



Synthesis, Crystal Structure and Luminescence Spectrum of a Binuclear Complex $[\text{Eu}_2(\text{HOC}_6\text{H}_4\text{CH}_2\text{COO})_6(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

HONG-XUN ZHANG, QUAN-YIN GUAN and GUO-LIANG ZHAO*

Xingzhi College, College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, P.R. China

*Corresponding author: Fax: +86 579 82282269; Tel: +86 579 82282061; E-mail: sky53@zjnu.cn

(Received: 29 February 2012;

Accepted: 7 January 2013)

AJC-12660

A binuclear complex $[\text{Eu}_2(\text{HOC}_6\text{H}_4\text{CH}_2\text{COO})_6(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**1**) was synthesized and characterized by X-ray diffraction single-crystal structure analysis. The synthesis was based on the reaction of *p*-hydroxyphenyl acetic acid, 4,4'-bipyridine and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in mixed solution of water and ethanol. The complex $\text{C}_{68}\text{H}_{64}\text{N}_4\text{O}_{21}\text{Eu}_2$, crystallizes in triclinic, space group Pn with $a = 1.17504(2)$ nm, $b = 1.62913(3)$ nm, $c = 1.84424(4)$ nm, $\alpha = 83.599(1)^\circ$, $\beta = 72.054(1)^\circ$, $\gamma = 71.038(1)^\circ$, $V = 3.17614(11)$ nm³, $M_r = 1577.15$, $\mu(\text{MoK}\alpha) = 2.039$ mm⁻¹, $D_c = 1.649$ g/cm³, $F(000) = 1588$, $Z = 2$, the final $R = 0.0255$, $wR = 0.0599$ for 11865 observed reflections [$I > 2\sigma(I)$]. Each Eu(III) atom is in a distorted monomeric square-antiprismatic environment, surrounded by eight oxygen atoms from carboxyl and water molecules, one nitrogen atom from 4,4'-bipyridine. The occurrence of numerous O-H...O involving coordinated and non-coordinated water molecules build up an intricate three dimensional network.

Key Words: Europium complex, *p*-Hydroxyphenylacetic acid, Crystal structure, Luminescence spectrum.

INTRODUCTION

There is great interest in the design and synthesis of coordination polymers in supramolecule and materials chemistry, due to their intriguing network topologies and promising applications in fields such as fluorescence, molecular magnets, optoelectronic devices, sensors and so on¹⁻⁴. By choosing appropriate metal ions and versatile bridging organic ligands, numerous 1D⁵, 2D⁶ and 3D⁷ coordination polymers have been synthesized so far.

In general, the architectures of such supramolecule networks are built-up using multidentate organic ligands containing O- and N- donors, such as polyacid with suitable spacers and 4,4'-bipyridine, to link metal centers to form polymeric structures⁸. It is well known that the coordination ability of aromatic carboxylic acids towards rare earth complexes has received considerable attention because of the strong coordination ability and varieties of the bridging modes of the carboxylate group with regard to the formation of extended frameworks^{9,10}. Considering the high coordination number of lanthanide ions, ancillary ligands can be employed to occupy some coordination sites and prevent the interpenetration of frameworks. 4,4'-Bipyridine (4,4'-bpy) is a neutral linear bifunctional ligand, widely used as an excellent spacer in the construction of metal coordination polymers carboxylates¹¹⁻¹⁶. In this paper, we have synthesized a new compound, $[\text{Eu}_2(\text{HOC}_6\text{H}_4\text{CH}_2\text{COO})_6(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

All reagents were of analytical grade quality and were used without further purification. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The FTIR spectra were obtained from KBr pellets in the range 4000–400 cm⁻¹ with a Nicolet NEXUS 670 FTIR spectrometer. Diffraction data were collected at 296(2) K on a Bruker APEXII CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm).

