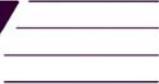


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Supporting Information

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**Relationship Between the Ligand Structure and the Luminescent Properties  
of Water Soluble Lanthanide Complexes containing Bis(bipyridine-anionic)  
Arms.**

Loïc J. Charbonnière,<sup>a\*</sup> Nicolas Weibel,<sup>a</sup> Pascal Retailleau,<sup>b</sup> and Raymond Ziessel<sup>a\*</sup>

<sup>a)</sup> *Laboratoire de Chimie Moléculaire, UMR 7509-CNRS, Ecole de Chimie, Polymères et Matériaux, 25 rue  
Becquerel, 67087 Strasbourg Cedex 02, France*

<sup>b)</sup> *ICSN-CNRS, 1 avenue de la Terrasse, 91198 Gif sur Yvette, France.*

**Preparation of compound 5.** In a Schlenk tube under argon were dissolved 6-aminomethylpyridine-2-carboxylic acid ethyl ester **4** (321 mg, 1.78 mmol), 6-bromo-6'-bromomethyl-2,2'-bipyridine **1** (1.285 g, 3.92 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (739 mg, 5.35 mmol) in 30 mL of dry acetonitrile. The solution was heated to 80°C for 19 hours. The mixture was then evaporated to dryness and the solid residue was partitioned between 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and 10 mL of water. The aqueous phase was further extracted with three portions of 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and evaporated to dryness. The residue was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane, 20/80 to 30/70) to give compound **5** (800 mg, 67%) as a pale yellow solid. *R<sub>f</sub>* = 0.56 (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>). Elemental analysis calcd (%) for C<sub>31</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: C 55.21, H 3.89, N 12.46; found: C 54.98, H 3.63, N 12.13. FAB<sup>+</sup>/MS: *m/z* 599.2 ([**5** - COOEt]<sup>+</sup>, 15%), 601.2 ([**5** - COOEt]<sup>+</sup>, 30%), 603.2 ([**5** - COOEt]<sup>+</sup>, 15%), 673.2 ([**5** + H]<sup>+</sup>, 50%), 675.2 ([**5** + H]<sup>+</sup>, 100%), 677.2 ([**5** + H]<sup>+</sup>, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): *d* = 1.40 (t, 3H, <sup>3</sup>*J* = 7.0 Hz), 3.99 (s, 4H), 4.13 (s, 2H), 4.44 (q, 2H, <sup>3</sup>*J* = 7.0 Hz), 7.43 (dd, 2H, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.56 (dd, 2H, <sup>3</sup>*J* = 7.0 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.60 (t, 2H, <sup>3</sup>*J* = 8.0 Hz), 7.75 (t, 2H, <sup>3</sup>*J* = 7.5 Hz), 7.78 (t, 1H, <sup>3</sup>*J* = 8.0 Hz), 7.89 (dd, 1H, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.95 (dd, 1H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz), 8.24 (dd, 2H, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz), 8.38 (dd, 2H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): *d* = 14.3, 60.1, 60.2, 61.7, 119.6, 119.7, 123.4, 123.5, 125.8, 127.8, 137.2, 137.3, 139.1, 141.4, 147.6, 153.7, 157.3, 158.6, 160.6, 165.2. IR (KBr, cm<sup>-1</sup>): 2959 (s), 2924 (s), 2853 (s), 1736 (m, ν<sub>C=O</sub>), 1640 (m), 1550 (m), 1576 (m), 1465 (m), 1451 (m), 1384 (m), 1262 (w), 1126 (w).

**Preparation of compound 6.** A solution of **5** (501 mg, 0.74 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (73 mg, 0.10 mmol) in a mixture of 25 mL of ethanol and 25 mL of triethylamine was heated to 70°C for 17 hours, under a continuous flow of CO at atmospheric pressure. The solution was evaporated to dryness, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered over Celite and evaporated to dryness. The residue was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>). The product still containing triphenylphosphine oxide was solubilized in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and was extracted three times with 5 mL of aqueous 3N HCl. The aqueous solution was neutralized with 15 mL of aqueous 3N NaOH and extracted with five portions of 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and evaporated to dryness to give compound **6** (223 mg, 45%) as a colourless oil. *R<sub>f</sub>* = 0.45 (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>). Elemental analysis calcd (%) for C<sub>37</sub>H<sub>36</sub>N<sub>6</sub>O<sub>6</sub>: C 67.26, H 5.49, N 12.72; found: C 67.02, H

5.33, N 12.64. FAB<sup>+</sup>/MS:  $m/z$  587.2 ([**6** - C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sup>+</sup>, 30%), 661.2 ([**6** + H]<sup>+</sup>, 100%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 1.38 (t, 3H, <sup>3</sup>*J* = 7.0 Hz), 1.43 (t, 6H, <sup>3</sup>*J* = 7.0 Hz), 4.00 (s, 4H), 4.13 (s, 2H), 4.42 (q, 2H, <sup>3</sup>*J* = 7.0 Hz), 4.44 (q, 4H, <sup>3</sup>*J* = 7.0 Hz), 7.58 (dd, 2H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.77 (t, 1H, <sup>3</sup>*J* = 7.5 Hz), 7.79 (t, 2H, <sup>3</sup>*J* = 7.5 Hz), 7.89 (t, 2H, <sup>3</sup>*J* = 8.0 Hz), 7.90 (dd, 1H, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz), 7.94 (dd, 1H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz), 8.07 (dd, 2H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz), 8.41 (dd, 2H, <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.0 Hz), 8.61 (dd, 2H, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 14.2, 60.0, 60.1, 61.7, 119.9, 123.4 (2C), 124.1, 124.7, 125.8, 137.2, 137.3, 137.7, 147.6, 147.7, 154.5, 156.4, 158.5, 160.6, 165.20, 165.24.

**Preparation of compound 8.** In a 250 mL round bottom flask equipped with a reflux condenser, **1** (870 mg, 2.65 mmol) and **7** (193 mg, 1.20 mmol) were dissolved in 60 mL CH<sub>3</sub>CN containing K<sub>2</sub>CO<sub>3</sub> (500 mg, 3.0 mmol). The solution was heated at 80°C during 3h. The cooled solution was evaporated to dryness and the residue partitioned between CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and water (25 mL). The aqueous layer was washed with 75 mL CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100/0 to 99/1) to afford **8** (368 mg, 47%) as a yellow sticky solid. *R*<sub>f</sub> = 0.16 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 98/2). Elemental analysis calcd (%) for C<sub>29</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: C 53.23, H 4.62, N 12.84; found: C 53.0, H 4.46, N 12.63. FAB<sup>+</sup>/MS:  $m/z$  653.5 ([**8**+H]<sup>+</sup>, 50%), 655.5 ([**8**+H]<sup>+</sup>, 100%), 657.5 ([**8**+H]<sup>+</sup>, 55%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  = 1.36 (s, 9H), 2.78 (t, 2H, <sup>3</sup>*J* = 5.8 Hz), 3.31 (q, br, 2H, <sup>3</sup>*J* = 5.6 Hz), 3.93 (s, 4H), 5.23 (s, br, 1H), 7.44 (d, 4H, <sup>3</sup>*J* = 7.6 Hz), 7.61 (t, 2H, <sup>3</sup>*J* = 7.7 Hz), 7.74 (t, 2H, <sup>3</sup>*J* = 7.7 Hz), 8.24 (d, 2H, <sup>3</sup>*J* = 7.7 Hz), 8.38 (d, 2H, <sup>3</sup>*J* = 7.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 28.3, 38.2, 53.5, 59.8, 78.8, 119.7, 123.6, 127.7, 137.3, 139.1, 141.4, 153.7, 155.9, 157.3, 158.7, 163.3.

