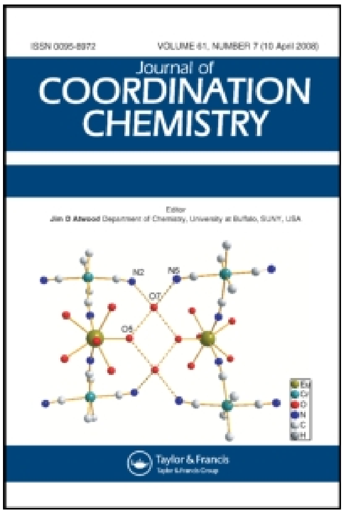

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Syntheses and crystal structures of two novel lanthanide coordination compounds of 3-aminobenzoic acid

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Syntheses and crystal structures of two novel lanthanide coordination compounds of 3-aminobenzoic acid

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Two new lanthanide coordination compounds, $RE(ABA)_3(H_2O)_3 \cdot H_2O$ ($RE = Sm$, Dy; ABA = 3-aminobenzoate), were obtained from ethanol solution and characterized structurally by X-ray diffraction methods. Both possess a monomeric molecular structure. Complex **1**, $Sm(ABA)_3(H_2O)_3$, is rhombohedral, space group $R3c$, with $a = 18.999(3)$, $c = 11.915(3)$ Å, $V = 3724.6(12)$ Å^3, $D_c = 1.784\,\mathrm{Mg\,m^{-3}}$, $Z = 6$, $F(000) = 2010$, GOF = 1.133 and $R_1 = 0.0204$. Complex **2**, $Dy(ABA)_3(H_2O)_3$, is isomorphous, with $a = 18.956(4)$, $c = 11.812(3)$ Å, $V = 3675.8(14)$ Å^3, $D_c = 1.840\,\mathrm{Mg\,m^{-3}}$, $Z = 6$, $F(000) = 2034$ and $R_1 = 0.0209$. Photophysical properties of the complexes were investigated.

Keywords: Lanthanide complex; 3-Aminobenzoic acid; Monomeric molecular structure; Hydrogen bonding

1. Introduction

Since a strongly photoluminescent europium complex was first reported by Weissmen in 1942 [1], lanthanide(III) complexes have attracted extensive interest because of their potential application as contrast agents for magnetic resonance imaging (MRI), catalysts in RNA hydrolysis, and special fluorescence properties [2–7]. In this field, much work has been focused on the design and assembly of lanthanide complexes with organic ligands such as aromatic carboxylic acids, β-diketones, cryptands, calixarenes and heterocyclic ligands. In particular, lanthanide complexes with aromatic carboxylic acids have been studied because of their novel structural features and potential applications in a number of areas. Dimeric and polymeric structures are frequently found for these species, and lanthanide complexes with aromatic carboxylic acids show greater thermal and photochemical stability than other lanthanide complexes [8–12].

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Mononuclear complexes of rare earth ions, particularly the lanthanides, are of continuing interest because of their electronic and nuclear properties with respect to contrast enhancement in MRI and roles as luminescent bioprobes and radiopharmaceuticals. Of special interest in this connection is the design of the luminescence, mononuclear, lanthanide complexes of multidentate ligands [13–21]. In this work, we report the syntheses and the crystal structures of two monomeric lanthanide complexes of 3-aminobenzoic acid (ABAH) acid, $RE(ABA)_3(H_2O)_3 \cdot H_2O$ (RE = Sm, Dy; ABA = 3-aminobenzoate). Photophysical properties of the complexes were studied by fluorescence spectroscopy.

