

Hydrothermal synthesis and crystal structure of a new europium fumarate compound

Xia Li⁽¹⁾ and Ying-Quan Zou^{(2)*}

Received August 25, 2004; accepted November 19, 2004

The complex $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ (H_2F = fumaric acid) has been synthesized and structurally characterized by single crystal X-ray diffraction methods. The complex crystallizes in the monoclinic system with space group $P2_1/n$, lattice parameters $a = 9.475(3)$ Å, $b = 14.700(5)$ Å, $c = 14.810(4)$ Å, $\alpha = 90^\circ$, $\beta = 91.250(5)^\circ$, $\gamma = 90^\circ$, $V = 2062.1(11)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.487$ Mg/m³. The Eu(III) center is in distorted tricapped trigonal prism coordination environment that is coordinated by nine oxygen atoms, seven from five F^{2-} groups, two from two water molecules. Eu(III) ions are connected into three-dimensional coordination network structure by the oxygen atoms of the carboxyl groups and hydrogen bonds.

KEY WORDS: Europium; fumaric acid; coordination polymer.

Introduction

In recent years, metal coordination polymers have attracted more attention due to their fascinating structures and potential application as magnetic, catalyst and luminescent materials.¹⁻⁴ Polycarboxylate anions are the suitable bridging ligands on construction network coordination polymers. Many metal coordination polymers with polycarboxylates have been reported,⁵⁻¹³ such as on rigid ligands aromatic polycarboxylic acids,⁵⁻⁷ and flexible ligands adipic acid,⁸ octanedioic acid and pentanedioic acid,⁹ suberic acid.¹⁰ Recently, several 2D and 3D open-frame-

works of transition metal bipy maleates and fumarates have been reported.¹¹⁻¹² The 3D frameworks of lanthanide coordination polymers with fumaric acid (H_2F), $[\text{M}_2\text{F}_3 \cdot 12\text{H}_2\text{O}]_n$ ($\text{M} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Y}, \text{Er}, \text{Lu}$) have been reported.¹³ Europium complexes have specific luminescent character as luminescent materials. A europium complex containing mixed-ligands displays intense fluorescence.¹⁴⁻¹⁶ We have selected H_2F and 2,2'-bipyridine as ligands to construct a coordination polymer with Eu(III) ion and obtain the title complex $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$, the expectant mixed-ligands complex has not been generated, possibly because 2,2'-bipyridine is weaker to coordinate lanthanide. But the structure of coordination polymer $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ is different from complex $[\text{Eu}_2\text{F}_3 \cdot 12\text{H}_2\text{O}]_n$,¹³ which belong to triclinic system with space group $P\bar{1}$, and 10 coordination numbers. Here, we report its structure.

⁽¹⁾Department of Chemistry, Capital Normal University, Beijing 100037, People's Republic of China.

⁽²⁾Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China.

* To whom correspondence should be addressed; e-mail: zouvq@263.net.

Experimental

Complex synthesis

An amount of 1.5 mmol fumaric acid was dissolved in appropriate amounts of ethanol and its pH was controlled in a range of 6–7 with 2 mol dm⁻³ NaOH solution. Then the ethanolic solution of 2,2'-bipyridine (0.5 mmol) and ethanolic solution of EuCl₃ (0.5 mmol) were dropped, successively. The mixture was heated under reflux with stirring for 2 h. Single crystals were obtained from the mother liquor after two weeks at room temperature.

X-ray crystallography

X-ray crystal data collection for a crystal size for complex 0.20 mm × 0.18 mm × 0.16 mm for complex on a Broker Smart 1000 CCD diffractometer with monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refinement on $|F|^2$ used the full-matrix least-squares methods of SHELXS-97.¹⁷ All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and details of the structure refinements are listed in Table 1.

Results and discussion

Coordination environment of the two Eu(III) ions in complex $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. The Eu(III) ion is coordinated by nine oxygen atoms, seven from five F²⁻ groups, two from two water molecules (Fig. 1). A distorted tricapped trigonal prism arrangement is found. Atoms O14, O3A and O13, and atoms O2, O5 and O8A, take the tips of the upper and lower triangles of the prism, respectively, and the dihedral angle between the two face is 6.6°. Atoms O1, O9 and O7A take the three cap

Table 1. Crystal Data and Structure Refinement for $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$