Synthesis of the complex: *p*-Hydroxyphenyl acetic acid (HPAA) (0.456 g, 3 mmol) and sodium hydroxide (0.12 g, 3 mmol) were mixed together in water (20 mL), then $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.446 g, 1 mmol) dissolved in water (10 mL) was added into the above solution, after stirred for an hour, an ethanol (5 mL) solution of 4,4'-bipyridine (0.156 g, 1 mmol) was slowly dripped into the above solution with stirring for three hours. After filtration, the filtrate was allowed to stand at room temperature, colourless single crystals suitable for X-ray analysis were obtained after a week. Yield: 35 % based on metal. Anal. calcd. For $\text{C}_{68}\text{H}_{64}\text{N}_4\text{O}_{21}\text{Eu}_2$ (%): C, 51.78; H, 4.09; N, 3.55 %. Found: C, 51.37; H, 4.00; N, 3.45 %. IR (KBr, ν_{max} , cm⁻¹): 3412 (m), 2905 (m), 2850 (w), 1597 (s), 1541 (s), 1451 (s), 1411 (s), 1239 (s), 1137 (s), 1028 (s), 805 (m), 619 (m).

Crystal structure determination: A single crystal of the title complex with dimensions of 0.30 mm \times 0.19 mm \times 0.08 mm was selected and mounted on a glass fiber and collected

diffraction data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm). Structure was solved by direct methods using SHELXS-97¹⁷ and refined on the F² by full-matrix least-square method with SHELXL-97¹⁸. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined by using a riding mode. Experimental details for X-ray data collection are presented in Table-1, CCDC No. 859091 of **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic data centre.

TABLE-1
CRYSTALLOGRAPHIC DATA OF
[Eu₂(HOC₆H₄CH₂COO)₆(C₁₀H₈N₂)₂(H₂O)₂].H₂O

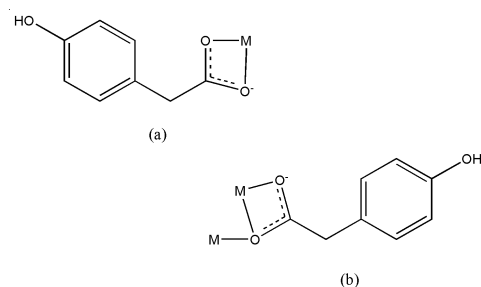
Formula	C ₆₈ H ₆₄ N ₄ O ₂₁ Eu ₂
Formula weight	1577.15
Temperature (K)	296(2)
Wavelength (nm)	0.071073
Crystal system,	Triclinic
Space group	Pn
a (nm)	1.17504(2)
b (nm)	1.62913(3)
c (nm)	1.84424(4)
α (°)	83.599(1)
β (°)	72.054(1)
γ (°)	71.038(1)
Volume (nm ³)	3.17614(11)
Z	2
Calculated density (g/cm ³)	1.649
Absorption coefficient (mm ⁻¹)	2.039
F(000)	1588
Crystal size (mm)	0.30 × 0.19 × 0.08
R(int)	0.032
Completeness (%)	99.2
Goodness-of-fit on F ²	0.98
Final R indices [I > 2 σ (I)]	R ₁ = 0.0255, wR ₂ = 0.0599
R indices (all data)	R ₁ = 0.0364, wR ₂ = 0.0658

RESULTS AND DISCUSSION

Structural description: The asymmetric unit of title compound [Eu₂(HOC₆H₄CH₂COO)₆(C₁₀H₈N₂)₂(H₂O)₂].H₂O consists of a binuclear unit, Eu³⁺ ion is coordinated with four hydroxyphenyl acetate ligands and a coordination water molecule. The structure of the present complex is similar to that of the Eu³⁺ complex of analogous ligands, namely [Eu₂(NDC)₃(H₂O)₂].H₂O¹⁹ and different from that of [Eu₂(NDC)₃(4,4'-bpy)_{0.5}(H₂O)₃].(4,4'-bpy)¹⁹, with each pair of Eu³⁺ ions are chelating bidentate by two hydroxyphenyl acetate anions and bridging tridentate by a hydroxyphenyl acetate carboxylate group. **Scheme-I** shows the coordination modes of the hydroxyphenyl acetate anion in complex **1**.

