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**CRYSTAL STRUCTURES AND CHARACTERIZATION OF TWO ONE-DIMENSIONAL
COORDINATION POLYMERS CONTAINING Ln³⁺ IONS
AND ANTHRANILATE (C₇H₆NO₂)⁻ ANIONS**

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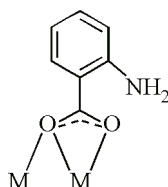
The syntheses, crystal structures and characterization (IR, TGA/DSC) of the isostructural one-dimensional coordination polymers [Ce(C₇H₆NO₂)₃]_n (**1**) and [Pr(C₇H₆NO₂)₃]_n (**2**) are described. The metal ions adopt distorted capped square anti-prismatic MO₉ coordination geometries. The anthranilate ligands bridge the metal ions in bridging-bidentate (O, μ²-O') mode to generate [010] chains in the crystal and each ligand features an intramolecular N—H···O hydrogen bond. It is notable that two very similar, but crystallographically distinct chains appear in the unit cell. Crystal data: **1**, C₂₁H₁₈CeN₃O₆, M_r = 548.51, monoclinic, P2₁/c (No. 14), a = 25.0476(10) Å, b = 7.4924(2) Å, c = 24.6366(7) Å, β = 119.424(1)°, V = 4027.1(2) Å³, R(F) = 0.037, wR(F²) = 0.068. **2**, C₂₁H₁₈N₃O₆Pr, M_r = 549.29, monoclinic, P2₁/c (No. 14), a = 25.0077(13) Å, b = 7.4497(3) Å, c = 24.6063(12) Å, β = 119.392(2)°, V = 3994.1(3) Å³, R(F) = 0.031, wR(F²) = 0.068.

Keywords: cerium, praseodymium, anthranilate anion, synthesis, crystal structure, one dimensional coordination polymer.

INTRODUCTION

Anthranilic acid (Hanth or 2-aminobenzoic acid), C₇H₇NO₂, has a minor structural claim to fame because it crystallizes with one neutral molecule and one zwitterionic molecule in the asymmetric unit [1]. In its deprotonated, anionic, anth⁻ form (see scheme below), it is an effective ligand for transition metal ions, which can bond in various different ways including O,O-bidentate [2], bridging-monodentate [3], O-monodentate [4] and N,O,O-bridging tridentate [5].

The structural chemistry of rare-earth anthranilates has been less studied. A preliminary report described the crystal structure of a bimetallic europium-anth complex [6] and a comprehensive study



Scheme 1. The anth⁻ anion in its (O,μ²-O') bridging-bidentate bonding mode

by Deacon *et al.* [7] revealed La, Nd, Eu and Er complexes with a wide variety of structures. As an extension of these studies, in this paper we describe the syntheses, characterization and single crystal structures of $[\text{Ce}(\text{C}_7\text{H}_6\text{NO}_2)_3]_n$ (**1**) and $[\text{Pr}(\text{C}_7\text{H}_6\text{NO}_2)_3]_n$ (**2**).

MATERIALS AND METHODS

Synthesis of 1. Solutions of cerium(III) nitrate hexahydrate (0.5 mmol, 0.217 g) in 10 ml distilled water and anthranilic acid (1.5 mol, 0.205 g) in 15 ml ethanol were prepared. Seven drops of 1 M sodium hydroxide solution were added to the anthranilic acid solution to raise the pH and the solutions were mixed and stirred for 30 minutes at room temperature. The solution was filtered and left at room temperature for crystallization. After 10 days, golden yellow blocks of **1** were recovered by vacuum filtration and rinsed with acetone. Yield: 42 %. Anal. calcd. (%) for $\text{C}_{21}\text{H}_{18}\text{CeN}_3\text{O}_6$: C 45.99; H 3.30; N 7.66. Found (%): C 46.92; H 3.42; N 8.18

Synthesis of 2. A solution of praseodymium(III) chloride hexahydrate (0.5 mmol, 0.187 g) in 10 ml distilled water was prepared. A solution of anthranilic acid (1 mmol, 0.137 g) in ethanol with six drops of 1 M NaOH added was mixed with the praseodymium solution and stirred for 1 h at room temperature. A white precipitate appeared which was then separated by filtration. The filtrate was kept at room temperature for crystallization: after seven days brown blocks of **2** were recovered. Yield: 38 %. Anal. calcd. (%) for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}_6\text{Pr}$: C 45.91; H 3.29; N 7.65. Found (%): C 47.61; H 3.46; N 8.32.

