Mild Hydrothermal Crystal Growth of New Uranium(IV) Fluorides, $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$: Structures, Optical and Magnetic Properties

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Abstract. Two new uranium(IV) fluorides, $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ (**1**) and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$ (**2**), were synthesized through an in situ mild hydrothermal route, and were structurally characterized by single crystal X-ray diffraction. The compounds exhibit complex crystal structures composed of corner- or edge-shared UF_9 and MF_6 (M= Mg, Mn) polyhedra, forming hexagonal channels in the three-dimensional framework, in which ordered or disordered divalent metal and sodium atoms reside. The large hexagonal voids contain the nearly regular M(II)F_6 octahedra and sodium ions, whereas the small hexagonal cavities include M(II) and sodium ions on a mixed-occupied site. Magnetic susceptibility measurements yielded effective magnetic moments of 8.36 and 11.6 μ_B for **1** and **2**, respectively, confirming the presence and oxidation states of U(IV) and Mn(II). The large negative Weiss constants indicate the spin gap between a triplet and a singlet state in the U(IV). Magnetization data as a function of applied fields revealed that **2** exhibits paramagnetic behavior due to the nonmagnetic singlet ground state of U(IV) at low temperature. UV-vis diffuse reflectance and X-ray photoelectron spectroscopy data were also analyzed.

Keywords: Uranium(IV); In situ reduction; Crystal growth; 3-D framework; Magnetism

1. Introduction

Materials containing uranium continue to be investigated because of their remarkable coordination chemistry [1-9] and important societal challenges, such as long-term nuclear waste storage [10-16]. Uranium can possess various oxidation states ranging from +3 to +6, among which tetra- and hexavalent species are more common. Most research, however, has focused predominantly on the U(VI) chemistry, even though U(IV) exhibits a rich crystal chemistry [17-25] and interesting magnetic properties [26-30] attributable to its large ionic size and unpaired electrons in the 5f orbitals. Presumably, the main reason for the limited investigations of U(IV) chemistry is the existence of only a limited number of such compounds, since the synthesis of U(IV) containing compounds, unlike the synthesis of U(VI) compounds, requires inert or reducing reaction conditions.

Hydrothermal synthesis is one technique widely used for exploratory crystal growth since solution-mediated reactions in closed reaction vessels can offer unique synthesis conditions when compared to the traditional high temperature ceramic methods. As a result, this method can lead to the discovery of distinctive compositions and topologies. In fact, many silicates and germanates containing U(IV) were prepared via hydrothermal methods involving the reduction of U(VI) by aluminum metal; however, this method requires extremely high temperatures and pressures that are difficult to achieve in a regular laboratory setting [31-36]. On the other hand, numerous organic reducing agents (solvents) are also effective for the creation of U(IV) containing compounds; however, this approach often results in organically templated U(IV) containing compounds where the organic group is incorporated into the crystal structures [37-46]. Thus, it continues to be a challenge to synthesize novel inorganic solids containing U(IV).

We recently developed a facile synthetic route to create U(IV) via an in situ reduction step of U(VI) to U(IV) under mild hydrothermal conditions, and successfully crystallized a host

of new U(IV) compounds, specifically U(IV) fluorides, which adopt various structure types [47-50]. The use of $\text{UO}_2(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ in an acidic environment played an important role to obtain the U(IV) fluorides because the acetate species in the starting uranium source readily reduced U(VI) to U(IV) during the reactions without incorporating into the final products. In the present study, we expanded this approach to explore new quaternary U(IV) fluorides that may possess interesting structural and magnetic features. With respect to quaternary U(IV) fluorides, we previously reported crystal structures based on a three-dimensional (3-D) $\text{U}_6\text{F}_{30}^{6-}$ building block that creates hexagonal channels in which transition metal polyhedra and sodium cations are located [47, 49]. Interestingly, the hexagonal channels can accommodate M(III)F_6 octahedra with a simultaneous reduction in the sodium content to maintain charge balance, suggesting that related compositions can be prepared. We therefore investigated this phase space of this quaternary uranium containing fluoride series that is based on the robust 3-D framework and successfully synthesized the title compounds that are closely related to the previously reported quaternary U(IV) fluorides. In this paper, we report on their synthesis, crystal structures, optical and magnetic properties of two new quaternary fluorides containing U(IV).

