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Synthesis and structural diversity of rare earth anthranilate complexes

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Dedicated to Professor Malcolm Chisholm F.R.S. on the occasion of his 60th birthday.

Abstract

Four structural classes have been established for rare earth anthranilates, which have been prepared from the lanthanoid chloride or triflate and anthranilic acid (anthH) followed by pH adjustment to 4. $[La(anth)_3]_n$ is a polymeric complex with nine coordinate lanthanum and bridging tridentate (O,O,O') anthranilate ligands, whereas $[Nd(anth)_3(H_2O)_3] \cdot 3H_2O$ is monomeric with nine coordinate neodymium and solely chelating (O,O) anthranilate groups. Both chelating (O,O) and bridging bidentate (O,O') ligands are observed in dimeric $[Er_2(anth)_6(H_2O)_4] \cdot 2H_2O$, in which erbium is eight coordinate and the water ligands are in a *trans* arrangement. A polymer is observed for $[Yb(anth)_3(H_2O)]_n$ with solely bridging bidentate (O,O') ligands and seven coordination for ytterbium. The NH₂ groups of the anthranilate ligands are not coordinated to the metal but is unusually involved in hydrogen-bond networks with water molecules for Ln = Er, Yb. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Although there have been widespread studies of complexes of rare earth ions with amino acids [1], there are only two structurally characterised complexes with anthranilate ions (anth) (Fig. 1), viz. $[Y(anth)_3(H_2O)]_n$ [2] and $[Eu_2(anth)_6(bpy)_2]$ (bpy = 2,2'-bipyridine) [3]. This contrasts the extensive structural chemistry of anthranilate ions with alkali metals [4,5], alkaline earth metals [6,7], and transition metals [8–12]. Structural proposals have been made for rare earth anthranilates $Ln(anth)_3 \cdot nH_2O$ (n = 0, Ln = La, Ce, Pr, Nd, Sm; n = 2, Ln = Y, Tb-Lu; and n = 1, Ln = Eu, Gd) on the basis of analytical, IR, and X-ray powder data [13,14]. It was suggested that the lighter rare earth anthranilates form two isostructural groups, (i) La-Sm, and (ii) Y, Eu, Gd [13]. A subsequent study found Tb-Lu to be isostructural [14]. IR data suggested coordination of both carboxylate and amino groups.

The insoluble nature of lanthanoid anthranilates makes growing crystals suitable for X-ray diffraction difficult. However because of our interest in lanthanoid anthranilates as possible "green" corrosion inhibitors [15], we have undertaken a study of the structures of representative lanthanoid anthranilates to assist in understanding the structural basis of corrosion inhibitors.

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Fig. 1. A line drawing of the anthranilate anion.

2. Experimental

2.1. Materials and instrumentation

Lanthanoid oxides (Nd₂O₃ and Yb₂O₃) were obtained from Honeywell. Er2O3 was supplied by Aldrich. Lanthanoid chlorides (other than LaCl₃) were prepared by dissolving lanthanoid oxides in hydrochloric acid. $Er(OTf)_3$ was prepared by dissolving Er_2O_3 in trifluoromethanesulfonic acid (HOTf). The resulting solutions were diluted, and the concentrations of the prepared solutions were accurately determined by complexometric titration with standardised 0.01 M Na₂H₂-EDTA. LaCl₃ · 7H₂O was obtained from Chempur. Reagent grade anthranilic acid was obtained from Merck, and used without further purification. All other starting materials were used as received. Microanalyses were performed in duplicate by the Campbell Microanalytical Laboratory of the University of Otago, Dunedin, New Zealand. Rare earth analyses were carried out by digesting accurately weighed samples in concentrated nitric and sulphuric acid and boiling the solutions to dryness. The resulting residues were diluted with water, and aliquots were buffered with hexamethylenetetramine and titrated against standardised 0.01 M Na₂H₂-EDTA with Xylenol Orange as the indicator. Infrared spectra were recorded as Nujol mulls sandwiched between NaCl plates using a Perkin Elmer 1600 FTIR instrument in the range $4000-500 \text{ cm}^{-1}$. ¹⁹F NMR spectra were recorded on a Bruker DPX 300 spectrometer, using $CFCl_3$ in d_6 -acetone as an external reference. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 1 instrument at a heating rate of 10 °C min⁻¹, using a platinum sample pan.