Physical measurements. The IR spectra of **1** and **2** were recorded on a Perkin-Elmer FTIR 180 spectrophotometer using KBr pellets over the frequency range 4000—400 cm^{-1} . Elemental analyses for C, H, and N were performed on a Varion Micro-Cube Analyzer. Thermal analyses (25—1200 °C) were recorded under a continuous N_2 flow with a ramp rate of 10 °C min^{-1} using a DSC/TGA model SDT Q 600, TA Instruments, USA. Alumina crucibles were used for recording the TG-DSC curves.

Crystal structure determinations. Intensity data for **1** (golden yellow block, 0.30×0.20×0.20 mm) and **2** (brown block, 0.25×0.20×0.10 mm) were collected at room temperature using a Bruker ApexII CCD diffractometer (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$). Multi-scan absorption corrections (transmission-factor ranges for **1** and **2** are 0.545—0.656 and 0.576—0.789, respectively) were made with SADABS [8] during data reduction. The structures were solved by direct methods with SHELXS-97 [9] in space group $P2_1/c$ and the structural models were developed and refined against $|F|^2$ using SHELXL-97 [9]. For both structures, the C-bound H atoms were geometrically placed ($\text{C—H} = 0.93 \text{ \AA}$) and refined as riding atoms with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ applied. The N-bound H atoms were located in difference maps, relocated to idealized positions ($\text{N—H} = 0.86 \text{ \AA}$), and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. Molecular graphics were generated with ORTEP-3 [10]. Crystal data for **1** and **2** are summarized in Table 1 and full details are available as supplementary material (cif format) (Table 1).

RESULTS

Infrared spectra. The IR spectra of **1** and **2** closely resemble each other (see supplementary materials), suggesting that they are isostructural, but are distinctly different to the spectrum of free anthranilic acid: in particular, the strong C—O(H) band at 1673 cm^{-1} in the free acid is not present in the spectra of **1** and **2**, indicating its deprotonation.

For **1**, intense vibrations at 1391 cm^{-1} and 1615 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the carboxylate group, respectively [11]. In **2**, the equivalent bands are observed at 1387 cm^{-1} and 1615 cm^{-1} , respectively, indicating that the oxygen atoms of the carboxylate groups are coordinated to the metal ion(s). There are no significant shifts in the asymmetric stretching (3474 cm^{-1}), symmetric stretching (3373 cm^{-1}), and bending vibrations (1509 cm^{-1}) for the —NH₂ amino group, which indicate that no bond is formed between its nitrogen atom and the metal atom [12], as confirmed by the crystal structures (*vide infra*). The spectra of both these complexes are destitute of any broad absorption bands around 3310 cm^{-1} , which indicates the absence of water mole-

Table 1

Crystallographic and data-collection parameters

| | 1 | 2 |
|--|---|--|
| Empirical formula | C ₂₁ H ₁₈ CeN ₃ O ₆ | C ₂₁ H ₁₈ N ₃ O ₆ Pr |
| Formula weight | 548.51 | 549.29 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 25.0476(10), 7.4924 (2), 24.6366 (7) | 25.0077(13), 7.4497 (3), 24.6063 (12) |
| β, deg. | 119.424(1) | 119.392(2) |
| <i>V</i> , Å ³ | 4027.1(2) | 3994.1(3) |
| <i>Z</i> | 8 | 8 |
| ρ _{calc} , g/cm ⁻³ | 1.809 | 1.827 |
| μ, mm ⁻¹ | 2.306 | 2.485 |
| Data scanned | 34323 | 35071 |
| Unique data | 9746 | 9823 |
| <i>R</i> _{int} | 0.047 | 0.040 |
| <i>R</i> (<i>F</i>) | 0.037 | 0.031 |
| <i>wR</i> (<i>F</i> ²) | 0.068 | 0.068 |
| Min., max. Δρ, e/Å ⁻³ | -0.82, +0.76 | -0.92, +0.91 |

cules [13]. The bands in the low frequency region 500—400 cm⁻¹ can be attributed to metal—oxygen bond vibrations [14].