2. Experimental section

2.1 Reagents

$\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (International Bio-Analytical Industries, Inc. ACS grade), NaF (Alfa Aesar, 99%), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Fisher, 99.3%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), and HF (Alfa Aesar, 48%) were used as received. *Warning: although the uranium precursors used contain depleted uranium, standard safety measures for handling radioactive substance should be followed. HF should be handled in an appropriate vented hood, and appropriate safety apparel should be worn when handling HF, as it is highly corrosive and toxic.*

2.2 Synthesis

Single crystals of the reported compounds were grown using a mild hydrothermal route. For typical reactions, 1 mmol (424.1 mg) of $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, 1 mmol (41.99 mg) of NaF, and 3 mL of HF were combined with 4 mmol of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (813.2 mg) or $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (791.6 mg).

The respective solutions were placed into 23 mL Teflon-lined autoclaves. The autoclaves were closed, heated to 200 °C at a rate of 5 °C m^{-1} , held for 1 day, and cooled to room temperature at a rate of 6 °C h^{-1} . The mother liquor was decanted from the single crystal products, which were isolated by filtration and washed with distilled water and acetone. In all cases, the reaction yielded a single phase product consisting of green hexagonal plate crystals in nearly quantitative yield based on $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$. The identity and phase purity of the products were confirmed by powder X-ray diffraction (see Fig. S1).

2.3 Single crystal X-ray diffraction

X-ray intensity data from green hexagonal plates were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo $K\alpha$ radiation, 0.71073 Å) [51]. The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs [51]. Final unit cell parameters were determined by least-squares refinement of a large number of reflections taken from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXS/L and ShelXle [52, 53].

The compounds crystallize in the space group $P \bar{3}c1$ (No. 165) as determined by the pattern of systematic absences in the intensity data and by structure solution. The asymmetric units consist of one uranium atom and five fluoride atoms on general positions (site 12g), magnesium Mg1 or Mn1 on site 2a, sodium Na2 on site 2b, a mixture of sodium (Na1) and

magnesium or manganese (Mg²⁺ or Mn²⁺) on site 4d, and a partially occupied sodium Na³⁺ on a general position but disordered about the two-fold axis of site 6f. All atoms were refined with anisotropic displacement parameters except for Na³⁺ (isotropic). Trial refinements of the uranium atom *sof* showed no deviation from full site occupancy. Crystallographic data and selected interatomic distances are listed in Tables 1 and 2, respectively. Detailed structure determination procedures can be found in the Supporting Information.

2.4 Powder X-ray diffraction

Powder X-ray diffraction data were collected on a Rigaku D/Max-2100 powder X-ray diffractometer using Cu K α radiation. The step-scan covered the angular range 5-70° 2 θ in steps of 0.02°. No impurities were observed, and the calculated and experimental PXRD patterns on ground crystals are in excellent agreement.

2.5 UV-vis diffuse reflectance spectroscopy

Diffuse reflectance spectra of polycrystalline powder samples of the reported materials were obtained using a Perkin Elmer Lambda 35 UV/vis scanning spectrophotometer equipped with an integrating sphere in the range 200 – 900 nm.

2.6 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K-alpha source. The energy scale of the system was calibrated using Au foil with Au 4f scanned for the Al radiation and Cu foil with Cu 2p scanned for Mg radiation resulting in a difference of 1081.70 ± 0.025 eV between these two peaks. The binding energy was calibrated using Ag foil with Ag 3d_{5/2} set at 368.21 ± 0.025 eV for the monochromatic Al X-ray source. The monochromatic Al K-alpha source was operated at 15 keV and 120 W. The pass energy was fixed at 40 eV for the detailed

scans. A charge neutralizer (CN) was used to compensate for the surface charge. The binding energy scale was corrected with the C1s (284.6 eV) as a reference.