2.2. Synthesis

2.2.1. $[La(anth)_3]_n$ (1)

Anthranilic acid (0.35 g, 2.6 mmol) was dissolved in 2 mL of MeOH, and the solution added to a stirred aqueous solution of LaCl₃ (5.0 mL, 5.0 mmol) heated to 70 °C. The pH of the reaction mixture was raised by the dropwise addition of 0.5 M NaOH. At a pH of approximately 4, a faint permanent precipitate formed. The reaction mixture was then cooled, and the precipitate filtered off. Crystals appeared following the slow evaporation of the reaction mixture at room temperature.

Yield: 0.21 g (45%). *Anal.* Calc. for $C_{21}H_{18}N_3O_6La$: C, 46.09; H, 3.32; N, 7.68; La, 25.38. Found: C, 46.23; H, 3.40; N, 7.83; La, 25.40%. Infrared (cm⁻¹): 3467 m, 3421 m, 3356 m, 3324 m, 1615 s, 1574 m, 1505 s, 1456 s, 1385 s, 1338 m, 1309 m, 1258 m, 1156 m, 1133 m, 1027 w, 978 w, 946 w, 875 m, 853 w, 811 m, 753 m, 707 m, 669 m.

2.2.2. $[Nd(anth)_3(H_2O)_3] \cdot 3H_2O(2)$

The compound was synthesised using the above procedure except that $NdCl_3$ (4.0 mL, 3.3 mmol) and anthranilic acid (0.21 g, 1.5 mmol) were used.

Yield: 0.12 g (36%). Anal. Calc. for $C_{21}H_{30}N_3O_{12}Nd$: C, 38.18; H, 4.58; N, 6.36; Nd, 21.83. Found: C, 38.17; H, 4.43; N, 6.16; Nd, 22.65%. Infrared (cm⁻¹): 3593 m, 3431 s, 1656 m, 1614 s, 1574 m, 1506 s, 1446 m, 1398 s, 1331 m, 1308 m, 1256 m, 1158 m, 1128 w, 1030 w, 981 w, 959 w, 875 m, 821 m, 770 s, 707 m, 672 m.

2.2.3. $[Er_2(anth)_6(H_2O)_4] \cdot 2H_2O(3)$

The compound was synthesised using the above procedure except that $Er(OTf)_3$ (4.0 mL, 3.5 mmol) and anthranilic acid (0.21 g, 1.5 mmol) were used. Single crystals of **3** were separated by hand picking. The bulk product analysed as $[Er_2(anth)_6(H_2O)_4] \cdot HO_3SCF_3 \cdot 2H_2O$, (**3** \cdot HO₃SCF₃).

Yield: 0.18 g. *Anal.* Calc. for $C_{43}H_{49}F_3N_6O_{21}SEr_2$ (**3** · HO₃SCF₃): C, 36.64; H, 3.50; N, 5.96; Er, 23.73. Found: C, 36.23; H, 3.54; N, 5.25; Er, 24.30%. Infrared (cm⁻¹): 3627 m, 3478 s, 3361 m, 3343 s, 3312 m, 1614 m, 1574 m, 1538 m, 1514 m, 1506 m, 1485 s, 1421 s, 1340 m, 1302 m, 1262 m, 1260 m, 1159 m, 1156 m, 1032 m, 960 w, 879 m, 820 m, 770 m, 750 m, 704 m, 673 m, 641 m. ¹⁹F NMR (*d*₆-acetone) $\delta = -37.66$ ppm.