Thermal analysis. The TGA trace for compound **1** shows that it is stable up to about 200 °C. Compound **1** then loses about 58 % of its initial weight by 1200 °C, without discernible intermediate steps and it appears that loss of volatile material is not complete, even at this elevated temperature. The calculated weight loss to generate Ce₂O₃ is 70 %.

Compound **2** is stable to 200 °C and then loses weight continuously to 1200 °C, at which point 68 % of the initial weight has been lost. This is in reasonably good agreement with a decomposition pathway that leads to a residue of Pr₂O₃ (calculated loss = 70 %).

Crystal structure of 1. Compound **1** is a one-dimensional coordination polymer: its asymmetric unit contains two Ce³⁺ ions and six C₇H₆NO₂⁻ anthranilate (anth⁻) anions (Fig. 1), which are both fragments of two completely separate but equivalent [Ce(anth)₃]_n infinite chains.

In the extended structure (Fig. 4), Ce1 is coordinated by nine oxygen atoms belonging to the C1-, C8- and C15-containing anions (Table 2), with the next-nearest O atom farther than 3.5 Å distant. The mean Ce—O separation is 2.541 Å and its bond-valence sum (BVS) [15] is 3.27 (expected value = 3.00), which suggests a degree of "over-bonding" [16].

If it is not to be merely regarded as irregular, the Ce1 coordination polyhedron could be described as a very-distorted capped square anti-prism [17] (Fig. 2) with the square faces defined by O1/O2/O3/O5ⁱ and O5/O3ⁱ/O4ⁱ/O1ⁱ (*i* = -*x*, 1/2+*y*, 1/2-*z*): the dihedral angle between these faces is 9.64(14)° and they are displaced by 1.0416(12) Å and -1.4250(12) Å, respectively from the metal ion. The displacement of the capping atom O6ⁱ through the O1 face is -1.388(3) Å.

Adjacent Ce1 atoms in the polymeric chain are linked *via* O1, O3, and O5 (*i.e.* one of the triangular side faces of the square anti-prism) to generate [010] chains, with each ligand bonding in bridging tridentate (O, μ²-O') mode (see scheme above), which obviously correlates with the nona-coordination of the metal ion. The separation of adjacent Ce1 atoms in the [010] chain is 3.8886(3) Å.

In the C1-containing anth⁻ ligand, the dihedral angle between the aromatic ring and the carboxylate group is 2.4(7)° and the chelated metal ion is displaced from the carboxylate plane by