2. Experimental

2.1. *RE(ABA)$_3$(H$_2$O)$_3$ (RE = Sm or Dy)*

$RE(NO_3)_3 \cdot 6H_2O$ (0.5 m mol) and ABAH (1.5 m mol) were separately dissolved in 95% C_2H_5OH. After adjusting the pH of the ABAH solution to 6.5 with aqueous 0.2 M NaOH solution, it was added dropwise to the ethanolic solution of $RE(NO_3)_3$. The mixture was stirred for 4 h, filtered, and the filtrate allowed to stand at room temperature. After 2 weeks, well-shaped, colorless single crystals suitable for X-ray analysis were obtained. Anal. Calcd. for $C_{21}H_{30}N_3O_{12}Sm$(%): C, 37.79; H, 4.50; N, 6.30. Found: C, 38.21; H, 4.42; N, 6.43. Anal. Calcd. for $C_{21}H_{30}N_3O_{12}Dy$(%): C, 37.11; H, 4.42; N, 6.19. Found: C, 37.89; H, 4.37; N, 6.11. IR spectra exhibited a complicated pattern of bands in the range 4000–400 cm^{-1}; for Complex **1** 1547 cm^{-1} (ν_{asCOO-}), 1411 cm^{-1} (ν_{sCOO-}) and for Complex **2** 1547 cm^{-1} (ν_{asCOO-}), 1411 cm^{-1} (ν_{sCOO-}) are characteristic.

2.2. *X-ray crystallography*

Diffraction data for crystals of dimensions 0.15 × 0.05 × 0.05 mm for Complex **1** and 0.20 × 0.08 × 0.05 mm for Complex **2** were collected using graphite-monochromated Mo Kα radiation on a CCD area detector four-circle diffractometer, using the ω–2θ scan technique. Structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [22,23]. A summary of the crystallographic data and refinement parameters is given in table 1.

Crystallographic data (excluding structure factors) for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 240168 for **1** and CCDC 240169 for **2**. 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 EL instrument. IR spectroscopy using KBr pellets was performed on a Nexus 912 AO446 FTIR spectrophotometer in the range 4000–400 cm^{-1}. Ultraviolet absorption spectra

Table 1. Crystal data and structure refinement details for $Sm(ABA)_3(H_2O)_3 \cdot H_2O$ and $Dy(ABA)_3(H_2O)_3 \cdot H_2O$.

	$Sm(ABA)_3(H_2O)_3 \cdot H_2O$	$Dy(ABA)_3(H_2O)_3 \cdot H_2O$
Empirical formula	$C_{21}H_{30}N_3O_{12}Sm$	$C_{21}H_{30}N_3O_{12}$ Dy
M	666.83	678.98
Temperature	293(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Rhombohedral	Rhombohedral
Space group	$R3c$	$R3c$
Unit cell dimensions	$a = 18.999(3)$ Å	$a = 18.956(4)$ Å
	$c = 11.915(3)$ Å	$c = 11.812(3)$ Å
Volume	3724.6(12) $Å^3$	3675.8(14) $Å^3$
Z	6	6
Calculated density	1.784 $Mg\,m^{-3}$	1.840 $Mg\,m^{-3}$
Absorption coefficient	2.434 mm^{-1}	3.119 mm^{-1}
$F(000)$	2010	2034
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0204$, $wR_2 = 0.0491$	$R_1 = 0.0209$, $wR_2 = 0.0414$
Largest diff. peak and hole	0.399, −0.653 e $Å^{-3}$	0.853, −0.526 e $Å^{-3}$

were obtained with an Agilent 8453 spectrophotometer. Excitation and emission spectra of solid samples of the complexes were measured with a Perkin Elmer LS-55 spectrophotometer.

3. Results and discussion

3.1. *Description of the structure*

Final atomic coordinates for nonhydrogen atoms of the isomorphous complexes are listed in table 2. Figure 1 shows the coordination geometry and atom labeling in the crystal structure of **1**, which consists of one Sm ion, three ABA ions, three coordinated water molecules and one lattice water molecule. All ABA anions are deprotonated and act as chelating bidentates. The central Sm ion is nine-coordinated, exclusively by oxygen atoms; the coordination geometry can be described in terms of a distorted square antiprism. The six oxygen atoms from the three chelated ABA groups have bond distances of 2.488(3) and 2.482(3) Å. Three oxygen atoms from coordinated water molecules bond at 2.452(3) Å. The average Sm–O distance is 2.475 Å. Analogous bond distances between Dy and carboxylate oxygen atoms are 2.431(3) and 2.447(3) Å, and to coordinated water 2.398(3) Å. The average Dy–O distance is 2.425 Å, much shorter than that for the Sm complex, in line with the ionic radii of the trivalent cations. The bond angle subtended at Sm by oxygen atoms of the carboxyl groups is 52.63(8)° and that at Dy is 53.28(9)°. Selected bond distances and angles for the complexes are listed in table 3.