Empirical formula	C ₁₂ H ₂₀ Eu ₂ O ₁₉
Formula weight	772.20
CCDC	247168
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 9.475(3) Å <i>b</i> = 14.700(5) Å <i>c</i> = 14.810(4) Å α = 90° β = 91.250(5)° γ = 90°
Volume	2062.1(11) Å ³
Z	4
Calculated density	2.487 Mg m ⁻³
Absorption coefficient	6.123 mm ⁻¹
Theta range for data collection	2.53–25.01°
Limiting indices	−11 ≤ <i>h</i> ≤ 10, −17 ≤ <i>k</i> ≤ 12, −17 ≤ <i>l</i> ≤ 17
Reflections collected/unique	10447/3639 [<i>R</i> _{int} = 0.0484]
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	3639/0/298
Goodness-of-fit on <i>F</i> ²	1.034
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0349, <i>wR</i> ₂ = 0.0703
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0581, <i>wR</i> ₂ = 0.0769
Largest diff. peak and hole	0.873 and −0.964 eÅ ⁻³

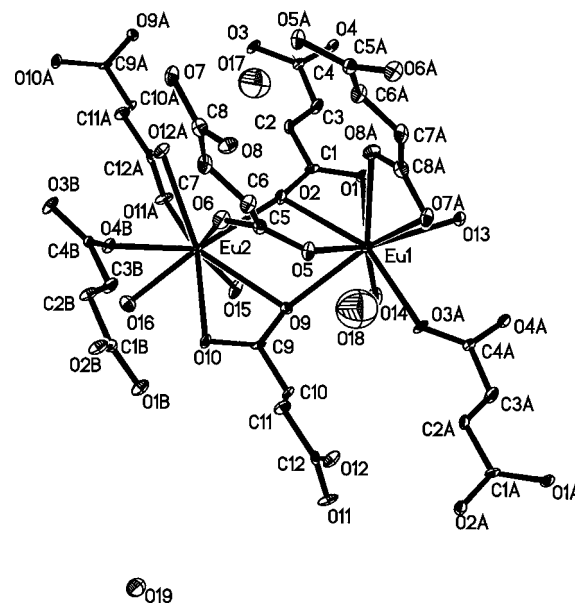


Fig. 1. Coordination environment of the two Eu(III) ions in complex $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ (all hydrogen atoms have been omitted for clarity). Thermal ellipsoids are shown at the 60% probability level.

Table 2. Bond Distances (Å) and Angles (deg) of the $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$

Eu(1)—O(3)#1	2.352(5)	Eu(1)—O(14)	2.412(5)
Eu(1)—O(9)	2.444(5)	Eu(1)—O(13)	2.448(5)
Eu(1)—O(5)	2.450(5)	Eu(1)—O(8)#2	2.458(5)
Eu(1)—O(1)	2.479(5)	Eu(1)—O(7)#2	2.533(5)
Eu(1)—O(2)	2.618(5)		
O(3)#1—Eu(1)—O(14)	77.08(18)	O(3)#1—Eu(1)—O(9)	88.56(17)
O(14)—Eu(1)—O(9)	70.06(17)	O(3)#1—Eu(1)—O(13)	79.31(16)
O(14)—Eu(1)—O(13)	78.21(18)	O(9)—Eu(1)—O(13)	147.86(17)
O(3)#1—Eu(1)—O(5)	91.79(17)	O(14)—Eu(1)—O(5)	137.65(19)
O(9)—Eu(1)—O(5)	68.92(17)	O(13)—Eu(1)—O(5)	140.33(17)
O(3)#1—Eu(1)—O(8)#2	124.66(18)	O(14)—Eu(1)—O(8)#2	146.67(17)
O(9)—Eu(1)—O(8)#2	128.76(17)	O(13)—Eu(1)—O(8)#2	81.59(17)
O(5)—Eu(1)—O(8)#2	71.96(17)	O(3)#1—Eu(1)—O(1)	141.00(17)
O(14)—Eu(1)—O(1)	75.81(18)	O(9)—Eu(1)—O(1)	107.64(16)
O(13)—Eu(1)—O(1)	68.11(16)	O(5)—Eu(1)—O(1)	127.00(17)
O(8)#2—Eu(1)—O(1)	72.14(17)	O(3)#1—Eu(1)—O(7)#2	72.69(19)
O(14)—Eu(1)—O(7)#2	140.52(17)	O(9)—Eu(1)—O(7)#2	132.64(16)
O(9)—Eu(1)—O(7)#2	71.78(16)	O(5)—Eu(1)—O(7)#2	68.68(17)
O(8)#2—Eu(1)—O(7)#2	52.01(17)	O(1)—Eu(1)—O(7)#2	114.24(18)
O(3)#1—Eu(1)—O(2)	154.40(19)	O(14)—Eu(1)—O(2)	88.38(17)
O(9)—Eu(1)—O(2)	66.53(15)	O(13)—Eu(1)—O(2)	118.58(15)
O(5)—Eu(1)—O(2)	84.86(15)	O(8)#2—Eu(1)—O(2)	78.35(17)
O(1)—Eu(1)—O(2)	50.52(15)	O(7)#2—Eu(1)—O(2)	128.41(17)

