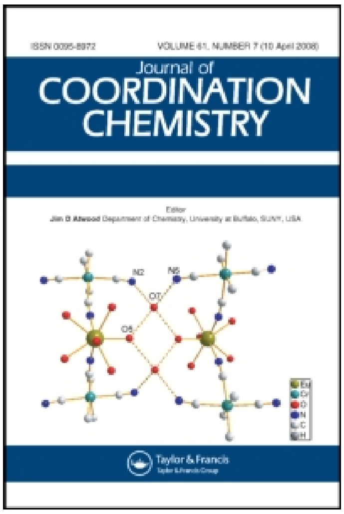

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# Synthesis and structure of a novel dimeric dysprosium complex of 3-amino-4-methylbenzoic acid

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# SYNTHESIS AND STRUCTURE OF A NOVEL DIMERIC DYSPROSIUM COMPLEX OF 3-AMINO-4-METHYLBENZOIC ACID

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A novel europium coordination complex $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$ has been obtained from ethanol solution and characterized structurally by X-ray diffraction (AMBAH=3-amino-4-methylbenzoic acid). The results reveal that it forms a dimeric molecular structure through bridging oxygen atoms of carboxylate groups. The title complex crystallizes in the triclinic system, space group $P1$, with lattice parameters $a=9.084(2)$, $b=12.331(3)$, $c=12.357(3)\,\text{Å}$, $\alpha=87.055(4)$, $\beta=69.657(3)$, $\gamma=81.866(3)^\circ$, $V=1284.8(6)\,\text{Å}^3$, $D_c=1.697\ \text{Mg}\,\text{m}^{-3}$, $Z=1$, $F(000)=660$, GOF $=1.050$, $R_1=0.0363$.

*Keywords:* Europium; Dimeric; Molecular structure; Hydrogen bonding; 3-amino-4-methylbenzoic acid

## INTRODUCTION

Rare earth coordination compounds have attracted great attention for their various molecular structures and photoactive properties which have potential practical value in such areas as luminescence labels for biological systems and active species for luminescent materials. Considerable studies have been focused on the design and assembly of rare earth complexes with organic ligands such as aromatic carboxylic acids, $\beta$-diketones, cryptands calixarenes and hetrocyclic ligands [1–6]. It is worth pointing out that rare earth complexes with aromatic carboxylic acids show higher thermal or luminescent stability for practical applications than other systems because they readily form dimeric or infinite chain polymeric structures, which are of great interest in extraction, separation, germicide preparation, catalysis, luminescence and functional material preparation [7–10]. As part of our continuing study of lanthanide carboxylate complexes, the present article reports the synthesis and the crystal structure of a novel europium complex, $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$ (AMBAH = 3-amino-4-methylbenzoic acid).

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# EXPERIMENTAL

## Synthesis of $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$

Stoichiometric amounts of $Eu(NO_3)_3 \cdot 6H_2O$ (0.2281 g, 0.5 mmol) and 3-amino-4-methylbenzoic acid (0.1846 g, 1.5 mmol) were separately dissolved in 95% $C_2H_5OH$. The pH of solution was adjusted to be about 6.5 with 0.2 M aqueous NaOH, then the solution of AMBAH was added dropwise to the solution of $Eu(NO_3)_3$; the mixed solution was stirred for 4 h. The resulting solution was filtered and the filtrate allowed to stand at room temperature. After three weeks, well-shaped, colourless, single crystals suitable for analysis were obtained. *Anal.* Calcd. for $C_{48}H_{60}Eu_2N_6O_{18}$%: C, 43.87; H, 4.57; N, 6.40. Found: C, 44.03; H, 4.46; N, 6.53. The IR spectrum exhibits a complicated pattern of bands in the range 4000–400 $cm^{-1}$: 1547 $cm^{-1}$ ($\nu_{sCOO-}$), 1411 $cm^{-1}$ ($\nu_{asCOO-}$).

## X-ray Crystallography

Diffraction data for a crystal with dimensions $0.10 \times 0.08 \times 0.05$ mm were collected using graphite-monochromated Mo K$\alpha$ radiation on an Enraf-Nonius CAD4 four-circle diffractometer using the $\omega$–$2\theta$ scan technique. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined.