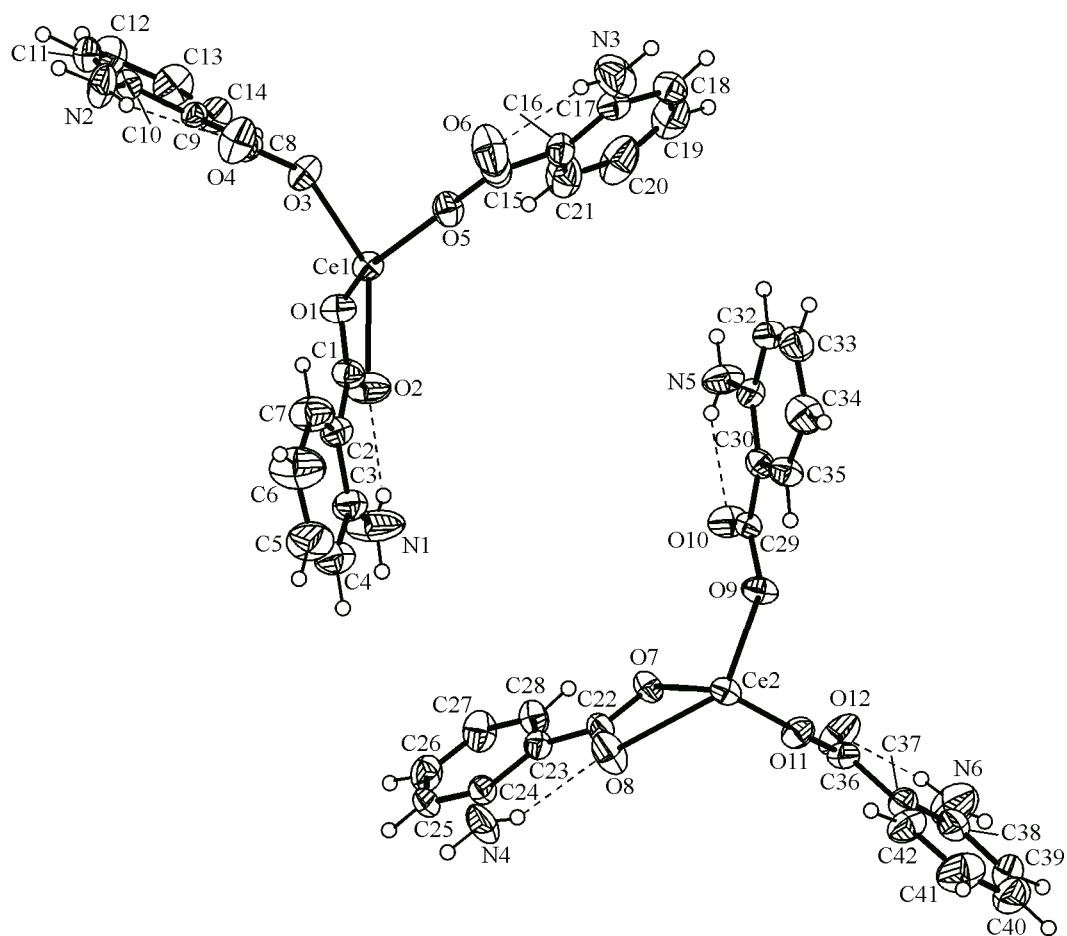


Fig. 1. The asymmetric unit of **1** showing 50 % displacement ellipsoids. The intra-ligand N—H \cdots O hydrogen bonds are shown as double-dashed lines

Table 2

Selected bond lengths (Å) and angles (deg. for **1**)

| | | | | | | | | |
|-----------------------|----------|-----------------------|----------|-----------------------------------|------|------|----------|-----|
| Ce1—O3 | 2.453(2) | Ce1—O5 | 2.458(2) | N1—H1B \cdots O2 | 0.86 | 2.05 | 2.690(4) | 130 |
| Ce1—O1 ⁱ | 2.484(2) | Ce1—O2 | 2.506(2) | N2—H2B \cdots O4 | 0.86 | 2.11 | 2.727(4) | 128 |
| Ce1—O6 ⁱ | 2.521(3) | Ce1—O4 ⁱ | 2.541(2) | N3—H3A \cdots O6 | 0.86 | 2.06 | 2.692(5) | 130 |
| Ce1—O5 ⁱ | 2.631(2) | Ce1—O1 | 2.636(2) | N4—H4A \cdots N2 ⁱⁱⁱ | 0.86 | 2.41 | 3.260(4) | 168 |
| Ce1—O3 ⁱ | 2.638(2) | | | N4—H4B \cdots O8 | 0.86 | 2.07 | 2.699(4) | 130 |
| Ce2—O11 | 2.454(2) | Ce2—O9 | 2.458(2) | N5—H5A \cdots N4 ^{iv} | 0.86 | 2.56 | 3.415(4) | 174 |
| Ce2—O7 ⁱⁱ | 2.467(2) | Ce2—O8 | 2.502(2) | N5—H5B \cdots O10 | 0.86 | 2.10 | 2.726(3) | 129 |
| Ce2—O12 ⁱⁱ | 2.518(2) | Ce2—O10 ⁱⁱ | 2.541(2) | N6—H6A \cdots O12 | 0.86 | 2.03 | 2.670(4) | 131 |
| Ce2—O9 ⁱⁱ | 2.631(2) | Ce2—O7 | 2.656(2) | | | | | |
| Ce2—O11 ⁱⁱ | 2.692(2) | | | | | | | |
| C1—O2 | 1.253(4) | C1—O1 | 1.291(4) | | | | | |
| C8—O4 | 1.251(4) | C8—O3 | 1.282(4) | | | | | |
| C15—O6 | 1.252(4) | C15—O5 | 1.287(4) | | | | | |
| C22—O8 | 1.257(4) | C22—O7 | 1.292(4) | | | | | |
| C29—O10 | 1.245(4) | C29—O9 | 1.292(4) | | | | | |
| C36—O12 | 1.252(4) | C36—O11 | 1.281(4) | | | | | |