**Preparation of compound 9.** Compound **8** (370 mg, 0.56 mmol) was dissolved in 6 mL CH<sub>2</sub>Cl<sub>2</sub> and trifluoroacetic acid (50 μL, 0.65 mmol) was added. The solution was agitated at room temperature for 3 hours, evaporated to dryness and co-evaporated twice with 5 mL MeOH containing 0.5 mL conc. HCl and twice with 5 mL MeOH. After evaporation to dryness and drying under reduced pressure **9** (368 mg, 92%) was obtained as its trihydrochloride salt as a beige powder. Elemental analysis calcd (%) for C<sub>24</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>6</sub>·3HCl·0.5H<sub>2</sub>O: C 42.28, H 4.00, N 12.33; found: C 42.14, H 3.76, N 12.16. FAB<sup>+</sup>/MS:  $m/z$  553.3 ([**9**+H]<sup>+</sup>, 50%), 555.6 ([**9**+H]<sup>+</sup>, 100%), 557.3 ([**9**+H]<sup>+</sup>, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/CD<sub>3</sub>OD, 1/1, 200 MHz):  $\delta$  = 3.66

(m, br, 2H), 3.83 (m, br, 2H), 4.93 (s, 4H), 7.61-7.77 (m, 4H), 7.91 (d, 2H,  $^3J = 7.6$  Hz), 8.25 (t, 2H,  $^3J = 7.6$  Hz), 8.35-8.40 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{CD}_3\text{OD}$ , 1/1, 50 MHz):  $\delta = 36.7, 54.1, 58.3, 122.9, 124.2, 127.5, 131.3, 141.8, 143.1, 144.0, 152.5, 153.0, 153.9$ .

**Preparation of compound 10.** Compound **9** (358 mg, 0.46 mmol) was dissolved in 40 mL  $\text{CH}_3\text{CN}$  and 6 mL EtOH containing  $\text{K}_2\text{CO}_3$  (232 mg, 1.7 mmol) and ethylbromoacetate (155  $\mu\text{L}$ , 1.4 mmol) and heated to  $80^\circ\text{C}$  for 2.5 h. The solution was then evaporated to dryness, partitioned between 50 mL  $\text{CH}_2\text{Cl}_2$  and 20 mL  $\text{H}_2\text{O}$ , the aqueous layer was separated and washed with 30 mL  $\text{CH}_2\text{Cl}_2$  and the combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 100/0 to 98/2) to give **10** (217 mg, 68%) as an oily residue.  $R_f = 0.11$  ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95/5).  $\text{FAB}^+/\text{MS}$ :  $m/z$  725.5 ( $[\mathbf{10}+\text{H}]^+$ , 50%), 727.2 ( $[\mathbf{10}+\text{H}]^+$ , 100%), 729.2 ( $[\mathbf{10}+\text{H}]^+$ , 50%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 1.18$  (t, 6H,  $^3J = 7.0$  Hz), 2.81 (t, br, 2H,  $^3J = 6.2$  Hz), 3.00 (t, br, 2H,  $^3J = 6.2$  Hz), 3.54 (s, 4H), 3.95 (s, 4H), 4.08 (q, 4H,  $^3J = 7.2$  Hz), 7.43 (d, 2H,  $^3J = 7.7$  Hz), 7.54 (d, 2H,  $^3J = 8.0$  Hz), 7.61 (t, 2H,  $^3J = 7.7$  Hz), 7.75 (t, 2H,  $^3J = 7.7$  Hz), 8.23 (d, 2H,  $^3J = 7.6$  Hz), 8.37 (d, 2H,  $^3J = 7.5$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta = 14.1, 29.6, 51.9, 52.7, 55.1, 60.3$  (2C), 119.5, 119.7, 123.5, 127.7, 137.2, 139.0, 141.4, 153.5, 157.4, 159.1, 171.1.

**Preparation of compound 13.** Compound **1** (951 mg, 2.90 mmol), dl-serine methyl ester hydrochloride **12** (205 mg, 1.32 mmol) and  $\text{K}_2\text{CO}_3$  (546 mg, 3.95 mmol) were placed in a Schlenk tube under nitrogen containing 20 mL  $\text{CH}_3\text{CN}$ . The solution was heated to  $80^\circ\text{C}$  for 17 hours, cooled and evaporated to dryness. The residue was partitioned between  $\text{CH}_2\text{Cl}_2$  (20 mL) and water (10 mL), the aqueous layer was further washed three times with 15 mL  $\text{CH}_2\text{Cl}_2$  and the combined organic layers were dried over  $\text{MgSO}_4$  and evaporated to dryness. Purification by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 100/0 to 99/1) afforded **13** (673 mg, 83%) as a white powder.  $R_f = 0.66$  ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95/5). Elemental analysis calcd (%) for  $\text{C}_{26}\text{H}_{23}\text{Br}_2\text{N}_5\text{O}_3$ : C 50.92, H 3.78, N 11.42; found: C 50.62, H 3.80, N 11.18.  $\text{FAB}^+/\text{MS}$ :  $m/z$  612.2 ( $[\mathbf{13}+\text{H}]^+$ , 50%), 614.2 ( $[\mathbf{13}+\text{H}]^+$ , 100%), 616.2 ( $[\mathbf{13}+\text{H}]^+$ , 50%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 3.67$  (s, 3H), 3.90 (s, br, 2+1H), 4.10-4.19 (m, 4H), 5.73 (s, br, 1H), 7.10 (d, 2H,  $^3J = 7.6$  Hz), 7.39 (d, 2H,  $^3J = 7.6$  Hz), 7.50 (t, 2H,  $^3J = 7.6$  Hz), 7.55 (t, 2H,  $^3J = 7.6$  Hz), 8.08 (d, 2H,  $^3J = 8.0$  Hz), 8.25 (d, 2H,  $^3J = 7.8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):

$d = 51.4, 57.3, 59.7, 66.0, 119.5, 119.8, 123.4, 127.7, 137.1, 139.1, 141.3, 153.9, 156.8, 158.7, 172.0.$

**Preparation of compound 14.** Compound **13** (300 mg, 0.49 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (34 mg, 49  $\mu$ mol) were dissolved in EtOH/Et<sub>3</sub>N (20 mL each), and heated at 70°C under a continuous flow of CO for 18 hours. The solution was evaporated to dryness, coevaporated with 20 mL CH<sub>2</sub>Cl<sub>2</sub>, and the residue was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100/0 to 99/1) to afford **14** (179 mg, 61%) as a colourless oil.  $R_f = 0.25$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95/5). HRMS:  $m/z$  559.2365 (calcd for C<sub>32</sub>H<sub>33</sub>N<sub>5</sub>O<sub>7</sub>: 559.2380). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $d = 1.46$  (t, 6H, <sup>3</sup> $J = 7.0$  Hz), 3.72 (s, 3H), 3.95 (m, br, 3H), 4.12-4.28 (m, 4H), 4.48 (q, 4H, <sup>3</sup> $J = 7.2$  Hz), 5.90 (m, br, 1H), 7.18 (d, 2H, <sup>3</sup> $J = 7.4$  Hz), 7.60 (t, 2H, <sup>3</sup> $J = 7.8$  Hz), 7.91 (t, 2H, <sup>3</sup> $J = 7.6$  Hz), 8.08 (d, 2H, <sup>3</sup> $J = 7.6$  Hz), 8.32 (d, 2H, <sup>3</sup> $J = 7.8$  Hz), 8.54 (d, 2H, <sup>3</sup> $J = 8.0$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $d = 14.4, 51.7, 57.4, 60.0, 61.9, 66.1, 120.4, 123.6, 124.2, 124.9, 137.6, 138.0, 147.9, 155.1, 156.2, 158.9, 165.3, 172.4.$

