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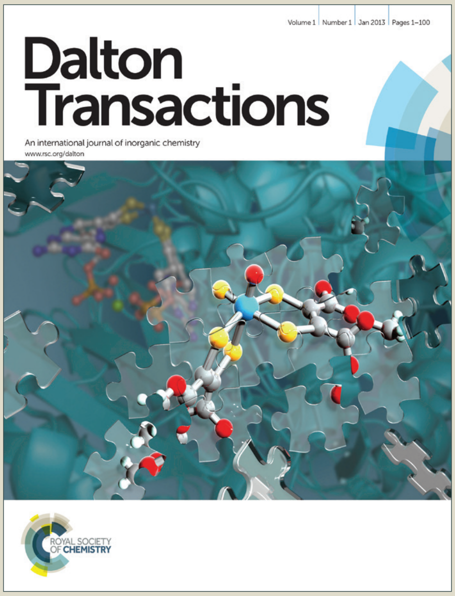

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Synthesis and Characterisation of a New Anion Exchangeable Layered Hydroxyiodide

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$Lu_4O(OH)_9I.3H_2O$ is a new member of the anion exchangeable lanthanide hydroxyanion family of materials which has been synthesised hydrothermally. Its structure comprises positively charged $[Lu_4O(OH)_9(H_2O)_3]^+$ layers with exchangeable charge balancing iodide anions located in the interlayer gallery. It has been found to undergo facile anion exchange reactions with dicarboxylate anions such as succinate and terephathalate at room temperature but reacts less readily with disulfonate anions such as 1,5- and 2,6-naphthalenedisulfonate under the same conditions. At reaction temperatures above 200 °C the cationic inorganic framework $Lu_3O(OH)_6I.2H_2O$ forms instead of the layered phase.

Introduction

Inorganic materials capable of undergoing anion exchange reactions have been the focus of much attention over many years as a result of their compositional diversity and structural flexibility giving them applications in fields as diverse as catalysis, separation science and medicine amongst others.[1-4] This area has traditionally been dominated by the layered double hydroxides (LDHs) which comprise extended 2D metal hydroxide sheets with exchangeable charge balancing anions between the layers.[5] The largest family of LDHs has the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$ where, for example, $M^{2+} = Mg^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}$ and $M^{3+} = Al^{3+}, Cr^{3+}, Fe^{3+}$. A^{n-} is the charge balancing anion which resides in interlayer regions within the structure which can range from small inorganic anions (e.g. carbonate, nitrate, chloride), to larger organic anions (e.g. succinate, terephthalate and surfactants) and even large, complex molecules such as DNA.[6-9] A second group of LDHs can be prepared by the intercalation of salts into the different $Al(OH)_3$ polymorphs.[10] These LDHs are just as flexible in terms of their anion exchange chemistry but are compositionally more limited with the reactions only being observed for lithium salts,[11-13] $M(NO_3)_2.xH_2O$ (M = Co, Ni, Cu, Zn),[14-16] $ZnSO_4$[17] and $MgCl_2.6H_2O$.[18]

The diversity of inorganic anion exchange hosts has recently been increased with the discovery of lanthanide hydroxyanion materials. These materials can be represented by the formula $Ln_2(OH)_5X.nH_2O$ and have been observed for the majority of the lanthanides including lutetium. Initially they were reported as having nitrate as the exchangeable anion[19-21] in the interlayer gallery but subsequent studies have reported analogous materials containing chloride,[22, 23] bromide[23] and sulfate.[24] As for the LDHs these lanthanide based materials readily undergo anion exchange reactions with a wide variety of anions at room temperature. These lanthanide based materials have the potential to extend the range of applications available to inorganic anion exchange materials and have shown promise as catalysts and for their optical properties.[25, 26]

Time resolved *in situ* energy dispersive X-ray diffraction investigations into the formation of $Yb_2(OH)_5NO_3.1.5H_2O$ revealed that its mechanism of formation is complex and that it transforms into $Yb_4O(OH)_9NO_3$ at high temperatures; a material which has a 3D cationic inorganic framework structure.[27] Whilst $Yb_4O(OH)_9NO_3$ does not undergo anion exchange its discovery subsequently led to the synthesis of $Yb_3O(OH)_6Cl.2H_2O$ which has a similar cationic inorganic framework structure which does undergo anion exchange reactions with small inorganic and organic anions.[28] $Yb_3O(OH)_6Cl.2H_2O$ is therefore a rare example of an anion exchangeable cationic inorganic framework of which we believe that only one other example, a thorium borate, has been reported.[29]