Symmetry codes: (i) $-x, y+1/2, 1/2-z$; (ii) $1-x, y-1/2, 1/2-z$; (iii) $-x, -y, -z$; (iv) $x, 1/2-y, z+1/2$. For the hydrogen bonds, the four values correspond to the D—H, H \cdots A and D \cdots A separations (Å) and the D—H \cdots A angle (°), respectively.

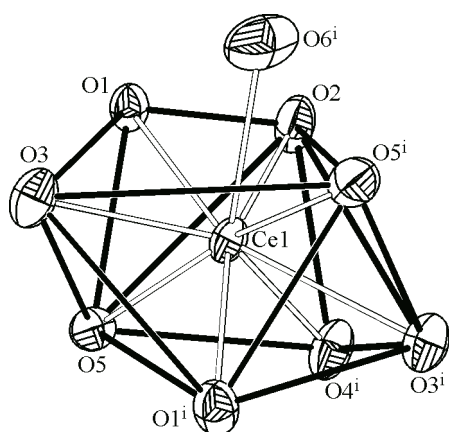


Fig. 2. The Ce1 coordination polyhedron in **1**.
Symmetry code: (i) $-x, y+1/2, 1/2-z$

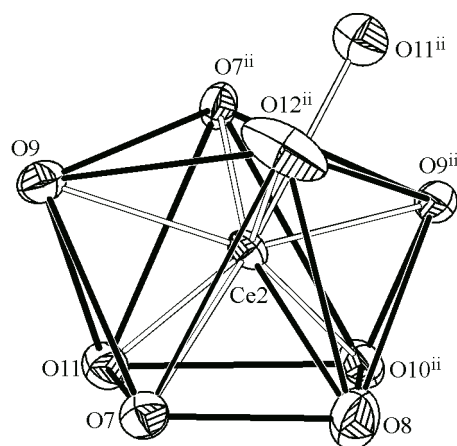


Fig. 3. The Ce2 coordination polyhedron in **1**.
Symmetry code: (ii) $1-x, y-1/2, 1/2-z$

$-0.122(1)$ Å. Equivalent data for the C8 ligand are $7.9(3)^\circ$ and $0.155(1)$ Å, respectively and for the C15 ligand are $2.8(3)^\circ$ and $-0.323(1)$ Å, respectively. Each ligand features an intramolecular N—H \cdots O hydrogen bond (Table 2), with the N—H \cdots O bond angles closely clustered in the range 128 – 130° .

Ce2 is also nine-coordinated by O atoms from the C22-, C29- and C36-containing ligands with a mean Ce—O distance of 2.547 Å and a BVS of 3.24. Its coordination can also be described as an extremely distorted capped square anti-prism, with O7/O8/O11/O10ⁱⁱ and O9/O7ⁱⁱ/O9ⁱⁱ/O12ⁱⁱ (ii = $1-x, y-1/2, 1/2-z$) defining the square faces and O11ⁱⁱ projecting through the second of these (Fig. 3). The dihedral angle between the squares is $4.43(12)^\circ$ and Ce2 is displaced by $-1.5300(12)$ Å from the first face and by $1.0075(11)$ Å from the second. The connectivity of the Ce2 atoms in the chain [via O7, O9 and O11 with Ce2 \cdots Ce2 = $3.8845(3)$ Å] and the bonding modes of the ligands are exactly equivalent to that of the equivalent species in the Ce1-chain.

