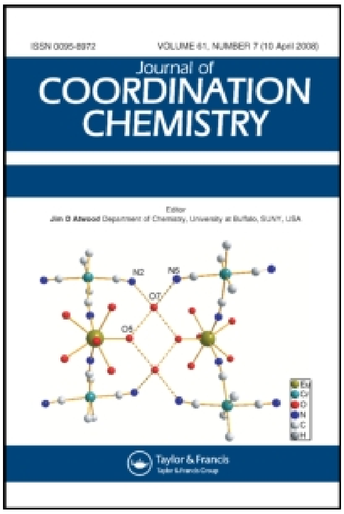

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A COMPLEX OF EUROPIUM PERCHLORATE WITH METHYLENE BIS(DIPHENYLPHOSPHINE OXIDE)

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A COMPLEX OF EUROPIUM PERCHLORATE WITH METHYLENE BIS(DIPHENYLPHOSPHINE OXIDE)*

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A complex of europium perchlorate with methylene bis(diphenylphosphine oxide) (HMPPO), $[Eu(HMPPO)_4](ClO_4)_3 \cdot 2H_2O$ has been synthesized and characterized by X-ray crystallography, infrared spectroscopy and thermal analysis. The X-ray structure of the complex shows Eu(III) is coordinated by eight oxygen atoms from four HMPPO ligands, forming a distorted square antiprism coordination geometry. The complex crystallizes in space group *P*-1 with cell parameters $a = 15.807(3)$, $b = 17.868(4)$, $c = 20.656(4)$ Å, $\alpha = 86.85(3)^\circ$, $\beta = 82.33(3)^\circ$, $\gamma = 66.75(3)^\circ$. The final R_f and R_w are 0.0803 and 0.1994, respectively, for 9540 observed reflections [$I > 2\sigma(I)$]. Its luminescent properties have also been studied.

Keywords: Europium; Methylene bis(diphenylphosphine oxide); Crystal structure; Absorption spectrum; Fluorescence properties

INTRODUCTION

One of the important applications of rare earth complexes is in the development of the luminescent materials because some of them exhibit

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sharp emission in the visible range, high quantum yields and long-lived emission [1,2]. For example, europium ion has been examined due to its pure red emission. At present, it is accepted that, after an efficient intersystem crossing from the lowest singlet to the triplet excited states of the ligand, energy transfers to a lower energy state of the rare earth ion. The atomic line emission of the rare earth ion is observed. Therefore, it is key to design the ligand containing the light-harvest group to collect light and to transfer the energy to the poorly absorbing rare earth ion. Numerous europium (III) complexes with β-diketones have been widely studied, as well as rare earth complexes with ligands containing P=O such as β-ketophosphine oxides and tetraphenylimidodiphosphinates [3-10]. We chose $Ph_2P(O)CH_2P(O)Ph_2$ (HMPPO) as the ligand since it is analogous to β-diketones but has twice as many aryl units to collect light. Recently, our group reported that it could also be used as an anionic ligand. In that case the complex of $Eu(TTA)(MPPO)(NO_3)(HMPPO)(H_2O)_2$ was obtained(TTA: thenoyltrifluoroacetone) at a high pH. Unfortunately, the single crystal of the complex was not good enough for X-ray diffraction analysis [5]. In this paper, mixing europium perchlorate with HMPPO at the same high pH, a europium complex $[Eu(HMPPO)_4](ClO_4)_3 \cdot 2H_2O$ was obtained. X-ray crystallography, infrared spectroscopy and thermal analysis are used to characterize its structure. Its luminescent properties have been studied, showing the complex has a long emission lifetime which contributes to four HMPPO ligands coordinating with Eu(III) and forming a shell to protect Eu(III) from quenching by the water molecules.

EXPERIMENTAL

The IR spectrum in the 400-4000 cm^{-1} range (as KBr pellets) was recorded on a Nicolet Magna-IR 750 model spectrometer. Thermogravimetric and differential thermal analysis in an N_2 atmosphere was carried out on a DuPont 951 system. An electronic spectrum in acetonitrile solution was recorded with a Shimadzu UV-3100 spectrophotometer in the range of 200-400 nm. A luminescence spectrum was recorded on a Hitachi F4500 Fluorescence Spectrophotometer at room temperature. Fluorescence lifetime measurements were performed on an SLM 48000 multiple frequency spectrofluorometer.