2.2.4. $[Yb(anth)_3(H_2O)]_n$ (4)

The compound was synthesised using the above procedure except that YbCl₃ (9.5 mL, 7.6 mmol) and anthranilic acid (0.52 g, 3.8 mmol) were used. Single crystals of **4** were separated but the bulk crystalline product analysed as $4 \cdot 2H_2O$ after prolonged desiccation at room temperature.

Yield: 0.22 g. *Anal.* Calc. for $C_{21}H_{24}N_3O_9Yb$ ($4 \cdot 2H_2O$): C, 39.69; H, 3.81; N, 6.61; Yb, 27.23. Found: C, 39.91; H, 4.10; N, 6.49; Yb, 27.26%. Infrared (cm⁻¹): 3479 m, 3394 m, 3343 m, 3278 m, 3178 m, 1682 m, 1613 m, 1572 m, 1542 m, 1521 m, 1506 m, 1483 m, 1416 s, 1339 w, 1303 m, 1272 w, 1260 m, 1155 m, 1024 w, 880 m, 820 w, 767 w, 750 m, 704 w, 674 w. TGA: % mass loss 50–200 °C: 8.2%. Calculated mass loss of three H₂O molecules: 8.5%.

2.3. X-ray crystallography

Intensity data for complexes 1–4 were collected using an Enraf–Nonius KAPPA CCD at 123 °K with Mo Kα radiation ($\lambda = 0.7170$ Å). Suitable crystals were immersed in viscous hydrocarbon oil, mounted on a glass fibre which was mounted on the diffractometer. Using psi and omega scans N_t (total) reflections were measured, which were reduced to No unique reflections, with $F_{o} > 2\sigma(F_{o})$ being considered observed. Data were corrected for absorption with a SORTAV multi-scan absorption correction [16]. The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2 , with anisotropic thermal parameters refined for non-hydrogen atoms. Aromatic hydrogen atoms were constrained in calculated positions and refined with a riding model. All other hydrogen atoms were found directly from the difference Fourier map and refined isotropically. Structure solutions and refinements were performed using the programs shelxs-97 [17] and shelxl-97 [18] through the graphical interface X-Seed [19]. Crystal data and structural refinement data for complexes 1-4 are given in Table 1. Selected bond lengths for complexes 1-4 are listed in Table 2, and hydrogen bond lengths and angles for complexes 2–4 are given in Table 3.

Bond angles and other crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication No. CCDC-270607 for compound 1, CCDC-270608 for compound 2, CCDC-270609 for compound 3 and CCDC-270610 for compound 4. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223 336 033; deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Synthesis of the complexes

Lanthanoid carboxylate complexes are typically synthesised by adding the carboxylate salt to a solution of the lanthanoid salt. An alternative procedure is to add the carboxylic acid to precipitated lanthanoid hydroxides, a method utilised by Brzyska and Rzaczynska [13,14] during their study of lanthanoid anthranilates. The insolubility of lanthanoid anthranilates limits the usefulness of these two methods to grow crystals suitable for single crystal X-ray analysis. The use of a diffusion apparatus yielded crystals of the complex $[Y(anth)_3(H_2O)]_n$ [2]. We have found that the use of a simpler method can yield suitable crystals. The addition of anthranilic acid to lanthanoid chloride solutions followed by the addition of NaOH dropwise to the reaction mixture to form the Na anthranilate salt led to the isolation of La, Nd, Er and Yb anthranilates after slow evaporation of the reaction mixture (pH ca. 4) at room temperature. This approach has been previously employed using higher pH conditions in the synthesis of lanthanoid hydroxo clusters [20].