**Preparation of compound 16.** In a Schlenk tube under argon were dissolved diethyl aminomalonate hydrochloride **15** (450 mg, 2.13 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.18 g, 8.54 mmol) in 150 mL of dry acetonitrile. The solution was heated to 80°C for 1 hour, 6-bromo-6'-bromomethyl-2,2'-bipyridine **1** (1.46 g, 4.45 mmol) was then added. The solution was heated to 80°C for 21 hours. The mixture was evaporated to dryness, 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and 20 mL of water were added, and the organic phase was separated. The aqueous phase was extracted twice with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and evaporated to dryness. The resulting solid was purified by column chromatography (SiO<sub>2</sub> flash, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 100/0 to 99/1) to give compound **16** (794 mg, 56%) as a pale yellow powder.  $R_f = 0.57$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97/3). Elemental analysis calcd (%) for C<sub>29</sub>H<sub>27</sub>Br<sub>2</sub>N<sub>5</sub>O<sub>4</sub>: C 52.04, H 4.07, N 10.46; found: C 51.93, H 3.93, N 10.31. FAB<sup>+</sup>/MS:  $m/z$  670.2 ([**16** + H]<sup>+</sup>, 100%), 672.2 ([**16** + H]<sup>+</sup>, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $d = 1.26$  (t, 6H, <sup>3</sup> $J = 7.0$  Hz), 4.22 (s, 4H), 4.23 (q, 4H, <sup>3</sup> $J = 7.0$  Hz), 4.47 (s, 1H), 7.43 (dd, 2H, <sup>3</sup> $J = 7.5$  Hz, <sup>4</sup> $J = 0.5$  Hz), 7.60 (t, 2H, <sup>3</sup> $J = 7.5$  Hz), 7.62 (d, 2H, <sup>3</sup> $J = 7.5$  Hz), 7.75 (t, 2H, <sup>3</sup> $J = 8.0$  Hz), 8.22 (dd, 2H, <sup>3</sup> $J = 7.5$  Hz, <sup>4</sup> $J = 1.0$  Hz), 8.37 (dd, 2H, <sup>3</sup> $J = 7.5$  Hz, <sup>4</sup> $J = 1.0$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $d = 14.1, 58.0, 61.4, 67.1, 119.7$  (2C), 123.4, 127.7, 137.4, 139.0, 141.4, 153.5, 157.4, 158.9, 168.1.

**Preparation of compound 17.** A solution of compound **16** (778 mg, 1.16 mmol) and  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (82 mg, 0.12 mmol) in a mixture of 75 mL of ethanol and 75 mL of triethylamine was heated to 70°C for 16 hours, under a continuous flow of CO at atmospheric pressure. The solution was evaporated to dryness, the resulting solid was dissolved in 75 mL of  $\text{CH}_2\text{Cl}_2$  and filtered over Celite. The organic layer was washed with 15 mL of water and the aqueous layer was extracted twice with 20 mL of  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and evaporated to dryness. The residue was purified by column chromatography ( $\text{SiO}_2$  flash,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 99.5/0.5 to 90/10). Fractions containing compound **17** and triphenylphosphine oxide were combined, evaporated to dryness, dissolved in 40 mL of  $\text{CH}_2\text{Cl}_2$  and extracted four times with 10 mL of aqueous 3N HCl. The combined aqueous layers were neutralised with NaOH and extracted with 30 mL of  $\text{CH}_2\text{Cl}_2$  three times. The resulting organic phase was dried over  $\text{MgSO}_4$ , filtered, and evaporated to dryness to give compound **17** (522 mg, 68%) as a colourless oil.  $R_f = 0.55$  ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 90/10). Elemental analysis calcd (%) for  $\text{C}_{35}\text{H}_{37}\text{N}_5\text{O}_8$ : C 64.11, H 5.69, N 10.68; found: C 63.81, H 5.43, N 10.43. FAB<sup>+</sup>/MS:  $m/z$  496.2 ( $[\mathbf{17} - \text{C}_7\text{H}_{11}\text{O}_4]^+$ , 35%), 656.1 ( $[\mathbf{17} + \text{H}]^+$ , 100%). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  = 1.26 (t, 6H,  $^3J = 7.0$  Hz), 1.45 (t, 6H,  $^3J = 7.0$  Hz), 4.23 (q, 4H,  $^3J = 7.0$  Hz), 4.24 (s, 4H), 4.47 (q, 4H,  $^3J = 7.0$  Hz), 4.48 (s, 1H), 7.64 (dd, 2H,  $^3J = 7.5$  Hz,  $^4J = 0.5$  Hz), 7.80 (t, 2H,  $^3J = 8.0$  Hz), 7.91 (t, 2H,  $^3J = 7.5$  Hz), 8.09 (dd, 2H,  $^3J = 7.5$  Hz,  $^4J = 1.0$  Hz), 8.40 (dd, 2H,  $^3J = 7.5$  Hz,  $^4J = 0.5$  Hz), 8.62 (dd, 2H,  $^3J = 8.0$  Hz,  $^4J = 1.5$  Hz). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  = 14.1, 14.3, 58.0, 61.4, 61.8, 67.1, 120.0, 123.4, 124.2, 124.7, 137.5, 137.7, 147.7, 154.4, 156.5, 158.8, 165.3, 168.2.

**Preparation of compound 20.** In a Schlenk tube under argon were dissolved **19** (200 mg, 0.30 mmol), diethylphosphite (90  $\mu\text{L}$ , 0.70 mmol) and triphenylphosphine (78 mg, 0.30 mmol) in 10 mL of anhydrous toluene containing 300  $\mu\text{L}$  of anhydrous *N,N*-diisopropylethylamine. The solution was flushed with argon for 20 min. at room temperature.  $[\text{Pd}(\text{PPh}_3)_4]$  (34 mg, 0.03 mmol) was added and the solution was heated to 100°C for 16 hours. Diethyl phosphite (40  $\mu\text{L}$ , 0.31 mmol) and  $[\text{Pd}(\text{PPh}_3)_4]$  (34 mg, 0.03 mmol) were then added and the solution was heated to 100°C for 16 hours. The mixture was evaporated to dryness and the residue was purified by column chromatography ( $\text{SiO}_2$  flash, 99/1 to 95/5  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ). Fractions containing **20** were evaporated, dissolved in 30 mL of  $\text{CH}_2\text{Cl}_2$  and washed with 10 mL of water. The organic phase was dried over  $\text{MgSO}_4$ , filtered, and evaporated to dryness. Compound **20** (72 mg, 31%) was isolated as an oil.  $R_f = 0.56$  ( $\text{SiO}_2$ ,

90/10 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): **d** = 1.35 (t, 12H, <sup>3</sup>J = 7.0 Hz), 2.02-2.22 (m, 2H), 2.37-2.71 (m, 2H), 3.47 (s, 3H), 3.54-3.61 (m, 1H), 3.75 (s, 3H), 4.01-4.17 (m, 4H), 4.18-4.36 (m, 8H), 7.47 (d, 2H, <sup>3</sup>J = 7.5 Hz), 7.73 (t, 2H, <sup>3</sup>J = 8.0 Hz), 7.81-7.97 (m, 4H), 8.32 (d, 2H, <sup>3</sup>J = 7.5 Hz), 8.59 (dt, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, <sup>3</sup>J<sub>H-P</sub> = <sup>4</sup>J<sub>H-H</sub> = 2.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): **d** = 16.3, 16.4, 24.7, 30.3, 51.4, 57.1, 61.9, 63.0, 63.1, 119.6, 123.2 (2), 123.4, 127.4, 127.9, 136.7, 137.0, 137.2, 149.0, 153.5, 154.5, 156.5, 156.9, 159.0, 173.1, 173.4. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): **d** = 11.73.

