Synthesis and Fluorescent and Magnetic Properties of a New Europium Complex $Eu(C_{20}H_{14}O_3N)_3(2,2'\text{-bipy})(H_2O)\cdot H_2O$①

YANG Ying-Qun[a, b②] KUANG Yun-Fei[a, b②] ZHU Xiao-Ming[a, b②]

[a] (*Key Laboratory of Functional Metal-organic Compounds of Hunan Province & Key Laboratory of Functional Organometallic Materials of Hunan Province College, Hengyang* 421008, *China*)

[b] (*Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang* 421008, *China*)

ABSTRACT A new europium(Ⅲ) complex $Eu(C_{20}H_{14}O_3N)_3(2,2'\text{-bipy})(H_2O)\cdot H_2O$ has been synthesized with 2-diphenylanine carbonyl benzoic acid and 2,2′-bipyridine as ligands. Crystal data for the complex are as follows: triclinic, space group $P\bar{1}$, a = 11.3334(5), b = 16.0883(7), c = 17.0116(8) Å, α = 70.411(4)º, β = 82.435(4)º, γ = 85.095(4)º, V = 2894.0(2) Å^3, D_c = 1.484 g/cm^3, Z = 2, μ = 1.15 mm^{-1}, F(000) = 1320 and the final R = 0.0447 and wR = 0.0578. The Eu(Ⅲ) ion is coordinated by nine atoms to give a monocapped square antiprism coordination geometry. The complex shows two intense fluorescence emission bands arising from the transitions of Eu^{3+}: $^5D_0 \rightarrow {}^7F_1$ (592 nm) and $^5D_0 \rightarrow {}^7F_2$ (616 nm), respectively. Also reported is the magnetic property of the complex. The complex exhibits antiferromagnetism in the temperature range of 300～2 K.

Keywords: europium(Ⅲ) complex, crystal structure, fluorescent and magnetic properties;

DOI: 10.14102/j.cnki.0254–5861.2011–2969

1 INTRODUCTION

Although the high and variable coordination numbers and flexible coordination environments of lanthanide ions make it difficult to control the reactions and the final structures of lanthanide complexes, the lanthanide organic frameworks have good optical, electrical and magnetic properties such as high color purity, long fluorescence lifetime, high efficiency of light conversion and wide emission spectrum wavelength distribution, and the design of novel lanthanide organic frameworks has attracted much attention in the field of crystal engineering[1-9]. It is well known that the aromatic carboxylic acid ligands play an important role in constructing novel and stable lanthanide organic frameworks mainly because of the versatile ligating abilities of -COO moieties including bidentate-chelating, bidentate-bridging or chelating-bridging modes, and also due to the enhanced affinity of lanthanide ions towards such O donors, which allows the formation of clusters, cage structures or open frameworks[10-15]. Among diverse aromatic carboxylic acid ligands, 2-diphenylanine carbonyl benzoic acid and its derivatives can be widely used as multidentate ligands to synthesize various complexes, such as $Tb(HDPAB)_3IP$[16] and $C_{32}H_{25}NO_3Sn\ C_7H_8$[17]. With the aim of proceeding previous jobs[18], we report herein a new lanthanide complex $Eu(C_{20}H_{14}O_3N)_3(2,2'\text{-bipy})(H_2O)\cdot H_2O$ based on 2-diphenylanine carbonyl benzoic acid. The complex shows two intense fluorescence emission bands arising from the transitions of Eu^{3+}: $^5D_0 \rightarrow {}^7F_1$ (592 nm) and $^5D_0 \rightarrow {}^7F_2$ (616 nm), respectively. In the temperature range of 300～2 K, the complex exhibits antiferromagnetism.

