A Novel 1-D Ladder-like Coordination Polymer $[Eu(dipic)_{1.5}(H_2O)_4{\cdot}3H_2O]_\infty$

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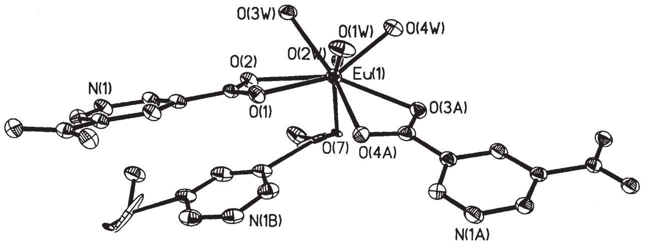
A novel one-dimensional infinite ladder-like lanthanide (Eu^{III}) coordination polymer was obtained by hydrothermal method and its structure and magnetic and photoemission properties were investigated.

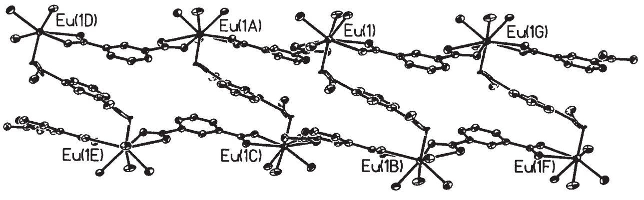
The design and construction of coordination polymers has been a field of rapid growth in materials chemistry because of their fascinating structures and applications as new materials.[1] The growing interest in this field is motivated by the ability of metalloligand coordination to provide a simple route to the controlled assembly of one-, two-, or three-dimensional materials.[2] Many advanced 2-D and 3-D materials has been prepared in this way with potential applications in catalysis, separation, ion exchange, sensors, and molecular recognition.[3] However, only a few examples of an infinite 1-D molecular ladder coordination polymer have been reported so far. In particular, the lanthanide complexes with ladder-like structure have received much less attention.[4] Eu^{III} complexes are characterized by the "narrow" red emission. As a result, Eu^{III} complexes are investigated as materials for light emission devices and fluorescence probes. Therefore, it is interesting to study new Eu^{III} complexes with interesting structures. Herein, we report the synthesis and structure of a ladder-like lanthanide coordination polymer formed from Eu^{III} and the $dipic^{2-}$ (H_2dipic = pyridine-3,5-dicarboxylic acid). Reaction of Eu_2O_3 with H_2dipic in H_2O under hydrothermal condition yields colorless crystalline blocks of $[Eu(dipic)_{1.5}(H_2O)_4{\cdot}3H_2O]_\infty$ (1),[5] its crystal structure was determined by X-ray diffraction.[6]



(a)

Figure 1a. ORTEP drawing of the asymmetric unit of complex 1, thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) ana angles (°): Eu(1)–O(7), 2.131(8); Eu(1)–O(1W), 2.296(5); Eu(1)–O(4W), 2.409(5); Eu(1)–O(2W), 2.424(5); Eu(1)–O(3W), 2.425(5); Eu(1)–O(4)#1, 2.506(5); Eu(1)–O(1), 2.734(5); Eu(1)–O(2), 2.755(5); Eu(1)–O(3)#1, 2.783(5); O(7)–Eu(1)–O(4)#1, 76.0(3); O(7)–Eu(1)–O(1), 98.4(3); O(4)#1–Eu(1)–O(1), 79.00(15); O(7)–Eu(1)–O(2), 82.3(2); O(4)#1–Eu(1)–O(2), 116.90(14); O(1)–Eu(1)–O(2), 46.61(14); O(7)–Eu(1)–O(3)#1, 72.1(2); O(1)–Eu(1)–O(3)#1, 131.47(14); O(2)–Eu(1)–O(3)#1, 153.93(13). #1: x, $-y+1$, $z+1/2$; #2: $-x+1$, y, $-z+1/2$; #3: x, $-y+1$, $z-1/2$.