**Table T1.** Crystal data and structure refinement .

Identification code	[Eu(L <sub>3</sub> H <sub>2</sub> )Cl]Cl.3H <sub>2</sub> O
Empirical formula	C <sub>27</sub> H <sub>28</sub> Cl <sub>2</sub> Eu N <sub>5</sub> O <sub>10</sub>
Formula weight	805.40
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.002(1) Å    α = 99.960(6) ° b = 12.793(2) Å    β = 96.173(6) ° c = 13.012(1) Å    γ = 106.178(3) °
Volume (Å <sup>3</sup> )	1553.5(2)
Z,	2
Calculated density (Mg/m <sup>3</sup> )	1.722
Absorption coefficient (mm <sup>-1</sup> )	2.254
F(000)	804
Crystal size (mm)	0.42 x 0.38 x 0.125
θ range for data collection	1.61 to 25.99 °
Limiting indices	-11 = h = 12 -11 = k = 15 -16 = l = 16
Reflections collected / unique	11750 / 5981 [R(int) = 0.0324]
Completeness to θ max	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.755 and 0.430
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5979 / 0 / 426
Goodness-of-fit on F <sup>2</sup>	1.051
Final R indices [I > 2σ(I)]	R1 = 0.0391, wR2 = 0.0973
R indices (all data)	R1 = 0.0468, wR2 = 0.1025
Largest diff. peak and hole (e. Å <sup>-3</sup> )	1.144 and - 1.824

**Table T2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{L}_3\text{H}_3$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

[Eu(L <sub>3</sub> H <sub>2</sub> )Cl]Cl.3H <sub>2</sub> O				
	X	Y	Z	$U(\text{eq})$
Eu(1)	1485(1)	3096(1)	2626(1)	27(1)
Cl(1)	185(1)	4570(1)	3375(1)	41(1)
Cl(2)	-4089(2)	-496(1)	7210(1)	56(1)
O(1)	3073(3)	2647(3)	1351(3)	38(1)
O(2)	5260(4)	2926(4)	991(3)	56(1)
O(3)	1454(4)	1171(3)	2392(3)	42(1)
O(4)	-2382(4)	-921(3)	2771(3)	57(1)
O(5)	-1976(5)	-159(4)	4498(3)	57(1)
O(6)	3077(3)	4838(3)	2514(2)	35(1)
O(7)	3560(5)	6347(3)	1815(3)	61(1)
N(1)	4017(4)	3260(3)	3421(3)	29(1)
N(2)	2012(4)	3021(3)	4607(3)	29(1)
N(3)	-580(4)	1754(3)	3467(3)	30(1)
N(4)	-885(4)	2119(3)	1356(3)	32(1)
N(5)	1078(4)	3719(3)	885(3)	30(1)
C(1)	4986(5)	3350(4)	2772(4)	33(1)
C(2)	6414(5)	3769(4)	3126(4)	38(1)
C(3)	6884(5)	4069(4)	4210(4)	38(1)
C(4)	5917(5)	3926(4)	4888(4)	36(1)
C(5)	4467(5)	3524(4)	4471(4)	31(1)
C(6)	4343(5)	2947(4)	1633(4)	35(1)
C(7)	3346(5)	3347(4)	5133(4)	32(1)
C(8)	3651(6)	3482(4)	6227(4)	39(1)
C(9)	2556(6)	3262(5)	6786(4)	44(1)
C(10)	1190(6)	2890(4)	6256(4)	42(1)
C(11)	958(5)	2771(4)	5169(3)	32(1)
C(12)	-519(5)	2371(4)	4560(4)	36(1)
C(13)	-312(5)	655(4)	3469(4)	35(1)
C(14)	302(5)	282(4)	2516(4)	40(1)
C(15)	-1665(5)	-240(4)	3548(4)	39(1)
C(16)	-1961(5)	1626(4)	2838(4)	35(1)
C(17)	-1949(5)	1406(4)	1671(4)	35(1)
C(18)	-3023(5)	613(5)	957(4)	46(1)
C(19)	-3020(6)	538(5)	-102(5)	58(2)
C(20)	-1987(6)	1319(5)	-439(4)	50(1)
C(21)	-940(5)	2115(4)	310(4)	37(1)
C(22)	111(5)	3075(4)	59(3)	33(1)
C(23)	51(6)	3361(5)	-925(4)	42(1)
C(24)	972(6)	4341(5)	-1043(4)	45(1)
C(25)	1935(6)	5020(5)	-178(4)	46(1)
C(26)	1968(5)	4672(4)	778(4)	35(1)
C(27)	2959(5)	5352(4)	1776(4)	36(1)
OW1	4393(7)	2392(6)	-989(4)	105(2)
OW2	-4433(6)	-1222(4)	4769(4)	72(1)
OW3	-7054(11)	-1911(6)	3292(6)	131(3)

**Table T3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

[Eu(L <sub>3</sub> H <sub>2</sub> )Cl]Cl.3H <sub>2</sub> O			
Eu(1)-O(6)	2.389(3)	C(12)-H(12B)	.9700
Eu(1)-O(3)	2.420(3)	C(13)-C(14)	1.504(7)
Eu(1)-O(1)	2.521(3)	C(13)-C(15)	1.537(7)
Eu(1)-N(5)	2.558(4)	C(13)-H(13)	.9800
Eu(1)-N(1)	2.568(4)	C(14)-H(14A)	.9700
Eu(1)-N(4)	2.589(4)	C(14)-H(14B)	.9700
Eu(1)-N(2)	2.599(4)	C(16)-C(17)	1.498(7)
Eu(1)-Cl(1)	2.6835(12)	C(16)-H(16A)	.9700
Eu(1)-N(3)	2.752(4)	C(16)-H(16B)	.9700
O(1)-C(6)	1.215(6)	C(17)-C(18)	1.378(7)
O(2)-C(6)	1.307(6)	C(18)-C(19)	1.365(8)
O(2)-H(2')	.8200	C(18)-H(18)	.9300
O(3)-C(14)	1.422(6)	C(19)-C(20)	1.390(8)
O(3)-H(3')	.8200	C(19)-H(19)	.9300
O(4)-C(15)	1.219(6)	C(20)-C(21)	1.387(7)
O(5)-C(15)	1.301(6)	C(20)-H(20)	.9300
O(5)-H(5)	.8200	C(21)-C(22)	1.488(7)
O(6)-C(27)	1.267(6)	C(22)-C(23)	1.390(7)
O(7)-C(27)	1.237(6)	C(23)-C(24)	1.378(8)
N(1)-C(5)	1.344(6)	C(23)-H(23)	.9300
N(1)-C(1)	1.346(6)	C(24)-C(25)	1.382(8)
N(2)-C(11)	1.344(6)	C(24)-H(24)	.9300
N(2)-C(7)	1.348(6)	C(25)-C(26)	1.391(7)
N(3)-C(16)	1.479(6)	C(25)-H(25)	.9300
N(3)-C(12)	1.488(6)	C(26)-C(27)	1.509(7)
N(3)-C(13)	1.503(6)	OW1-H(11)	.99(12)
N(4)-C(17)	1.347(6)	OW1-H(12)	1.06(12)
N(4)-C(21)	1.355(6)	OW2-H(21)	1.06(9)
N(5)-C(26)	1.334(6)	OW2-H(22)	.96(9)
N(5)-C(22)	1.340(6)	OW3-H(31)	1.06(15)
C(1)-C(2)	1.373(7)	OW3-H(32)	.97(15)
C(1)-C(6)	1.491(7)		
C(2)-C(3)	1.389(7)	O(6)-Eu(1)-O(3)	137.64(11)
C(2)-H(2)	.9300	O(6)-Eu(1)-O(1)	73.64(11)
C(3)-C(4)	1.374(7)	O(3)-Eu(1)-O(1)	68.17(11)
C(3)-H(3)	.9300	O(6)-Eu(1)-N(5)	64.48(11)
C(4)-C(5)	1.408(6)	O(3)-Eu(1)-N(5)	113.57(12)
C(4)-H(4)	.9300	O(1)-Eu(1)-N(5)	66.64(11)
C(5)-C(7)	1.478(6)	O(6)-Eu(1)-N(1)	69.45(11)
C(7)-C(8)	1.392(7)	O(3)-Eu(1)-N(1)	77.27(12)
C(8)-C(9)	1.371(7)	O(1)-Eu(1)-N(1)	63.02(11)
C(8)-H(8)	.9300	N(5)-Eu(1)-N(1)	118.60(12)
C(9)-C(10)	1.375(8)	O(6)-Eu(1)-N(4)	123.80(11)
C(9)-H(9)	.9300	O(3)-Eu(1)-N(4)	79.30(12)
C(10)-C(11)	1.384(6)	O(1)-Eu(1)-N(4)	97.00(11)
C(10)-H(10)	.9300	N(5)-Eu(1)-N(4)	61.25(12)
C(11)-C(12)	1.502(7)	N(1)-Eu(1)-N(4)	153.64(12)
C(12)-H(12A)	.9700	O(6)-Eu(1)-N(2)	103.63(11)