$Eu(HMPPO)_4(ClO_4)_3(H_2O)_2$

HMPPO was synthesized according to the literature procedure [12]. Anal. Calcd. for $C_{25}H_{22}O_2P_2$(%): C, 72.11; H, 5.33. Found: C, 72.12; H, 5.47. The

HMPPO was also identified by its ^{1}HNMR spectrum. Europium perchlorate (0.2 mmol) aqueous solution was added dropwise to an ethanol solution (20 ml) of HMPPO(0.4 mmol) and NaOH (0.4 mmol). The mixture was stirred at 70–80°C for 6 hours. The resulting solid was filtered off, dried and recrystallized from hot ethanol to give colorless single crystals. Anal. Calcd. for $C_{100}H_{92}Cl_3EuO_{22}P_8$(%): C, 55.82; H, 4.31. Found: C, 55.60; H, 3.97.

Crystal Structure Determination and Refinement

A crystal with dimensionality $0.21 \times 0.11 \times 0.07\,mm^3$ was mounted on a PC Rigaku diffractometer. Data collections were performed with MoK_α graphite-monochromated radiation ($\lambda = 0.71073$ Å) at 293 K. A total of 12108 independent reflections were collected in the range of $0.99° \leq \theta \leq 25.00°$, of which 9540 observed reflections [$I > 2\sigma(I)$] were used for structural refinement. The structure was solved by direct method (SHELXS 97) [14] and refined by full-matrix least squares method based on F^2. Hydrogen atoms were added in calculated positions and hydrogen atoms of water molecules were not found from difference election density map. Oxygen atoms of perchlorate anions were refined isotropically with the same free variables while other non-hydrogen atoms were refined anisotropically are refined. The residual electron density varied from -1.130 to $0.917\,Å^{-3}$. The largest shift on final cycles is 0.003. The final R_l and R_w are 0.0803 and 0.1994, respectively.

Crystal data, $C_{100}H_{92}Cl_3EuO_{22}P_8$:, space group P-1, triclinic, $a = 15.807(3)$, $b = 17.868(4)$, $c = 20.656(4)$ Å, $\alpha = 86.85(3)°$, $\beta = 82.33(3)°$, $\gamma = 66.75(3)°$, $V = 5312.3(18)\,Å^3$, $M = 2151.81$, $Dx = 1.345\,Mg/m^3$, $u = 0.852\,mm^{-1}$, $F(000) = 2204$, $Z = 2$, GOF = 1.020.

RESULTS AND DISCUSSION

Description of the Structure

Selected bond lengths (Å) and angles (°) for the complex are listed in Table I. In the complex, the Eu—O bond distances range from 2.404(7) to 2.528(7) Å with an average of 2.444(6) Å, longer than that of europium (III) complexes with β-diketones(2.39 Å)^3 and the sum of the ionic radius of 2.42 Å (eight-coordinated Eu^{3+} 1.07 Å and effective ionic radius of O^{2-} 1.35 Å). This may result from the bulkiness of four HMPPO ligands with sixteen phenyl groups which form a cage around the europium ion. Compared with the rare earth complexes with ligands containing P=O, the four additional phenyl