2 EXPERIMENTAL

2. 1 Reagents and instruments

The reagents were obtained from commercial sources and used without further purification. C, H and N analyses were conducted with a PE-2400(II) apparatus. A fluorescence spectrum was obtained at room temperature on a HORIBA QuantaMaster 8000 fluorescence spectrophotometer. Magnetic measurements in the range of 300～2 K were performed

Received 24 August 2020; accepted 10 October 2020 (**CCDC 1848487**)

① This project was supported by the Foundation of Key Laboratory of Functional Metal-organic Compounds of Hunan Province (MO20K05), and the Foundation of Key Laboratory of Functional Organometallic Materials, University of Hunan Province

② Corresponding authors. E-mail: yingqunyq@163.com or zxmhnhy@163.com.

Yang Ying-Qun and Kuang Yun-Fei made equal contributions to this work

on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode (1 kOe = 7.96×10^4 A·m^{-1}).

2. 2 Synthesis of the complex

A mixture of 2,2′-bipyridine (0.25 mmol) and europium(Ⅲ) nitrate hexahydrate (0.10 mmol) was dissolved in 9 mL mixed solvent of ethanol and water (volume ratio 2:7), and heated under a water-bath at 323 K for 0.5 h. The solution was poured into a glass test-tube. Then 5 mL ethanol solution with pH 5～6 containing sodium hydroxide and 2-diphenylanine carbonyl benzoic acid (0.15 mmol) was added to this test-tube which was covered with plastic film. The mixture was put at room temperature for slow diffusion. Colorless single crystals suitable for X-ray diffraction analysis were obtained after three weeks. Yield: 30.2%. Anal. Calcd. (%) for $C_{70}H_{54}EuN_5O_{11}$: C, 65.01; H, 4.21; N, 5.41. Found (%): C, 64.94; H, 4.20; N, 5.40. IR(ν/cm^{-1}): 1649(vs), 1589(vs), 1551(s), 1489(s), 769(m), 700(m), 619 (w), 542 (w), 442 (w), 420 (w).

2. 3 Structure determination and refinement

The X-ray diffraction measurement for the complex was carried out on a Bruker SMART APEX CCD area detector at 100.00(10) K by using graphite-monochromatized Mo$K\alpha$ (λ = 0.71073 Å) radiation. The structure was solved by direct methods and refined by full-matrix least-squares with the SHELXL-2015 program package[19]. Corrections for *Lp* factors and empirical adsorption adjustment were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to R = 0.0447 and wR = 0.0578 ($w = 1/[\sigma^2(F_o^2) + (0.0078P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{max} = 0.002$ and S = 0.959.

3 RESULTS AND DISCUSSION

3. 1 Structural description

Fig. 1 shows the molecular structure of the complex and the coordination polyhedron for the central Eu(III) ion. Selected bond lengths and bond angles are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of the Complex