In this paper we report the synthesis and characterisation of a new member of the layered lanthanide hydroxyanion family, $Lu_4O(OH)_9I.3H_2O$. Whilst there are numerous studies involving the intercalation of iodide e.g. from sea water or waste water streams it is much rarer to have iodide as the exchangeable anion within an inorganic system.[30-33]

Experimental Section

Synthesis

$Lu_4O(OH)_9I.3H_2O$ was synthesised under hydrothermal conditions. In a typical reaction, LuI_3 (3.3mmol, 1.834g), NaOH (5.25mmol, 0.21g) and NaI (3.6mmol, 0.54g) were placed into a Teflon liner with 10mL deionised water and treated hydrothermally in an oven for 45 hours at 150°C with a heating rate of 3°C/min and a cooling rate of 0.1°C/min. The product, which was a white microcrystalline powder, was then filtered under vacuum, washed with deionised water and dried with ethanol.

Anion exchange reactions were performed by suspending 50 mg of $Lu_4O(OH)_9I.3H_2O$ in 5mL of an aqueous solution containing a 3-fold molar excess of the guest anion. The anions used in these reactions, as sodium salts, were succinate, phthalate, 1,5-naphthalenedisulfonate (1,5-NDS) and 2,6-naphthalenedisulfonate (2,6-NDS). The mixtures were stirred overnight at room temperature. The solid intercalation product was retrieved as described above.

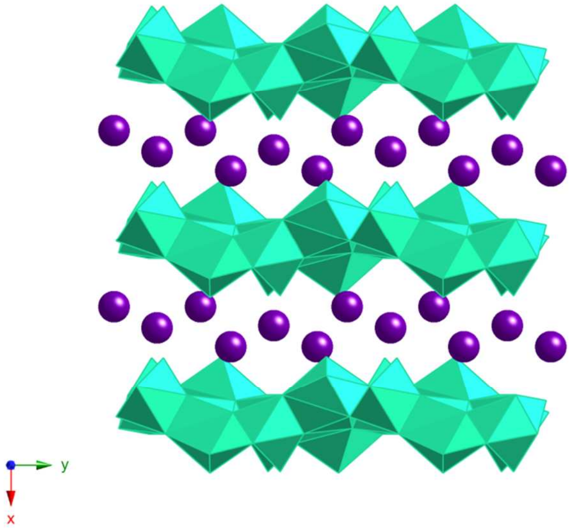

Fig. 1 Crystal structure of $Lu_4O(OH)_9I.3H_2O$.

Characterisation

Powder X-ray diffraction (XRD) patterns were obtained with Cu Kα_1 radiation on a Stoe Stadi-P diffractometer in either Bragg-Brentano or Debye-Scherrer geometry. Further characterisation was provided by TGA performed on a Perkin-Elmer STA6000 instrument where the sample was heated to 990˚C at a rate of 5˚C/min in a nitrogen atmosphere and Fourier transform infrared (FTIR) spectroscopy where spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer fitted with the Universal Diamond/ZnSe ATR. CHN analysis was performed on a Flash EA 1112 instrument.

X-ray Crystallography

Single crystal X-ray diffraction data for $Lu_4O(OH)_9I.3H_2O$ were collected on Beamline I19 of the Diamond Light Source. The beamline operates at a typical energy of 18 keV (Zr K absorption edge) and the experimental hutch (EH1) is equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724+ CCD detector and an Oxford Cryosystems Cryostream plus cryostat. Unit cell determination and refinement and data reduction was performed using CrystalClear-SM Expert 2.0 r5.[34] Structure solution was performed with SUPERFLIP[35] and refined using SHELXL2013 within OLEX2.[36, 37] Full details of the refinement and structural parameters are included in the ESI.

Results and Discussion

$Lu_4O(OH)_9I.3H_2O$ has been synthesised hydrothermally and represents a new member of the family of anion exchangeable lanthanide hydroxide phases which have been the focus of much attention in recent years. It was prepared as a white microcrystalline powder which contained small rod shaped single crystals. Structure determination was performed from synchrotron single crystal X-ray diffraction data which revealed that it crystallises in the orthorhombic space group Pbcm with the unit cell parameters *a* = 9.399(7) Å, *b* = 12.413(9) Å, *c* = 13.5909(10) Å. The crystal data and structural refinement parameters are summarised in Table 1. The crystal structure is shown in Figure 1 from which it can be seen that it comprises $[Lu_4O(OH)_9(H_2O)_3]^+$ layers which extend in the *yz* plane with uncoordinated iodide anions situated in the interlayer gallery. The asymmetric unit contains three independent Lu^{3+} cations each of which is eight coordinate to oxygen atoms from hydroxide ions, water molecules and/or the oxide anion with bond lengths of 2.184(16) Å for the oxide, 2.282(16) – 2.507(17) for hydroxide and 2.36(4) and 2.43(3) for the water molecules. The distinction between the hydroxide anions and water molecules was made by inspection of the structure with hydroxide ions bridging between three Lu^{3+} cations and water molecules coordinated to a single Lu^{3+} cation and oriented into the interlayer gallery. A diffraction pattern calculated from the crystal structure is compared to the experimental pattern in Figure 2 showing that the structure is representative of the major phase in the sample.