TABLE I Selected bond lengths (Å) and angles (°) for the title complex

Eu(1)-O(5)	2.404(7)	Eu(1)-O(3)	2.413(6)
Eu(1)-O(7)	2.416(7)	Eu(1)-O(8)	2.436(6)
Eu(1)-O(1)	2.441(7)	Eu(1)-O(2)	2.443(6)
Eu(1)-O(4)	2.468(6)	Eu(1)-O(6)	2.528(7)
P(1)-O(1)	1.494(7)	P(2)-O(2)	1.488(7)
P(3)-O(3)	1.505(7)	P(4)-O(4)	1.501(7)
P(5)-O(5)	1.494(8)	P(6)-O(6)	1.508(7)
P(7)-O(7)	1.510(7)	P(8)-O(8)	1.505(7)
O(5)-Eu(1)-O(3)	99.3(2)	O(5)-Eu(1)-O(7)	136.0(2)
O(3)-Eu(1)-O(7)	100.0(3)	O(5)-Eu(1)-O(8)	76.1(2)
O(3)-Eu(1)-O(8)	70.5(2)	O(7)-Eu(1)-O(8)	73.7(2)
O(5)-Eu(1)-O(1)	151.9(2)	O(3)-Eu(1)-O(1)	73.3(2)
O(7)-Eu(1)-O(1)	72.0(2)	O(8)-Eu(1)-O(1)	123.8(2)
O(5)-Eu(1)-O(2)	95.8(3)	O(3)-Eu(1)-O(2)	135.6(2)
O(7)-Eu(1)-O(2)	97.4(2)	O(8)-Eu(1)-O(2)	153.9(2)
O(1)-Eu(1)-O(2)	73.9(2)	O(5)-Eu(1)-O(4)	71.0(2)
O(3)-Eu(1)-O(4)	72.4(2)	O(7)-Eu(1)-O(4)	152.9(2)
O(8)-Eu(1)-O(4)	124.6(2)	O(1)-Eu(1)-O(4)	80.9(2)
O(2)-Eu(1)-O(4)	73.6(2)	O(5)-Eu(1)-O(6)	71.8(2)
O(3)-Eu(1)-O(6)	150.7(2)	O(7)-Eu(1)-O(6)	72.0(2)
O(8)-Eu(1)-O(6)	80.2(2)	O(1)-Eu(1)-O(6)	127.1(2)
O(2)-Eu(1)-O(6)	73.7(2)	O(4)-Eu(1)-O(6)	126.8(2)
P(1)-O(1)-Eu(1)	145.3(4)	P(2)-O(2)-Eu(1)	141.9(4)
P(3)-O(3)-Eu(1)	147.0(4)	P(4)-O(4)-Eu(1)	146.1(4)
P(5)-O(5)-Eu(1)	147.5(4)	P(6)-O(6)-Eu(1)	144.4(4)
P(7)-O(7)-Eu(1)	144.1(4)	P(8)-O(8)-Eu(1)	146.4(4)

groups contribute to the fact that the P—O bond distance of the titled complex (1.501 Å) is longer than that of the complex $Ce(NO_3)_3[Ph_2P(O)CH_2C(O)Ph]$ with the bidentate ligand (1.493 Å) [11]. Figure 1 shows the structure and labeling scheme of the title complex. Figure 2 shows the arrangement of the coordinated oxygen atoms surrounding the europium atom. Each europium (III) ion is coordinated by the eight oxygen atoms from four bidentate neutral HMPPO ligands, yielding a distorted square antiprism configuration, in which the dihedral angle between the top and bottom planes defining the O(1), O(3), O(7), O(8) and O(2), O(4), O(5), O(6) respectively is 0.86°. Although the deviations of the atoms from the planes are large, the polyhedron cannot be described as dodecahedral or bi-capped triangular prism [15].

Thermal Analysis and IR Spectrum

The TG and DTA curves of the complex show that the water molecules are easily dissociated from the complex at 40°C. It can be explained that the water molecules are not coordinated with the europium ion, consistent with the results of the X-ray crystallography that the water molecules are outside

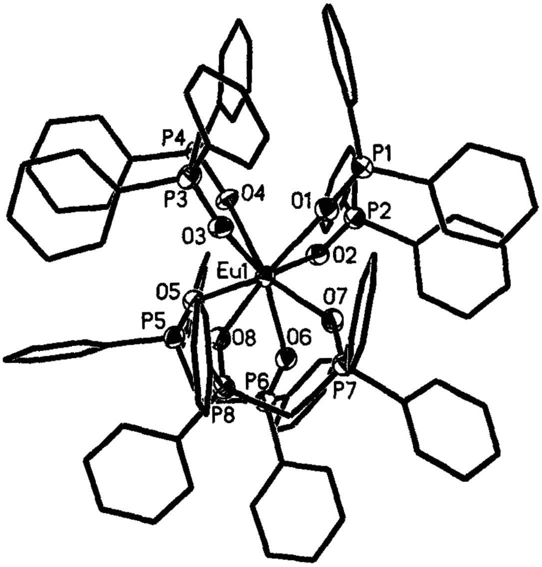

FIGURE 1 The labeling scheme of the complex.