O(3)-Eu(1)-N(2)	81.67(12)	C(22)-N(5)-Eu(1)	122.4(3)
O(1)-Eu(1)-N(2)	121.03(11)	N(1)-C(1)-C(2)	123.4(4)
N(5)-Eu(1)-N(2)	164.69(12)	N(1)-C(1)-C(6)	112.9(4)
N(1)-Eu(1)-N(2)	61.52(11)	C(2)-C(1)-C(6)	123.7(4)
N(4)-Eu(1)-N(2)	126.37(12)	C(1)-C(2)-C(3)	118.2(5)
O(6)-Eu(1)-Cl(1)	76.97(9)	C(1)-C(2)-H(2)	120.9
O(3)-Eu(1)-Cl(1)	144.78(8)	C(3)-C(2)-H(2)	120.9
O(1)-Eu(1)-Cl(1)	145.42(8)	C(4)-C(3)-C(2)	119.4(4)
N(5)-Eu(1)-Cl(1)	84.51(9)	C(4)-C(3)-H(3)	120.3
N(1)-Eu(1)-Cl(1)	121.85(8)	C(2)-C(3)-H(3)	120.3
N(4)-Eu(1)-Cl(1)	84.44(9)	C(3)-C(4)-C(5)	119.4(4)
N(2)-Eu(1)-Cl(1)	83.28(8)	C(3)-C(4)-H(4)	120.3
O(6)-Eu(1)-N(3)	154.14(11)	C(5)-C(4)-H(4)	120.3
O(3)-Eu(1)-N(3)	64.79(11)	N(1)-C(5)-C(4)	121.0(4)
O(1)-Eu(1)-N(3)	131.79(11)	N(1)-C(5)-C(7)	115.5(4)
N(5)-Eu(1)-N(3)	124.87(11)	C(4)-C(5)-C(7)	123.5(4)
N(1)-Eu(1)-N(3)	114.47(11)	O(1)-C(6)-O(2)	124.3(5)
N(4)-Eu(1)-N(3)	64.77(11)	O(1)-C(6)-C(1)	121.6(4)
N(2)-Eu(1)-N(3)	61.72(11)	O(2)-C(6)-C(1)	114.1(4)
Cl(1)-Eu(1)-N(3)	80.03(8)	N(2)-C(7)-C(8)	122.3(4)
C(6)-O(1)-Eu(1)	120.0(3)	N(2)-C(7)-C(5)	115.7(4)
C(6)-O(2)-H(2')	109.5	C(8)-C(7)-C(5)	122.0(4)
C(14)-O(3)-Eu(1)	124.6(3)	C(9)-C(8)-C(7)	118.8(5)
C(14)-O(3)-H(3')	109.5	C(9)-C(8)-H(8)	120.6
Eu(1)-O(3)-H(3')	121.0	C(7)-C(8)-H(8)	120.6
C(15)-O(5)-H(5)	109.5	C(8)-C(9)-C(10)	119.5(5)
C(27)-O(6)-Eu(1)	125.3(3)	C(8)-C(9)-H(9)	120.3
C(5)-N(1)-C(1)	118.5(4)	C(10)-C(9)-H(9)	120.3
C(5)-N(1)-Eu(1)	122.0(3)	C(9)-C(10)-C(11)	118.8(5)
C(1)-N(1)-Eu(1)	117.5(3)	C(9)-C(10)-H(10)	120.6
C(11)-N(2)-C(7)	117.6(4)	C(11)-C(10)-H(10)	120.6
C(11)-N(2)-Eu(1)	120.7(3)	N(2)-C(11)-C(10)	122.8(4)
C(7)-N(2)-Eu(1)	121.3(3)	N(2)-C(11)-C(12)	116.7(4)
C(16)-N(3)-C(12)	108.6(4)	C(10)-C(11)-C(12)	120.5(4)
C(16)-N(3)-C(13)	112.4(4)	N(3)-C(12)-C(11)	111.6(4)
C(12)-N(3)-C(13)	111.5(4)	N(3)-C(12)-H(12A)	109.3
C(16)-N(3)-Eu(1)	107.9(3)	C(11)-C(12)-H(12A)	109.3
C(12)-N(3)-Eu(1)	106.1(3)	N(3)-C(12)-H(12B)	109.3
C(13)-N(3)-Eu(1)	110.0(3)	C(11)-C(12)-H(12B)	109.3
C(17)-N(4)-C(21)	118.7(4)	H(12A)-C(12)-H(12B)	108.0
C(17)-N(4)-Eu(1)	120.2(3)	N(3)-C(13)-C(14)	111.9(4)
C(21)-N(4)-Eu(1)	119.2(3)	N(3)-C(13)-C(15)	110.9(4)
C(26)-N(5)-C(22)	119.8(4)	C(14)-C(13)-C(15)	110.7(4)
C(26)-N(5)-Eu(1)	117.5(3)		

**Table T4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for  $\text{Li}_3\text{H}_3$ . The anisotropic displacement factor exponent takes the form:  $-2 \mathbf{p}^2 [ h^2 a^{*2} U11 + \dots + 2 h k a^* b^* U12 ]$