Both the La and Nd anthranilates crystallise as large (diameter greater than 2 mm) single crystals, and the micro and metal analysis results of the La and Nd anthranilates confirm the stoichiometry obtained from the X-ray crystallography results. The Er and Yb anthranilates crystallise as clusters of thin needles, the clusters partially decomposing into watery solution as they are broken apart with a needle. Consequently, suitable crystals

Table 1

Crystallographic and data collection parameters for complexes 1-4

Complex	1	2	3	4
Formula	C42H36La2N6O12	C ₂₁ H ₃₀ N ₃ NdO ₁₂	C ₂₁ H ₂₄ ErN ₃ O ₉	$C_{21}H_{20}N_{3}O_{7}Yb$
Formula weight	1094.59	660.72	629.69	599.44
Colour, habit	brown block	dark brown block	light brown needle	light brown needle
Crystal size (mm)	$0.20 \times 0.20 \times 0.10$	$0.30 \times 0.25 \times 0.20$	$0.25 \times 0.25 \times 0.20$	$0.20 \times 0.10 \times 0.10$
Crystal system	monoclinic	hexagonal	orthorhombic	monoclinic
Space group	$P2_1/c$	R3c	Pbca	C2/c
Unit cell dimensions				
a (Å)	24.760(5)	18.566(3)	8.4910(17)	31.234(6)
b (Å)	7.4954(15)	18.566(3)	19.645(4)	9.0441(18)
<i>c</i> (Å)	24.485(5)	12.282(3)	28.129(6)	15.596(3)
α (°)	90	90	90	90
β (°)	119.29(3)	90	90	108.44(3)
γ (°)	90	120	90	90
Volume (Å ³)	3963.1(14)	3666.4(10)	4692.0(16)	4179.2(14)
Ζ	4	6	8	8
$D_{\rm calc} ({\rm g/cm}^3)$	1.835	1.795	1.783	1.905
<i>F</i> (000)	2160	1998	2488	2344
Measured reflections	25192	12462	43956	30452
Independent reflections	9027	1871	4612	4094
R _(int)	0.0272	0.0502	0.0804	0.0544
Goodness-of-fit on F^2	1.084	1.064	1.006	1.065
R	0.0264	0.0195	0.0378	0.0247
R_w	0.0582	0.0428	0.0929	0.0577

Table 2 Selected bond lengths (Å) for complexes 1–4

Complex 1	
La(1) - O(1)	2.635(2)
La(1)–O(1)#1	2.473(2)
La(1)–O(2)	2.567(2)
La(1)–O(3)	2.634(2)
La(1)–O(3)#2	2.507(2)
La(1)–O(4)	2.530(2)
La(1)–O(5)	2.636(2)
La(1)–O(5)#1	2.475(2)
La(1)–O(6)	2.548(2)
La(2)–O(7)	2.634(2)
La(2)–O(7)#3	2.473(2)
La(2)–O(8)	2.566(2)
La(2)–O(9)	2.683(2)
La(2)–O(9)#3	2.475(2)
La(2)–O(10)	2.543(2)
La(2)–O(11)	2.655(2)
La(2)–O(11)#4	2.487(2)
La(2)–O(12)	2.524(2)
Complex 2	
Nd(1)–O(1)	2.464(2)
Nd(1)–O(2)	2.549(2)
Nd(1)–O(3)	2.492(2)
Complex 3	
$\operatorname{Er}(1) - O(1)$	2.397(4)
$\operatorname{Er}(1) - \operatorname{O}(2)$	2.400(4)
$\operatorname{Er}(1) - \operatorname{O}(3)$	2.369(4)
$\operatorname{Er}(1)$ – $O(4)$	2.356(4)
Er(1) - O(5)	2.272(4)
Er(1) - O(6) #1	2.241(4)
Er(1) - O(7)	2.354(4)
Er(1)–O(8)	2.360(4)
Complex 4	
Yb(1)–O(1)	2.285(3)
Yb(1)–O(2)	2.276(2)
Yb(1)–O(3)#1	2.317(3)
Yb(1)–O(4)	2.301(3)
Yb(1)–O(5)#1	2.274(2)
Yb(1)–O(6)#1	2.199(3)
Yb(1)–O(7)	2.213(3)

Symmetry transformations used to generate equivalent atoms for: Complex (1): #1 -x, y + 1/2, -z + 1/2; #2 -x, y-1/2, -z + 1/2; #3 -x + 1, y - 1/2, -z + 1/2; #4 -x + 1, y + 1/2, -z + 1/2. Complex (3): #1 -x + 1, -y, -z + 1.