Note. Symmetry transformations used to generate equivalent atoms: #1 $x - 1, y, z$; #2 $-x + 1, -y + 2, -z + 1$; #3 $x - 1/2, -y + 3/2, z - 1/2$; #4 $x + 1, y, z$; #5 $x + 1/2, -y + 3/2, z + 1/2$.

positions (Fig. 2). The Eu—O (carboxyl group) bond lengths range from 2.352(5) to 2.618(5) Å, among them Eu—O(2) is the longest, [–14pc] which may be due to the stronger strain in

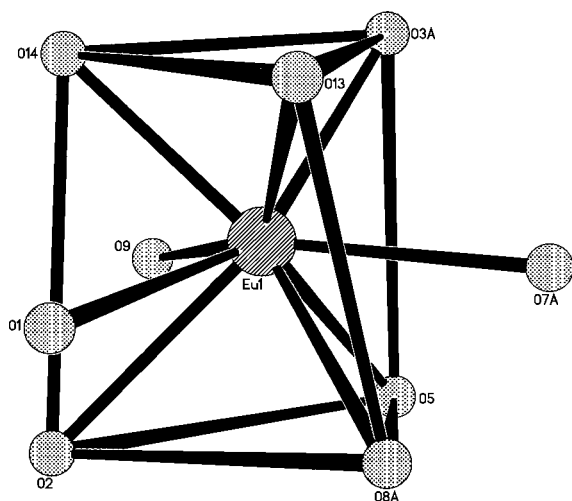
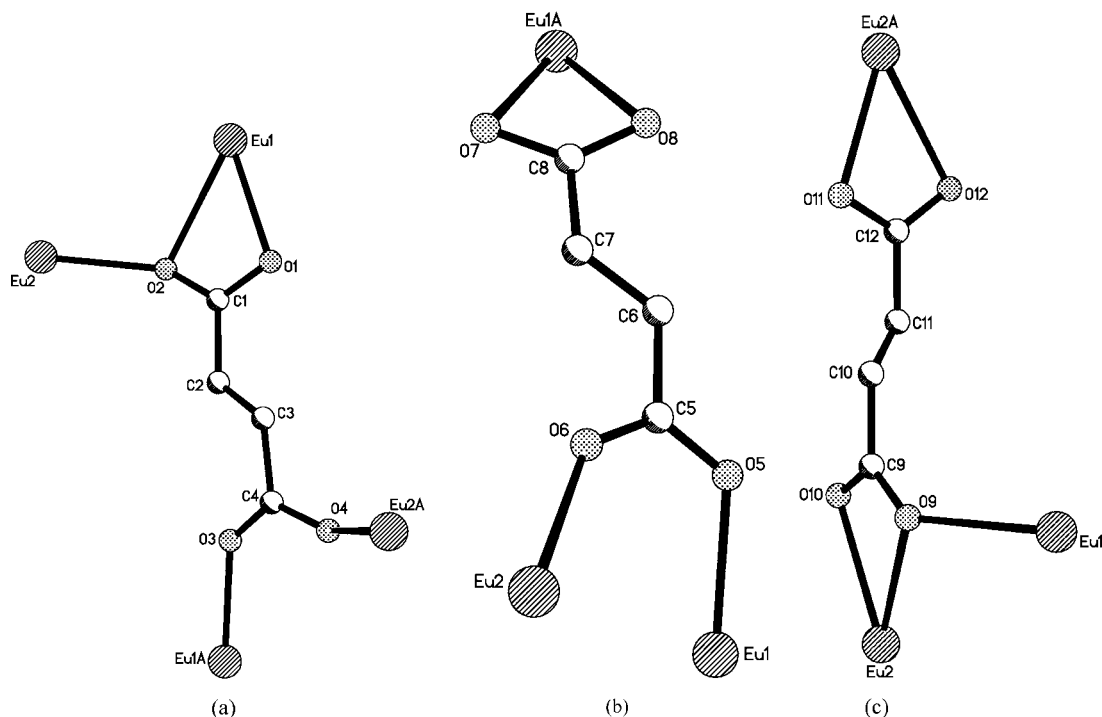


