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## Lanthanide complexes based on ethyl 2-hydroxymethylidene-3-oxobutanoate

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The reaction of europium(III) or terbium(III) chlorides with ethyl 2-hydroxymethylidene-3-oxobutanoate in the presence of 2,2'-bipyridine (2,2'-bipy) resulted in the luminescent complexes  $[LnL_3] \cdot 2,2'$ -bipy (L = ethyl 2-hydroxymethylidene-3-oxobutanoate, Ln = Tb<sup>III</sup> or Eu<sup>III</sup>), whose molecular structure has been determined by X-ray analysis.

The synthesis of new trivalent rare earth complexes is of great interest due to their wide applications in medicine and materials science.<sup>1–3</sup> The substituents of ligands influence the properties of metal complexes.<sup>4–7</sup> The use of  $\beta$ -diketones in complexation with rare earth metal ions is an efficient approach to metal complexes possessing very bright luminescence.<sup>8,9</sup> However, organic ligands based on 2-substituted 1,3-dicarbonyl compounds are less examined.

Here we studied ethyl 2-(hydroxymethylidene)-3-oxobutanoate with different substituents in carbonyl fragments as a ligand for the preparation of the luminescent complexes of europium(III) and terbium(III).

Tricarbonyl-substituted derivatives can be synthesized from  $\beta$ -dicarbonyl compounds by (i) acylation with acyl halides under basic conditions<sup>10–12</sup> or (ii) condensation with triethyl orthoformate with the subsequent hydrolysis.<sup>13</sup> To obtain target non-symmetric tricarbonyl compound **2**, 2-ethoxymethylidene-3-oxobutanoate **1** was initially synthesized by a known procedure<sup>14</sup> in 83–87% yield *via* the condensation of ethyl acetoacetate with triethyl orthoformate in the presence of acetic anhydride. The following hydrolysis of an ethoxy substituent in ester **1** afforded ethyl 2-hydroxymethylidene-3-oxobutanoate **2** (Scheme 1).<sup>†</sup> Previously, the hydrolysis of ethoxymethylidene group proceeding through the copper(II) salt formation was reported.<sup>15</sup> In this work, the direct hydrolysis was performed in water at room temperature

Synthesis of ethyl 2-hydroxymethylidene-3-oxobutanoate 2.

*Method A*. A solution of compound **1** (9.31 g, 0.05 mol) in water (100 ml) was stirred at room temperature for 1 h. Then, the mixture was extracted with Et<sub>2</sub>O (2×30 ml). The organic layer was washed with water (3×20 ml) and dried over MgSO<sub>4</sub> for 4 h. The distillation of a crude residue *in vacuo* gave target compound **2** as colorless oil.



Scheme 1 Reagents and conditions: i,  $H_2O$ , room temperature; ii, 1% aqueous NaOH, room temperature.

without catalysts. Desired product **2** was isolated by vacuum distillation in 68% yield. The use of a 1% aqueous solution of NaOH in this process decreased the yield of compound **2** to 54% because of formation of ethyl acetoacetate as a by-product.

Published data on the structure of compound **2** are contradictory.<sup>15–17</sup> For example, the product of hydrolysis of methyl 2-methoxymethylidene-3-oxobutanoate was described<sup>16</sup> as an aldehyde. Hydroxy tautomer **2** was reported<sup>15</sup> to exist as a mixture of two tautomers, whereas only one hydroxy derivative was described more recently.<sup>17</sup> Based on spectral data, the enol form of product **2** was confirmed.<sup>†</sup> Thus, there is one high-frequency absorption band of the ethoxycarbonyl group (1719 cm<sup>-1</sup>) in the IR spectrum of ester **2** and a low-field OH group signal (17.09 ppm) in the <sup>1</sup>H NMR spectrum. Regardless of the solvent used, enol **2** mainly exists in *E*-form (90%).