As illustrated in Fig. 1, the Eu³⁺ ion is nine coordinated in an distort monomeric square-antiprismatic geometry, being coordinated by seven oxygen atoms from four hydroxyphenyl acetate ligands, one coordination water molecule and one nitrogen atom from 4,4'-bipyridine. The cap is occupied by the chelating carboxy group oxygen atom O8. The atoms O10, O2, O7, O1w and O1, O4, O5, N3 constitute the upper bottom and lower base of square-antiprismatic respectively. The

carboxylate group in hydroxyphenyl acetate ligands adopt two coordination modes: bidentate chelating and bridging tridentate. The distance between Eu₁ and Eu₂ of binuclear unit is 0.4149 nm. The Eu-O bond lengths range from 0.2462(3)-0.2643(2)nm. The Eu-N distances range from 0.2674(3)-2.653(3)nm. The Eu-O(water) bond length is slightly shorter than the other Eu-O bond length, which are similar to those found in other europium complexes with similar coordination¹⁹.



Scheme-I: Coordination modes of hydroxyphenyl acetate ligand in the compound

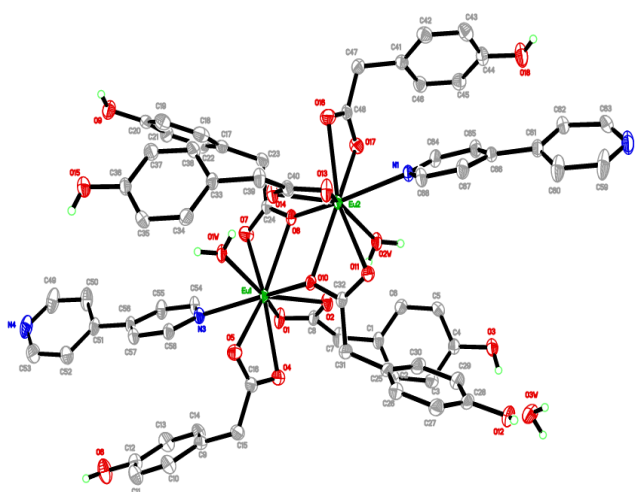


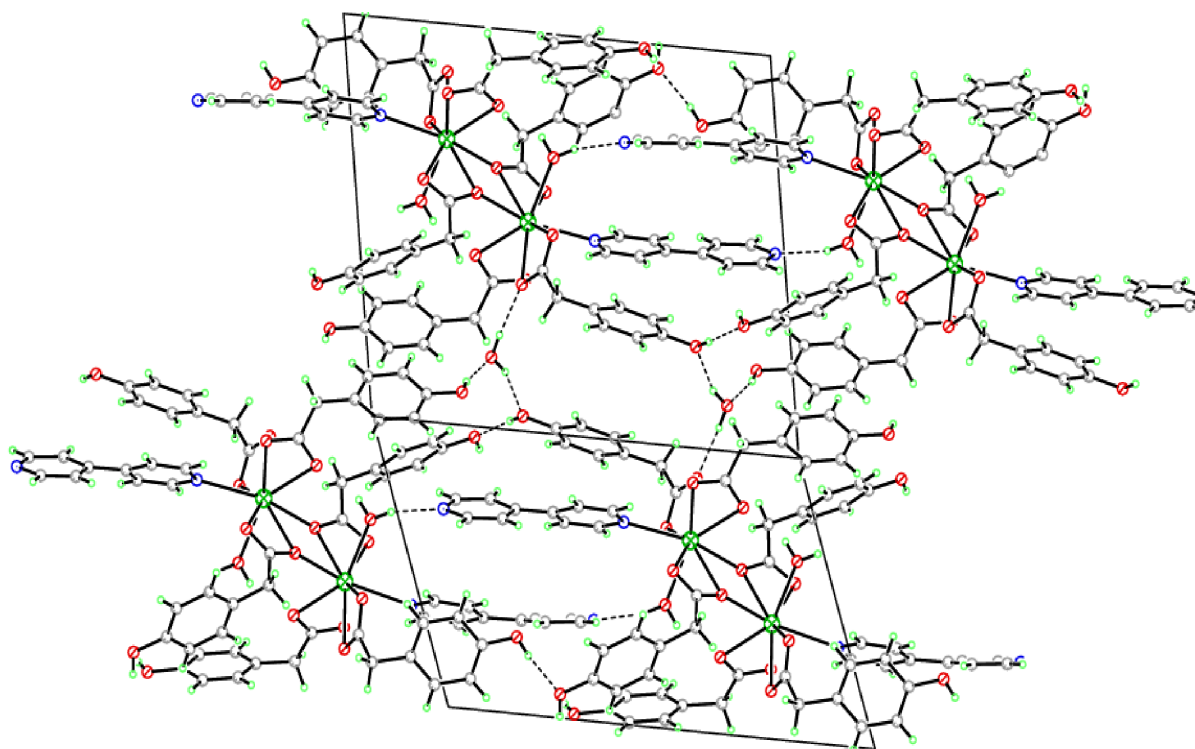
Fig. 1. Molecular structure of the [Eu₂(HOC₆H₄CH₂COO)₆(C₁₀H₈N₂)₂(H₂O)₂].H₂O (displacement ellipsoids are drawn at the 30 % probability level)