Fig. 2. A schematic representation of the coordination geometry of the Eu(III) ion in $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$.

the O2Eu1C1O1 four-membered ring. The mean Eu—O (carboxyl group) distance is 2.476 Å. The Eu—O (aqua) bond lengths are 2.412(5) and 2.448(5) Å, respectively. They are a little shorter than corresponding average distances found in the $[\text{Eu}_2\text{F}_3 \cdot 12\text{H}_2\text{O}]_n$ ¹³ complex, attributable to the differences in coordination environment of Eu(III) ion. In $[\text{Eu}_2\text{F}_3 \cdot 12\text{H}_2\text{O}]_n$, Eu(III) is ten coordinated by eight oxygen atoms from fumarate ligands and two water molecules. The O—Eu—O bond angles are in the range of 50.52(15)–154.40(19)°. The calculated results of the least-squares plane show that four carbon atoms of fumarate groups are roughly coplanar, while coordinated fumarate ligand are twisted. The fumarate groups coordinate metal in three coordination modes. (i) Two carboxylate groups of one F²⁻ coordinate metal in bridging and chelating-bridging modes, respectively, to form a pentadentate bridging (Scheme 1(a)). Carboxylate group O1—C1—O2 is in a bridging-chelating mode, in which two O atoms chelate one Eu(III) ion and one of them also simultaneously links another



Scheme 1. Coordination modes of fumarate in complex $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$.

Eu(III) ion. Carboxylate group O3—C4—O4 is in a bridging mode, in which two O atoms link two different Eu(III) ions. (ii) Two carboxylate groups of one F^{2-} coordinate metal in bridging and chelating modes, respectively, to form a tetradentate bridging (Scheme 1(b)). Carboxylate group O5—C5—O6 is in a bridging mode to coordinate Eu(III) ion, similar to carboxylate group O3—C4—O4. Carboxylate group O7—C8—O8 is in a chelating mode, in which two O atoms chelate one Eu(III) ion. (iii) Two carboxylate groups of one F^{2-} coordinate metal in chelating-bridging and chelating modes, respectively, to form a pentadentate bridging (Scheme 1(c)). Carboxylate group O9—C9—O10 is in a chelating-bridging mode to coordinate Eu(III) ion, similar to carboxylate group O1—C1—O2. Carboxylate group O11—C12—O12 is in a chelating mode to coordinate Eu(III) ion, similar to carboxylate group O7—C8—O8. The two Eu(III) ions are linked together by two COO^- groups in chelating-bridging mode and one in bridging

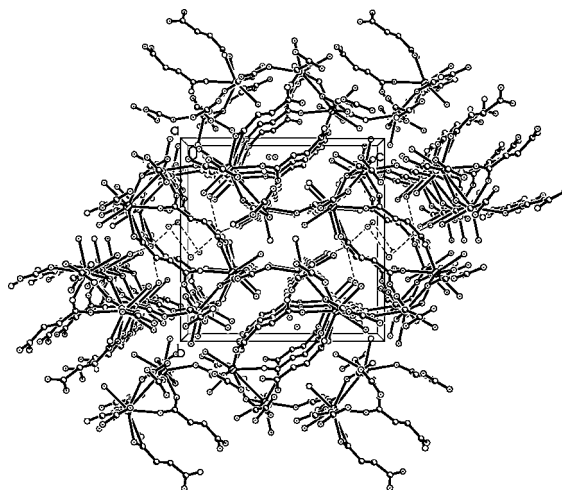


Fig. 3. Packing diagram of $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ viewed along α -axis.

to form a centrosymmetric dimer with Eu...Eu distance of 4.1526(9) Å. The dimeric units as building block are connected to framework through “OOCCHCHCOO” groups in

Table 3. Hydrogen Bonds for $\{[\text{Eu}_2\text{F}_3 \cdot 4\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$ [Å and deg]