Although ethyl 2-hydroxymethylidene-3-oxobutanoate **2** is an O,O,O-tridentate ligand, there was no data on its metal complexes so far. We showed that the reaction of compound **2** with lanthanide chlorides (TbCl<sub>3</sub> and EuCl<sub>3</sub>) gave complexes **3a**, $b^{\ddagger}$  (Scheme 2). To fulfill the coordination number of a lanthanide

<sup>‡</sup> Lanthanide complexes **3** (general procedure). Compound **2** (1.58 g, 10 mmol) and 2,2'-bipyridine (0.47 g, 3 mmol) were added to a solution of NaOH (0.40 g, 10 mmol) in ethanol (50 ml). The resulting mixture was stirred at room temperature for 15 min. Then, the previously prepared solution of TbCl<sub>3</sub> or EuCl<sub>3</sub> (3 mmol) in water (5 ml) was added dropwise and the reaction mixture was stirred at room temperature. After 5 h, a precipitate was filtered. After filtrate evaporation, Et<sub>2</sub>O (10 ml) was added to the crude residue with the formation of a solid. The precipitate was filtered and crystallized from hexane–Et<sub>2</sub>O (3:1) mixture to give complexes **3a,b** as white solids.

<sup>&</sup>lt;sup>†</sup> All commercially available reagents and solvents were used without additional purification.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) in CDCl<sub>3</sub>. The IR spectra were obtained on a Perkin-Elmer Spectrum One spectrometer (FT-IR) (400–4000 cm<sup>-1</sup>). Elemental analysis was performed using a Perkin-Elmer PE 2400 (series II CHNS-O EA 1108) analyzer. Melting points were measured on a Stuart SMP3 apparatus in open capillaries. The luminescence spectra were recorded on a Varian Cary Eclipse spectrofluorimeter within 286–800 nm wavelength range with selective luminescence excitation at  $\lambda_{exc} = 281$  (for **3a**) and 276 nm (for **3b**). Reactions were monitored by TLC with 0.20 mm Alugram Sil G/UV254 pre-coated silica gel plates (60 F<sub>254</sub>).

*Method B*. A solution of ethyl 2-ethoxymethylidene-3-oxobutanoate **1** (9.31 g, 0.05 mol) in 1% aqueous NaOH (200 ml) was stirred at room temperature for 1 h. Then, the reaction mixture was treated with a 10% aqueous solution of HCl to reach pH 6 and extracted with  $Et_2O$  (2×30 ml). The product was isolated as described in *method A*.

Yield of **2**, 5.38 g (68%) (A), 4.27 g (54%) (B), bp 75–76 °C (10 Torr). IR (KBr,  $\nu/cm^{-1}$ ): 2985, 2938 (C–H), 1719 (br., C=O), 1636 (C=C), 1265, 1078 (C–O). <sup>1</sup>H NMR,  $\delta$ : 9.19 (d, 1H, CH, J 6.1 Hz), 17.09 (d, 1H, OH, J 6.1 Hz); E (90%): 1.33 (t, 3H, OCH<sub>2</sub>Me, J 7.1 Hz), 2.56 (s, 3H, Me), 4.26 (q, 2H, OCH<sub>2</sub>Me, J 7.1 Hz); Z (10%): 1.39 (t, 3H, OCH<sub>2</sub>Me, J 7.1 Hz), 2.53 (s, 3H, Me), 4.39 (q, 2H, OCH<sub>2</sub>Me, J 7.1 Hz). <sup>13</sup>C NMR,  $\delta$ : E: 14.23 (CH<sub>2</sub>), 26.28 (*Me*CH<sub>2</sub>), 60.30 (*Me*CO), 107.92 (*C*=COH), 165.03 (*C*O<sub>2</sub>Et), 187.32 (CHOH), 199.49 (MeCO). Found (%): C, 52.98; H, 6.37. Calc. for C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> (%): C, 53.16; H, 6.28.



Scheme 2

ion, 2,2'-bipyridine (2,2'-bipy) was used as a co-ligand. Coordination compounds of Tb<sup>III</sup> and Eu<sup>III</sup> exhibit strong ionic fluorescence due to efficient energy transfer from a triplet state of the organic ligand to the resonance level of a lanthanide ion.<sup>18</sup> For this reason, the luminescence spectrum of a substance is mostly determined by the complexing ion.

The structure of complex **3a** was refined by XRD analysis (Figure 1).<sup>§</sup> The complex formation occurs through the coordination of a Tb<sup>III</sup> ion with three ligands and one 2,2'-bipy molecule. The central Tb<sup>III</sup> cation is bonded with the oxygen atoms of hydroxyl and acyl groups and its coordination sphere is saturated through coordination with the nitrogen atoms of 2,2'-bipy. The complex has a trigonal prismatic geometry.