In the unit cell of **1**, the existence of noncoordinated water molecules gives rise to a complex hydrogen-bonding network. Three types of intermolecular $O–H \cdots O$ hydrogen bonds are evident. One involves the oxygen atom of the lattice water and an oxygen atom of the chelated ABA anion [$O(4)–H(4B) \cdots O(2)^c$, bond angle 121(6)°]; the corresponding bond angle in **2** is 120(5)°. The second is between the oxygen atom of a coordinated water molecule and an oxygen atom of chelated ABA [$O(1)–H(1B) \cdots O(3)^e$, bond angle 176(4)°]; the corresponding bond angle in **2**

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3/\text{Å}^2$) for $Sm(ABA)_3(H_2O)_3 \cdot H_2O$, **1**, and $Dy(ABA)_3(H_2O)_3 \cdot H_2O$, **2**.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Complex **1**				
Sm(1)	0	0	−1277(1)	17(1)
N(1)	6839(2)	9941(2)	2566(3)	37(1)
O(1)	9704(2)	8967(2)	−2718(2)	30(1)
O(2)	8522(2)	9056(2)	−982(2)	28(1)
O(3)	9115(1)	10101(1)	169(2)	24(1)
C(1)	8486(2)	9453(2)	−151(3)	24(1)
C(2)	7699(2)	9167(2)	446(3)	21(1)
C(3)	7018(2)	8425(2)	161(4)	29(1)
C(4)	6291(2)	8183(2)	723(4)	34(1)
C(5)	6232(2)	8658(2)	1547(3)	30(1)
C(6)	6900(2)	9405(2)	1817(3)	25(1)
C(7)	7640(2)	9650(2)	1275(3)	25(1)
O(4)	324(2)	7875(2)	7616(3)	39(1)
Complex **2**				
Dy(1)	0	0	11132(1)	19(1)
N(1)	9939(2)	3100(2)	7294(3)	39(1)
O(1)	10103(2)	971(2)	9704(2)	27(1)
O(2)	9062(2)	520(2)	10855(2)	27(1)
O(3)	8993(2)	−728(2)	12557(3)	31(1)
O(4)	6347(2)	888(2)	588(3)	41(1)
C(1)	9456(3)	947(3)	10024(3)	27(1)
C(2)	9170(2)	1455(2)	9429(3)	22(1)
C(3)	9646(2)	2000(2)	8595(3)	25(1)
C(4)	9405(3)	2495(3)	8050(3)	28(1)
C(5)	8660(3)	2418(3)	8325(3)	31(1)
C(6)	8179(3)	1876(3)	9156(4)	35(1)
C(7)	8428(2)	1395(2)	9717(3)	30(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

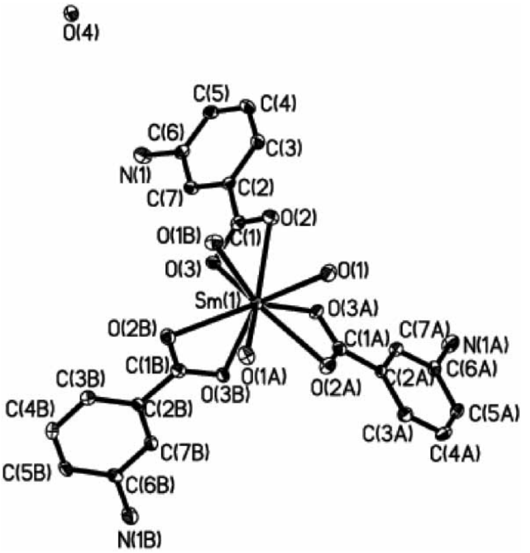

Figure 1. An ORTEP drawing of $Sm(ABA)_3(H_2O)_3 \cdot H_2O$ with the atom labeling scheme. $Dy(ABA)_3(H_2O)_3 \cdot H_2O$ is isomorphous.