Bond	Dist.	Bond	Dist.	Bond	Dist.
Eu(1)–O(1)	2.459(2)	Eu(1)–O(5)	2.525(3)	Eu(1)–O(10)	2.487(3)
Eu(1)–O(2)	2.457(2)	Eu(1)–O(7)	2.449(3)	Eu(1)–N(1)	2.554(3)
Eu(1)–O(4)	2.379(3)	Eu(1)–O(8)	2.454(2)	Eu(1)–N(2)	2.527(3)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Eu(1)–O(5)	142.14(9)	O(4)–Eu(1)–O(7)	78.23(9)	O(7)–Eu(1)–N(1)	153.73(9)
O(1)–Eu(1)–O(10)	65.21(9)	O(4)–Eu(1)–O(8)	93.60(9)	O(7)–Eu(1)–N(2)	141.17(10)
O(1)–Eu(1) –N(1)	70.96(10)	O(4)–Eu(1)–O(10)	152.70(9)	O(8)–Eu(1)–O(1)	137.69(9)
O(1)–Eu(1)–N(2)	79.39(9)	O(4)–Eu(1)–N(1)	78.39(10)	O(8)–Eu(1)–O(2)	135.61(9)
O(2)–Eu(1)–O(1)	53.45(8)	O(4)–Eu(1)–N(2)	124.61(10)	O(8)–Eu(1)–O(5)	71.78(9)
O(2)–Eu(1)–O(5)	128.80(9)	O(5)–Eu(1)–N(1)	72.35(9)	O(8)–Eu(1)–O(10)	72.56(9)
O(2)–Eu(1)–O(10)	94.38(9)	O(5)–Eu(1)–N(2)	76.48(9)	O(8)–Eu(1)–N(1)	140.19(9)
O(2)–Eu(1)–N(1)	81.59(9)	O(7)–Eu(1)–O(1)	114.51(9)	O(8)–Eu(1)–N(2)	91.20(9)
O(2)–Eu(1)–N(2)	129.06(9)	O(7)–Eu(1)–O(2)	82.35(8)	O(10)–Eu(1)–O(5)	136.43(8)
O(4)–Eu(1)–O(1)	125.72(8)	O(7)–Eu(1)–O(5)	102.53(8)	O(10)–Eu(1)–N(1)	127.24(9)
O(4)–Eu(1)–O(2)	78.99(8)	O(7)–Eu(1)–O(8)	53.40(8)	O(10)–Eu(1)–N(2)	80.08(10)
O(4)–Eu(1)–O(5)	53.36(8)	O(7)–Eu(1)–O(10)	74.63(9)	N(2)–Eu(1)–N(1)	63.96(10) .

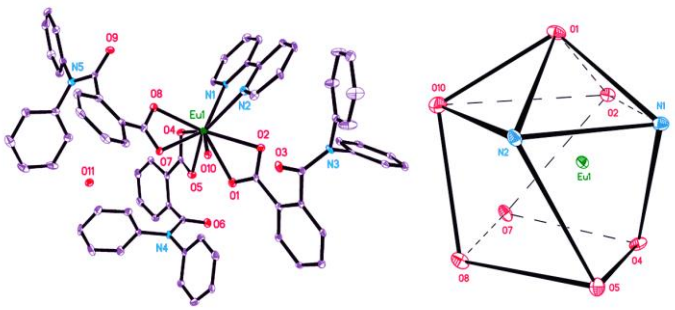

Fig. 1. Molecular structure of the title complex and the coordination polyhedron for the Eu(III) ion at 30% displacement ellipsoids

As shown in Fig. 1, the complex consists of one central Eu(III) ion, three 2-diphenylanine carbonyl benzoic acid anions, one 2,2′-bipyridine molecule and two water molecules. Eu(III) ion is coordinated by seven oxygen atoms from three 2-diphenylanine carbonyl benzoic acid anions and one water molecule, respectively, and two nitrogen atoms from one 2,2′-bipyridine molecule. The central Eu(III) ion adopts a distorted monocapped square antiprism coordination geometry. In the coordination polyhedron (EuN_2O_7), the cap position is occupied by O(1) atom. Atoms N(1), N(2), O(10) and O(2) give the upper plane of the square antiprism, and atoms O(8), O(5), O(4) and O(7) determine the plane below. Their plane equations are $2.800x + 15.838y + 6.925z = 14.5218$ and $3.235x + 15.747y + 5.430z = 16.0981$, respectively. The dihedral angle of the two planes is 6.0°. The O–Eu–O angles are between 53.36(8) and 152.70(9)°, and the N–Eu–O angles range from 70.96(10) to 153.73(9)°. The Eu–O bond lengths change from 2.379(3) to 2.525(3) Å, and their average is 2.459 Å, which falls in the normal range[20].

Compared with $Tb(HDPAB)_3IP$[16] synthesized by the same ligand 2-diphenyl carbonyl benzoic acid, the title complex with water molecules contains extensive hydrogen bonds, which is conducive to the stability of the complex. The bond lengths of O(10)–H(10A)···O(1), O(10)–H(10A)···O(3), O(10)–H(10B)···O(11), O(11)–H(11A)···O(9) and O(11)–H(11B)···O(9) are 2.665(5), 3.315(4), 2.695(4), 2.898(4) and 2.784(4) Å, respectively. Their bond angles are 102, 145, 142, 174 and 147°, respectively. In addition, π-π stacking interaction can be observed between adjacent 2,2′-bipy molecules in the title complex, and the shortest centroid-to-centroid distance is 3.495 Å (Fig. 2).