For the C22 ligand, the dihedral angle between the aromatic ring and the carboxylate group is $2.4(7)^\circ$ and the displacement of the metal ion from the carboxylate plane by $-0.122(15)$ Å. Equivalent data for the C29 ligand are $7.9(3)^\circ$ and $0.231(14)$ Å, respectively and for the C36 ligand are $2.8(3)^\circ$ and $0.292(15)$ Å, respectively. Each ligand features an intramolecular N—H \cdots O hydrogen bond (Table 2): in each case the acceptor O atom is the one bonded to the metal atom in μ^1 -mode.

It is notable that the carboxylate groups of all six ligands have distinctly different C—O bond lengths (Table 2), with the mean values of the shorter and longer bond lengths being 1.253 Å and

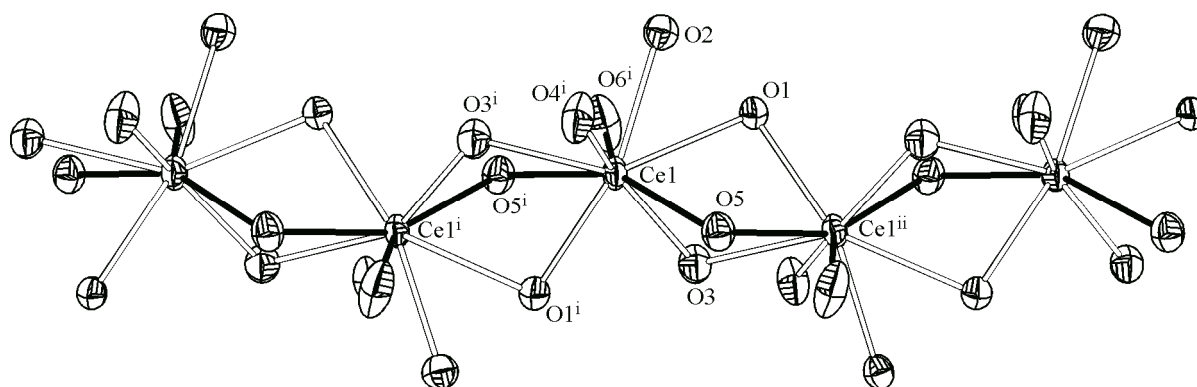


Fig. 4. Fragment of the Ce1-containing [010] polymeric chain in **1** showing only the O atoms. The bonds arising from the C1-, C7- and C15-containing ligands are colored blue, orange, and black, respectively.
Symmetry codes: (i) $-x, y+1/2, 1/2-z$; (ii) $-x, y-1/2, 1/2-z$

