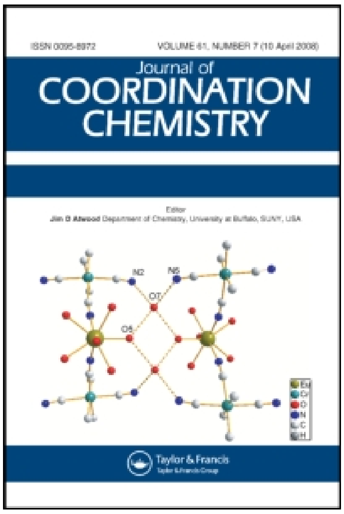

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A novel dimeric europium complex of 5-amino-2-chlorobenzoic acid: Structure and photophysical properties

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A novel dimeric europium complex of 5-amino-2-chlorobenzoic acid: Structure and photophysical properties

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A novel europium complex, $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$, where AClBA = 5-amino-2-chlorobenzoic acid, has been characterized structurally by X-ray diffraction methods. The complex has a dimeric structure formed by bridging oxygen atoms of carboxylate groups. It is triclinic, space group $P\bar{1}$, with $a = 9.849(3)$, $b = 11.000(3)$, $c = 12.790(4)$ Å, $\alpha = 106.828(4)$, $\beta = 103.588(4)$, $\gamma = 93.493(4)^\circ$, $V = 1276.7(6)$ Å^3, $D_c = 1.867\,\mathrm{Mg\,m^{-3}}$, $Z = 1$, $F(000) = 708$, goodness-of-fit = 1.034, $R1 = 0.0283$. Photophysical properties (UV absorption, excitation and emission) of the complex have been determined.

Keywords: Europium complex; Dimer; Molecular structure; Hydrogen bonding; Photophysical properties

1. Introduction

Considerable attention has been devoted to the design and synthesis of luminescent lanthanide complexes because of their interesting photophysical properties and potential applications in sensors, liquid crystal materials, optical fiber lasers and amplifiers, luminescent labels for specific biomolecule interactions, and magnetic molecular and electroluminescent materials [1–6]. Many studies have focused on the design and assembly of lanthanide complexes with organic ligands such as aromatic carboxylic acids, β-diketones, cryptands, calixarenes and heterocycles [7–14]. In particular, lanthanide complexes of aromatic carboxylic acids show higher thermal or luminescent stability than other lanthanide complex systems because they readily form dimeric or infinite chain polymeric structures, with practical applications in several of the above-mentioned areas [15–18].

Most luminescent lanthanide(III) aromatic carboxylate complexes contain Tb(III) or Eu(III). These ions are frequently sensitized by coordinated aromatic carboxylic acids. As part of our continuing study of lanthanide carboxylate complexes, we report here

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Table 1. Crystal data and structure refinement details for $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$.

Formula	$C_{42}H_{42}Cl_6Eu_2N_6O_{18}$
M	1325.67
Color	Colorless
Temperature	298(2) K
Wavelength	0.71073 Å
Radiation	Mo Kα
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.849(3)$ Å $b = 11.000(3)$ Å $c = 12.790(4)$ Å $\alpha = 106.828(4)^\circ$ $\beta = 103.588(4)^\circ$ $\gamma = 93.493(4)^\circ$
V	1276.7(6) Å^3
Z	1
Calculated density	1.867 Mg m^{-3}
Absorption coefficient	2.826 mm^{-1}
$F(000)$	708
Crystal size	$0.15 \times 0.15 \times 0.10$ mm
θ range for data collection	1.72 to 27.12°
Reflections collected/unique	6374/5378 [$R(\text{int}) = 0.0132$]
Completeness to $2\theta = 25.01^\circ$	95.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5378/9/358
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0283$, $wR2 = 0.0671$
Largest diff. peak and hole	0.998 and −0.872 e Å^{-3}

