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Synthesis, Crystal Structure and Fluorescence of 2-D Polymeric Eu(III) Complex with Fumarate and 2-Chlorofumarate as Bridging Ligands

by S.C. Zhu, J.M. Shi*, Q.Y. Liu and C.J. Wu

Department of Chemistry, Shandong Normal University, Jinan 250014, P. R. China

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For a long time much interest has been focused on crystal engineering of coordination compounds because such compounds may afford new materials with useful properties [1–2]. Many complexes dealing with fumarate as bridging ligand have been synthesized [3–4], while the complex with fumarate and 2-chloro-fumarate as bridging ligand has not yet been reported. Here we report the synthesis, crystal structure and the fluorescence of the novel two-dimensional complex: $[Eu_2(\mathit{fum})(\mathit{cfum})_2(H_2O)_4]\cdot 4H_2O$ (*fum* = fumarate; *cfum* = 2-chlorofumarate).

The two-dimensional complex $[Eu_2(fum)(cfum)_2(H_2O)_4]\cdot 4H_2O$ was prepared in the following way: $Eu(ClO_4)_3\cdot 6H_2O$ (0.51058 g, 0.91 mmol) was added into the solution (about 15 cm^3) of fumaric acid (0.05502 g, 0.47 mmol) and 2-chlorofumaric acid (0.13905 g, 0.92 mmol), then the diluted NaOH solution was added to the solution to adjust pH to 3.5 and the solution was stirred for a few minutes. Colorless transparent single crystals were obtained after the solution was allowed to stand at room temperature for two weeks. Found C, 16.32; H, 1.97; Eu, 35.90%. Calc. For $C_6H_{10}ClEuO_{10}$: C, 16.78; H, 2.35; Eu, 35.38%. IR absorption bands of the complex appear at 3300 cm^{-1} (br. vs) for vibration of H_2O, 1610 (vs), 1570 (vs) cm^{-1} for $\nu_{as}(C{=}O)$, 1405 (s) and 1360 cm^{-1} (s) for $\nu_s(C{=}O)$. The separation values between $\nu_{as}(C{=}O)$ and $\nu_s(C{=}O)$ indicate that the carboxylate groups as monodentate and multidentate ligand may take part in the coordination and this is in agreement with the X-ray result. The determination of the crystal structure was carried out on a X-ray Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) at 301(2) K using a single crystal of the dimensions of 0.20 mm × 0.15 mm × 0.10 mm. A total of 2397 reflections were collected in the range of $5.77° \le \theta \le 23.29°$, of which 1622 were independent reflections and 1361 were observed reflections with $I > 2\sigma(I)$. The SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) [5] programs of structure solution and refinement were used. The semi-empirical absorption correction was performed on equivalent reflections. The selected bond lengths and the

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* Author to whom all correspondence should be directed.

associated angles are listed in Table 1. The fluorescence spectra were obtained on a Perkin-Elmer LS-50 fluorescence spectrophotometer.

The crystal is triclinic, space group $P\bar{1}$ with a = 8.872(3) Å, b = 9.422(3) Å, c = 9.545(3) Å, α = 103.520(4)°, β = 101.355(4)°, γ = 94.076(5)°, V = 754.8(4) Å^3, Z = 1, D_c = 1.890 g/cm^3, $F(000)$ = 412, $\mu(MoK_\alpha)$ = 4.366 mm^{-1}, $R1$ = 0.0340 and $wR2$ = 0.0665 for 1361 observed reflections ($I > 2\sigma(I)$). The completeness to θ = 23.29° is 74.5% and the goodness of fit on F^2 is 0.982. The maximum peak in the final difference Fourier map is 0.901 and the minimum one –0.456 e·Å^{-3}.