Herein, the water molecules are not only a hydrogen-bond acceptor but also proton donor. The coordinated water O1w and O2w involve in hydrogen bond to the oxygen atoms from carboxylate group and nitrogen atoms from 4,4'-bipyridine, the lattice water O3w make intermolecular hydrogen bond to the O3 (acceptor, \angle O-H...O = 160°) and share its hydrogen atoms with O6 [donor, \angle O-H...O = 161(4)°] and O4 [donor, \angle O-H...O = 176(4)°] (Table-2). In crystal, O-H...O and O-H...N hydrogen bonds link the molecules into a three dimensional network (Fig. 2).

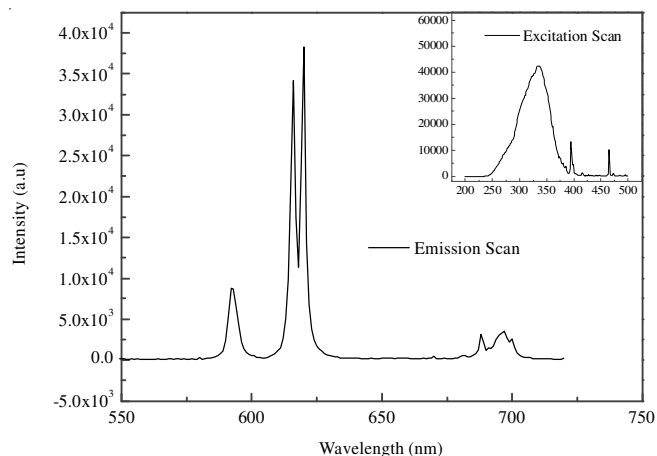
Luminescence property: The fluorescence spectrum of complex **1** at room temperature was studied using an excitation wavelength of 338 nm. Its photoluminescence spectra is given in Fig. 3. The main emission band is suppressed followed by the strong red luminescence, characteristics of the ⁵D₀→⁷F_J (J = 0, 1, 2, 3, 4) emission bands of the Eu³⁺ ion²⁰. The emission at 580, 591, 615(620), 688 and 697 nm corresponds to ⁵D₀→⁷F₀, ⁵D₀→⁷F₁, ⁵D₀→⁷F₂, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄ transitions, respectively. It has been observed that the emission band of

TABLE-2
 HYDROGEN BOND GEOMETRY FOR $[\text{Eu}_2(\text{HOC}_6\text{H}_4\text{CH}_2\text{COO})_6(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$

D-H...A	d(D-H)/ nm	d(H...A)/ nm	d(D-H...A)/ nm	$\angle\text{DHA}/^\circ$
O3—H3A...O3W	0.082	0.185	0.2639 (3)	160
O3—H3A...O3W	0.082	0.193	0.2743 (3)	173
O15—H15A...O3 ^{iv}	0.082	0.190	0.2721 (3)	174
O9—H9A...O16 ⁱⁱ	0.082	0.186	0.2674 (3)	173
O12—H12A...O11 ⁱⁱⁱ	0.082	0.194	0.2747 (3)	168
O18—H18A...O9 ^v	0.082	0.195	0.2765 (3)	174
O2W—H2WA...N4 ^v	0.0839(18)	0.2012 (18)	0.2839 (3)	169 (3)
O1W—H1WA...O14	0.082 (4)	0.1956 (19)	0.2753(2)	162 (4)
O1W—H1WB...N2 ⁱ	0.0814 (18)	0.200 (2)	0.2743 (3)	160 (4)
O9—H9A...O16 ⁱⁱ	0.083 (4)	0.201 (2)	0.2761 (3)	150 (3)
O3W—H3WA...O6 ^v	0.085 (4)	0.194	0.2747 (3)	168
O3W—H3WB...O4 ^{iv}	0.0842 (18)	0.1933 (18)	0.2774 (3)	176 (4)

