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Na_nMTh₆F₃₀ – a Large Family of Quaternary Thorium Fluorides

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Abstract

Recently we reported the synthesis, crystal structures and magnetic properties of compounds in the Na_nMU₆F₃₀ series, where n = 4 or 3, and where M is a divalent or trivalent metal cation, respectively. In this article we advance our investigation of this structure type by expanding it to the thorium containing compounds Na_nMTh₆F₃₀, where n = 3 in the case of M^{III} = Al, Sc, Ti, V, Cr, Fe, Ga, or In; n = 4 when M^{II} = Mg, Mn, Co, Ni, Cu, or Zn; and n varies from 3.87 to 4.39 when the M site is partially occupied by a trivalent rare earth element. Magnetic properties of the compounds containing magnetic ions M = Ti³⁺, V³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, and Cu²⁺ were studied to demonstrate that the substitution of Th(IV) for U(IV) prevents the magnetic ions from coupling magnetically and, therefore, exhibit simple paramagnetic behavior.

Introduction

Despite their radioactivity and the associated difficulties and risks of handling them, the actinide elements have been actively studied since the beginning of the 20th century. Among the many reasons, the most important one is their use in nuclear power and the consequent problems related to refinement and enrichment of the uranium ore, nuclear fuel preparation and finally spent nuclear fuel management.^{1–6} All except the last step have been extensively studied at the dawn of the nuclear age and most of the required procedures have been thoroughly worked out. On the last step, nuclear waste management,⁷ there remain challenges that need to be addressed prompting us to investigate the synthesis and study of new actinide-bearing materials.^{8–12}

Apart from its application in nuclear chemistry, the actinide elements attract interest because of their specific properties attributable to the presence of the partially filled 5*f* shell. The most intensively studied actinide element is undoubtedly uranium. The variety of its oxidation states coupled with the sometimes intriguing magnetic properties of U(IV) and the predominance of the uranyl cation in U(VI) chemistry makes this element a perfect candidate for study. Furthermore, the comparatively low radioactivity of uranium allows one to consider uranium-based compounds as potential materials for some applications.^{13–15} Actinium, protactinium and all the transuranium (TRU) elements are significantly more radioactive, hindering their potential applications in a non-nuclear context. Thorium does not exhibit a diversity of stable oxidation states and exists predominantly in the +4 oxidation state; only a limited number of Th³⁺ and even fewer Th²⁺ compounds have been reported.^{16–18} The low radioactivity makes thorium a practical candidate for use as a surrogate for other actinide elements that exist in the +4 oxidation state, including U(IV) containing compounds. This, along with the ongoing development of thorium-based nuclear fuel cycle, has attracted renewed attention to thorium and herein we are exploring its role as an elemental substitute for uranium in fluoride structures.^{19–22}

Uranium fluorides have been extensively studied because of their use in nuclear power, which has not precluded the recent synthetic advances in this field that resulted in the synthesis of new complex fluorides as well as in the improved characterization of older, known, fluorides and oxyfluorides.^{23–29} Our study of uranium(IV) fluorides resulted in a report of a rather unique structure type that can accommodate both di- and trivalent p- and d-metals along with uranium and which has the general formula Na_nMU₆F₃₀, where $M = Mn^{2+}$, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and M =

Al³⁺, Ga³⁺, Ti³⁺, V³⁺, Cr³⁺, Fe³⁺, with n = 4 and 3, respectively, to maintain charge balance.^{30–32} Our further investigation of this series resulted in the synthesis of $Na_{3,13}Mg_{1,43}U_6F_{30}$ and Na_{2.50}Mn_{1.75}U₆F₃₀, which established the existence of compositions with partial occupancy of both the Na and the metal sites. The mild hydrothermal syntheses utilizing $UO_2(CH_3CO_2) \cdot 2H_2O$ as the uranium source did not result the formation of compounds with M cations larger than Ti³⁺, suggesting that there is a phase stability boundary that restricts the size of the M cation and that lies approximately between Ti³⁺ and Sc³⁺. A well-established fact about the actinide series is the actinide contraction, which means that the radii of the actinides decrease with the increase of the effective nuclear charge. Due to this, the Th⁴⁺ cation is slightly larger than the U⁴⁺ cation, which can be confirmed by their Shannon ionic radii of 1.09 and 1.05 Å for nine-fold coordinated Th and U, respectively. Given the $Na_nMU_6F_{30}$ formula unit, there are six uranium atoms per one M atom, which suggests that in this structure type the replacement of uranium by thorium should expand the framework in general, thereby influencing the M site and, thus, potentially enabling the incorporation of a larger cations in this position. To prove this suggestion, we performed synthesis and structure characterization of a series of compounds with the general formula Na_nMTh₆F₃₀ to probe how large a M cation can be adopted by this thorium based structure type and how it will influence the magnetic properties of resulting compounds.

Experimental section

Caution: Hydrofluoric acid is toxic and corrosive, and must be handled with extreme caution and the appropriate protective gear! If contact with the liquid or vapor occurs, proper treatment procedures should immediately be followed.