TABLE I Crystal data and structure refinement details for the complex

| *Complex* | $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$ |
|---|---|
| Formula | $C_{48}H_{60}Eu_2N_6O_{18}$ |
| Relative molecular weight *M* | 1312.94 |
| Colour | Colourless |
| Temperature (K) | 298(2) |
| Wavelength (Å) | 0.71073 Å |
| Radiation | Mo K$\alpha$ |
| Crystal system | $P\bar{1}$ |
| Space group | Triclinic |
| Unit dimensions | $a = 9.084(2)$ Å |
| | $b = 12.331(3)$ Å |
| | $c = 12.357(3)$ Å |
| | $\alpha = 87.055(4)°$ |
| | $\beta = 69.657(3)°$ |
| | $\gamma = 81.866(3)°$ |
| Volume (Å$^3$) | 1284.8(6) Å$^3$ |
| *Z* | 1 |
| Calculated density (Mg m$^{-3}$) | 1.697 Mg/m$^3$ |
| Absorption coefficient (mm$^{-1}$) | 2.498 mm$^{-1}$ |
| *F*(000) | 660 |
| Crystal size (mm) | $0.10 \times 0.08 \times 0.05$ mm |
| $\theta$ range for data collection (°) | 1.76° to 25.00° |
| Reflections collected/unique (*R*(int)) | 5424/4468[*R*(int)= 0.0233] |
| Completeness to $2\theta = 25.01$/% | 98.5% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4468/2/362 |
| Goodness-of-fit on $F^2$ | 1.050 |
| Final *R* indices $R_1$, $wR_2$ [$I > 2\sigma(I)$] | $R_1 = 0.0363$, $wR_2 = 0.0827$ |
| Largest diff. peak and hole | 1.541 and $-0.840$ e Å$^{-3}$ |

All calculations were performed using SHELXS-97 and SHELXL-97 [11,12]. A summary of crystallographic data and refinement parameters is given in Table I. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No: CCDC-230258. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

## Physical Measurements

Elemental analyses (C, H, N) were determined on an Elementar Cario EL instrument. Infrared spectroscopy (KBr pellets) was performed on a Nexus 912 AO446 FT-IR

TABLE II Final atomic coordinates and equivalent isotropic displacement parameters ($10^3$ Å$^2$) for the complex

| *Atom* | *x/a* | *y/b* | *z/c* | *U(eq)* |
|---|---|---|---|---|
| Eu(1) | 7539(1) | 101(1) | 11000(1) | 22(1) |
| N(1) | 6477(11) | 5827(7) | 9940(9) | 137(4) |
| N(2) | 6461(5) | −621(4) | 5428(4) | 38(1) |
| N(3) | 3847(12) | −3716(9) | 15792(9) | 48(3) |
| N(3′) | 2287(15) | −4414(10) | 12819(11) | 65(3) |
| O(1) | 8226(4) | 1738(3) | 10048(3) | 39(1) |
| O(2) | 10856(4) | 1586(3) | 9235(4) | 38(1) |
| O(3) | 10370(4) | −390(3) | 8436(3) | 33(1) |
| O(4) | 7767(4) | −310(3) | 9065(3) | 32(1) |
| O(5) | 5670(5) | −1304(3) | 11321(3) | 42(1) |
| O(6) | 6201(4) | −885(3) | 12830(3) | 34(1) |
| O(7) | 5126(5) | 1075(4) | 10663(4) | 35(1) |
| O(8) | 6114(5) | 1443(4) | 12592(4) | 45(1) |
| O(9) | 4628(10) | 3489(7) | 2120(8) | 152(3) |
| C(1) | 9498(7) | 2122(4) | 9515(5) | 32(1) |
| C(2) | 9392(7) | 3317(4) | 9208(5) | 34(1) |
| C(3) | 10731(8) | 3756(5) | 8513(5) | 49(2) |
| C(4) | 10640(10) | 4866(6) | 8281(6) | 61(2) |
| C(5) | 9263(11) | 5549(6) | 8728(7) | 63(2) |
| C(6) | 7932(10) | 5120(6) | 9436(7) | 65(2) |
| C(7) | 7990(8) | 3999(5) | 9668(6) | 50(2) |
| C(8) | 9176(13) | 6765(6) | 8420(9) | 96(3) |
| C(9) | 9102(6) | −453(4) | 8263(4) | 27(1) |
| C(10) | 9169(6) | −741(4) | 7095(4) | 24(1) |
| C(11) | 10567(6) | −1240(4) | 6299(5) | 31(1) |
| C(12) | 10577(6) | −1569(5) | 5256(5) | 34(1) |
| C(13) | 9243(6) | −1410(4) | 4932(4) | 30(1) |
| C(14) | 7853(6) | −847(4) | 5710(4) | 27(1) |
| C(15) | 7839(6) | −539(4) | 6778(4) | 26(1) |
| C(16) | 9291(7) | −1817(5) | 3796(5) | 41(1) |
| C(17) | 5601(6) | −1486(4) | 12341(5) | 30(1) |
| C(18) | 4770(6) | −2412(4) | 12997(5) | 33(1) |
| C(19) | 3913(7) | −2979(5) | 12543(6) | 43(2) |
| C(20) | 3126(7) | −3814(5) | 13159(7) | 52(2) |
| C(22) | 4015(8) | −3528(6) | 14723(6) | 52(2) |
| C(23) | 4822(7) | −2702(5) | 14080(5) | 46(2) |
| C(24) | 2233(11) | −4985(7) | 14956(8) | 91(3) |

