral complex $[\text{Ln}(\text{Q}^{\text{Cy}})_3]$, step followed at 415 °C by full decomposition of the organic part and combustion of coal. The total weight loss (86%) is in accordance with theoretical (85.5%), calculated for the Eu_2O_3 residue.

Complex **1** is not stable in water solution, $[\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4]$ immediately dissociating to $[\text{Eu}(\text{Q}^{\text{Cy}})_3(\text{H}_2\text{O})_x]$, Q^- and H_3O^+ . Conductivity measurements in organic solvents have been performed in order to verify the stability of **1**. The degree of dissociation (α) has been calculated by the formula $\Lambda = \alpha(\lambda_+ + \lambda_-)$ (where λ_i = ion mobility). Assuming that protons mobility in infinitely diluted solution is approximately equal to that in the investigated solutions, λ_+ has been assumed $\gg \lambda(\text{Eu}(\text{Q}^{\text{Cy}})_4^-)$ taking into account the large radius of anion (14 Å) ($\lambda \sim |Z_i|e_0^2N_A/6\pi\mu r$, where Z_i – charge of ion, e_0 – charge of electron, N_A – Avogadro's constant, μ – viscosity of solvent, r – ion radius). From the data obtained ($\Lambda([\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4], \text{EtOH}, 0.005 \text{ M}) = 4.0 \text{ ohm}^{-1} \text{ cm}^2/\text{mol}$, $\Lambda(\text{HQ}^{\text{Cy}}, \text{EtOH}, 0.005 \text{ M}) = 1.28 \text{ ohm}^{-1} \text{ cm}^2/\text{mol}$, $\alpha([\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4])_{\text{calc}} = 6.8\%$, $\alpha(\text{HQ}^{\text{Cy}})_{\text{calc}} = 0.02\%$) we can propose that $[\text{Eu}(\text{Q}^{\text{Cy}})_4]^-$ is stable in solution because its formation strongly increases acidity in comparison with ligand. Partial dissociation even in the diluted solution allows to assume that the complex occurs in solution as a ionic pair in which H_5O_2^+ (or H_3O^+) is connected to the nitrogen of the pyrazolone ring. The conductivity values in ethanol and acetone are well correlated to the mobilities of H^+ in these solvents ($\lambda_{\text{H}^+}^\infty(\text{EtOH}) = 59.6 \text{ ohm}^{-1} \text{ cm}^2/\text{mol}$, $\lambda_{\text{H}^+}^\infty(\text{acetone}) = 88 \text{ ohm}^{-1} \text{ cm}^2/\text{mol}$).

This study has demonstrated that lanthanide pyrazolones are excellent hosts for oxonium ions in the solid and solution state that can contemporaneously possess both luminescent and acid properties. With a suitable choice of the anionic ligand Q and of the reaction conditions, it is possible to stabilize the H_5O_2^+ cation in rare earth com-

plexes of acylpyrazolone due to strong hydrogen bonding with the diketonate ligand that is in accordance with the relatively high thermal stability of $[\text{H}_5\text{O}_2][\text{Eu}(\text{Q}^{\text{Cy}})_4]$ with respect to other similar acid complexes and with its ionic character in ethanol and acetone solutions.

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- (d, 8H, C₆H₅ of Q^{Cy}), 7.3 (d, 20H, C₆H₅ of Q^{Cy} + CH₂ of Q^{Cy}), 8.1 (d, 8H, C₆H₅ of Q^{Cy}). Data collection for **1** was carried out at room temperature on an IPDS (Stoe) diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). C₆₈H₈₁EuN₈O₁₀, Monoclinic, C2/c, $a = 14.908(3) \text{ \AA}$, $b = 25.261(4) \text{ \AA}$, $c = 17.003(4) \text{ \AA}$, $\beta = 94.53(3)^\circ$. $V = 6383(2) \text{ \AA}^3$, $D_c = 1.372 \text{ g cm}^{-3}$, $Z = 4$, $\mu = 1.308 \text{ mm}^{-1}$; 6450 reflections measured at 293 K, 5468 observed [$I > 2\sigma(I)$], 396 parameters. $R_1 = 0.0374$; $wR_2 = 0.0962$.
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