Caution: Both thorium and uranium, although the uranium precursor used in this synthesis contains depleted uranium, require that proper procedures for handling radioactive materials are observed. All handling of radioactive materials was performed in labs specially designated for the study of radioactive actinide materials.

Reagents

Th(NO₃)₄·4H₂O (Baker Analyzed), UF₄ (International Bioanalyitical Industries), NaF (Alfa Aesar), MgO (Alfa Aesar 99.998% metal basis), CuO (Alfa Aesar, 99.7% metal basis), ZnF₂ (Alfa Aesar, 99%), Al₂O₃ activated (Acros), Sc₂O₃ (Aran Isles Chemicals, 99.9%), Ti₂O₃ (Cerac, 99.8%), V₂O₃ (Alfa Aesar, >99.7%), CrF₃·3H₂O (Alfa Aesar), FeC₂O₄·2H₂O (Alfa

Aesar, 99.999% metal basis), $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (Alfa Aesar, 98%), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (MCB), $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (Aldrich), and $CuC_2O_4 \cdot 0.5H_2O$ (Strem Chemicals), $GaF_3 \cdot 3H_2O$ (Strem Chemicals, 99.5%), In_2O_3 (Alfa Aesar, 99.9% metal basis), Y_2O_3 (Alfa Aesar, 99.9%), Lu_2O_3 (Alfa Aesar, 99.9%), Tm_2O_3 (Alfa Aesar, 99.9%), and hydrofluoric acid solution (EMD, $\geq 48\%$), were used as received. ThF₄ was obtained by dissolving thorium nitrate (1.50 g) in 5 mL of distilled water in a 23 mL PTFE liner and adding 1 mL of hydrofluoric acid. The PTFE liner with the mixture was sealed in an autoclave and placed into a programmable oven at a temperature of 140 °C. After dwelling at this temperature for 24 hours, the resulting fine powder of ThF₄ was filtered and washed with distilled water and acetone and then dried for 5 h at a temperature of 140 °C in a drying oven. The phase purity of the resulting ThF₄ was confirmed by powder X-ray diffraction.

Synthesis

All the reported compounds were obtained via mild hydrothermal route using ThF₄, NaF and respective di- or trivalent metal oxides, fluorides, or acetates as precursors. The specific synthetic conditions for crystal growth of all the phases are listed in Table 1. In general, 0.150 g of ThF₄, the appropriate amount of NaF and a di- or trivalent metal source (listed in the reagents section above) were loaded into a PTFE-lined autoclave in the molar ratios listed in Table 1. Once added, a corresponding amount of distilled water and hydrofluoric acid were added to the mixture, and the autoclaves were sealed and placed into a programmable oven. The oven was ramped up to 200 °C, kept at that temperature for 24 hours, and then cooled down to 40 °C with a cooling rate of 0.2 °C/min. The resulting product was filtered and washed with distilled water and acetone. In most cases the product was found to be a mixture of a target phase and another fluoride.

To explore the magnetic properties of the phases containing magnetic ions, i.e. Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+} , the reaction conditions were optimized to produce phase pure samples. Na₄CoTh₆F₃₀ and Na₄NiTh₆F₃₀ were obtained by a reaction of ThF₄, cobalt or nickel acetates, and NaF in a 2:1:3 respective molar ratio. To obtain Na₄CrTh₆F₃₀, Na₄MnTh₆F₃₀, Na₃FeTh₆F₃₀, Na₄CuTh₆F₃₀, CrF₃·3H₂O, Mn(CH₃CO₂)₂·4H₂O, FeC₂O₄·2H₂O, and CuC₂O₄·0.5H₂O, respectively, were combined in a 2:1:2 ratio. To obtain phase pure samples of Na₃VTh₆F₃₀ and Na₃TiTh₆F₃₀ a Th : M : Na molar ratio of 1:4:1 and 1:8:1 was employed. In all

cases, the solution consisted of 0.75 mL HF and 0.75 mL H₂O and the temperature profile was as follows: the reactions were kept for 36 hours at 200 °C and then cooled to room temperature by switching off the oven. The yields (based on Th) for the phase pure samples are 83% (Mn), 93% (Co), 87% (Ni), 76% (Cu), 58% (Ti), 77% (V), 71% (Cr), and 83% (Fe). The purity of the resulting phases was confirmed by PXRD (Figure S1-S8). Although many attempts were committed to obtain the phase pure samples of the lanthanide-containing quaternary fluorides, they were always found to be accompanied by ternary sodium thorium fluorides.

Table 1. Specific synthetic conditions for obtaining Na_nMTh₆F₃₀.