Complex (4): #1 - x + 3/2, y + 1/2, -z + 1/2.

of Er and Yb anthranilates for X-ray analysis were handpicked from the bulk product. The unit cells of several crystals obtained from the Yb anthranilate reaction mixture were in agreement with that of the crystal of the solved structure. The discrepancy between the X-ray determined composition and the observed micro and metal analysis values is likely to be due to the presence of additional water molecules trapped within the clusters of crystals. Microanalyses of bulk products from two preparations and a metal analysis were all consistent with [Yb(anth)₃(H₂O)] \cdot 2H₂O, i.e., $4 \cdot$ 2H₂O, as was the TGA weight loss over 60–200 °C. Prior to analysis,

Table 3 Hydrogen bond lengths (Å) and bond angles (°) for complexes 2-4

		0 () 1		
D–H···A	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)
Complex 2				
O(3) - H(3A) - O(2) = 0	0.971(19)	1.796(19)	2.765(3)	176(4)
$O(3) - H(3B) \cdots O(4) \# 1$	0.955(18)	1.840(19)	2.794(3)	177(3)
Complex 3				
O(7)−H(7A)···O(9)#3	0.99(2)	1.67(3)	2.644(6)	166(8)
$O(7)-H(7B)\cdots N(1)#3$	0.99(2)	1.89(3)	2.864(6)	166(6)
O(8) - H(8B) - O(1) #2	0.98(2)	2.01(6)	2.825(6)	138(6)
$O(9)-H(9A)\cdots O(3)$	0.99(2)	1.76(2)	2.748(6)	171(6)
Complex 4				
$O(1)-H(4A)\cdots N(3)#3$	0.79(5)	2.07(5)	2.845(5)	171(5)
$O(1)-H(4B)\cdots N(1)#4$	0.85(5)	2.01(5)	2.845(5)	170(4)
~ ~ ~				

Symmetry transformations used to generate equivalent atoms for: Complex (2): #1 - x + y, -x + 1, z; #3 x, x - y + 1, z + 1/2. Complex (3): #2 - x + 2, -y, -z + 1; #3 x - 1/2, -y + 1/2, -z + 1.

Complex (3): #2 - x + 2, -y, -2 + 1, #3 - 1/2, -y + 1/2, -2 + 1. Complex (4): #3 - x + 3/2, -y + 3/2, -z + 1; #4 - x, -y + 2, z + 1/2.

the samples were dried in a desiccator to constant weight and they remained at constant weight for 2 days after removal from the desiccator. No disordered water was evident in the crystal structure but it is possible that highly disordered waters could be present in holes in the lattice. The issue of hydration in lanthanoid anthranilates is also observed in comparing the anhydrous Nd(anth)₃ composition proposed by Brzyska and Rzaczynska [13] from a synthesis in water with the composition of **2**, which contains six water molecules. Possibly small differences in reaction conditions and drying techniques have a major effect on hydration and structure.

An even more marked difference between single crystal structure and bulk composition is observed with **3**, where the bulk composition corresponds more closely to $\mathbf{3} \cdot \text{HO}_3\text{SCF}_3$, and the ¹⁹F NMR spectrum shows clear evidence of a CF₃ resonance, somewhat paramagnetically shifted (by Er³⁺) from the free acid value ($\delta = -77.9$ ppm). Plausibly, isolation at pH 4 leads to protonation of one amino group of **3** giving **3**H⁺(OTf⁻).