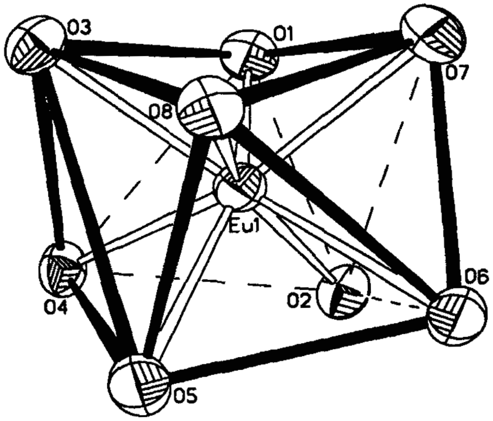

FIGURE 2 The coordination polyhedron of Eu^{3+} iron.

of the coordination sphere. The complex is chemically stable from 40°C to 330°C, but from 350°C–550°C, four HMPPO molecules are lost and the cumulative weight loss is 73% (calc. 77%), which corresponds to the strong exothermic peak in the range of 336°C to 380°C in the DTA spectrum.

In the IR spectrum of the complex, the P=O bond is shifted to frequencies ($1162\,cm^{-1}$) that are lower than those of the free ligand

HMPPO (1188 cm^{-1}), indicating the P=O bond is weakened upon coordination. The frequency of OH stretches around 3431 cm^{-1} shows the existence of the water molecule. Although the absorption bands from the perchlorate group overlap with those of the coordinated P=O group, it is apparent that no coordinated perchlorate groups are present from the characteristic singlet peaks of the perchlorate ion at 1185 cm^{-1} and 623 cm^{-1}.

Absorption, Fluorescence Spectra and Lifetime

The absorption spectra of the complex and the free ligand HMPPO in the acetonitrile solution show that there are three absorption bands in the ultraviolet range. The peak centered at 222 nm can be assigned as $\pi \rightarrow \pi^*$ transition, while the other two centered at 266 nm and 274 nm can be assigned as $n \rightarrow \pi^*$ bands because the former has larger molar extinction coefficient than the latter two.

When the emission light was fixed at 614 nm, the excitation spectrum of the complex in the solid state and in the acetonitrile solution presents three main excitation bands: 238, 266 and 350 nm (Fig. 3). Among them, the band around 266 nm is the strongest. The band around 350 nm is the weakest but broad. However, for the solid and solution samples the ratios of the relative intensity of the band around 266 nm and around 350 nm (I_{350}/I_{266}) are quite different from each other. In the solid state I_{350}/I_{266} is about 0.04 while that in solution is about 0.4. The bigger ratio in the acetonitrile solution results from solvent effects.

When the excitation light was fixed at 266 nm, the emission spectrum from the solid powder and acetonitrile solution (Fig. 4) are both characteristic of Eu(III), which can be attributed to the $^5D_0 \rightarrow {}^7F_j (j = 1-4)$ electronic transitions. In both cases the electric dipolar $^5D_0 \rightarrow {}^7F_2$ transition is the strongest and then the magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transition. Some fluorescence data are listed in Table II. When the emission light slit is reduced from 5 nm to 1 nm, it is observed that the $^5D_0 \rightarrow {}^7F_1$ transition of the complex in the solid state is split into two bands (589.4 and 592.8 nm) and the $^5D_0 \rightarrow {}^7F_2$ transition is split into three bands (611.6, 613.8 and 625.5 nm), suggesting Eu(III) is located in a low symmetry environment. It is in agreement with the crystallographic results revealing that Eu has C_1 symmetry.

The fluorescence lifetime is evaluated by measuring the phase shift and the relative modulation of the samples [13]. When the excitation light is fixed at 266 nm, the lifetime measurements are monoexponential and the emission