Fig. 1 shows the coordination diagram of the title complex with the atom numbering scheme. It indicates that the Eu(1) ion is coordinated by eight oxygen atoms, in which O(7) and O(8) are from H_2O molecules and the other oxygen atoms come from carboxylic groups. The four oxygen atoms of each fumarate coordinate four Eu(III) ions, and it means that fumarate plays a role of μ_4 bridging ligand. Two carboxylic groups of 2-chlorofumarate coordinate to three Eu(III) ions. One of the carboxylic groups that close to the chlorine atom coordinates Eu(III) ion as a two-dentate ligand and a chelated four-member ring is formed. The other carboxylic group coordinates two Eu(III) ions, in which one of the two oxygen atoms as a bridging ligand coordinates two Eu(III) ions and a four-member ring is also formed. The coordination bond lengths and the associated angles indicate that the Eu(III) ion lies in a distorted dodecahedral environment. Fig. 2 shows two-dimensional net structure and it indicates that the structure is constructed through the coordination of Eu(III) ions and the two kinds of bridging ligands. The two-dimensional structure as a two-deck sheet is located on YZ plane as shown in Fig. 3. Because of hydrogen bond formed, the sheets pile up along X direction and a three-dimensional structure is formed. The uncoordinated H_2O molecules are located between the layers. The deposition number of the crystal at CCDC is 178986. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Selected bond lengths (Å) and the associated angles (°).

Eu(1)–O(1)	2.378(6)	Eu(1)–O(2)	2.403(6)	Eu(1)–O(8)	2.418(6)
Eu(1)–O(7)	2.433(6)	Eu(1)–O(4)	2.447(5)	Eu(1)–O(5)	2.522(5)
Eu(1)–O(3)	2.541(5)	Eu(1)–O(6)	2.608(5)		

O(1)–Eu(1)–O(2)	134.9(2)	O(1)–Eu(1)–O(8)	79.7(2)
O(2)–Eu(1)–O(8)	141.6(2)	O(1)–Eu(1)–O(7)	141.9(2)
O(2)–Eu(1)–O(7)	69.8(2)	O(8)–Eu(1)–O(7)	71.8(3)
O(1)–Eu(1)–O(4)	127.1(2)	O(2)–Eu(1)–O(4)	81.5(2)
O(8)–Eu(1)–O(4)	88.2(2)	O(7)–Eu(1)–O(4)	77.5(2)

Table 1 (continuation)

O(1)–Eu(1)–O(5)	76.8(2)	O(2)–Eu(1)–O(5)	93.6(2)
O(8)–Eu(1)–O(5)	76.8(2)	O(7)–Eu(1)–O(5)	72.5(2)
O(4)–Eu(1)–O(5)	149.4(2)	O(1)–Eu(1)–O(3)	76.3(2)
O(2)–Eu(1)–O(3)	124.1(2)	O(8)–Eu(1)–O(3)	72.6(2)
O(7)–Eu(1)–O(3)	116.8(2)	O(4)–Eu(1)–O(3)	51.1(2)
O(5)–Eu(1)–O(3)	142.2(2)	O(1)–Eu(1)–O(6)	69.97(19)
O(2)–Eu(1)–O(6)	70.50(19)	O(8)–Eu(1)–O(6)	122.67(18)
O(7)–Eu(1)–O(6)	104.9(2)	O(4)–Eu(1)–O(6)	148.5(2)
O(5)–Eu(1)–O(6)	49.94(17)	O(3)–Eu(1)–O(6)	138.22(19)