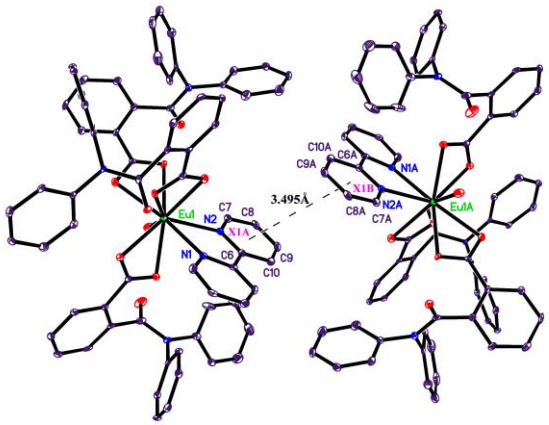

Fig. 2. π-π stacking of the neighboring molecules

3. 2 Fluorescent property

The complex and 2-diphenylanine carbonyl benzoic acid ligand were dissolved in a mixture of ethanol and water (volume ratio of 5:1), respectively. The fluorescent properties of these two solutions were measured at room temperature in the range of 357～675 nm. The emission spectra of the complex and 2-diphenylamine carbonyl benzoic acid ligand are shown in Fig. 3. As shown in Fig. 3, under 349 nm excitation, 2-diphenylamine carbonyl benzoic acid ligand shows one wide fluorescence emission band in the range of 360 to 395 nm. When the excitation wavelength is 396 nm, the complex shows two intense fluorescence emission bands at 592 and 616 nm, corresponding to the transitions of Eu^{3+}: $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively. They are the characteristic fluorescence peaks of Eu(Ⅲ) ion, and the fluorescence is stronger at 616 nm.

3. 3 Magnetic properties

The magnetic susceptibility of the complex was investigated in the temperature range of 300～2 K with an applied magnetic field of 2 kOe. The temperature dependence of the molar magnetic susceptibility of the complex is revealed in Fig. 4 in the forms of X_mT and $1/X_m$ *vs.* T. The product of X_mT is 1.13666 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K. Upon cooling, the X_mT gradually decreases to the corresponding product of 0.01733 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. In addition, as shown in Fig. 4, in the temperature range of 300～150 K, the data are in linear relationship in the form of $1/X_m$ *vs.* T. The linear regression equation is $1/X_m = 0.419T + 134.18$, and the correlation coefficient is 0.9907. According to the Curie-Weiss law, $X_m = C/(T - \theta)$, the Weiss constant (θ) can be obtained as negative value. Such magnetic behavior indicates that the title complex is an antiferromagnetism system at low temperature[21].