*U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

spectrophotometer in the range 4000–400 cm$^{-1}$. Phosphorescence and fluorescence spectra were measured with a Perkin-Elmer LS-55 spectrophotometer.

## RESULTS AND DISCUSSION

### Description of the Crystal Structure

Final atomic coordinates for non-hydrogen atoms are listed in Table II. Fig. 1 shows the coordination geometry and atom labeling in the crystal structure of $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$. X-ray analysis reveals a dimeric formulation $[Eu(AMBA)_3(H_2O)_2 \cdot H_2O]_2$ with two equivalent structural units (one half of the dimer) related by a crystallographic inversion centre. The symmetry-related europium ions are bridged by four AMBA anions, with two additional AMBA anions chelating them. Each central europium ion is eight-coordinate; geometry can be described as a distorted square antiprism. Four bridging oxygen atoms have Eu–O distances of 2.314(3) ~ 2.402(3) Å. Chelated AMBA groups have longer distances, 2.509(4) Å and 2.516(4) Å. In addition, two coordinated water molecules (O(7) and O(8)) have bond

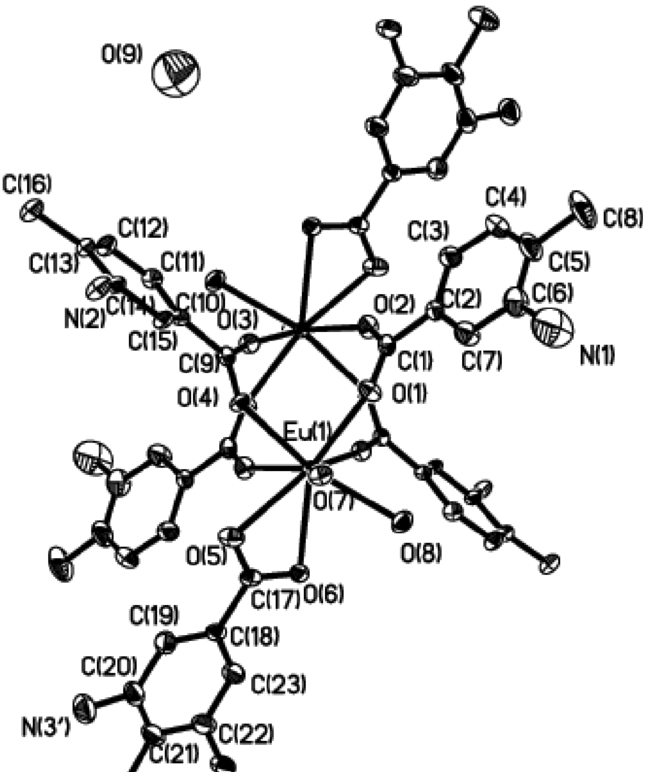

FIGURE 1 Molecular structure of the complex showing the title atom labeling scheme.

distances of 2.498(4) and 2.502(4) Å. The average Eu(1)–O distance is 2.427 Å. The bond angle at Eu ion made by the oxygen atoms of chelated AMBA is 51.81(9)°. Selected bond distances and angles for the complex are listed in Table III.

The existence of water molecules gives rise to hydrogen bonding involving all nitrogen atoms of AMBA anions. The O–H···N bond between the nitrogen atom of the bridged AMBA and the oxygen atoms of a coordinated water molecule has a bond angle of 172(7)° In addition there are three types of N–H···O hydrogen bonds: one is between nitrogen of the bridged AMBA and the oxygen atoms of the coordinated water molecules (bond angle 117.4°). Others are between nitrogen of the bridged AMBA and oxygen atoms of chelated AMBA (angles 166.0 and 165.2°, respectively). Besides these, there also exist three types of O–H···O hydrogen bonds: one is between the oxygen atoms of bridged AMBA and coordinated water molecules (angle 167(10)°); another is water molecules and chelated AMBA (angle 137(5)°) and the final is between coordinated and lattice water molecules (angle 134(5)°). The hydrogen bonding links the complex units, resulting in a 3-D network. Details of hydrogen bonding are given in Table IV.