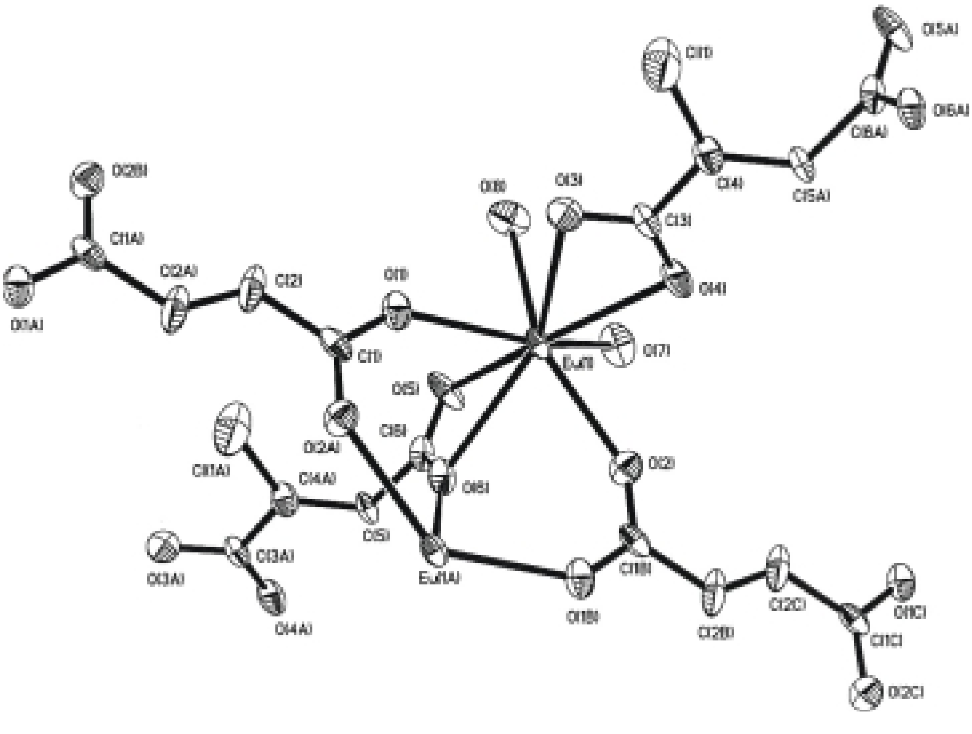

Figure 1. The coordination diagram of the complex with atom numbering scheme.

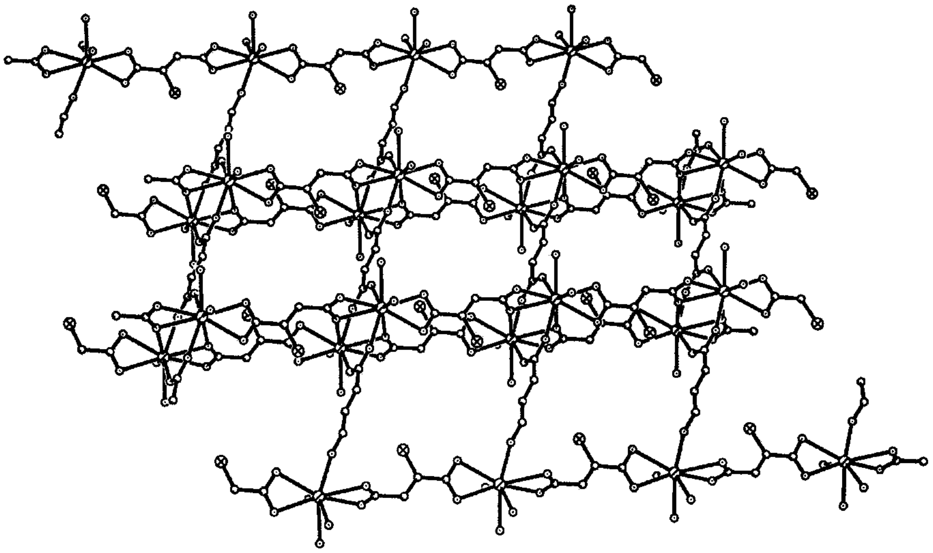

Figure 2. The diagram of two-dimensional net structure of the complex.

