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Poly(tetrafluoroethylene) Impregnation for Ion-Exchange Reactions with Layered Ce(IV) Fluorides

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The preparation of new low-dimensional and open-framework solids with ion-exchange, sorption, or catalytic properties are significant areas of current development owing to the potential technological applications of these materials.[1−7] The utilization of mild hydrothermal conditions combined with the use of organic structure-directing agents has played a key role in the successful isolation of these types of compounds.[8,9] Among the materials prepared by this method are a series of organically templated uranium fluorides[10−16] and oxyfluorides[14,15,17−19] that possess unusual structural motifs and atypical physical properties such as metamagnetic transitions and ferromagnetic interactions.[15] One difficulty faced in the advancement of this chemistry is the potential hazards associated with working with radioactive substances, particularly if useful materials are to be developed.

A facile solution to this problem is the substitution of Ce(IV) for U(IV) because the structural chemistry of these cations is often quite similar.[20] Therefore, isostructural Ce(IV) analogues of U(IV) solids should be isolable. The resultant Ce(IV) compounds will be diamagnetic, whereas U(IV) materials are typically antiferromagnetic. However, these products will still possess desirable chemical properties derived from their robust extended metal−fluoride networks. In particular, layered Ce(IV) fluorides should display similar ion-exchange reactions as previously found with layered U(IV) compounds.[10] For example, the ion exchange of organic templates for alkali metals and Co(II) in $(H_3N(CH_2)_n NH_3)U_2F_{10}$ ($n = 3, 5, 6$) has been reported. However, the products are isolated as crystalline powders, inhibiting the accurate determination of the structural identity of the products and whether the $[U_2F_{10}]^{2-}$ layers remain intact during the ion-exchange reaction.[10]

We have focused our efforts on preparing ion-exchangeable Ce(IV) fluorides where the ion-exchange products can be prepared in the form of single crystals, allowing for determination of whether the layers in these compounds remain intact throughout the ion-exchange processes and if ion selectivity can be achieved in these systems. The completion of a series of hydrothermal reactions in the compositional space diagram[21−23] of CeF_4/HF/ethylenediamine at 180 °C for 3 days has allowed for the isolation of one-dimensional $(C_2H_{10}N_2)_2Ce_2F_{12}$ and two-dimensional $(C_2H_{10}N_2)Ce_2F_{10}$ (**1**) in the form of colorless crystals.[24] These materials are the first organically templated lanthanide fluorides to be reported. Compound **1** was characterized by single-crystal X-ray diffraction[25] and proved to be isostructural with $(C_2H_{10}N_2)U_2F_{10}$ as desired.[15]

The structure of **1** consists of $[Ce_2F_{10}]^{2-}$ layers separated by ethylenediammonium dications. A view along (010) shows the layered structure with the ethylenediammonium dications separating the layers (Figure 1). Each layer consists of CeF_9 tricapped trigonal prisms that share three edges and two corners with neighboring polyhedra. This is a well-known structural motif for U(IV) fluorides and has been observed in products from high-temperature solid-state reactions of alkali metal fluorides and UF_4.[26] This is a strong indication of the robust nature of these metal−fluoride frameworks. In these layers, one of the fluoride ligands is not involved in intralayer bonding and instead points between layers. These and other fluoride ligands in the layers form

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(24) $(C_2H_{10}N_2)Ce_2F_{10}$ (**1**). CeF_4 (0.865 g, 4 mmol), ethylenediamine (0.14 mL, 2 mmol), HF (0.54 mL, 15 mmol), and water (2 mL) were loaded in a 23-mL PTFE-lined autoclave. The autoclave was heated at 180 °C for 3 days and cooled at 9 °C/h to 23 °C. The product consisted of small colorless crystals. The mother liquor was decanted from the crystals, which were then washed with methanol and allowed to dry; yield, 944 mg (89% yield based on Ce). Anal. Calcd for $C_2H_{10}N_2F_{10}Ce_2$: C, 4.51; H, 1.89; N, 5.26. Found: C, 4.49; H, 1.84; N, 5.14.

(25) Crystallographic data: **1** (193 K), monoclinic, space group $C2/c$, $a = 15.933(1)$ Å, $b = 7.0420(5)$ Å, $c = 8.6696(6)$ Å, $\beta = 91.661(1)°$, $V = 970.1(1)$ Å^3, $Z = 4$, Mo Kα, $\lambda = 0.71073$, $R_1 = 0.0165$, wR2 = 0.0419; **2** (193 K), monoclinic, space group $P2_1/c$, $a = 10.9439(9)$ Å, $b = 6.9769(6)$ Å, $c = 8.7108(8)$ Å, $\beta = 94.031(1)°$, $V = 663.5(1)$ Å^3, $Z = 2$, Mo Kα, $\lambda = 0.71073$, $R_1 = 0.0188$, wR2 = 0.0463.