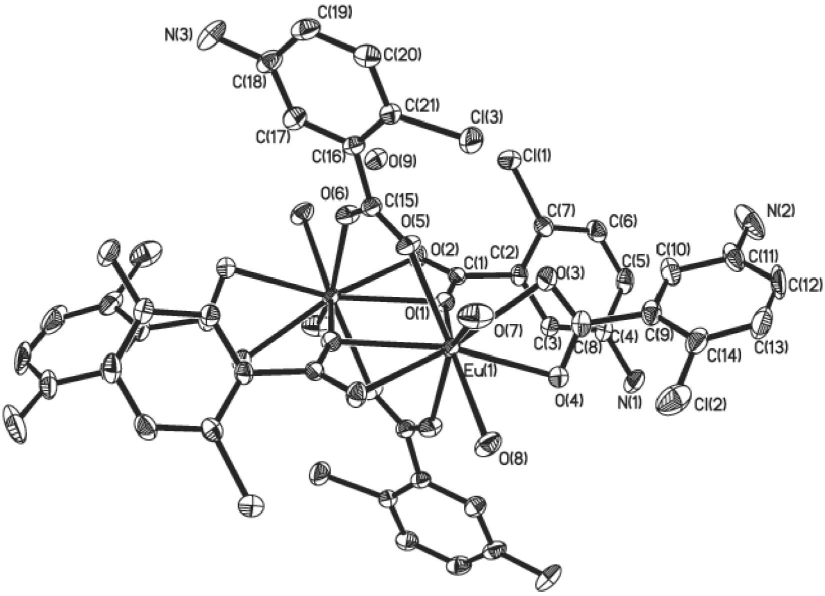

Figure 1. The molecular structure of $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$ showing the atom numbering scheme.

the synthesis and structure of a novel dimeric europium complex, $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$ (AClBA = 5-amino-2-chlorobenzoic acid).

2. Experimental

2.1. *Synthesis of* $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$

Stoichiometric amounts of $Eu(NO_3)_3 \cdot 6H_2O$ (0.2281 g, 0.5 mmol) and AClBA (0.2586 g, 1.5 mmol) were dissolved in 95% C_2H_5OH. The pH of the AClBA solution was adjusted to about 6.5 with 0.2 M NaOH solution, and then the solution was added dropwise to the solution of $Eu(NO_3)_3$ and the mixture stirred for 4 h. The resulting solution was filtered and the filtrate allowed to stand at room temperature. After 2 weeks, well-shaped light colorless single crystals suitable for analysis were obtained.

Table 2. Final atomic coordinates for nonhydrogen atoms ($\times 10^5$) and equivalent isotropic displacement parameters (Å^2, $\times 10^3$) for the complex.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Eu(1)	11430(1)	9926(1)	9128(1)	24(1)
Cl(1)	6547(1)	5500(1)	7677(1)	52(1)
Cl(2)	14523(1)	7863(2)	6891(1)	72(1)
Cl(3)	8330(1)	9895(1)	5711(1)	58(1)
N(1)	12433(4)	4566(3)	9219(3)	45(1)
N(2)	10482(6)	3091(4)	5272(4)	92(2)
N(3)	3892(4)	12587(4)	7447(4)	56(1)
O(1)	9770(2)	8558(2)	9481(2)	31(1)
O(2)	7983(3)	7723(2)	9897(2)	36(1)
O(3)	10768(3)	8079(3)	7341(2)	46(1)
O(4)	12648(3)	8010(2)	8641(2)	37(1)
O(5)	9250(2)	10343(2)	8164(2)	36(1)
O(6)	7556(3)	10206(2)	9037(2)	36(1)
O(7)	11719(3)	10765(3)	7579(3)	55(1)
O(8)	13929(3)	10560(3)	9362(3)	47(1)
O(9)	4834(4)	6977(3)	9665(3)	53(1)
C(1)	8973(3)	7590(3)	9439(3)	27(1)
C(2)	9303(4)	6277(3)	8911(3)	28(1)
C(3)	10678(4)	6037(3)	9244(3)	31(1)
C(4)	11047(4)	4805(3)	8899(3)	36(1)
C(5)	9987(4)	3812(3)	8190(3)	41(1)
C(6)	8633(4)	4044(3)	7830(3)	40(1)
C(7)	8278(4)	5266(3)	8187(3)	34(1)
C(8)	11833(4)	7570(3)	7652(3)	35(1)
C(9)	12138(4)	6415(4)	6818(3)	40(1)
C(10)	11184(5)	5302(4)	6421(3)	48(1)
C(11)	11392(6)	4223(4)	5593(4)	64(2)
C(12)	12511(8)	4360(6)	5132(4)	85(2)
C(13)	13432(7)	5467(7)	5514(5)	83(2)
C(14)	13293(5)	6486(5)	6384(4)	55(1)
C(15)	8020(3)	10421(3)	8261(3)	29(1)
C(16)	7014(3)	10864(3)	7401(3)	29(1)
C(17)	5945(4)	11503(3)	7756(3)	35(1)
C(18)	4997(4)	12010(4)	7069(4)	41(1)
C(19)	5146(4)	11881(4)	5987(4)	44(1)
C(20)	6180(4)	11250(4)	5613(3)	42(1)
C(21)	7107(4)	10741(3)	6308(3)	34(1)