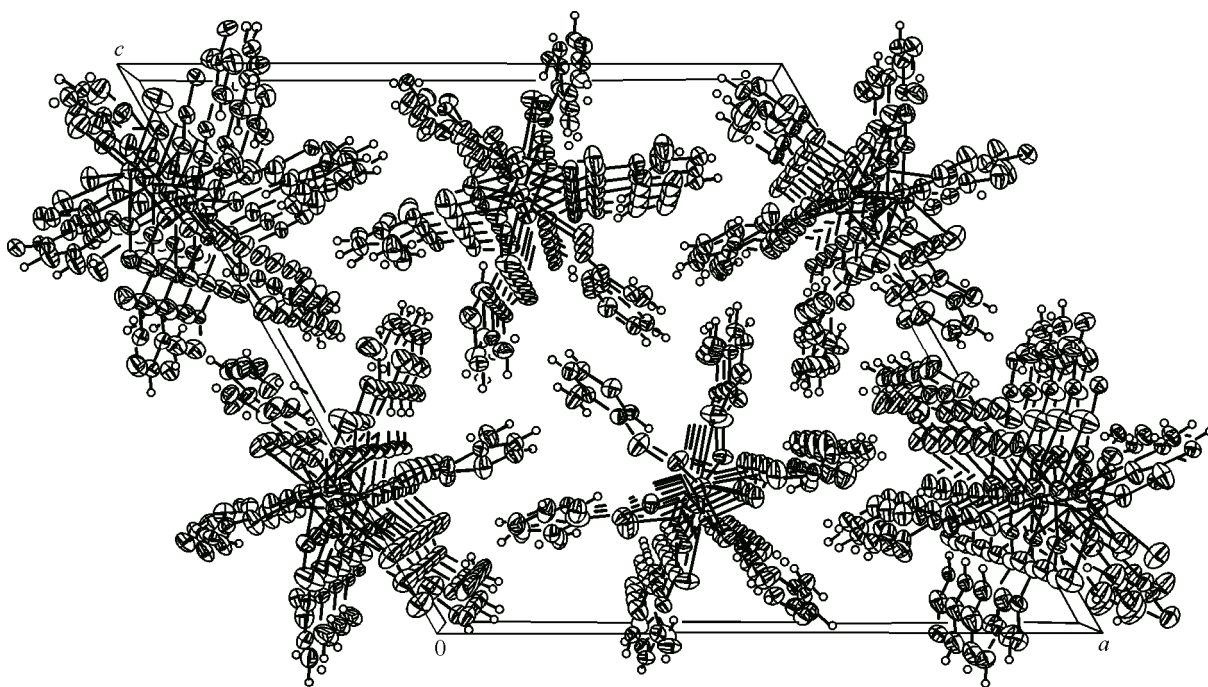


Fig. 5. The unit-cell packing in **1** viewed approximately down [010] showing the "snowflake" motif of the chains in projection

1.283 Å, respectively: this correlates perfectly with the bridging-bidentate coordination mode of the ligand, with the longer C—O bond bearing the μ^2 -O atom in each case.

In the crystal, the Ce1 and Ce2 polymeric strands are completely separate and the [010] chains interact only by way of possible very weak N—H \cdots N hydrogen bonds (Table 2), which both arise from the Ce2 chain. Some possible weak aromatic π — π stacking interactions were identified in a PLATON [18] analysis of the structure, with centroid—centroid separations in the range of 3.649(3) Å to 3.972(3) Å. When viewed down [010] (Fig. 5), the [Ce(anth)₃]_n chains in projection have a "snowflake" appearance and possess *pseudo* six-fold rotation symmetry. The Ce1 and Ce2 chains alternate in the [100] direction.

Crystal structure of 2. Compound **2** is isostructural with **1** and only significant differences will be described here: its geometrical data are summarized in Table 3. The mean Pr1—O and Pr2—O separations are 2.521 Å and 2.527 Å, respectively and the Pr1 and Pr2 BVSs are 3.25 and 3.22, respectively. The dihedral angles between the ring plane and the carboxylate group in the C1-, C8-, C15-, C22-, C29- and C36-containing anth⁻ species are 2.7(7)°, 7.6(3)°, 3.4(3)°, 1.1(3)°, 6.3(6)° and 2.3(4)°, respectively. Each ligand in **2** features an intramolecular N—H \cdots O hydrogen bond, with almost identical geometries to the equivalent bonds in **1**. In the extended structure of **2**, the bridging-bidentate anth⁻ ligands lead to the same [010] polymeric chains as in **1**.

DISCUSSION

Although it has been previously noted that rare-earth anthranilates are highly insoluble and difficult to crystallize [5], single crystals of **1** and **2** were grown by a straightforward solution method. Their spectroscopic data are consistent with previous results and they display reasonable thermal stability. Their golden/brown color is consistent with that of other rare-earth anthranilates [5], in which the color of the ligand apparently overwhelms the pale "natural" color of the lanthanide ion.