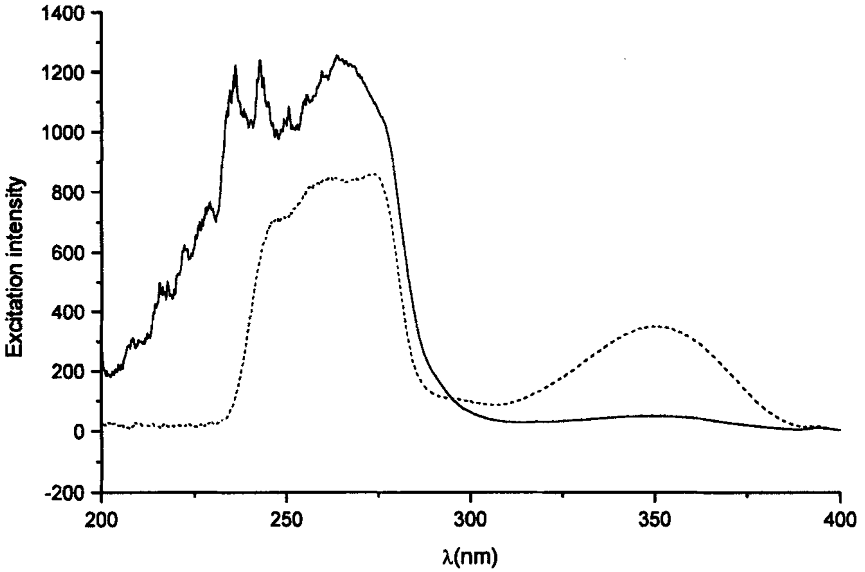

FIGURE 3 Fluorescence excitation spectra of the complex in different states. Solid powder(solid line), acetonitrile solution(dotted line, × 70 times).

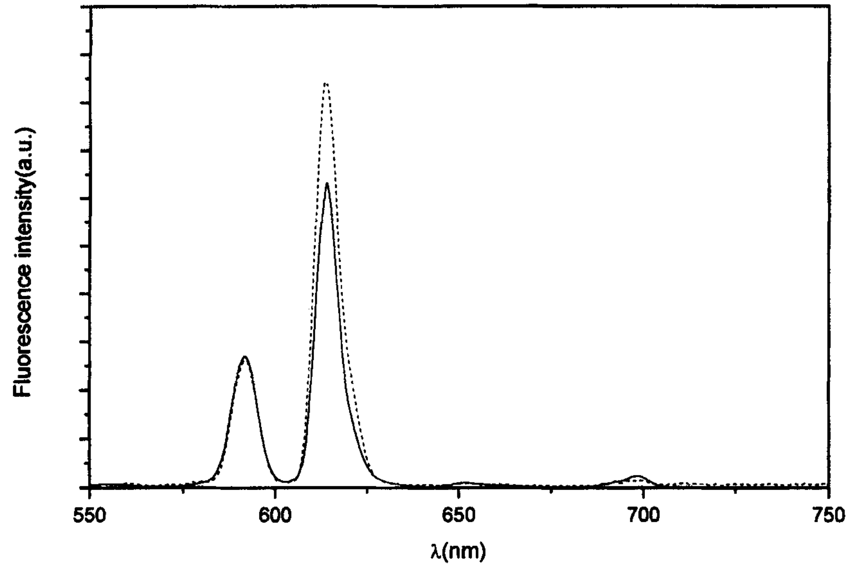

FIGURE 4 Fluorescence spectra of complex in different states. Solid powder(solid line), acetonitrile solution(dotted line, × 50 times).

TABLE II Comparison of the fluorescence spectra of the complex in the solid state and in the acetonitrile solution

		Emission position(intensity)*			
State	$\lambda_{max}^{EX}(nm)$	$j=1$	$j=2$	$j=3$	$j=4$
Solid powder	266	592(1.00)	614(2.20)	652(0.05)	699(0.09)
Acetonitrile solution	266	592(1.00)	614(3.37)	652(0.01)	699(0.04)

* The fluorescence intensity is normalized by each one's magnetic($^5D_0 \rightarrow {}^7F_1$) transition.

lifetime is 1.6 ms. It shows the complex in the solid state exhibits a long lifetime, about two to three times longer than those observed from europium complexes with β-diketones [5, 13], but shorter than that of Eu[$Ph_2P(O)NP(O)Ph_2$]$_3$ [4]. The four HMPPO ligands especially 16 phenyl groups, form a shell around europium ion and protect it from quenching by water molecules and the emission lifetimes is usually longer in the case of ligands featuring phosphine oxide functionalities. However, HMPPO containing a C—H bond in the inner coordination sphere contributes to quenching of the complex.

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