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$Yb_3O(OH)_6Cl \cdot 2H_2O$: An Anion-Exchangeable Hydroxide with a Cationic Inorganic Framework Structure

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Abstract: The first anion-exchangeable framework hydroxide, $Yb_3O(OH)_6Cl \cdot 2H_2O$, has been synthesized hydrothermally. This material has a three-dimensional cationic ytterbium oxyhydroxide framework with one-dimensional channels running through the structure in which the chloride anions and water molecules are located. The framework is thermally stable below 200 °C and can be reversibly dehydrated and rehydrated with no loss of crystallinity. Additionally, it is able to undergo anion-exchange reactions with small ions such as carbonate, oxalate, and succinate with retention of the framework structure.

Materials that adopt framework structures have been the focus of much attention in recent years because of their potential applications in a diverse range of fields, including catalysis and sorption among many others. Examples of such materials include zeolites,[1] alumino- and gallophosphates,[2] and metal−organic frameworks (MOFs).[3] In the vast majority of cases, the framework structure is either neutral or negatively charged. Materials having a cationic charge on the inorganic component are much rarer and are primarily limited to layered materials, such as layered double hydroxides (LDHs) and those adopting the structure of francisite, $Cu_3BiSeO_8[X^-]$.[4]

Among those materials having a cationic charge on the inorganic component, the LDHs have been the most widely studied as a consequence of their flexible composition, leading to a wide range of applications in areas such as catalysis, molecular recognition, and pharmaceuticals.[5] These materials, which typically contain a divalent cation (e.g., Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) and a trivalent cation (e.g., Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}) within the hydroxide layers, are able to undergo anion-exchange reactions with a diverse range of inorganic and organic species. Recent investigations in this area have resulted in the discovery of a related series of anion-exchange host lattices with cationic lanthanide hydroxide layers, $[Ln_2(OH)_5]X \cdot nH_2O$ (Ln = Sm−Lu, Y; X = NO_3, Cl, Br).[6] These new materials have shown potential for applications in catalysis, optics, and medicine. In situ energy-dispersive X-ray diffraction experiments observing the synthesis of $[Yb_2(OH)_5]NO_3 \cdot 1.5H_2O$ revealed the formation of $Yb_4O(OH)_9NO_3$ at temperatures above 200 °C.[7] This material has a three-dimensional framework structure with nitrate anions located in channels, but no capacity for anion exchange has been demonstrated for this structure. A recent study has shown that anion exchange occurs for the thorium borate framework $[ThB_5O_6(OH)_6][BO(OH)_2] \cdot 2.5H_2O$.[8]

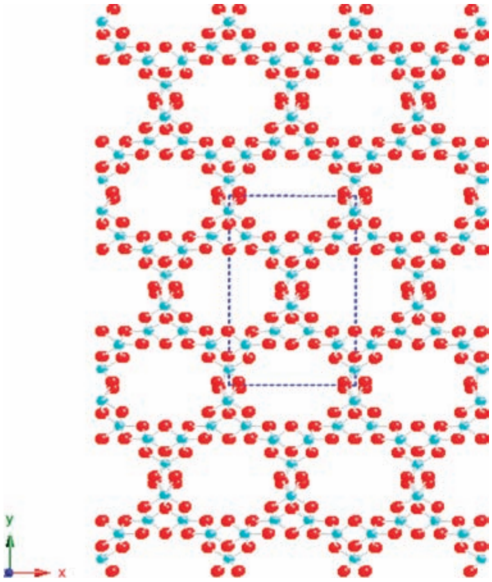

Figure 1. Cationic framework of the crystal structure of $Yb_3O(OH)_6Cl \cdot 2H_2O$. The Cl^- anions and water molecules are located in the channels but are disordered and have not been shown.

In this communication, we report the synthesis, crystal structure, and anion-exchange reactions of a new cationic inorganic framework hydroxide, $Yb_3O(OH)_6Cl \cdot 2H_2O$. This phase is the first framework hydroxide structure to display such properties and as a result represents a significant breakthrough in this area of chemistry. $Yb_3O(OH)_6Cl \cdot 2H_2O$ was synthesized hydrothermally in a reaction analogous to the synthesis of the layered $[Ln_2(OH)_5]Cl \cdot 1.5H_2O$ phases but at an elevated temperature of 220 °C. This synthesis yielded a microcrystalline powder with a needle morphology that contains extremely small single crystals of $Yb_3O(OH)_6Cl \cdot 2H_2O$. A small amount of an unknown impurity was also present, and it has not been possible to completely remove it from the synthesis despite extensive screening. Characterization data for $Yb_3O(OH)_6Cl \cdot 2H_2O$ are given in the Supporting Information.

The crystal structure of $Yb_3O(OH)_6Cl \cdot 2H_2O$ was determined to be orthorhombic (space group *Cmcm*) from data collected on beamline I19 of the Diamond Light Source and is shown in Figure 1. The structure consists of oxide-centered Yb_4 tetrahedra linked by μ_3- and μ_2-bridging hydroxide groups (minor disorder is described in the Supporting Information), creating a three-dimensional framework structure that contains one-dimensional channels. The oxide ions therefore act as nodes in the structure around which the framework can form, overcoming the strong preference of the hydroxides to form layered phases. There are two