3.2. Crystal structure descriptions

Complexes 1–3 represent new structural classes of lanthanoid anthranilates, while complex 4 is isostructural with the previously reported Y anthranilate [2]. In all four structures, the anthranilate ligand is bound to the lanthanoid solely through the carboxylate group, in contrast to carboxylate and NH₂ coordination found in transition metal anthranilates and proposed for rare earth anthranilates [13,14]. Although the amino group is not bound to the lanthanoid cation, the amino group participates in hydrogen bonding in complexes 3 and 4, stabilising the crystal structures. The results of this study demonstrate that lanthanoid anthranilates exhibit a range of structural classes, even more diverse than the closely related lanthanoid *p*-aminobenzoates [21].

Complex 1 crystallises as an anhydrous species in the monoclinic space group $P2_1/c$. Selected bond lengths are given in Table 2. The structure consists of two crystallographically distinct polymer chains. The bonding in the two chains is almost identical with only negligible differences in bond lengths (Table 2). Only bridging tridentate (O,O,O') ligands are present. The asymmetric unit consists of two independent La mononuclear units, each bound to three anthranilate ligands. Each polymer strand (Fig. 2) is built up from the monomeric units by links to two adjacent La cations, through bridging tridentate anthranilate ligands. Overall, each lanthanum is surrounded by six bridging tridentate ligands, three of which chelate (O,O) to a given lanthanum, and three are unidentate (O). Consequently, each La ion displays a coordination number of nine. In chain 1 the average La(1)–O (carboxylate) bond distance is 2.556 Å, and the distances between adjacent La ions is 3.901 Å. In chain 2, the average La(2)-O carboxylate distance is 2.560 Å and the distance between adjacent La ions is 3.893 Å. The coordination environment around La(1) is best described as a doubled trigonal prism [22], while for La(2) the coordination environment most closely resembles a capped cube [22]. The presence of two independent polymer chains with the same composition but slightly different structures in the same crystal is uncommon, but it has been previously reported in a praseodymium β -alanine complex [23].

Complex 2 crystallises in the hexagonal space group R3c and is monomeric. Selected bond lengths are listed in Table 2. As displayed in Fig. 3, the Nd cation is surrounded by three chelating anthranilate ligands, and three water O atoms giving a coordination number of nine. The coordination environment around the Nd

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La1

most closely resembles a doubled trigonal prism [22]. The Nd-O (carboxylate) distances are markedly different, being 2.464 (2) Å (Nd-O(1)) and 2.549 (2) Å (Nd–O(2)), indicating asymmetric chelation of the anthranilate ligands. The carboxylate angles (O(1)-C(1)-O(2)) are 119.1 (3)°. The angle between the Nd cation and centroids generated between the carboxylate oxygens of the anthranilate ligands is 99.36°, indicating that the anthranilate ligands adopt a *cisoid* geometry around the Nd cation. The Nd-O (water) distances are 2.492 (2) Å, comparable with the Nd–O carboxylate distances. The angle between the O atoms of coordinated water molecules and the Nd is 74.25 (10)°, indicating the coordinated water molecules are also arranged in a cisoid geometry. Three water molecules (two are symmetry generated) reside in the lattice and hydrogen bonding links coordinated water and lattice water molecules. Hydrogen bonding also occurs between the coordinated water and the carboxylate oxygen of the anthranilate ligand. Hydrogen bond lengths and angles are given in Table 3. Surprisingly, the structure is isostructural with the closely related lanthanoid m-aminobenzoate hydrate structures, despite the different positions of the NH₂ substituent. Lanthanoid complexes of *m*-aminobenzoates have been shown to be isostructural from La to Lu including Y [24], unlike the anthranilates.

Complex 3 crystallises in the orthorhombic space group *Pbca* and is a dimer. Selected bond lengths are listed in Table 2. In addition to two bound water molecules, each Er cation is encircled by four anthranilate ligands which exhibit two different binding modes (Fig. 4). Two chelating anthranilate ligands and two bridging bidentate anthranilate ligands give an overall



04

C3



Fig. 3. An ORTEP representation of 2, exhibiting the chelating anthranilate ligands. Lattice water molecules and hydrogen atoms on anthranilate ligands have been omitted for clarity (ellipsoids at 50% probability). Inset – stylised diagram displaying the ligand connectivity (aromatic groups omitted for clarity).