	<i>U11</i>	<i>U22</i>	<i>U33</i>	<i>U23</i>	<i>U13</i>	<i>U12</i>
Eu(1)	23(1)	32(1)	24(1)	8(1)	2(1)	5(1)
Cl(1)	39(1)	45(1)	44(1)	13(1)	12(1)	17(1)
Cl(2)	49(1)	61(1)	55(1)	4(1)	4(1)	21(1)
O(1)	31(2)	47(2)	33(2)	5(1)	3(1)	8(2)
O(2)	39(2)	86(3)	38(2)	7(2)	15(2)	10(2)
O(3)	34(2)	39(2)	59(2)	13(2)	16(2)	14(2)
O(4)	53(2)	47(2)	56(2)	8(2)	3(2)	-6(2)
O(5)	56(3)	57(3)	49(2)	17(2)	16(2)	-3(2)
O(6)	29(2)	39(2)	33(2)	10(1)	-1(1)	2(1)
O(7)	71(3)	43(2)	53(2)	18(2)	2(2)	-9(2)
N(1)	26(2)	32(2)	28(2)	6(2)	2(2)	8(2)
N(2)	29(2)	34(2)	26(2)	8(2)	1(2)	10(2)
N(3)	29(2)	32(2)	30(2)	7(2)	2(2)	9(2)
N(4)	27(2)	38(2)	30(2)	9(2)	-1(2)	7(2)
N(5)	27(2)	38(2)	25(2)	10(2)	4(2)	7(2)
C(1)	30(2)	33(2)	37(3)	10(2)	5(2)	11(2)
C(2)	27(2)	41(3)	49(3)	12(2)	9(2)	14(2)
C(3)	23(2)	38(3)	48(3)	2(2)	-3(2)	10(2)
C(4)	30(2)	37(3)	37(3)	2(2)	-6(2)	10(2)
C(5)	29(2)	30(2)	32(2)	5(2)	0(2)	10(2)
C(6)	31(3)	41(3)	34(2)	12(2)	9(2)	10(2)
C(7)	34(2)	28(2)	32(2)	4(2)	3(2)	11(2)
C(8)	42(3)	46(3)	27(2)	4(2)	-2(2)	14(2)
C(9)	55(3)	55(3)	21(2)	6(2)	3(2)	18(3)
C(10)	53(3)	47(3)	31(3)	11(2)	12(2)	17(2)
C(11)	32(2)	37(2)	26(2)	9(2)	8(2)	9(2)
C(12)	33(3)	40(3)	32(2)	6(2)	9(2)	8(2)
C(13)	32(2)	35(2)	35(2)	11(2)	2(2)	8(2)
C(14)	36(3)	32(3)	53(3)	10(2)	10(2)	8(2)
C(15)	36(3)	36(3)	45(3)	15(2)	4(2)	7(2)
C(16)	26(2)	39(3)	40(3)	15(2)	4(2)	5(2)
C(17)	25(2)	41(3)	38(3)	13(2)	2(2)	7(2)
C(18)	29(3)	51(3)	48(3)	13(2)	-3(2)	-4(2)
C(19)	42(3)	58(4)	49(3)	2(3)	-9(3)	-10(3)
C(20)	41(3)	66(4)	31(3)	7(2)	-4(2)	1(3)
C(21)	30(2)	46(3)	31(2)	5(2)	1(2)	8(2)
C(22)	27(2)	44(3)	26(2)	5(2)	1(2)	10(2)
C(23)	41(3)	55(3)	26(2)	8(2)	0(2)	10(2)
C(24)	51(3)	62(3)	27(2)	18(2)	7(2)	18(3)
C(25)	53(3)	49(3)	40(3)	24(2)	14(2)	12(3)
C(26)	33(3)	45(3)	29(2)	14(2)	8(2)	11(2)
C(27)	32(2)	37(3)	35(3)	12(2)	6(2)	1(2)
OW1	95(4)	121(5)	49(3)	9(3)	8(3)	-40(4)
OW2	69(3)	76(3)	66(3)	11(2)	23(3)	13(3)
OW3	217(9)	75(4)	97(5)	15(4)	40(5)	33(5)
Eu(1)	23(1)	32(1)	24(1)	8(1)	2(1)	5(1)
Cl(1)	39(1)	45(1)	44(1)	13(1)	12(1)	17(1)

Cl(2)	49(1)	61(1)	55(1)	4(1)	4(1)	21(1)
O(1)	31(2)	47(2)	33(2)	5(1)	3(1)	8(2)
O(2)	39(2)	86(3)	38(2)	7(2)	15(2)	10(2)
O(3)	34(2)	39(2)	59(2)	13(2)	16(2)	14(2)
O(4)	53(2)	47(2)	56(2)	8(2)	3(2)	-6(2)
O(5)	56(3)	57(3)	49(2)	17(2)	16(2)	-3(2)
O(6)	29(2)	39(2)	33(2)	10(1)	-1(1)	2(1)
O(7)	71(3)	43(2)	53(2)	18(2)	2(2)	-9(2)
N(1)	26(2)	32(2)	28(2)	6(2)	2(2)	8(2)
N(2)	29(2)	34(2)	26(2)	8(2)	1(2)	10(2)
N(3)	29(2)	32(2)	30(2)	7(2)	2(2)	9(2)
N(4)	27(2)	38(2)	30(2)	9(2)	-1(2)	7(2)

**Table T5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $[\text{Eu}(\text{L}_3\text{H}_2)\text{Cl}]\text{Cl}\cdot 3\text{H}_2\text{O}$

	X	Y	Z	$U(eq)$
H(2')	4843	2689	380	67
H(3')	2188	1007	2489	51
H(5)	-2798	-527	4471	69
H(2)	7049	3850	2651	46
H(3)	7843	4364	4475	45
H(4)	6218	4092	5615	44
H(8)	4581	3718	6571	47
H(9)	2736	3362	7519	53
H(10)	435	2723	6622	51
H(12A)	-1131	1888	4928	43
H(12B)	-861	3005	4526	43
H(13)	381	754	4099	42
H(14A)	622	-351	2605	49
H(14B)	-416	54	1890	49
H(16A)	-2221	2300	3041	42
H(16B)	-2672	1015	3000	42
H(18)	-3746	131	1195	56
H(19)	-3700	-27	-592	69
H(20)	-1996	1308	-1156	60
H(23)	-606	2895	-1497	51
H(24)	946	4544	-1696	55
H(25)	2549	5696	-234	55
H(11)	3600(130)	1740(100)	-1370(90)	158
H(12)	5280(130)	2830(100)	-1290(90)	158
H(21)	-4480(90)	-890(70)	5570(80)	108
H(22)	-5430(100)	-1460(80)	4510(70)	108
H(31)	-6760(150)	-1110(120)	3110(110)	197
H(32)	-6880(150)	-2530(130)	2840(110)	197