X-ray analysis revealed that complex **1** comprises a two-leg ladder running along the [001] direction. An ORTEP view of complex **1** is shown in Figures 1a and 1b. Each Eu^{III} ion is nine coordinated with tricapped trigonal prism environment by four water molecules (average Eu–O bond length 2.388 Å) and five carboxyl oxygen atoms (mean Eu–O bond length 2.582 Å), four of which are from two neighboring $dipic^{2-}$ ligands (along the leg of ladder) and the other one is provided by another $dipic^{2-}$ ligand (rung of the ladder). The legs of such a ladder are made of $[Eu(dipic)(H_2O)_4]_\infty$ chains in which Eu^{III} ions are bridged by $dipic^{2-}$ ligands and each of the two carboxyl of $dipic^{2-}$ in a bidentate coordination mode. The rungs are made up of $dipic^{2-}$, in which each of carboxyl group in a monodentate coordination mode bridge two Eu^{III} atoms belonging to either side of the ladder. In the rungs, $dipic^{2-}$ ions are C_2-rotation disordered. In this ladder, Eu(III)–Eu(III) separation among the leg is 6.294 Å, and the Eu(III)–Eu(III) separation in the rungs is 7.136 Å.



(b)

Figure 1b. ORTEP view of ladder structure of the complex **1**.

Thermal gravimetric analysis (TGA) was performed on crystalline samples of complex **1** in the range of 23 to 600 °C. The TGA curve of complex **1** is shown in Figure 2. The weight loss of 23.98% between 60 to 280 °C corresponds to the loss of all uncoordinated and coordinated water molecules (calcd. 23.98%). This is in agreement with the elemental analysis result that reveals the presence of seven water molecules in complex **1**.

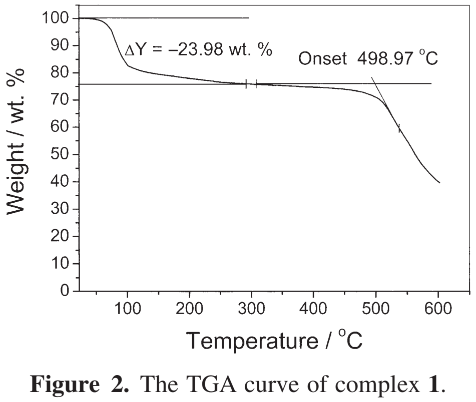


Figure 2. The TGA curve of complex **1**.

The temperature dependence of the magnetic susceptibility of **1** is shown in Figure 3, where χ_m is the corrected molar magnetic susceptibility per Eu^{III} unit. The observed $\chi_m T$ at room temperature is 1.42 cm^3 mol^{-1} K, slightly less than the value 1.5 cm^3 mol^{-1} K for the isolated Eu^{III} ion calculated by Van Vleck equation allowing for population of the excited state at 293 K. As the temperature is lowered, $\chi_m T$ decreases continuously, which should be attributed to the depopulation of the Stark levels for a single Eu^{III} ion.[7] Owing to the presence of thermal populated excited states, the ^{7}F ground term of Eu^{III} is splitted by the spin-orbit coupling into seven states ^7F_J ($J = 0$–6). The magnetic data were fitted by previously reported equations,[8] leading to spin-orbit coupling parameter $\lambda = 358\,cm^{-1}$ (the agreement factor $R = \Sigma_i[(\chi_m)_{obs}(i) - (\chi_m)_{calc}(i)]^2/\Sigma_i[(\chi_m)_{obs}(i)]^2 = 3.79 \times 10^{-5}$). The $\chi_m T$ versus kT/λ plot is shown in Figure 3 (inset). At the lowest temperature, $\chi_m T$ is close to zero, indicating a $J = 0$ ground state of the Eu^{III} ion ($^7F_0$). Above 140 K, the magnetic susceptibility of the ^{7}F term is the sum of an orbital contribution and a spin contribution, and it follows the Curie–Weiss law due to the presence of thermally populated excited state.

Complex **1** exhibits intense red fluorescence under UV light. The luminescence spectrum of **1** corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 1$–2) transitions in the range of 580 to 650 nm is shown in Figure 4. It is well known that the $^5D_0 \rightarrow {}^7F_2$ transition induced by the electric dipole moment is hypersensitive to the environment of the Eu^{III} ion, while the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition which is fairly insensitive to the coordination environment of the Eu^{III} ion. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)$ / $I(^5D_0 \rightarrow {}^7F_1)$ is equal to 4.36, which indicates that the symmetry of the Eu^{III} ion site in complex **1** is low.[9] This is in agreement with the result of the single crystal X-ray analysis.