Anal. Calc. for $C_{42}H_{42}Cl_6Eu_2N_6O_{18}$(%): C, 35.11; H, 2.93; N, 5.85. Found: C, 35.67; H, 2.87; N, 5.94. IR spectra exhibited a complicated pattern of bands in the 4000–400 cm^{-1} range; 1547 cm^{-1} (ν_{sCOO^-}), 1411 cm^{-1} (ν_{asCOO^-}).

2.2. *X-ray crystallography*

Diffraction data for a crystal of dimensions 0.15 × 0.15 × 0.10 mm were measured with graphite-monochromated Mo Kα radiation on an Enraf-Nonius CAD4 four-circle diffractometer, and collected by the ω–2θ scan technique. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [19, 20]. A summary of crystallographic data and refinement parameters is given in table 1.

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as CCDC No. 255230. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. *Physical measurements*

Elemental analyses (C, H, N) were determined on an Elementar Cario instrument. IR spectroscopy (KBr pellets) was performed on a Nexus 912 AO446 FTIR spectrophotometer in the 4000–400 cm^{-1} range. Ultraviolet absorption spectra were measured

Table 3. Selected bond distances (Å) and angles (°) for the complex.

Eu(1)–O(5)	2.354(2)	Eu(1)–O(4)	2.484(2)
Eu(1)–O(1)	2.363(2)	Eu(1)–O(2)#1	2.487(2)
Eu(1)–O(6)#1	2.375(2)	Eu(1)–O(3)	2.496(3)
Eu(1)–O(8)	2.441(3)	Eu(1)–O(1)#1	2.617(2)
Eu(1)–O(7)	2.480(3)	–	–
O(5)–Eu(1)–O(1)	76.83(9)	O(8)–Eu(1)–O(2)#1	71.26(9)
O(5)–Eu(1)–O(6)#1	136.32(9)	O(7)–Eu(1)–O(2)#1	77.46(11)
O(1)–Eu(1)–O(6)#1	73.87(8)	O(4)–Eu(1)–O(2)#1	139.33(9)
O(5)–Eu(1)–O(8)	137.50(10)	O(5)–Eu(1)–O(3)	77.47(9)
O(1)–Eu(1)–O(8)	145.45(9)	O(1)–Eu(1)–O(3)	77.38(9)
O(6)#1–Eu(1)–O(8)	78.55(10)	O(6)#1–Eu(1)–O(3)	125.28(9)
O(5)–Eu(1)–O(7)	69.51(10)	O(8)–Eu(1)–O(3)	102.95(11)
O(1)–Eu(1)–O(7)	138.77(9)	O(7)–Eu(1)–O(3)	72.74(11)
O(6)#1–Eu(1)–O(7)	147.27(10)	O(4)–Eu(1)–O(3)	52.46(9)
O(8)–Eu(1)–O(7)	70.23(11)	O(2)#1–Eu(1)–O(3)	149.70(10)
O(5)–Eu(1)–O(4)	129.50(9)	O(5)–Eu(1)–O(1)#1	68.37(8)
O(1)–Eu(1)–O(4)	85.43(8)	O(1)–Eu(1)–O(1)#1	74.53(8)
O(6)#1–Eu(1)–O(4)	79.51(9)	O(6)#1–Eu(1)–O(1)#1	73.01(8)
O(8)–Eu(1)–O(4)	69.26(9)	O(8)–Eu(1)–O(1)#1	116.62(9)
O(7)–Eu(1)–O(4)	97.87(11)	O(7)–Eu(1)–O(1)#1	112.40(10)
O(5)–Eu(1)–O(2)#1	87.25(9)	O(4)–Eu(1)–O(1)#1	149.49(8)
O(1)–Eu(1)–O(2)#1	124.66(8)	O(2)#1–Eu(1)–O(1)#1	50.48(7)
O(6)#1–Eu(1)–O(2)#1	83.58(9)	O(3)–Eu(1)–O(1)#1	139.65(9)