Table 1 Crystal data and structural refinement parameters for $Lu_4O(OH)_9I.3H_2O$.

Empirical formula	$H_{15}ILu_4O_{13}$	
Formula weight	1049.9	
Temperature	100(2) K	
Wavelength	0.6889 Å	
Crystal system	Orthorhombic	
Space group	*Pbcm*	
Unit cell dimensions	*a* = 9.399(7) Å	α = 90°
	b = 12.413(9) Å	β = 90°
	c = 13.5909(10) Å	γ = 90°
Volume	1585.6(17) $Å^3$	
Z	8	
Density (calculated)	4.398 Mg / m^3	
Absorption coefficient	24.440 mm^{-1}	
F(000)	1824	
Crystal	colourless rod	
Crystal size	0.06 x 0.01 x 0.01 mm^3	
θ range for data collection	2.64 – 26.64°	
Index ranges	$-12 \le h \le 11$, $-16 \le k \le 14$, $-17 \le l \le 11$	
Reflections collected	8292	
Independent reflections	1898 [R_{int} = 0.1397]	
Completeness to θ = 27.500°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1898 / 0 / 61	
Goodness-of-fit on F^2	0.988	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0833, *wR2* = 0.2135	
R indices (all data)	*R1* = 0.1148, *wR2* = 0.2367	
Extinction coefficient	n/a	
Largest diff. peak and hole	9.746 and –5.078 e $Å^{-3}$	

One unusual feature of the layers is the presence of the oxide anion which has not been observed in the related nitrate, chloride, bromide and sulfate materials. Oxide anions have, however, been seen in the cationic inorganic framework phases $Ln_4O(OH)_9NO_3$ (Ln = Er – Lu) and $Ln_3O(OH)_6Cl.2H_2O$ (Ln = Yb, Lu) which are formed from the same reaction mixtures as the layered phases but at higher temperatures (> 200 °C).[27, 28] Time resolved *in situ* energy dispersive X-ray diffraction data have shown that the layered phases form first and then convert to the framework materials and therefore the layered phases can be considered to be precursors to the frameworks at high temperatures. When this synthesis is performed at 220 °C a framework material with the composition $Lu_3O(OH)_6I.2H_2O$ is formed which whilst less crystalline appears to be isostructural with the previously reported

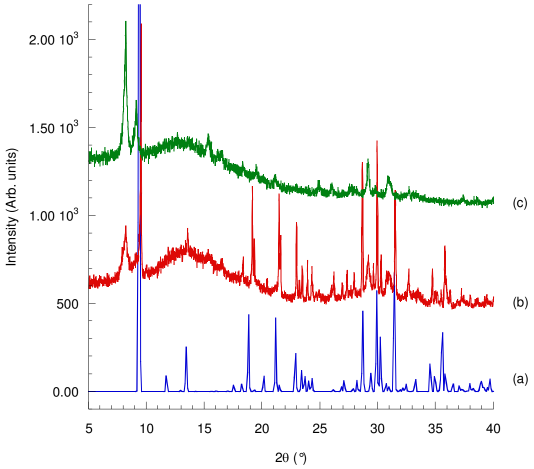

Fig. 2 Powder XRD patterns of $Lu_4O(OH)_9I.3H_2O$ (a) calculated and (b) experimental and (c) powder XRD pattern of $Lu_3O(OH)_6I.2H_2O$.

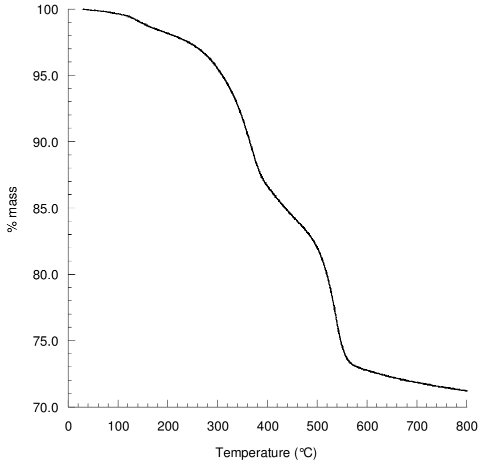

Fig. 3 TGA trace of $Lu_4O(OH)_9I.3H_2O$.