**Table T6.** Torsion angles [deg] for [Eu(L<sub>3</sub>H<sub>2</sub>)Cl]Cl·3H<sub>2</sub>O.

O(6)-Eu(1)-O(1)-C(6)	57.8(4)	O(1)-Eu(1)-N(1)-C(5)	-177.1(4)
O(3)-Eu(1)-O(1)-C(6)	-103.4(4)	N(5)-Eu(1)-N(1)-C(5)	144.5(3)
N(5)-Eu(1)-O(1)-C(6)	126.6(4)	N(4)-Eu(1)-N(1)-C(5)	-133.1(3)
N(1)-Eu(1)-O(1)-C(6)	-17.0(3)	N(2)-Eu(1)-N(1)-C(5)	-18.0(3)
N(4)-Eu(1)-O(1)-C(6)	-178.9(4)	Cl(1)-Eu(1)-N(1)-C(5)	42.4(4)
N(2)-Eu(1)-O(1)-C(6)	-38.5(4)	N(3)-Eu(1)-N(1)-C(5)	-51.0(4)
Cl(1)-Eu(1)-O(1)-C(6)	90.7(4)	O(6)-Eu(1)-N(1)-C(1)	-62.4(3)
N(3)-Eu(1)-O(1)-C(6)	-116.7(4)	O(3)-Eu(1)-N(1)-C(1)	91.0(3)
O(6)-Eu(1)-O(3)-C(14)	-179.8(3)	O(1)-Eu(1)-N(1)-C(1)	19.2(3)
O(1)-Eu(1)-O(3)-C(14)	-152.6(4)	N(5)-Eu(1)-N(1)-C(1)	-19.2(4)
N(5)-Eu(1)-O(3)-C(14)	-102.5(4)	N(4)-Eu(1)-N(1)-C(1)	63.2(4)
N(1)-Eu(1)-O(3)-C(14)	141.6(4)	N(2)-Eu(1)-N(1)-C(1)	178.3(4)
N(4)-Eu(1)-O(3)-C(14)	-50.6(4)	Cl(1)-Eu(1)-N(1)-C(1)	-121.3(3)
N(2)-Eu(1)-O(3)-C(14)	79.1(4)	N(3)-Eu(1)-N(1)-C(1)	145.3(3)
Cl(1)-Eu(1)-O(3)-C(14)	13.4(5)	O(6)-Eu(1)-N(2)-C(11)	130.7(3)
N(3)-Eu(1)-O(3)-C(14)	16.5(3)	O(3)-Eu(1)-N(2)-C(11)	-92.2(3)
O(3)-Eu(1)-O(6)-C(27)	106.2(4)	O(1)-Eu(1)-N(2)-C(11)	-150.4(3)
O(1)-Eu(1)-O(6)-C(27)	80.0(4)	N(5)-Eu(1)-N(2)-C(11)	93.2(5)
N(5)-Eu(1)-O(6)-C(27)	8.5(4)	N(1)-Eu(1)-N(2)-C(11)	-172.2(4)
N(1)-Eu(1)-O(6)-C(27)	146.7(4)	N(4)-Eu(1)-N(2)-C(11)	-22.1(4)
N(4)-Eu(1)-O(6)-C(27)	-7.5(4)	Cl(1)-Eu(1)-N(2)-C(11)	55.9(3)
N(2)-Eu(1)-O(6)-C(27)	-161.2(4)	N(3)-Eu(1)-N(2)-C(11)	-26.4(3)
Cl(1)-Eu(1)-O(6)-C(27)	-81.6(4)	O(6)-Eu(1)-N(2)-C(7)	-42.1(3)
N(3)-Eu(1)-O(6)-C(27)	-109.3(4)	O(3)-Eu(1)-N(2)-C(7)	95.0(3)
O(6)-Eu(1)-N(1)-C(5)	101.3(3)	O(1)-Eu(1)-N(2)-C(7)	36.8(4)
O(3)-Eu(1)-N(1)-C(5)	-105.3(3)	N(5)-Eu(1)-N(2)-C(7)	-79.6(5)
N(1)-Eu(1)-N(2)-C(7)	15.1(3)	O(3)-Eu(1)-N(3)-C(12)	132.2(3)
N(4)-Eu(1)-N(2)-C(7)	165.1(3)	O(1)-Eu(1)-N(3)-C(12)	145.9(3)
Cl(1)-Eu(1)-N(2)-C(7)	-116.9(3)	N(5)-Eu(1)-N(3)-C(12)	-125.6(3)
N(3)-Eu(1)-N(2)-C(7)	160.8(4)	N(1)-Eu(1)-N(3)-C(12)	71.0(3)
O(6)-Eu(1)-N(3)-C(16)	94.2(3)	N(4)-Eu(1)-N(3)-C(12)	-138.1(3)
O(3)-Eu(1)-N(3)-C(16)	-111.5(3)	N(2)-Eu(1)-N(3)-C(12)	38.1(3)
O(1)-Eu(1)-N(3)-C(16)	-97.9(3)	Cl(1)-Eu(1)-N(3)-C(12)	-49.5(3)
N(5)-Eu(1)-N(3)-C(16)	-9.3(3)	O(6)-Eu(1)-N(3)-C(13)	-142.9(3)
N(1)-Eu(1)-N(3)-C(16)	-172.7(3)	O(3)-Eu(1)-N(3)-C(13)	11.4(3)
N(4)-Eu(1)-N(3)-C(16)	-21.8(3)	O(1)-Eu(1)-N(3)-C(13)	25.1(3)
N(2)-Eu(1)-N(3)-C(16)	154.4(3)	N(5)-Eu(1)-N(3)-C(13)	113.6(3)
Cl(1)-Eu(1)-N(3)-C(16)	66.7(3)	N(1)-Eu(1)-N(3)-C(13)	-49.7(3)
O(6)-Eu(1)-N(3)-C(12)	-22.1(4)	N(4)-Eu(1)-N(3)-C(13)	101.2(3)
N(2)-Eu(1)-N(3)-C(13)	-82.6(3)	N(5)-Eu(1)-N(4)-C(21)	24.6(3)
Cl(1)-Eu(1)-N(3)-C(13)	-170.3(3)	N(1)-Eu(1)-N(4)-C(21)	-72.5(4)
O(6)-Eu(1)-N(4)-C(17)	-154.6(3)	N(2)-Eu(1)-N(4)-C(21)	-171.2(3)
O(3)-Eu(1)-N(4)-C(17)	64.2(3)	Cl(1)-Eu(1)-N(4)-C(21)	111.3(3)
O(1)-Eu(1)-N(4)-C(17)	130.4(3)	N(3)-Eu(1)-N(4)-C(21)	-167.1(4)
N(5)-Eu(1)-N(4)-C(17)	-171.2(4)	O(6)-Eu(1)-N(5)-C(26)	1.8(3)
N(1)-Eu(1)-N(4)-C(17)	91.8(4)	O(3)-Eu(1)-N(5)-C(26)	-131.5(3)
N(2)-Eu(1)-N(4)-C(17)	-7.0(4)	O(1)-Eu(1)-N(5)-C(26)	-80.5(3)
Cl(1)-Eu(1)-N(4)-C(17)	-84.4(3)	N(1)-Eu(1)-N(5)-C(26)	-43.5(4)
N(3)-Eu(1)-N(4)-C(17)	-2.8(3)	N(4)-Eu(1)-N(5)-C(26)	166.6(4)
O(6)-Eu(1)-N(4)-C(21)	41.1(4)	N(2)-Eu(1)-N(5)-C(26)	42.8(6)
O(3)-Eu(1)-N(4)-C(21)	-100.0(4)	Cl(1)-Eu(1)-N(5)-C(26)	80.0(3)
O(1)-Eu(1)-N(4)-C(21)	-33.9(4)	N(3)-Eu(1)-N(5)-C(26)	153.8(3)