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

with an Aligent 8453 spectrophotometer. Excitation and emission spectra were measured with a Perkin-Elmer LS-55 spectrophotometer.

3. Results and discussion

3.1. *Description of the crystal structure*

Figure 1 shows the coordination geometry and atom numbering for the crystal structure of $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$. Final atomic coordinates for the nonhydrogen atoms are listed in table 2. The structure is dimeric with two equivalent structural units related by a crystallographic inversion center. The two symmetry-related europium ions are bridged by four AClBA ligands, with two additional chelating AClBA groups. The Eu ion is coordinated by nine oxygen atoms, with a coordination geometry that can be described as distorted square monoantiprismatic. Among the five oxygen atoms of the four bridging AClBA groups [O(1), O(5), O(1#), O(2#) and O(6#) for Eu(1)], bond distances range from 2.354(2) to 2.617(2) Å. The other two oxygen atoms of the chelated AClBA groups [O(3) and O(4) for Eu(1)] have bond distance of 2.496(3) and 2.484(2) Å, respectively. In addition, there are two coordinated oxygen atoms of coordinated water molecules [O(7) and O(8) for Eu(1)] with bond distances of 2.480(3) and 2.441(3) [Eu(1)–O(8)] Å, respectively. The average Eu(1)–O distance is 2.455 Å. The chelating O(4)–Eu(1)–O(3) bond angle is 52.46(9)°. Selected bond distances and angles for the dimer are listed in table 3. All AClBA anions are deprotonated and all oxygen atoms take part in coordination to the central metal

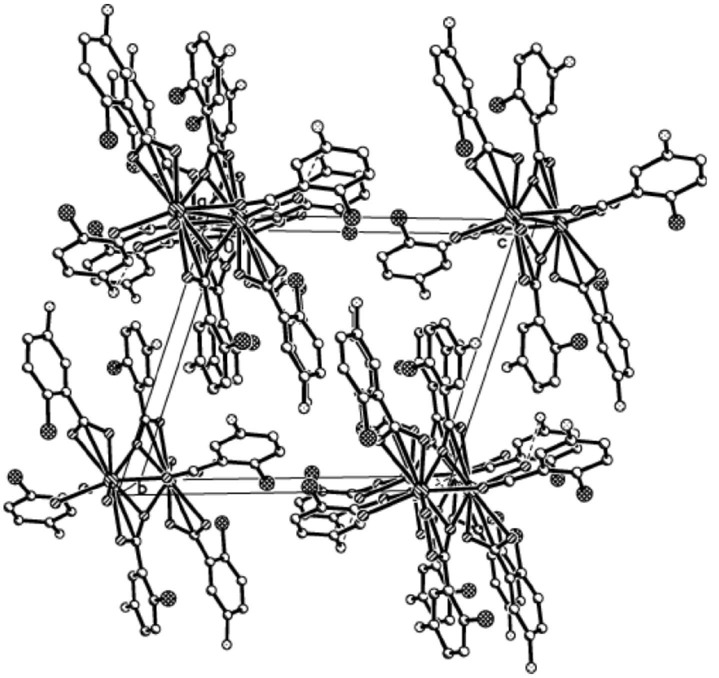

Figure 2. Packing view in the unit cell.

ion with three coordination modes: (a) chelating-bridging tridentate, (b) bridging didentate ligand and (c) chelating didentate ligand. The two Eu ions in the dimer are connected by modes (a) and (b).