2.7 Magnetic property measurements

The magnetic properties of the microcrystalline compounds (approximately 30 mg) were measured using a Quantum Design Physical Property measurement System (QD-PPMS) equipped with a vibrating-sample magnetometer. Temperature dependent susceptibility measurements were made in both zero-field cooled (ZFC) and field cooled (FC) conditions in applied fields of 1000 Oe. Magnetization measurements at 2 K were carried out in applied fields up to 8 T.

3. Results and discussion

3.1 Synthesis

The title compounds, $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ (**1**) and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$ (**2**), were synthesized by utilizing in situ mild hydrothermal conditions that used $\text{UO}_2(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ as a convenient starting reagent, in which the acetate species, functioning as the reducing agent, is already included. The reactions promoted the reduction of U^{6+} to U^{4+} in a hydrofluoric acid environment, and resulted in intense green single crystals, shown in Fig. 1, as the sole products in nearly quantitative yield based on the $\text{UO}_2(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. The purity of ground crystals was confirmed by powder X-ray diffraction (PXRD), which was in excellent agreement with the calculated patterns from the single crystal data (see Fig. S1). The obtained crystals are stable to air and moisture for at least several months. For the synthesis of **2**, great care must be taken to distinguish between the desired product and the competing phase, $\text{Na}_4\text{MnU}_6\text{F}_{30}$ (**4**) that we previously reported, due to their similar color and morphology. In order to ensure the formation of **2**, we collected multiple single crystal and PXRD data on several products, all of which were

identical, confirming the reported compositions. For comparison, the calculated powder patterns of **2** and **4** are present in Fig. S2, showing the difference in PXRD.

3.2 Structures

The title compounds, **1** and **2**, crystallize in the trigonal space group $P\bar{3}c1$ and exhibit three-dimensional (3-D) crystal structures consisting of corner- or edge-shared UF_9 and MF_6 polyhedra with the charge balance maintained by sodium ions as depicted in Fig. 2. There is one crystallographically unique uranium site forming a distorted tricapped trigonal prismatic UF_9 polyhedron with U-F distances of 2.190(3) – 2.454(4) Å that are consistent with what has been observed from previously reported U(IV) fluorides [47-50]. Each UF_9 polyhedron shares one edge with another UF_9 polyhedron, giving rise to U_2F_{16} dimeric units that are further linked to each other via corner- and edge-sharing to create two types of one-dimensional (1-D) chains parallel to the c-axis. The 1-D chains connect to create the 3-D framework that contains two distinct hexagonal channels along the c-axis. The large hexagonal cavities built from corner-shared 1-D chains contain M^{2+} (M= Mg or Mn) and $\text{Na}(2)^+$ cations, and are surrounded by six small hexagonal voids. The M^{2+} cations are found in nearly regular octahedra with M-F distances of 1.966(3) – 2.061(3) Å, where all six fluorine atoms connect to six U^{4+} cations. The small hexagonal channels are created by two sets of corner-shared UF_9 polyhedra forming two 3-membered rings, which are further connected by three additional UF_9 polyhedra through edge-sharing between the rings.

There are three crystallographic sodium sites in the structure, all of which exhibit irregular NaF_x polyhedra with Na-F distances between 2.239(4) Å and 2.93(6) Å. The Na(1) atoms in the small hexagonal voids have mixed-occupancy and contain both sodium and the divalent metal atom in ratios of 78/22 (Na/Mg) and 37/63 (Na/Mn) for **1** and **2**, respectively, resulting in the non-integer stoichiometries of the title compounds. The Na(2) atoms are located

entirely in the large hexagonal voids, while the Na(3) atoms are located between the framework where they are disordered over two sites around a two-fold axis with Na-Na separation of 1.09(5) – 1.26(11) Å. Bond valence sum calculations [54, 55] yielded values of 0.94 -1.25, 2.10 – 2.25, and 4.14 – 4.15 for Na⁺, M²⁺, and U⁴⁺, respectively, consistent with the expected values.