Table 3. Selected bond distances (Å) and angles (°) for $Sm(ABA)_3(H_2O)_3 \cdot H_2O$ and $Dy(ABA)_3(H_2O)_3 \cdot H_2O$.

Sm(1)–O(1)	2.452(3)	Dy(1)–O(1)	2.431(3)
Sm(1)–O(3)	2.482(3)	Dy(1)–O(2)	2.447(3)
Sm(1)–O(2)	2.488(3)	Dy(1)–O(3)	2.398(3)
O(1)–Sm(1)–O(1A)	76.38(12)	O(3A)–Dy(1)–O(3)	76.10(14)
O(1)–Sm(1)–O(1B)	76.38(12)	O(3A)–Dy(1)–O(3B)	76.10(14)
O(1)–Sm(1)–O(3A)	145.30(9)	O(3)–Dy(1)–O(3B)	76.10(14)
O(1B)–Sm(1)–O(3A)	88.96(9)	O(3A)–Dy(1)–O(1B)	144.80(11)
O(1)–Sm(1)–O(3A)	88.96(9)	O(3)–Dy(1)–O(1B)	88.99(10)
O(1A)–Sm(1)–O(3B)	145.30(9)	O(3A)–Dy(1)–O(1)	88.99(10)
O(3A)–Sm(1)–O(3B)	77.08(10)	O(3)–Dy(1)–O(1)	131.46(11)
O(1)–Sm(1)–O(3)	130.93(9)	O(3B)–Dy(1)–O(1)	144.80(12)
O(1A)–Sm(1)–O(3)	88.96(9)	O(1B)–Dy(1)–O(1)	77.21(11)
O(1B)–Sm(1)–O(3)	145.30(9)	O(3)–Dy(1)–O(1A)	144.80(11)
O(3A)–Sm(1)–O(3)	77.08(10)	O(3B)–Dy(1)–O(1A)	88.99(10)
O(3B)–Sm(1)–O(3)	77.08(10)	O(1B)–Dy(1)–O(1A)	77.21(11)
O(1)–Sm(1)–O(2A)	143.46(11)	O(1)–Dy(1)–O(1A)	77.21(11)
O(1A)–Sm(1)–O(2A)	78.33(10)	O(3)–Dy(1)–O(2A)	142.77(12)
O(1B)–Sm(1)–O(2A)	72.32(9)	O(3B)–Dy(1)–O(2A)	71.87(11)
O(3B)–Sm(1)–O(2A)	126.00(10)	O(1B)–Dy(1)–O(2A)	126.66(10)
O(3)–Sm(1)–O(2A)	73.99(8)	O(1)–Dy(1)–O(2A)	73.96(9)
O(1)–Sm(1)–O(2)	78.33(10)	O(3A)–Dy(1)–O(2)	71.87(10)
O(1A)–Sm(1)–O(2)	72.32(9)	O(3)–Dy(1)–O(2)	78.22(11)
O(1B)–Sm(1)–O(2)	143.46(11)	O(3B)–Dy(1)–O(2)	142.77(12)
O(3A)–Sm(1)–O(2)	126.00(10)	O(1B)–Dy(1)–O(2)	73.96(9)
O(3B)–Sm(1)–O(2)	73.99(8)	O(1)–Dy(1)–O(2)	53.28(9)
O(3)–Sm(1)–O(2)	52.63(8)	O(1A)–Dy(1)–O(2)	126.66(10)
O(2A)–Sm(1)–O(2)	118.03(3)	O(2A)–Dy(1)–O(2)	118.25(3)
O(1)–Sm(1)–O(2B)	72.32(9)	O(3A)–Dy(1)–O(2B)	142.77(12)
O(1A)–Sm(1)–O(2B)	143.46(11)	O(3)–Dy(1)–O(2B)	71.87(11)
O(3A)–Sm(1)–O(2B)	73.99(8)	O(1)–Dy(1)–O(2B)	126.66(10)
O(3)–Sm(1)–O(2B)	126.00(10)	O(1B)–Dy(1)–O(2B)	73.96(9)
O(2A)–Sm(1)–O(2B)	118.03(3)	O(2B)–Dy(1)–O(2B)	118.25(3)
O(2)–Sm(1)–O(2B)	118.03(3)	O(2)–Dy(1)–O(2B)	118.25(3)