Figure 2 shows the packing in the unit cell. The water molecules, nitrogen and chlorine atoms are involved in hydrogen bonding. N–H···O hydrogen bonds between the bridging AClBA anions have an angle of 114.0° [N(1)–H(1A)···O(2)#2]. N–H···O hydrogen bonds between the nitrogen atoms of bridging AClBA anions and the oxygen atoms of the lattice water molecules have an angle of 143.2° [N(1)–H(1B)···O(9)#4]. N–H···N hydrogen bonding is also present [N(1)–H(1A)···N(3)#3, 136.2°] together with N–H···Cl [N(2)–H(2A)···Cl(3)#5, 147.1°], O–H···Cl [O(7)–H(7A)···Cl(3), 168(4)°] and O–H···N [O(7)–H(7B)···N(3)#4, 166(5)°]. O–H···O interactions involve lattice water molecules and chelated AClBA anions [O(9)–H(9A)···O(4)#6, 160(4)°] and lattice water alone [O(8)–H(8A)···O(9)#1, 176(6)°]. Finally, O–H···Cl bonds are present [O(9)–H(9B)···Cl(1), 169(4)°]. These result in a 3D network and make the structure stable. Detailed data for the hydrogen bonding network are given in table 4.

Table 4. Hydrogen bonding data (Å,°) for the complex.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)–H(1A)···O(2)#2	0.86	2.63	3.086(4)	114.0
N(1)–H(1A)···N(3)#3	0.86	2.64	3.316(5)	136.2
N(1)–H(1B)···O(9)#4	0.86	2.54	3.268(5)	143.2
N(2)–H(2A)···Cl(3)#5	0.86	2.78	3.536(4)	147.1
O(7)–H(7A)···Cl(3)	0.826(19)	2.697(19)	3.508(3)	168(4)
O(7)–H(7B)···N(3)#4	0.840(19)	2.09(2)	2.910(5)	166(5)
O(9)–H(9A)···O(4)#6	0.846(18)	1.93(2)	2.734(4)	160(4)
O(9)–H(9B)···Cl(1)	0.837(19)	2.63(2)	3.451(4)	169(4)
O(8)–H(8A)···O(9)#1	0.834(19)	1.87(2)	2.703(4)	176(6)

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

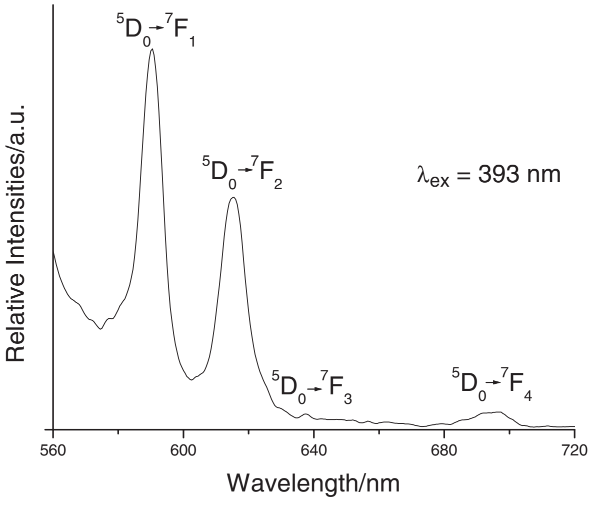

Figure 3. Emission spectrum of $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$.

3.2. *Photophysical properties*

The ultraviolet absorption spectrum of $[Eu(AClBA)_3(H_2O)_2 \cdot H_2O]_2$ (10^{-4} mol dm^{-3} in ethanol) shows an absorption band at 296 nm, attributed to AClBA. This indicates that AClBA is the energy donor and the luminescence sensitizer of the Eu^{3+} ion. The solid-state excitation spectrum shows that effective energy absorption mainly takes place in the ultraviolet region (290–400 nm) and emission at 613 nm with two main excitation peaks at 307 and 393 nm. Emission spectra generated by selective excitation at the two excitation wavelengths showed similar emission positions with little difference in luminescence intensities. Emission spectra at room temperature (figure 3) show four apparent emission bands at 393 nm excitation (590, 615, 637 and 696 nm), attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) for the Eu^{3+} ion.

Acknowledgements

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