As mentioned earlier, the crystal structures of **1** and **2** are closely related to those of Na₃MU₆F₃₀ (**3**) (M= trivalent metals) [47] and Na₄MU₆F₃₀ (**4**) (M= divalent metals) [49] that we previously reported. All members of the series contain the same 3-D framework consisting of the U₆F₃₀⁶⁻ building blocks that create two types of hexagonal channels. The structures differ in the content of those channels, where the differences in the amounts of sodium atoms and the oxidation states of metal atoms are delineated in Fig. 3. There are three available crystallographic sites in the 3-D framework, labeled as **M**, **A**, and **B**, for metal and sodium atoms. For all members of this structural family, the **M** site contains ordered sodium and metal atoms, however, depending on the amount of sodium elsewhere in the structure, the oxidation states of the metal ranges from 2+ to 3+, resulting in di- and trivalent metal ions for **3** and **4**, respectively. **1**, **2**, and **4** have sodium atoms on the **B** site, which is disordered over two positions related by two-fold symmetry; however, no sodium atoms are located on the **B** site for **3**, which is the main reason why only **3** contains the trivalent metal ions in the structure. In other words, the decrease in cationic charge due to the loss of disordered sodium atoms can be compensated for by an increase in the oxidation state of metal atoms. On the **A** site, **1** and **2** exhibit site mixing of sodium and divalent metal atoms, while **3** and **4** have only ordered sodium atoms on the **A** site. From a structural standpoint, it can thus be inferred that a variety of other isostructural compositions can be prepared by judiciously choosing different metal ions for the M and A sites.

3.3 UV-vis optical and X-ray photoelectron spectroscopy

The UV-vis diffuse reflectance data were collected on ground crystals of **1** and **2**. Fig. 4 shows the absorbance data converted from the reflectance data using the Kubelka-Munk function [56]. The two spectra look very similar to each other due to the presence of U^{4+} f-f transitions in both materials. The absorption bands above 400 nm are attributed to the transitions from the ground state of 3H_4 to several excited states of the U^{4+} . Although d-d transitions are expected for Mn^{2+} , the bands are not noticeable in the spectrum, likely due to the strong and sharp f-f transitions that obscure the d-d transitions. The estimated band gaps are approximately 3.5 eV, indicating semiconducting behavior for the title compounds.

The U 4f XPS data were collected to confirm the valence state of uranium, and are shown in Fig. 5 and Fig. S3. The binding energies (BEs) for the data were referenced to the adventitious C 1s at 284.6 eV. The main peaks located at 393.3 and 382.5 eV, and 389.4 and 378.7 eV for **1** and **2**, respectively, are assigned to the $4f_{5/2}$ and $4f_{7/2}$ states of the U^{4+} . The peak separations are 10.8 and 10.7 eV, which are likely caused by spin-orbit interactions between the two levels, consistent with previously observed values [31-33, 36]. The minor peaks at around 400 and 390 eV are thought to be satellites of the 4f peaks generated by the loss of the initial energy of the photoelectrons. The peak separations of the satellites from the primary peaks are important factor for assigning the valence state of elements since the positions of the satellites are dependent on the oxidation states of species. For uranium, the satellites are generally found at higher BEs than the 4f peaks, for example, 6 – 7 eV for U^{4+} , 7.8 – 8.5 eV for U^{5+} , and 4 and 10 eV for U^{6+} , respectively [57]. In the present cases, the peak separations are between 6.5 eV and 6.9 eV, confirming the valence state of the U^{4+} .

3.4 Magnetic properties

The temperature dependence of the magnetic susceptibility for **1** and **2** was measured under an applied field of 1000 Oe. No differences were observed between the zero-field cooled

(zfc) and field cooled (fc) data for either composition. The magnetic susceptibility of **1** shown in Fig. 6 indicates the typical behavior for U^{4+} species related to the coupling between the singlet ground state and low lying excited states that are thermally accessible. The temperature dependent behavior above 150 K is shown in Fig. 6. The linear high temperature range of the inverse susceptibility data was fitted to the Curie-Weiss (C-W) law, resulting in values of $8.74(1)$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and $-125(1)$ K for the Curie and Weiss constants, respectively. The large negative Weiss temperature relates to the spin gap between triplet and singlet states associated with the U^{4+} , rather than strong antiferromagnetic interactions. The effective magnetic moment of $3.41 \mu_B$ per U^{4+} compares well with the theoretical value of $3.58 \mu_B$, confirming the presence of U^{4+} .