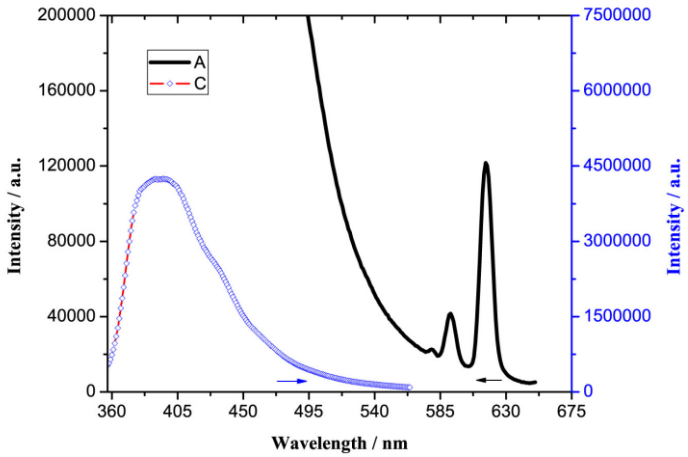

Fig. 3. Both excitation and emission spectra of the complex at room temperature

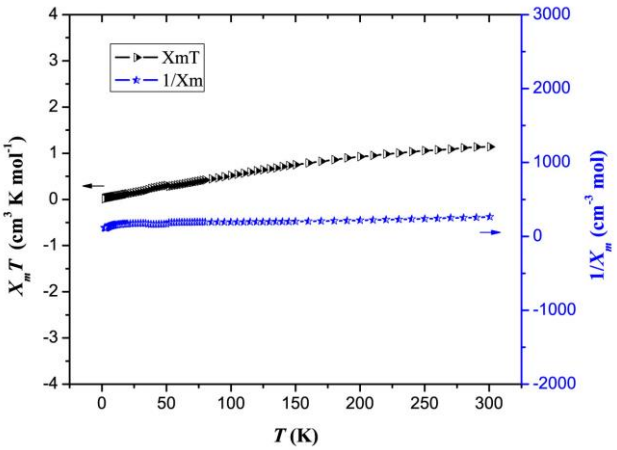

Fig. 4. Temperature dependence of the magnetic susceptibility of the complex in the form of X_mT and $1/X_m$ *vs*. T

REFERENCES

(1) Ghandour, Y.; Mestiri, I.; Belkhiria, M. S. Synthesis, crystal structure, electrochemical and catalytic properties of hybrid polyoxomolybdate clusters-based terbium complex. *J. Inorg. Organomet. Polym.* **2017**, 27, 685–691.

(2) Gándara, F.; Andrés, A.; Gómez-Lor, B.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Proserpio, D. M.; Snejko, N. A rare-earth MOF series: fascinating structure, efficient light emitters, and promising catalysts. *Cryst. Growth Des.* **2008**, 8, 378–380.

(3) Aillaud, I.; Collin, J.; Duhayon, C.; Guillot, R.; Lyubov, D.; Schulz, E.; Trifonov, A. New chiral lanthanide amide ate complexes for the catalysed-synthesis of scalemic nitrogen-containing heterocycles. *Chem. Eur. J.* **2008**, 14, 2189–2200.

(4) Zhang, Z. H.; Okamura, T.; Hasegawa, Y.; Kawaguchi, H.; Kong, L. Y.; Sun, W. Y.; Ueyama, N. Syntheses, structures, and luminescent and magnetic properties of novel three-dimensional lanthanide complexes with 1,3,5-benzenetriacetate. *Inorg. Chem.* **2005**, 44, 6219–6227.

(5) Lu, D.; Tang, Y. P.; Zheng, Y. H. Fluorescence sensing behavior for the detection of alcoholic strength and water based on two novel metallic complex edifices. *J. Fluores.* **2018**, 28, 1269–1273.

(6) Chen, M. H.; Zheng, Y. H.; Gao, J. W.; Li, C.; Yu, C. F.; Wang, Q. M. Fluorometric determination of dopamine by using a terbium(III) inorganic-organic network. *Microchim Acta* **2017**, 184, 2275–2280.

(7) Zhang, C. V.; Luo, J. X.; Li, W. J.; Ou, L. J. Preparation and sensing properties of covalent-linked europium complex monodisperse polystyrene microspheres. *Chem. J. Chin. U.* **2019**, 40, 153–159.

(8) Schnable, D.; Freedman, K.; Ayers, K. M.; Schley, N. D.; Kol, M.; Ung, G. Synthesis of enantiopure lanthanide complexes supported by hexadentate N,N′-bis(methylbipyridyl)bipyrrolidine and their circularly polarized luminescence. *Inorg. Chem.* **2020**, 59, 8498–8504.