D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O(13)—H(13B)...O(4)#1	0.85	2.28	2.699(7)	110.7
O(14)—H(14B)...O(12)#5	0.85	1.91	2.737(7)	164.0
O(15)—H(15B)...O(8)#5	0.85	2.16	2.806(7)	132.7
O(16)—H(16A)...O(1)#6	0.85	2.31	2.785(7)	115.9
O(14)—H(14A)...O(19)#7	0.85	2.21	2.847(8)	131.9
O(15)—H(15A)...O(19)#7	0.85	2.34	2.831(8)	117.3
O(17)—H(17B)...O(8)#4	0.85	2.26	2.783(7)	120.12
O(18)—H(18B)...O(17)#1	0.92	2.06	2.783(7)	133.89

Note. Symmetry transformations used to generate equivalent atoms: #1 $x - 1, y, z$; #2 $-x + 1, -y + 2, -z + 1$; #3 $x - 1/2, -y + 3/2, z - 1/2$; #4 $x + 1, y, z$; #5 $x + 1/2, -y + 3/2, z + 1/2$; #6 $-x + 3/2, y - 1/2, -z + 3/2$; #7 $-x + 1/2, y + 1/2, -z + 3/2$.

coordination modes Scheme 1(a–c), which above are discussed. Three-dimensional network viewed along the crystallographic *a*-axis as shown in Fig. 3. The dissociative water fills in the crystal lattice and available for hydrogen bonding. Variety hydrogen bonds exist in the crystal: between coordinated water and carboxylate groups, such as O14—H14B...O12; between coordinated water and lattice water, such as O15—H15A...O19; between lattice water and carboxylate groups O(17)—H(17B)...O(8); in addition, between lattice waters, such as O18—H18A...O17. Hydrogen bonding distances and angles are presented in Table 3. These hydrogen bonds interactions affords extra stabilization to the complex.

Supplementary material CCDC-247168 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

We are grateful to the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government and the Project Sponsored by the Scientific Research Foundation for the Returned

Overseas Chinese Scholars, State Education Ministry.

References

- Pujita, M.; Kwon, Y.J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.
- Guilhem, J.; Tchertanov, L.; Nakatani, K. *J. Am. Chem. Soc.* **2000**, *122*, 9444.
- Zhang, X.X.; Chui, S.S.Y.; Williams, I.D. *J. Appl. Phys.* **2000**, *87*, 6007.
- Zhang, H.; Wang, X.; Teo, B.K. *J. Am. Chem. Soc.* **1996**, *118*, 11813.
- Sun, D.F.; Rong, C.; Liang, Y.C.; Shi, Q.; Su, W.P.; Hong, M.Ch. *J. Chem. Soc., Dalton Trans.* **2001**, 2335.
- Wan, Y.H.; Jin, L.P.; Wang, K.Zh.; Zhang, L.P.; Zheng, X.J.; Lu, Sh.Zh. *New J. Chem.* **2002**, *26*, 1590.
- Pan, L.; Woodlock, E.B.; Wang, X.T. *Inorg. Chem.* **2000**, *39*, 4174.
- Kiritisis, V.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L. *Inorg. Chem.* **1998**, *37*, 3407.
- Devereux, M.; McCann, G.M.; Cronin, J.F.; Ferguson, G.; McKee, V. *Polyhedron* **1999**, *18*, 2141.
- Zheng, Y.Q.; Lin, J.L.; Kong, Z.P. *Polyhedron* **2003**, *22*, 2699.
- Shi, Z.; Zhang, L.; Gao, S.; Yang, G.; Hua, J.; Gao, L.; Feng, S. *Inorg. Chem.* **2000**, 1990, 39.
- Tao, J.; Tong, M.-L.; Shi, J.-X.; Chen, X.-M.; Ng, S.W. *Chem. Commun.* **2000**, 2043.
- Ma, J.F.; Wei, G.H.; Ni, J.Z. *Acta Phys.-Chim. Sin. (in Chinese)* **1993**, *9*, 752.
- Li, X.; Zheng, X.J.; Jin, L.P.; Lu, Sh.Zh.; Zhang, J.H. *J. Mol. Struct.* **2001**, *559*, 341.
- Jin, L.P.; Wang, R.F.; Li, L.Sh.; Lu, Sh.Zh.; Huang, Sh.H. *Polyhedron* **1998**, *18*, 487.
- Li, X.; Zheng, X.J.; Jin, L.P.; Lu, Sh.Zh.; Huang, Sh.H. *J. Coord. Chem.* **2000**, *51*, 115.
- Sheldrick, G.M., SHELXL97, University of Gottingen, Germany, **1997**.