The temperature dependence of the magnetic susceptibility for **2** is shown in Fig. 7, where the paramagnetic behavior related to Mn^{2+} (high-spin, $S = 5/2$) becomes evident. Due to the above mentioned U^{4+} ground state properties, the absence of magnetic coupling between the U^{4+} and the Mn^{2+} ions is expected. Also, dipolar interactions between Mn^{2+} ions are not expected due to their separation of over $6 \text{ \AA}$. The inverse susceptibility data above 150 K for **2** were fitted to the C-W law, and the extracted values are $16.8(1) \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and $-45.1(1)$ K for the Curie and Weiss constants, respectively. From the Curie constant, an effective magnetic moment of $11.6 \mu_B$ per f.u. was obtained, which is in excellent agreement with the theoretical value of $11.8 \mu_B$ per f.u., confirming the oxidation state of U^{4+} and Mn^{2+} . $\chi_m T$ for **1** and **2** along with the difference, $\Delta\chi_m T$, are plotted in Fig. 8, where it can be clearly seen that the $\Delta\chi_m T$ data nearly follows the theoretical Mn^{2+} single ion behavior, indicating that the Mn^{2+} ions are well isolated and non-interacting with each other. This phenomenon is also supported by the field dependence of magnetization data as seen in Fig. 9. The magnetization plot for **2** is in reasonable agreement with the Brillouin function [58] derived for 1.75 non-interacting Mn^{2+} ions per f.u. at 2 K.

4. Conclusions

We have successfully synthesized and characterized two new quaternary U(IV) fluorides. U(VI) in the starting reagent was fully reduced to U(IV) via an in situ reduction step under mild hydrothermal conditions. The compounds exhibit complex crystal structures based on the 3-D $\text{U}_6\text{F}_{30}^{6-}$ building block, creating two distinct hexagonal channels. The large channels contain almost regular MF_6 polyhedra, whereas the small ones contain disordered divalent metal and sodium atoms. The U 4f XPS data confirmed the valence state of U(IV). Magnetic property measurements indicated a spin gap between a triplet state at high temperature and a nonmagnetic singlet ground state at low temperature for U(IV). The presence of Mn^{2+} is corroborated for **2** as well as the absence of significant magnetic exchange coupling between the 3d-5f ions.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at <http://www.sciencedirect.com>. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany; fax: +49-7247-808-666; *E-mail address*: crystdata@fizkarlsruhe.de on quoting the depository numbers CSD - 429361 ($\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$); 429362 ($\text{Na}_{2.50}\text{Mg}_{1.75}\text{U}_6\text{F}_{30}$).

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Table 1Crystallographic data for Na_{3.13}Mg_{1.43}U₆F₃₀ and Na_{2.50}Mn_{1.75}U₆F₃₀.

formula	Na _{3.13} Mg _{1.43} U ₆ F ₃₀	Na _{2.50} Mn _{1.75} U ₆ F ₃₀
fw	2145.08	2151.69
temperature	100(2) K	100(2) K
crystal system	Trigonal	Trigonal
space group	<i>P</i> $\bar{3}c1$	<i>P</i> $\bar{3}c1$
<i>a</i> (Å)	9.8594(3)	9.8578(3)
<i>c</i> (Å)	13.0211(8)	13.1920(8)
<i>V</i> (Å ³)	1096.17(9)	1110.20(10)
<i>Z</i>	2	2
density (Mg/m ³)	6.378	6.437
absorption coefficient (mm ⁻¹)	44.508	44.841
crystal size (mm ³)	0.08×0.06×0.04	0.06×0.06×0.05
completeness to $\theta_{\max}$ /%	99.9	99.9
<i>R</i> (int)	0.0493	0.0501
GOF (<i>F</i> ²)	1.190	1.190
<i>R</i> (<i>F</i>) ^{<i>a</i>}	0.0256	0.0307
<i>R_w</i> (<i>F_o</i> ²) ^{<i>b</i>}	0.0535	0.0687
<i>R</i> (<i>F</i>) ^{<i>a</i>} = $\Sigma F_o - F_c /\Sigma F_o $. <i>R_w</i> (<i>F_o</i> ²) ^{<i>b</i>} = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$		

Table 2

Selected interatomic distances (Å) for Na_{3.13}Mg_{1.43}U₆F₃₀ and Na_{2.50}Mn_{1.75}U₆F₃₀.