O(6)-Eu(1)-N(5)-C(22)	175.0(4)	C(4)-C(5)-C(7)-N(2)	176.2(4)
O(3)-Eu(1)-N(5)-C(22)	41.7(4)	N(1)-C(5)-C(7)-C(8)	173.8(4)
O(1)-Eu(1)-N(5)-C(22)	92.7(3)	C(4)-C(5)-C(7)-C(8)	-5.3(7)
N(1)-Eu(1)-N(5)-C(22)	129.7(3)	N(2)-C(7)-C(8)-C(9)	.9(7)
N(4)-Eu(1)-N(5)-C(22)	-20.2(3)	C(5)-C(7)-C(8)-C(9)	-177.4(4)
N(2)-Eu(1)-N(5)-C(22)	-144.1(4)	C(7)-C(8)-C(9)-C(10)	1.4(8)
Cl(1)-Eu(1)-N(5)-C(22)	-106.9(3)	C(8)-C(9)-C(10)-C(11)	-1.2(8)
N(3)-Eu(1)-N(5)-C(22)	-33.1(4)	C(7)-N(2)-C(11)-C(10)	3.5(7)
C(5)-N(1)-C(1)-C(2)	-4.5(7)	Eu(1)-N(2)-C(11)-C(10)	-169.5(4)
Eu(1)-N(1)-C(1)-C(2)	159.8(4)	C(7)-N(2)-C(11)-C(12)	-177.9(4)
C(5)-N(1)-C(1)-C(6)	175.5(4)	Eu(1)-N(2)-C(11)-C(12)	9.1(5)
Eu(1)-N(1)-C(1)-C(6)	-20.2(5)	C(9)-C(10)-C(11)-N(2)	-1.3(7)
N(1)-C(1)-C(2)-C(3)	3.0(7)	C(9)-C(10)-C(11)-C(12)	-179.8(5)
C(6)-C(1)-C(2)-C(3)	-177.0(4)	C(16)-N(3)-C(12)-C(11)	-166.4(4)
C(1)-C(2)-C(3)-C(4)	.8(7)	C(13)-N(3)-C(12)-C(11)	69.2(5)
C(2)-C(3)-C(4)-C(5)	-2.8(7)	Eu(1)-N(3)-C(12)-C(11)	-50.6(4)
C(1)-N(1)-C(5)-C(4)	2.3(6)	N(2)-C(11)-C(12)-N(3)	31.1(6)
Eu(1)-N(1)-C(5)-C(4)	-161.3(3)	C(10)-C(11)-C(12)-N(3)	-150.3(4)
C(1)-N(1)-C(5)-C(7)	-176.8(4)	C(16)-N(3)-C(13)-C(14)	84.8(5)
Eu(1)-N(1)-C(5)-C(7)	19.6(5)	C(12)-N(3)-C(13)-C(14)	-153.0(4)
C(3)-C(4)-C(5)-N(1)	1.3(7)	Eu(1)-N(3)-C(13)-C(14)	-35.5(4)
C(3)-C(4)-C(5)-C(7)	-179.7(4)	C(16)-N(3)-C(13)-C(15)	-39.5(5)
Eu(1)-O(1)-C(6)-O(2)	-167.7(4)	C(12)-N(3)-C(13)-C(15)	82.8(5)
Eu(1)-O(1)-C(6)-C(1)	14.0(6)	Eu(1)-N(3)-C(13)-C(15)	-159.7(3)
N(1)-C(1)-C(6)-O(1)	4.7(7)	Eu(1)-O(3)-C(14)-C(13)	-41.5(5)
C(2)-C(1)-C(6)-O(1)	-175.4(5)	N(3)-C(13)-C(14)-O(3)	49.0(5)
N(1)-C(1)-C(6)-O(2)	-173.8(4)	C(15)-C(13)-C(14)-O(3)	173.3(4)
C(2)-C(1)-C(6)-O(2)	6.2(7)	N(3)-C(13)-C(15)-O(4)	100.1(6)
C(11)-N(2)-C(7)-C(8)	-3.3(6)	C(14)-C(13)-C(15)-O(4)	-24.8(7)
Eu(1)-N(2)-C(7)-C(8)	169.7(3)	N(3)-C(13)-C(15)-O(5)	-77.3(5)
C(11)-N(2)-C(7)-C(5)	175.1(4)	C(14)-C(13)-C(15)-O(5)	157.8(5)
Eu(1)-N(2)-C(7)-C(5)	-11.9(5)	C(12)-N(3)-C(16)-C(17)	159.0(4)
N(1)-C(5)-C(7)-N(2)	-4.7(6)	C(13)-N(3)-C(16)-C(17)	-77.1(5)
Eu(1)-N(3)-C(16)-C(17)	44.4(4)	Eu(1)-N(5)-C(22)-C(21)	14.7(5)
C(21)-N(4)-C(17)-C(18)	5.7(7)	N(4)-C(21)-C(22)-N(5)	8.7(6)
Eu(1)-N(4)-C(17)-C(18)	-158.7(4)	C(20)-C(21)-C(22)-N(5)	-176.9(5)
C(21)-N(4)-C(17)-C(16)	-167.7(4)	N(4)-C(21)-C(22)-C(23)	-165.9(5)
Eu(1)-N(4)-C(17)-C(16)	28.0(5)	C(20)-C(21)-C(22)-C(23)	8.5(8)
N(3)-C(16)-C(17)-N(4)	-50.5(6)	N(5)-C(22)-C(23)-C(24)	-2.1(8)
N(3)-C(16)-C(17)-C(18)	136.2(5)	C(21)-C(22)-C(23)-C(24)	172.2(5)
N(4)-C(17)-C(18)-C(19)	.1(8)	C(22)-C(23)-C(24)-C(25)	-.1(8)
C(16)-C(17)-C(18)-C(19)	172.9(5)	C(23)-C(24)-C(25)-C(26)	1.9(8)
C(17)-C(18)-C(19)-C(20)	-4.7(9)	C(22)-N(5)-C(26)-C(25)	-.7(7)
C(18)-C(19)-C(20)-C(21)	3.6(9)	Eu(1)-N(5)-C(26)-C(25)	172.7(4)
C(17)-N(4)-C(21)-C(20)	-6.7(7)	C(22)-N(5)-C(26)-C(27)	177.1(4)
Eu(1)-N(4)-C(21)-C(20)	157.8(4)	Eu(1)-N(5)-C(26)-C(27)	-9.6(5)
C(17)-N(4)-C(21)-C(22)	167.9(4)	C(24)-C(25)-C(26)-N(5)	-1.5(8)
Eu(1)-N(4)-C(21)-C(22)	-27.6(5)	C(24)-C(25)-C(26)-C(27)	-179.1(5)
C(19)-C(20)-C(21)-N(4)	2.2(9)	Eu(1)-O(6)-C(27)-O(7)	162.3(4)
C(19)-C(20)-C(21)-C(22)	-172.0(5)	Eu(1)-O(6)-C(27)-C(26)	-16.5(6)
C(26)-N(5)-C(22)-C(23)	2.5(7)	N(5)-C(26)-C(27)-O(7)	-162.3(5)
Eu(1)-N(5)-C(22)-C(23)	-170.5(3)	C(25)-C(26)-C(27)-O(7)	15.4(8)
C(26)-N(5)-C(22)-C(21)	-172.2(4)	N(5)-C(26)-C(27)-O(6)	16.5(6)

C(25)-C(26)-C(27)-O(6)      -165.8(5)

**Table 7** Hydrogen-bond geometry (Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2')...OW1	.82	1.74	2.537(6)	164.5
O(5)-H(5)...OW2	.82	1.75	2.551(6)	165.2
OW1-H(12)...O(7)				
#1	1.06(12)	1.63(13)	2.680(7)	168(10)
OW1-H(11)...O(4)				
#2	.99(12)	2.01(12)	2.888(7)	147(10)
OW2-H(22)...OW3	.96(9)	2.02(9)	2.896(11)	150(8)
OW3-H(32)...O(7)				
#3	.97(15)	1.97(15)	2.927(8)	172(14)
O(3)-H(3')...Cl(2) #4	.82	2.19	3.014(4)	176.8
OW2-H(21)...Cl(2)	1.07(9)	2.07(10)	3.103(5)	162(7)
OW3-H(31)...Cl(2)				
#5	1.06(15)	2.12(15)	3.179(8)	173(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x,-y,-z #3 x-1,y-1,z #4 -x,-y,-z+1 #5 -x-1,-y,-z+1

**Table T8.** Relative intensities ratio  $I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$  of the europium complexes with ligands **L**<sub>1</sub> to **L**<sub>4</sub> and **L**<sub>6</sub>.

	<b>L</b> <sub>1</sub>	<b>L</b> <sub>2</sub>	<b>L</b> <sub>3</sub>	<b>L</b> <sub>4</sub>	<b>L</b> <sub>6</sub>
$I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$	2.6	3.8	3.2	3.1	2.1