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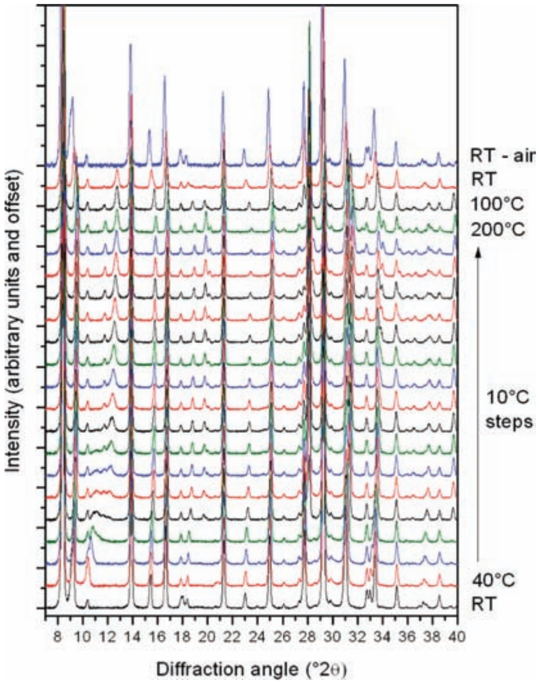

Figure 2. Powder XRD patterns showing the reversible dehydration–rehydration and structural evolution of $Yb_3O(OH)_6Cl \cdot 2H_2O$ between room temperature and 200 °C.

crystallographically independent Yb atoms in the structure, both of which are seven-coordinate. The channels in the framework, which run along the [001] direction, contain chloride anions and uncoordinated water molecules that are highly disordered and could not be modeled as discrete atoms. The windows to the channels have approximate dimensions of 7.6×4.8 Å. Analysis of the structure with PLATON revealed that the solvent-accessible volume would be 30.3% when these channels are empty, and in that case each unit cell would contain two 135 Å^3 voids. However, no solvent-accessible volume was predicted for the as-synthesized material. This was confirmed by gas sorption measurements, which indicated that $Yb_3O(OH)_6Cl \cdot 2H_2O$ is not porous toward N_2, CO_2, or H_2, suggesting that the large chloride anions block access to the channels. Comparison of a powder X-ray diffraction (XRD) pattern calculated from the structure to the experimental data (Figure S1 in the Supporting Information) confirmed that the structure is representative of the bulk sample.

The thermogravimetric analysis (TGA) trace of $Yb_3O(OH)_6Cl \cdot 2H_2O$ (Figure S2) confirms the bulk composition of the sample and indicates that the cointercalated water molecules can be removed. Powder XRD patterns of $Yb_3O(OH)_6Cl \cdot 2H_2O$ as a function of temperature (Figure 2) show that the phase can be reversibly dehydrated and rehydrated below 200 °C without any loss of crystallinity. New reflections corresponding to the onset of dehydration (e.g., at $2\theta = 19.8$ and 28.2°) are observed upon heating above 70 °C, and these are subsequently lost upon cooling. After exposure to air for 30 min at room temperature, the material is fully rehydrated, and the diffraction pattern matches the original one. Heating to 500 °C results in collapse of the structure, forming Yb_2O_3 (Figure S4). A detailed analysis of the structure as a function of temperature is underway, and full details will be reported elsewhere. The thermal stability of the structure up to 200 °C will be essential in developing future applications of cationic inorganic frameworks.

Synthetic screening with other lanthanides revealed that this cationic inorganic framework can also be prepared with Lu (Figure S5) but that the larger lanthanides Er and Tm form the layered $[Ln_2(OH)_5]Cl \cdot 1.5H_2O$ phase under these conditions.

The presence of uncoordinated, disordered chloride anions within the channels in the structure suggests that they are mobile, and as a result, it should be possible to perform anion-exchange reactions, a characteristic property of the layered hydroxides, on $Yb_3O(OH)_6Cl \cdot 2H_2O$. Successful anion exchange was achieved by reacting $Yb_3O(OH)_6Cl \cdot 2H_2O$ with an aqueous solution containing a 3-fold molar excess of small inorganic (e.g., carbonate) or organic (e.g., oxalate or succinate) anions at room temperature, forming phases with the general composition $Yb_3O(OH)_6X_{0.5} \cdot nH_2O$. As in the thermal cycling, the framework is stable under these conditions, leading to little change in the powder XRD patterns as a consequence of the exchange reactions. Successful anion exchange was confirmed by elemental analysis, TGA, and FTIR spectroscopy of the resulting products, and the data are summarized in the Supporting Information. In each case, there is strong evidence for the inclusion of the new anions into the structure (e.g., the presence of strong bands characteristic of the anion in the FTIR spectra), and the elemental analysis suggests that in most cases the exchange is complete. Additionally, it was possible to precipitate AgCl from the resulting reaction solution, confirming the removal of chloride from the host lattice. When $Yb_3O(OH)_6Cl \cdot 2H_2O$ was suspended in water overnight and the resulting solution similarly treated with $AgNO_3$, no precipitate formed, confirming that chloride was removed only via the anion-exchange reaction. SEM images of the anion-exchange products (Figure S11) show that the needle morphology of the crystals is unchanged during the reaction, suggesting that the reaction proceeds directly rather than through a dissolution–reprecipitation mechanism.

In conclusion, an anion-exchangeable three-dimensional cationic inorganic framework has been synthesized via a hydrothermal route. This material, $Ln_3O(OH)_6Cl \cdot 2H_2O$ (Ln = Yb, Lu), has an oxyhydroxide framework formed from O-centered Ln_4 tetrahedra by μ_2 and μ_3-bridging hydroxides. One-dimensional channels containing disordered chloride ions and water molecules run through the structure along the [001] direction. The framework is thermally stable below 200 °C and can be reversibly hydrated and dehydrated below this temperature. It is also stable toward room-temperature anion-exchange reactions with small inorganic and organic anions.

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Supporting Information Available: Experimental details, crystallographic data for $Yb_3O(OH)_6Cl \cdot 2H_2O$ (CIF), and characterization data (powder XRD, TGA, FTIR, elemental analysis) for $Yb_3O(OH)_6Cl.2H_2O$ and its anion-exchange derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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