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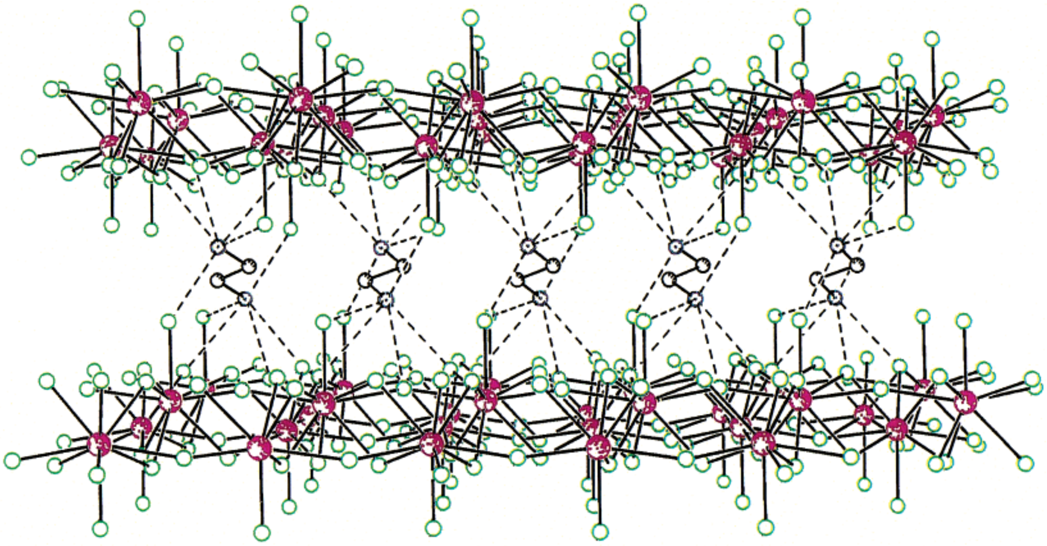

Figure 1. View along (010) shows the layered structure of $(C_2H_{10}N_2)Ce_2F_{10}$ (**1**) with the ethylenediammonium dications separating the layers.

strong hydrogen bonds with the ethylenediammonium dications. Ce−F bond distances range from 2.278(1) to 2.444(1) Å for bridging fluorides and are 2.182(2) Å for terminal ligands. These distances compare well with U−F distances found in $(C_2H_{10}N_2)U_2F_{10}$.[15] The organic templates lie at an acute angle of 23.4° normal to the cerium fluoride layers, which provides an interlayer spacing of ≈8.0 Å.

Given the significant interlayer spacing in **1**, ion-exchange reactions should be possible. However, the direct addition of ion-exchange reagents to either **1**, or reaction mixtures that should lead to the formation of **1**, only yields polycrystalline powders. For example, the reaction of aqueous Ni(II) sources with $(C_2H_{10}N_2)_2Ce_2F_{10}$ only produced a blue-green powder whose X-ray diffraction pattern has no obvious relationship with **1**.

In an attempt to slow the rate of addition of Ni(II) to this reaction to allow for crystal growth, we made use of the semipermeable properties of the poly(tetrafluoroethylene) (PTFE) liners[27] in the autoclaves employed in these reactions by pretreating them with 2.75 M $NiCl_2 \cdot 6H_2O$ for 24 h at 200 °C. The heating of 480 mg of $(C_2H_{10}N_2)Ce_2F_{10}$ in aqueous media for 3 days at 180 °C in these Ni(II)-impregnated liners resulted in the formation of $[Ni(H_2O)_6][Ce_2F_{10}] \cdot 2H_2O$ (**2**) in the form of single crystals with an aquamarine coloration in 10% yield. A comparison of the X-ray diffraction pattern from the blue-green crystalline powder resulting from the direct reaction of $(C_2H_{10}N_2)Ce_2F_{10}$ with Ni(II) under these same conditions demonstrates that this product is not **2**. X-ray fluorescence measurements provide a Ni:Ce ratio of 3:8, which is quite different from that of **2**.

The structure of $[Ni(H_2O)_6][Ce_2F_{10}] \cdot 2H_2O$ (**2**) is depicted in Figure 2 viewed down the *b* axis and consists of $[Ce_2F_{10}]^{2-}$ layers separated by octahedral $[Ni(H_2O)_6]^{2+}$ dications.[25] The layers in **2** are essentially identical to those found in **1**, indicating that either the layers remain intact during the ion-exchange reaction or that $[Ni(H_2O)_6]^{2+}$ also directs the formation of these same layers. The interlayer spacing in **2** has increased from 8.0 Å in **1** to ≈11.0 Å to accommodate the increased size of the $[Ni(H_2O)_6]^{2+}$ dications versus the ethylenediammonium dications. The Ni(II) ions in $[Ni(H_2O)_6]^{2+}$ adopt nearly ideal octahedral coordination environments and form a hydrogen-bonding network with each other and