	Na _{3.13} Mg _{1.43} U ₆ F ₃₀	Na _{2.50} Mn _{1.75} U ₆ F ₃₀
U(1)-F(4)	2.238(3)	2.190(3)
U(1)-F(2)	2.267(3)	2.274(3)
U(1)-F(5)	2.301(3)	2.284(3)
U(1)-F(3)	2.327(3)	2.338(3)
U(1)-F(1)	2.321(3)	2.351(4)
U(1)-F(5)	2.329(3)	2.317(3)
U(1)-F(2)	2.331(3)	2.354(3)
U(1)-F(3)	2.441(3)	2.431(3)
U(1)-F(1)	2.421(3)	2.454(4)
M(1)-F(4)	1.966(3) × 6	2.061(3) × 6

Fig. 1. Optical image of single crystals of $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ (left) and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$ (right).
The crystal size is up to 1 mm.

Fig. 2. Polyhedral representation of the UF_9 polyhedron showing a distorted tricapped trigonal prismatic coordination environment (a), and a view down to the c axis (b) for $Na_{3.13}Mg_{1.43}U_6F_{30}$ and $Na_{2.50}Mn_{1.75}U_6F_{30}$. The 3-D framework created from U_6F_{30} building blocks creates two types of hexagonal channels in which MF_6 polyhedra and $Na(2)$ atoms are located. The small hexagonal voids contain a mixed-occupied site of M^{2+} ions and $Na(1)$ atoms. The disordered $Na(3)$ atoms are located between the 3-D framework. Green, blue, and orange polyhedra/spheres represent U^{4+} , M^{2+} , and Na^{+} cations, respectively.

Fig. 3. The structural relationship of the three families is shown. The 3-D framework is common to all series, but the amount of sodium atoms and the oxidation state of metal ions are different. The disordered sodium or metal atoms are identified by red ovals.

Fig. 4. UV-vis absorption spectra for $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$. The absorption bands above 400 nm are attributed to the f-f transitions in the U(IV).

Fig. 5. U 4f X-ray photoelectron spectroscopy data for $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$.

Fig. 6. Temperature dependence of the molar magnetic susceptibility and the inverse susceptibility of $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ measured in an applied field of 1000 Oe. The magnetic susceptibility deviates from the Curie-Weiss behavior below around 150 K due to the singlet ground state of U^{4+} . The black solid line indicates the Curie-Weiss fit. Only zfc data are present because no difference between zfc and fc data was found.

Fig. 7. Temperature dependence of the molar magnetic susceptibility and the inverse susceptibility of $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$ measured in an applied field of 1000 Oe, showing nearly paramagnetic behavior at a low temperature region originating from the Mn^{2+} . The black solid line indicates the Curie-Weiss fit. Only zfc data are present because no difference between zfc and fc data was found.

Fig. 8. The $\chi_m T$ and $\Delta\chi_m T$ data for $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$, where the $\Delta\chi_m T$ plot nearly follows the theoretical Mn^{2+} single ion behavior.

Fig. 9. The field dependence of the magnetic moment of $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$ measured at 2 K along with the Brillouin function fit for the non-interacting Mn^{2+} cations.

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Table of Contents Caption

Two new quaternary U(IV) fluorides, $\text{Na}_{3.13}\text{Mg}_{1.43}\text{U}_6\text{F}_{30}$ and $\text{Na}_{2.50}\text{Mn}_{1.75}\text{U}_6\text{F}_{30}$, were crystallized via an in situ reduction step of U(VI) to U(IV) under mild hydrothermal conditions. The compounds show complex crystal structures based on the 3-D building block of U_6F_{30} . Magnetic property measurements revealed that the U(IV) exhibits a nonmagnetic singlet ground state at low temperature with a spin gap.