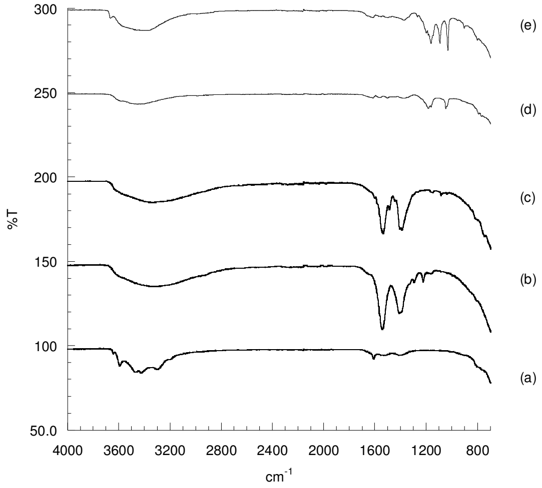

Fig. 4 FTIR spectra of (a) $Lu_4O(OH)_9I.3H_2O$, (b) $Lu_4O(OH)_9(C_4H_4O_4)_{0.5}.3H_2O$, (c) $Lu_4O(OH)_9(C_8H_4O_4)_{0.5}.3H_2O$, (d) $Lu_4O(OH)_9(1,5\text{-NDS})_{0.25}I_{0.5}.3H_2O$ and (e) $Lu_4O(OH)_9(2,6\text{-NDS})_{0.25}I_{0.5}.3H_2O$.

$Yb_3O(OH)_6Cl.2H_2O$ phase (Figures S1 and S2) suggesting that the observation of the oxide ion in the layered phase is reasonable (Figure 2(c)). Inspection of the powder XRD diffraction pattern of $Lu_4O(OH)_9I.3H_2O$ (Figure 2(b)) shows that a small amount of the $Lu_3O(OH)_6I.2H_2O$ is formed simultaneously as well as some unidentified amorphous material. Despite screening of the synthetic conditions it was not possible to prepare the layered phase without a small amount of the framework being present. Full details of the synthesis including *in situ* diffraction data, structure and anion exchange chemistry of the halide frameworks $Ln_3O(OH)_6X.2H_2O$ (X = Cl, Br, I) will be published elsewhere.

Additional characterisation of $Lu_4O(OH)_9I.3H_2O$ was provided by TGA, FTIR and CHN analysis. The TGA trace of $Lu_4O(OH)_9I.3H_2O$ is shown in Figure 3 and shows three mass losses. The first two mass losses overlap giving a combined mass loss of 13.4 % below 400 °C corresponds to the loss of the bound water and decomposition of the hydroxide layers (calculated mass loss is 12.9 % for pure $Lu_4O(OH)_9I.3H_2O$). This is followed by loss of the iodide with a further mass loss of 13.8 % (calculated – 11.3 %) with decomposition complete by 700 °C. The residue is Lu_2O_3. The FTIR spectrum is shown in Figure 4(a) and shows bands in the 3200 – 3600 cm^{-1} region due to the O-H stretches of the hydroxide anions and water molecules with an additional band at 1610 cm^{-1} due to the bending mode of water. CHN analysis showed that the sample contained 1.09 % H compared to a calculated value of 1.44 % with only trace amounts of C suggesting little carbonate contamination consistent with the other lanthanide hydroxyanion phases.

One characteristic property of many layered hydroxide phases, including the previously reported lanthanide hydroxyanion materials and the widely studied LDHs, is their ability to undergo facile anion exchange reactions. The anion exchange capability of $Lu_4O(OH)_9I.3H_2O$ has been demonstrated by reactions with aqueous solutions containing a threefold molar excess of the disodium salts of succinic, phthalic, 1,5-naphthalenedisulfonic (1,5-NDS) and 2,6-naphthalenedisulfonic (2,6-NDS) acids. Powder X-ray diffraction patterns of the resulting compounds are shown in Figure 5 and show the loss of the (100) reflection characteristic of $Lu_4O(OH)_9I.3H_2O$ coupled with the appearance of a new

Table 2 Characterising data for the anion exchange products of $Lu_4O(OH)_9I.3H_2O$.