Symmetry transformations used to generate equivalent atoms are: (A) $-x+y+2, -x+1, z$; (B) $-y+1, x-y-1, z$.

is 173(5)°. Third, similar bonds exist between a coordinated water molecules and the lattice water molecule [O(1)–H(1A)$\cdots$O(4)^f, bond angles 175(5) and 129(5)° in **1** and **2**, respectively. In addition, there are O–H$\cdots$N and N–H$\cdots$O hydrogen bonds between lattice water molecules and amine groups of the chelated ABA anion [O(4)–H(4A)$\cdots$N(1)^d, bond angles 159(4) and 163(4)° in **1** and **2**, respectively; N(1)–H(1C)$\cdots$O(4)^g, bond angles 147.5 and 147.1° in **1** and **2**, respectively]. The hydrogen-bonding network links the complexes into a 3D network and lends the structure extra stability. Details of the hydrogen-bonding scheme are listed in table 4.

3.2. *Photophysical properties*

Excitation at 596 nm of the solid complex **1** gave rise to one main peak at 247 nm and excitation of **2** at 484 nm gave five main peaks at 202, 208, 227, 288 and 398 nm. For Complex **1**, excitation of 247 nm gave rise to emission at 560 and 596 nm, attributed to the $^4G_{5/2} \rightarrow {}^6H_J$ ($J=5/2$ and $7/2$) transitions of the Sm^{3+} ion. For Complex **2**, the luminescence spectrum shows two emission peaks with excitation at 398 nm,

Table 4. Hydrogen bond details (Å, °) for $Sm(ABA)_3(H_2O)_3 \cdot H_2O$, **1**, and $Dy(ABA)_3(H_2O)_3 \cdot H_2O$, **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
Complex **1**				
O(4)–H(4B)···O(2)^{c}	0.84(2)	2.60(7)	3.123(4)	121(6)
O(4)–H(4A)···N(1)^{d}	0.809(18)	2.21(2)	2.982(5)	159(4)
O(1)–H(1B)···O(3)^{e}	0.841(19)	1.935(19)	2.774(4)	176(4)
O(1)–H(1A)···O(4)^{f}	0.819(19)	2.06(2)	2.880(4)	175(5)
N(1)–H(1C)···O(4)^{g}	0.86	2.31	3.068(5)	147.5
Complex **2**				
O(4)–H(4B)···O(2)^{c}	0.825(19)	2.63(5)	3.131(4)	120(5)
O(4)–H(4A)···N(1)^{d}	0.825(17)	2.18(2)	2.981(5)	163(4)
O(3)–H(3B)···O(1)^{e}	0.798(18)	1.99(2)	2.785(4)	173(5)
O(3)–H(3A)···O(4)^{f}	0.797(19)	2.32(5)	2.885(5)	129(5)
N(1)–H(1A)···O(4)^{g}	0.86	2.29	3.044(5)	147.1

Symmetry transformations used to generate equivalent atoms are: $^{a}-x+y+1, -x+2, z$; $^{b}-y+2, x-y+1, z$; $^{c}-y+1, x-y+1, z+1$; $^{d}x-2/3, y-1/3, z+2/3$; $^{e}x, x-y+1, z-1/2$; $^{f}x+1, y, z-1$; $^{g}-y+4/3, x-y+5/3, z-1/3$.

and emission at 478 and 576 nm. These correspond with the characteristic $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2, 13/2$) transitions of the Dy^{3+} ion.

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