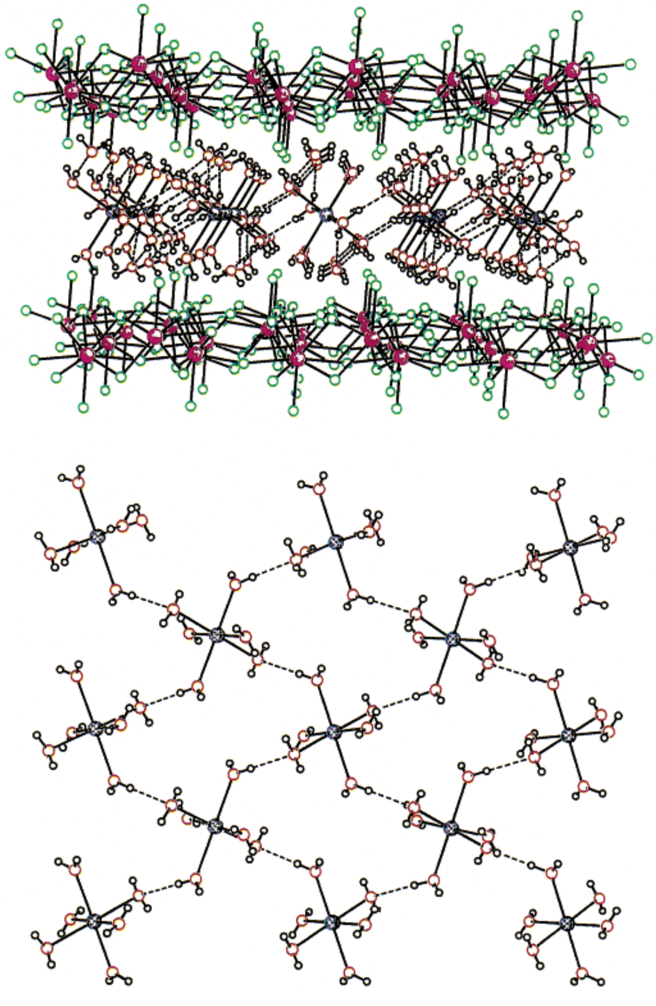

Figure 2. (top) View down the *b* axis of the structure of $[Ni(H_2O)_6][Ce_2F_{10}] \cdot 2H_2O$ (**2**). (bottom) The hydrogen-bonding network of octahedral $[Ni(H_2O)_6]^{2+}$ dications in **2**.

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with the $[Ce_2F_{10}]^{2-}$ layers as shown in Figure 2 (bottom).

While oxygen atoms can be difficult to distinguish from fluorine atoms on the basis of X-ray scattering alone, Ni−O(H_2O) bond distances are typically longer than those found for fluoride. The Ni−O bond distances in **2** range from 2.034(2) to 2.066(2) Å. Furthermore, owing to the high quality of the diffraction data obtained from these crystals, all of the hydrogen atoms on both the coordinated and interstitial water molecules were located. Finally, bond valence sum calculations[28,29] on the Ni(II) centers provide a value of 2.06, which is consistent with the present formulation.

An important feature of this new method for performing ion-exchange reactions is that additional ions besides Ni(II) can also be used to impregnate the PTFE liners. We have found that Cu(II), Co(II), and SO_4^{2-} all undergo sorption into the PTFE under mild hydrothermal conditions. Subsequent reactions in these adulterated Teflon inserts allow for the crystal growth of new ion-exchange products.

In recent experiments we impregnated PTFE liners with both Cu(II) and Ni(II) and performed a series of reactions in these pretreated liners with **1**. Only $[Ni(H_2O)_6][Ce_2F_{10}]\cdot 2H_2O$ was obtained from these reactions. We were quite surprised to discover that this finding held true even if Cu(II) sources were added directly to the reaction solutions. In contrast, if Cu(II) is reacted with $(C_2H_{10}N_2)Ce_2F_{10}$ in Ni-free liners, Cu-containing cerium fluorides can be isolated in crystalline form. These experiments suggest that selectivity is possible in the cerium fluoride system. The development of Ni(II)-selective ion-exchange materials is critical to current environmental remediation needs.

Ion selectivity may be achievable for three reasons. First, some hydrated metal ions may provide more optimal hydrogen bonding to the fluoride layers than others. This might be true for instance in the present study of Ni(II) vs Cu(II), as the latter is a Jahn−Teller ion, and probably creates a substantially different hydrogen-bonding network in the solid state with the $[Ce_2F_{10}]^{2-}$ layers. Second, there may be an optimum interlayer distance allowing for selectivity based upon the size of the hydrated cation. Third, there may be ion discrimination based upon differences in charge, for example, $[Cr(H_2O)_6]^{3+}$ vs $[Ni(H_2O)_6]^{2+}$. A future full report will detail these ion-exchange studies.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** in CIF format and XRD powder patterns comparing **2** with the Ni(II)-substituted cerium fluoride. This material is available free of charge via the Internet at http://pubs.acs.org.

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