(9) Santos, M. C. D.; Runser, A.; Bartenlian, H.; Nonat, A. M.; Charbonnière, L. J.; Klymchenko, A. S.; Hildebrandt, N.; Reisch, A. Lanthanide-complex-loaded polymer nanoparticles for background-free single-particle and live-cell imaging. *Chem. Mater.* **2019**, 31, 4034–4041.

(10) Li, D. P.; Feng, Y. L.; Chen, Z. M.; Kuang, D. Z.; Zhang, C. H.; Yang, Y. Q.; Li, W. Synthesis, crystal structure of a binuclear terbium complex with 2,4,6-trimethylbenzoic acid and 1,10-phenanthroline. *Chin. J. Inorg. Chem*. **2006**, 22, 2097−2100.

(11) Wei, C.; Sun, B. X.; Zhao, Z. F.; Cai, Z. L.; Liu, J. J.; Tan, Y.; Wei, H. B.; Liu, Z. W.; Bian, Z. Q.; Huang, C. H. A family of highly emissive lanthanide complexes constructed with 6-(diphenylphosphoryl)picolinate. *Inorg. Chem.* **2020**, 59, 8800–8808.

(12) Liu, M. S.; Yu, Q. Y.; Cai, Y. P.; Su, C. Y.; Lin, X. M.; Zhou, X. X.; Cai, J. W. One-, two-, and three-dimensional lanthanide complexes constructed from pyridine-2,6-dicarboxylic acid and oxalic acid ligands. *Cryst. Growth Des*. **2008**, 8, 4083–4091.

(13) Lei, Q.; Liu, Q. Y.; Wang, Y. L. Two three-dimensional terbium-1,4-benzenedicarboxylate coordination polymers: syntheses, structures, and luminescence. *Chin. J. Struct. Chem.* **2016**, 35, 566−576.

(14) Shen, P. P.; Ren, N.; Zhang, J. J.; Geng, L. N.; Wang, S. P.; Shi, S. K. Crystal structures, luminescent and thermal properties of lanthanide complexes with 3,4-dimethylbenzoic acid and 2,2′ -bipyridine. *J. Therm. Anal. Calorim.* **2018**, 131, 1699−1707.

(15) Tao, P.; Zeng, C. H.; Zheng, K.; Huang, C. Q.; Zhong, S. L. Uniform terbium coordination polymer microspheres: preparation and luminescence. *J. Inorg. Organomet Polym*. **2016**, 26, 1087−1094.

(16) Ren, X. M.; Wei, C. P.; Lu, Z. J. Synthesis and photoluminescence of novel terbium(III) ternary complexes with carboxylic acid. *Spectrosc. Spect. Anal*. **2011**, 31, 436−439.

(17) Xiao, X.; Han, X.; Mei, Z. M.; Zhu, D. S.; Shao, K. Z.; Liang, J. W.; Tian, M.; Xu, L. Organotin(IV) carboxylates based on amide carboxylic acids: syntheses, crystal structures and characterizations. *J. Organomet. Chem*. **2013**, 729, 28−39.

(18) Yang, Y. Q.; Yang, Y.; Li, J. D.; Li, W. Synthesis, fluorescent, magnetic and thermal stability properties of a new terbium(III) complex $Tb(C_{20}H_{14}O_3N)_3(C_{12}H_8N_2)(H_2O)\cdot H_2O$. *Chin. J. Struct. Chem.* **2019**, 38, 2129−2134.

(19) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, 71, 3−8.

(20) Wang, L.; Shen, Z.; Lan, Q.; Luo, B. M.; Yang, H.; Zhao, Q. Structure and luminescence of carboxylic acid samarium and europium complexes. *Chin. J. Struct. Chem*. **2019**, 38, 1182−1187.

(21) Li, D. P.; Wang, Q.; Xie, Y. B.; Zhang, J.; Lian, Q. Y.; Li, Y. X. Mononuclear Dy(III) and Ho(III) complexes with slow magnetic relaxation behavior. *Chin. J. Inorg. Chem*. **2018**, 34, 1547−1554.