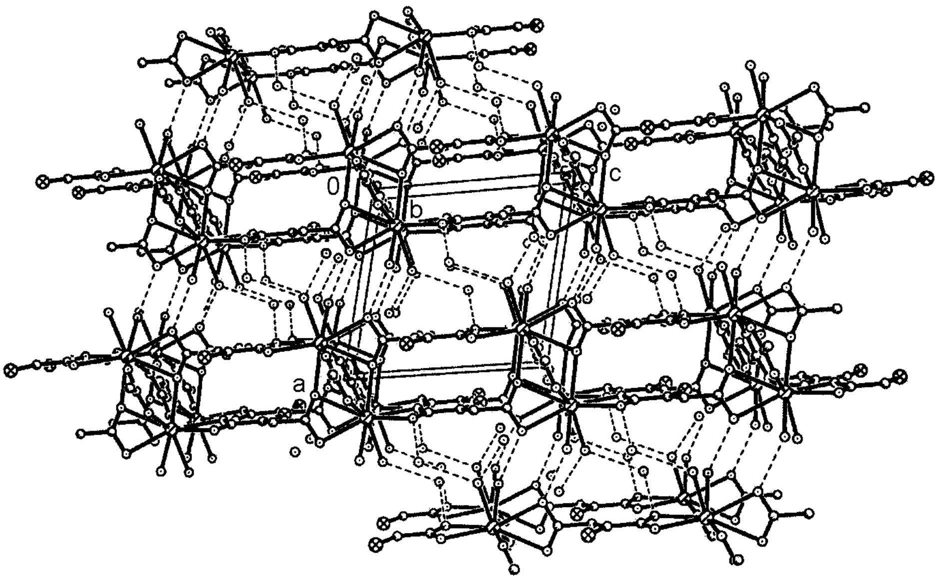

Figure 3. The unit cell and the arrangement of two-dimensional two-deck sheets in the crystal.

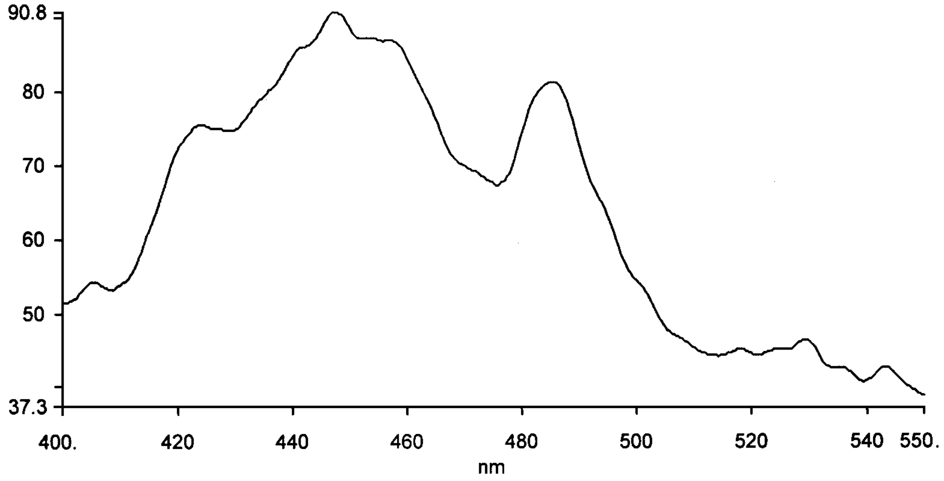

Figure 4. The fluorescent spectrum of the complex in solid state.

The fluorescence spectrum of the complex, shown in Fig. 4, was measured at room temperature in the solid state. The maximum excited wavelength is 306 nm and the maximum emission peaks are at about 448 nm and 485 nm. Generally, the compounds of Eu(III) exhibit strong and sharp fluorescent emission peaks in visible range [6]. They origin from the transitions of $^5D_0$–$^7F_2$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_4$ of Eu(III). The present fluorescent spectrum shows no fluorescent peaks from Eu(III), while a strong absorption band appears at 430 nm to 650 nm for the present complex in the solid state. This may be the strong absorption property of the complex at visible range that makes the energy transfers from Eu(III) to the complex and quench the fluorescent emissions of Eu(III).

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