TABLE III Selected bond distances (Å) and angles (°) for the complex

| | |
|---|---|
| Eu(1)–O(3)#1 2.314(3) | Eu(1)–O(8) 2.498(4) |
| Eu(1)–O(2)#1 2.334(4) | Eu(1)–O(7) 2.502(4) |
| Eu(1)–O(1) 2.335(4) | Eu(1)–O(6) 2.509(4) |
| Eu(1)–O(4) 2.402(3) | Eu(1)–O(5) 2.516(4) |
| O(3)#1–Eu(1)–O(2)#1 74.75(13) | O(8)–Eu(1)–O(7) 70.88(15) |
| O(3)#1–Eu(1)–O(1) 78.40(13) | O(3)#1–Eu(1)–O(6) 93.54(12) |
| O(2)#1–Eu(1)–O(1) 127.01(14) | O(2)#1–Eu(1)–O(6) 77.65(13) |
| O(3)#1–Eu(1)–O(4) 124.76(12) | O(1)–Eu(1)–O(6) 149.19(14) |
| O(2)#1–Eu(1)–O(4) 80.61(13) | O(4)–Eu(1)–O(6) 128.23(12) |
| O(1)–Eu(1)–O(4) 78.56(13) | O(8)–Eu(1)–O(6) 69.76(15) |
| O(3)#1–Eu(1)–O(8) 80.42(14) | O(7)–Eu(1)–O(6) 98.69(15) |
| O(2)#1–Eu(1)–O(8) 137.31(16) | O(3)#1–Eu(1)–O(5) 137.89(13) |
| O(1)–Eu(1)–O(8) 79.56(16) | O(2)#1–Eu(1)–O(5) 75.09(14) |
| O(4)–Eu(1)–O(8) 141.65(15) | O(1)–Eu(1)–O(5) 143.71(13) |
| O(3)#1–Eu(1)–O(7) 142.32(14) | O(4)–Eu(1)–O(5) 77.69(12) |
| O(2)#1–Eu(1)–O(7) 142.69(14) | O(8)–Eu(1)–O(5) 103.33(15) |
| O(1)–Eu(1)–O(7) 72.91(15) | O(7)–Eu(1)–O(5) 74.06(15) |
| O(4)–Eu(1)–O(7) 72.76(14) | O(6)–Eu(1)–O(5) 51.52(12) |

Symmetry transformation used to generate equivalent atoms: #1 $-x+2$, $-y$, $-z+2$.

TABLE IV Hydrogen bond data (Å) for the complex

| *D–H···A* | *d(D–H)* | *d(H···A)* | *d(D···A)* | *d(DHA)* |
|---|---|---|---|---|
| O(7)–H(7B)···O(4)#2 | 0.78(9) | 2.06(9) | 2.822(5) | 167(10) |
| O(7)–H(7A)···O(5)#2 | 0.76(6) | 2.17(6) | 2.778(6) | 137(5) |
| O(8)–H(8E)···N(2)#2 | 0.78(2) | 2.21(2) | 2.987(7) | 172(7) |
| O(8)–H(8D)···O(9)#3 | 0.86(2) | 2.15(4) | 2.821(10) | 134(5) |
| N(2)–H(2B)···O(6)#4 | 0.86 | 2.49 | 3.335(6) | 166.0 |
| N(2)–H(2A)···O(8)#2 | 0.86 | 2.49 | 2.987(7) | 117.4 |
| N(2)–H(2A)···O(6)#2 | 0.86 | 2.23 | 3.073(6) | 165.2 |

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

Flourscence spectra of the title complex under excitation at 242 mm showed very weak, characteristic, red emission of $Eu^{3+}$ at 615 mm ($^5D_0 \rightarrow {}^7F_2$ transistion), which suggests there is no efficient energy transfer between the triplet state AMBA and the emission level of $Eu^{3+}$. We further measured the phosphorescence spectrum and found the maximum phosphorescence peak around 385 nm. The triplet state of AMBA was determined to be about 26000 $cm^{-1}$ and much higher than the resonant emissive energy level of $Eu^{3+}$ (17300 $cm^{-1}$).

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