Anion	Formula	Interlayer separation (Å)	Elemental Analysis	
			Observed (%)	Calculated [a] (%)
Iodide	$Lu_4O(OH)_9I.3H_2O$	9.4	H 1.09 C 0.1	H 1.44 C 0
Succinate	$Lu_4O(OH)_9(C_4H_4O_4)_{0.5}.3H_2O$	10.8	H 1.43 C 4.45	H 1.74 C 2.44
Phthalate	$Lu_4O(OH)_9(C_8H_4O_4)_{0.5}.3H_2O$	13.1	H 1.36 C 6.68	H 1.71 C 4.78
1,5-NDS	$Lu_4O(OH)_9(C_{10}H_6(SO_3)_2)_{0.25}I_{0.5}.3H_2O$	14.9	H 1.12 C 2.32	H 1.22 C 2.42
2,6-NDS	$Lu_4O(OH)_9(C_{10}H_6(SO_3)_2)_{0.25}I_{0.5}.3H_2O$	15.3	H 1.19 C 3.18	H1.22 C 2.42

[a] Calculated values are for the given formula and do not take into account the presence of the framework phase.

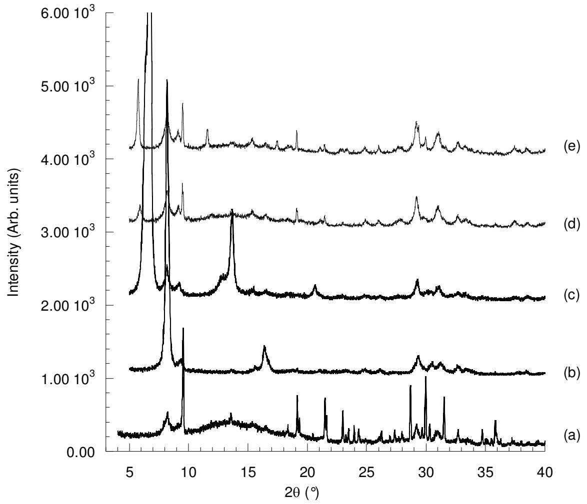

Fig. 5 Powder XRD patterns of (a) $Lu_4O(OH)_9I.3H_2O$, (b) $Lu_4O(OH)_9(C_4H_4O_4)_{0.5}.3H_2O$, (c) $Lu_4O(OH)_9(C_8H_4O_4)_{0.5}.3H_2O$, (d) $Lu_4O(OH)_9(1,5\text{-NDS})_{0.25}I_{0.5}.3H_2O$ and (e) $Lu_4O(OH)_9(2,6\text{-NDS})_{0.25}I_{0.5}.3H_2O$.

reflection indicating an increase of the interlayer separation resulting from the successful intercalation of the organic anion. The framework phase is unaffected by the anion exchange reactions. From the data it is apparent that the carboxylate anions, succinate and phthalate, have fully exchanged whilst the sulfonates, 1,5- and 2,6-NDS, have only partially reacted under these conditions with a significant amount of the host material remaining. Elemental analysis suggests that the degree of exchange is approximately 50 % for the reactions with the sulfonates. The loss of iodide from the materials was confirmed by the addition of $AgNO_3$ to the residual solution resulting from the precipitation of AgI in each case. The characterising data for the anion exchange products is summarised in Table 2. Further evidence for the inclusion of the organic anions comes from FTIR spectra (Figure 4) which all show bands characteristic of the organic species in addition to the O-H bands. For example, carboxylate stretches are observed at 1548 and 1545 cm^{-1} for the succinate and phthalate compounds respectively.

Conclusions

$Lu_4O(OH)_9I.3H_2O$, a new member of the lanthanide hydroxyanion family of anion exchange hosts has been synthesised hydrothermally. Structure determination has revealed that it comprises positively charged $[Lu_4O(OH)_9(H_2O)_3]^+$ layers with uncoordinated iodide anions located in the interlayer gallery. These iodide anions can be exchanged readily at room temperature for dicarboxylate anions such as succinate and phthalate but it was observed that the reactivity towards the disulfonate anions 1,5- and 2,6-NDS was less resulting in only partial exchange under these conditions. As the reaction temperature is increased the layered phase is no longer observed with the cationic inorganic framework $Lu_3O(OH)_6I.2H_2O$ forming instead.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Additional characterising data and structural parameters for $Lu_4O(OH)_9I.3H_2O$ is available. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the CSD number 427333]. See DOI: 10.1039/b000000x/

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Synthesis and Characterisation of a New Anion Exchangeable Layered Hydroxyiodide

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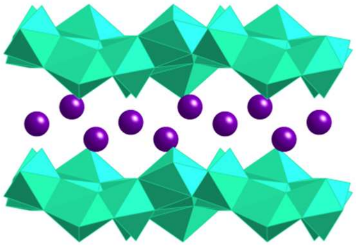
Graphical Abstract



A new anion exchangeable lanthanide hydroxyiodide has been synthesised, structurally characterised and its anion exchange chemistry investigated.