Figure 1 ORTEP view of complex 3a (thermal ellipsoids at a 50% probability at 295 K).

*Terbium(III)* (2,2'-*bipyridine)-tris(ethyl-2-hydroxymethylidene-3-oxo-butanoate)* **3a.** Yield, 2.08 g (88%), mp 135–136 °C. IR (DRA,  $\nu/cm^{-1}$ ): 3060, 2984 (C–H), 1700 (br.), 1639 (C=O), 1604 (C=C). Found (%): C, 47.34; H, 4.45; N, 3.50. Calc. for  $C_{31}H_{35}N_2O_{12}Tb$  (%): C, 47.34; H, 4.49; N, 3.56.

Europium(III) (2,2'-bipyridine)-tris(ethyl-2-hydroxymethylidene-3-oxo*butanoate*) **3b**. Yield, 2.15 g (92%), mp 106–107 °C. IR (NPVO, *v*/cm<sup>-1</sup>): 3061, 2984 (C-H), 1699, 1635 (C=O), 1608 (C=C). Found (%): C, 47.85; H, 4.48; N, 3.60. Calc. for  $C_{31}H_{35}N_2O_{12}Eu~(\%)$ : C, 47.76; H, 4.53; N, 3.59. § Crystallographic data for 3a. The single crystal (colorless prism, 0.20×0.14×0.07 mm) of complex 3a ( $C_{31}H_{35}N_2O_{12}Tb$ ) was used for X-ray analysis at 295(2) K on an Xcalibur 3 diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) and a CCD detector. Crystal is triclinic, space group  $P\bar{1}$  with a = 11.5924(7), b = 11.7977(5)and c = 13.1915(9) Å,  $\alpha = 93.542(5)^{\circ}$ ,  $\beta = 102.551(6)^{\circ}$ ,  $\gamma = 106.352(5)^{\circ}$ ,  $V = 1675.15(17) \text{ Å}^3$ , Z = 2. On the angles  $2.84 < \theta < 30.51^\circ 19043$  reflections were measured, among them 10059 unique reflections ( $R_{int} = 0.0248$ ), 6282 reflections with  $I > 2\sigma(I)$ . Completeness to  $\theta_{\text{max}} = 26.00$  is 99.3%. The structure was solved by a direct method and refined by full-matrix least squares at  $F^2$  using the SHELXTL program package.<sup>19</sup> All nonhydrogen atoms were refined anisotropically, the positions of the hydrogen atoms were calculated as a riding model in isotropic approximation. An absorption correction was not applied ( $\mu = 2.174 \text{ mm}^{-1}$ ). Goodness of fit at  $F^2$  0.988; final R values  $[I > 2\sigma(I)]$ ,  $R_1 = 0.0282$ ,  $wR_2 = 0.0486$ ; R value (all reflections)  $R_1 = 0.0563$ ,  $wR_2 = 0.0486$ . Largest difference peak and hole were 2.032 and -0.669 eÅ<sup>-3</sup>.

CCDC 1408322 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



Figure 2 Photoluminescence spectrum of terbium(III) complex 3a in ethanol.



Figure 3 Photoluminescence spectrum of europium(III) complex 3b in ethanol.

Under photoexcitation, complexes **3a,b** have luminescence characteristic of terbium and europium (green and red, respectively). The luminescence spectrum of **3a** (Figure 2) contained characteristic luminescence bands corresponding to the  ${}^{5}D_{4} \rightarrow {}^{7}F_{j}$ (j = 6, 5, 4, 3) electron transitions of Tb<sup>III</sup> at 490, 546, 583 and 621 nm, respectively; the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of Tb<sup>III</sup> at 546 nm was the strongest. In the fluorescence emission spectrum of europium complex **3b** (Figure 3), five emission peaks were observed, which were attributed to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$  (j = 0, 1, 2, 3, 4) transitions at 580, 592, 612, 654 and 705 nm, respectively; the strongest transition of Eu<sup>III</sup> was the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  at 612 nm.

In summary, we synthesized luminescent europium(III) and terbium(III) complexes based on an O,O,O-tridentate ligand, ethyl 2-hydroxymethylidene-3-oxobutanoate. The regiospecific coordination of the lanthanide ion to the oxygen atoms of a 1,3-dicarbonyl moiety was demonstrated.

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