Fig. 4. An ORTEP representation of **3**, displaying the dimeric structure. Lattice water molecules and hydrogen atoms on anthranilate ligands have been omitted for clarity (ellipsoids at 50% probability). Inset – stylised diagram showing the ligand connectivity (aromatic groups omitted for clarity).

coordination number of eight for each Er cation. The coordination geometry around each Er centre most closely resembles a square antiprism [22]. The average carboxylate bite angle for the chelating anthranilate ligands is 118.95°, while for the bridging anthranilate ligands it is 122.82°. The chelating anthranilate ligands adopt a *cisoid* geometry around the Er cation, while the coordinated water molecules are arranged in a *transoid* geometry. The average Er–O distance for chelating anthranilate ligands is 2.381 Å, and for bridging anthranilate ligands is 2.257 Å. The average Er–O (water) distance is 2.357 Å. Two water molecules reside in the lattice. Hydrogen bonding links the lattice water molecule to the carboxylate group of the anthranilate ligand. The coordinated water molecules also participate in hydrogen bonding, and are linked to lattice water molecules and additionally to the amino groups of anthranilate ligands bound to neighbouring Er cations, therefore generating a polymeric supramolecular structure. Hydrogen bond lengths and angles are given in



Fig. 5. An ORTEP representation of **4**, illustrating the bridging bidentate anthranilate ligands present in the polymeric structure. Hydrogen atoms on anthranilate ligands have been omitted for clarity (ellipsoids at 50% probability). Inset – stylised diagram displaying the ligand connectivity (aromatic groups omitted for clarity).

Table 3. The structure of complex **3** is similar to that of the related Er salicylate [25].

Complex 4 crystallises in the monoclinic space group C2/c. Selected bond lengths are listed in Table 2. The polymeric structure consists of Yb cations linked by six bridging bidentate anthranilate ligands, resulting in the formation of linear polymer chains (Fig. 5). In addition to one O atom from each of six anthranilate ligands, each Yb cation is also bound to one water molecule giving a coordination number of seven. The coordination environment around the Yb cation is best described as a pentagonal bipyramid [22]. The average Yb–O carboxylate distance is 2.263 Å, while the Yb–O (water) distance corresponds closely (2.285 Å). The Yb...Yb distance is 4.714 Å. Hydrogen bonding links the coordinated water molecule to the amino groups of two anthranilate ligands in an adjacent polymer chain. Hydrogen bond lengths and angles are given in Table 3. The complex is isostructural with the reported Y anthranilate [2]. Significant differences in the C–O distances of the carboxylate groups were reported for the Y anthranilate, but in the Yb anthranilate structure the C-O carboxylate distances are comparable. The Y-O

(water) distance (2.301 Å) and the Y···Y distance (4.742 Å), are comparable with analogous values for complex 4 allowing for ionic radius differences.

Selected rare earth anthranilate complexes have been tested as potential "green" corrosion inhibitors. The results of these tests indicate that rare earth anthranilates do act as corrosion inhibitors; however they are less effective inhibitors than the closely related rare earth salicylates [15].

4. Conclusions

By employing an alternative synthetic route we have synthesised and crystallised a range of lanthanoid anthranilates, and probed the solid state structures using X-ray crystallography. The results reveal a diverse range of structural classes exhibited by lanthanoid anthranilates. In all cases, the amino group of the anthranilate ligand is not coordinated to the lanthanoid cation. The carboxylate groups of the anthranilate ligand exhibited three different binding modes, chelating, bridging bidentate and bridging tridentate. The variations in structural class can be related to the lanthanoid contraction, with a decline from nine coordination (La) to seven (Yb). However other factors such as slight variations in reaction conditions including pH may influence the structural class isolated. Further investigation is required to unravel completely the origin of the structural diversity.

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