 Symmetry codes: (i) $x, y-1, z$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+2, -y+2, -z$; (iv) $x+1, y-1, z$; (v) $x, y+1, z$; (vi) $-x+1, -y+2, -z$

 Fig. 2. Three dimensional supermolecular structure viewed along the c -axis formed through hydrogen bonding(dashed lines)

the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ peaks also give an idea about the coordination environment. For example, a $(2J + 1)$ splitting is observed in the emission band for a single type of environment (coordination environment and site symmetry) around the metal ion²¹. In the present case, only one very weak emission band has been observed in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ degenerate transition around 580 nm. This indicates that the Eu^{3+} ion occupies only one of the three crystallographic sites. The emission at 593 nm corresponds to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, which is induced by magnetic dipole moment and is fairly insensitive to the coordination environment²⁰. The emission at 620 nm corresponds to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, which is induced by the electric dipole moment and also sensitive to the environment. The intensity of $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$ is much stronger than $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$, which indicates a lower symmetry level of the coordination environment of the Eu^{3+} occupied site²¹.


 Fig. 3. Excitation and emission curves of $[\text{Eu}_2(\text{HOC}_6\text{H}_4\text{CH}_2\text{COO})_6(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$

REFERENCES

1. S. Surble, C. Serre, F. Millange, F. Pellé and G. Férey, *Solid State Sci.*, **7**, 1074 (2005).
2. S. Ferlay, T. Mallah, R. Ouahes, M. Verdaguer and P. Veillet, *Nature*, **378**, 701 (1995).
3. S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, **43**, 2334 (2004).
4. N.E. Leadbeater and M. Marco, *Chem. Rev.*, **102**, 3217 (2002).
5. L. Yi, X. Yang and P. Cheng, *Cryst. Growth Des.*, **5**, 1215 (2005).
6. K. Mitsurs, M. Shimamura and S.L. Noro, *Chem. Mater.*, **12**, 1288 (2000).
7. J.M. Sheng, *Asian J. Chem.*, **22**, 6622 (2010).
8. C.-B. Liu, C.-Y. Sun and L.-P. Jin, *New J. Chem.*, **28**, 1019 (2004).
9. Y. Li, F.-K. Zheng and X. Liu, *Inorg. Chem.*, **45**, 6308 (2006).
10. T. Fiedler, M. Hilder and P.C. Junk, *Eur. J. Inorg. Chem.*, 291 (2007).
11. Y. Rodriguez-Martin, C. Ruiz-Perez, J. Sanchiz, F. Lloret and M. Julve, *Inorg. Chim. Acta*, **318**, 159 (2001).
12. J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C.-L. Lin and X.-Y. Huang, *J. Li. Chem. Commun.*, 1342 (2002).
13. S. Dalai, P.S. Mukherjee, E. Zangrando, F. Lloret and N.R. Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 822 (2002).
14. R. Carballo, A. Castineiras, B. Covelos and E.M. Vazquez-Lopez, *Polyhedron*, **20**, 899 (2001).
15. K. Seki, *Phys. Chem. Chem. Phys.*, **4**, 1968 (2002).
16. X.J. Zheng, L. Li C, S. Gao and L.P. Jin, *Polyhedron*, **23**, 1257 (2003).
17. G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany (1997).
18. G.M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany (1997).
19. X.-J. Zhang, L.-P. Jin, S. Gao and S.-Z. Lu, *New J. Chem.*, **29**, 798 (2005).
20. N. Sabbatini, M. Guardigli and J.M. Lehn, *Coord. Chem. Rev.*, **123**, 201 (1993).
21. A. Thirumurugan and S. Natarajan, *J. Mater. Chem.*, **15**, 4588 (2005).