Their one-dimensional polymeric crystal structures complement that of isostructural [La(anth)₃]_n as described by Deacon *et al.* [5], who also reported several other structure types for the heavier rare-earth anthranilates. The global mean metal—oxygen bond distances in [La(anth)₃]_n, **1**, and **2** are

Table 3

Selected bond lengths (Å) and angles (deg.) for **2**

| | | | | | | | | |
|-----------------------|------------|-----------------------|------------|----------------------------|------|------|----------|-----|
| Pr1—O3 | 2.434(2) | Pr1—O5 | 2.441(2) | N1—H1B···O2 | 0.86 | 2.06 | 2.693(4) | 130 |
| Pr1—O1 ⁱ | 2.459(2) | Pr1—O2 | 2.481(2) | N2—H2B···O4 | 0.86 | 2.10 | 2.722(4) | 128 |
| Pr1—O6 ⁱ | 2.498(3) | Pr1—O4 ⁱ | 2.516(2) | N3—H3A···O6 | 0.86 | 2.05 | 2.689(4) | 130 |
| Pr1—O1 | 2.6122(19) | Pr1—O5 ⁱ | 2.625(2) | N4—H4A···N2 ⁱⁱⁱ | 0.86 | 2.42 | 3.267(4) | 167 |
| Pr1—O3 ⁱ | 2.626(2) | | | N4—H4B···O8 | 0.86 | 2.07 | 2.697(4) | 130 |
| Pr2—O11 | 2.436(2) | Pr2—O9 | 2.441(2) | N5—H5A···N4 ^{iv} | 0.86 | 2.57 | 3.423(4) | 174 |
| Pr2—O7 ⁱⁱ | 2.447(2) | Pr2—O8 | 2.481(2) | N5—H5B···O10 | 0.86 | 2.09 | 2.720(3) | 129 |
| Pr2—O12 ⁱⁱ | 2.492(2) | Pr2—O10 ⁱⁱ | 2.521(2) | N6—H6A···O12 | 0.86 | 2.04 | 2.675(4) | 130 |
| Pr2—O9 ⁱⁱ | 2.6127(19) | Pr2—O7 | 2.6335(19) | | | | | |
| Pr2—O11 ⁱⁱ | 2.681(2) | | | | | | | |
| C1—O2 | 1.257(3) | C1—O1 | 1.289(4) | | | | | |
| C8—O4 | 1.251(3) | C8—O3 | 1.285(4) | | | | | |
| C15—O6 | 1.248(4) | C15—O5 | 1.278(4) | | | | | |
| C22—O8 | 1.252(4) | C22—O7 | 1.289(3) | | | | | |
| C29—O10 | 1.256(3) | C29—O9 | 1.285(3) | | | | | |
| C36—O12 | 1.255(3) | C36—O11 | 1.274(4) | | | | | |

Symmetry codes: (i) $-x, y+1/2, 1/2-z$; (ii) $1-x, y-1/2, 1/2-z$; (iii) $-x, -y, -z$; (iv) $x, 1/2-y, z+1/2$.
For the hydrogen bonds, the four values correspond to the $D-H$, $H\cdots A$ and $D\cdots A$ separations (Å) and the $D-H\cdots A$ angle ($^\circ$), respectively.

2.558 Å, 2.544 Å, and 2.524 Å, respectively, which is the expected trend based on the lanthanide contraction effect [19]. All the ligands adopt the same bridging-bidentate bonding mode. There seems to be no obvious reason why these compounds should crystallize with two very similar polymeric strands in the unit-cell, beyond some vague appeal to "packing effects".

This work is also consistent with the earlier results of Brzyska and Rzaczyńska [20], who reported that Y, La and light lanthanides (to Sm) form an isomorphous series of anhydrous compounds of the empirical formula $M(\text{anth})_3$, although no structural data were reported.

CONCLUSIONS

The one-dimensional coordination polymers $[\text{Ce}(\text{anth})_3]_n$ and $[\text{Pr}(\text{anth})_3]_n$ have been prepared as single crystals and characterized. They feature distorted MO_9 capped square anti-prismatic coordination geometries for the metal ions. Two very similar but crystallographically distinct polymeric chains occur in their monoclinic unit cells. They complement $[\text{La}(\text{anth})_3]_n$ described previously [17]. The trend in the mean metal–oxygen bond lengths in these isostructural compounds is in line with that expected from the lanthanide contraction.

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IR spectra for **1** and **2**. Full details of the crystal structures of **1**(CCDC 933801) and **2**(CCDC 933802) in cif format are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, or e-mail deposit@ccdc.cam.ac.uk.

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