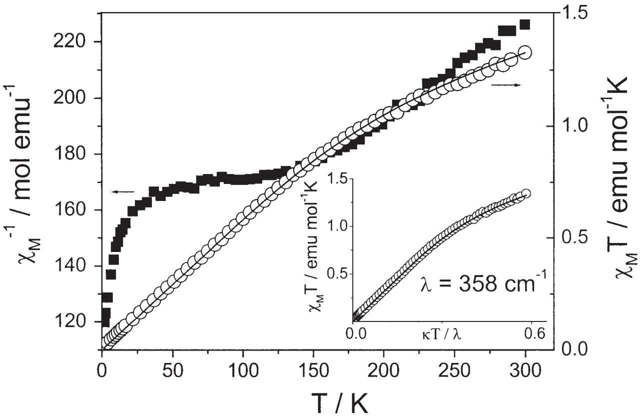


Figure 3. Polt of $1/\chi_m$ and $\chi_m T$ vs T for complex **1**, the solid line corresponds to the best theoretical fit. The best fit parameter $\lambda = 358\,cm^{-1}$; plot of $\chi_m T$ vs kT/λ for **1** (inset).

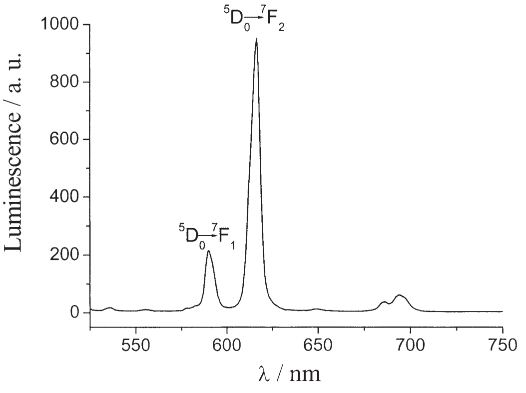


Figure 4. Luminececescence spectrum of **1**, $\lambda_{exc} = 260$ nm.

In summary, a new 1-D coordination polymer of Eu^{III} with ladder-like structure was prepared and crystallographically characterized. Its magnetic and photoemission properties were measured and studied.

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References and Notes

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5 A mixture of H_2dipic (1.5 mmol, 0.25 g), Eu_2O_3 (0.5 mmol, 0.176 g), and H_2O (12 mL) was added into a Teflon-lined stainless-steel Parr acid digestion vessel (20 mL) and heated at 180 °C for three days under autogenous pressure. After slow cooling to room temperature, colourless crystals were obtained as a pure phase. Yield: 0.37 g (68%). Found: C, 23.68; H, 3.59; N, 4.00%. Calcd. for $C_{10.5}H_{4.5}EuN_{1.5}O_6 \cdot 7H_2O$: C, 23.97; H, 3.52; N, 4.00%.

6 Crystal data: $C_{10.5}H_{4.5}EuN_{1.5}O_6 \cdot 7H_2O$, M = 525.62, monoclinic, $C2/c$, $a = 17.519(4)$ Å, $b = 10.991(2)$ Å, $c = 19.983(4)$ Å, $\beta = 111.82(3)°$, $V = 3572.0(12)$ Å^3, $Z = 8$, $D_c = 1.899\,g\,cm^{-3}$; F(000) = 1956, μ(Mo Kα) = 3.577 mm^{-1}. 3848 reflections of which 2866 are ($R_{int} = 0.0673$) were collected to a θ limit of 31.63° on a Rigaku RAXIS RAPID IP instrument at 153(2) K. The structure was solved by direct methods and refined by a least-squares matrix method. The final cycle of full-matrix least-square refinement was based on 1377 observed reflections [$I > 2\sigma(I)$] and 298 variable parameters and converged to $R_1 = 0.0452$, $wR_2 = 0.1203$.

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