	Th:M:Na			
Composition	molar	Solution composition	Temperature profile	
	ratio			
$Na_4MgTh_6F_{30}(1)$	1:2:2			
$Na_4MnTh_6F_{30}(2)^*$	1:2:2			
$Na_4CoTh_6F_{30}(3)^*$	1:2:2	2.0 mI H $O \pm 1.0 \text{ mI}$ HE		
$Na_4NiTh_6F_{30}(4)*$	1:1:1	2.0 IIIL H_2O +1.0 IIIL HF		
$Na_4CuTh_6F_{30}(5)^*$	1:2:2			
$Na_{4}ZnTh_{6}F_{30}(6)$	1:2:2			
$Na_{3}AlTh_{6}F_{30}(7)$	ן 1:2:1	0.25 mJ H ₂ O + 0.50 mJ HE		
$Na_{3}ScTh_{6}F_{30}(8)$	1:2:1 5	$0.23 \text{ mL } \text{m}_2\text{O} + 0.30 \text{ mL } \text{m}_2$		
$Na_{3}TiTh_{6}F_{30}(9)*$	1:4:1 ไ	0.75 mL H + 0.75 mL HE		
$Na_{3}VTh_{6}F_{30}$ (10)*	1:2:1 5	$0.75 \text{ mL } \text{m}_2\text{O} + 0.75 \text{ mL } \text{m}_2$	200 °C for 24h,	
$Na_3CrTh_6F_{30}(11)^*$	2:1:1	$0.50 \text{ mL H}_2\text{O} + 0.50 \text{ mL HF}$	cooling down to 40	
$Na_{3}FeTh_{6}F_{30}$ (12)*	1:2:2	$2.0 \text{ mL H}_2\text{O} + 1.0 \text{ mL HF}$	with 0.2 °C/min	
$Na_{3}GaTh_{6}F_{30}$ (13)	1:2:1	1.0 mL CH ₃ OH + 0.50 HF		
$Na_{3}InTh_{6}F_{30}(14)$	1:1:1 J			
$Na_{3.87}Y_{0.71}Th_{6}F_{30}$ (15)	2:1:2			
$Na_{4.39}Lu_{0.54}Th_{6}F_{30}$ (16)	2:1:2			
$Na_{3+3x}Yb_{1-x}Th_{6}F_{30}(17)$	2:1:2	0.25 mJ H ₂ O + 0.50 mJ HF		
$Na_{4.11}Tm_{0.63}Th_6F_{30}$ (18)	2:1:2	0.25 HIL 1120 + 0.50 HIL 11		
$Na_{3+3x}Er_{1-x}Th_{6}F_{30}$ (19)	2:1:2			
$Na_{3+3x}Ho_{1-x}Th_{6}F_{30}(20)$	2:1:2			
$Na_{3+3x}Dy_{1-x}Th_{6}F_{30}(21)$	2:1:2			
*reactions afforded phase	e pure sample	es. The M cation sources are list	ed in the reagents section.	

Single-Crystal X-ray Diffraction

Single-crystal X-ray diffraction data were collected at 300(2)–302(2) K on a Bruker D8 QUEST diffractometer equipped with an Incoatec IµS 3.0 microfocus radiation source (MoK α , λ

= 0.71073 Å) and a PHOTON II area detector. The crystals were mounted on a microloop with immersion oil. The raw data reduction and absorption correction were performed using SAINT and SADABS programs.^{33,34} The structure models for previously reported quaternary uranium fluorides were used for refinement, and the setting of the unit cells was changed by a (-1 0 0 0 -1 0 0 0 1) transformation matrix after image integration when necessary. Full-matrix least-square refinements against F² were performed with the SHELXL software.³⁵ All the structures were checked for missing symmetry with the Addsym program implemented into the PLATON software and no higher symmetry was found.³⁶ The crystallographic characteristics and results of the diffraction experiments are summarized in Tables 2–4. The rare-earth elements in the structures of **15-17**, listed in Table 4, were found to occupy the M site partially. Due to this, a second free variable was introduced to the model and the occupancies of the M and Na3 sites were refined together, and constrained to charge balance. The respective occupancies for Y, Lu, and Tm are 0.711(6), 0.535(4), and 0.628(4).

Powder X-ray diffraction (PXRD) data for phase identification and phase purity confirmation were collected on ground samples. Data were collected on a Bruker D2 PHASER diffractometer utilizing Cu K α radiation. The data were collected over the range from 10° to 65° 20 with a step size of 0.02°.

Energy-Dispersive Spectroscopy (EDS)

EDS was performed on product single crystals using a Tescan Vega-3 SEM equipped with a Thermo EDS attachment. The SEM was operated in low-vacuum mode. Crystals were mounted on an SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an 80 s accumulating time. The results of EDS confirm the presence of elements found by single-crystal X-ray diffraction.

Magnetism

Magnetic property measurements were performed on a Quantum Design MPMS 3 SQUID magnetometer. Zero-field-cooled magnetic susceptibility measurements were performed from 2 to 300 K in an applied field of 0.1 T. The raw data were corrected for radial offset and sample shape effects according to the method described in the literature.³⁷ All magnetic data were collected on polycrystalline powders obtained by grinding the product single crystals.

Crystal chemical calculations

Crystal structure analysis was performed using the TOPOS 4.0 software package.^{38,39} The method of intersecting spheres was employed for coordination number determination using the AutoCN program.⁴⁰ Dirichlet and ADS programs were employed for Voronoi polyhedra construction and topological analysis, respectively. The standard structure simplification procedure was employed to obtain the underlying net of the compounds.⁴¹

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Chemical formula	Mg (1) Mn (2)		Co (3)	Ni (4)	Cu (5)	Zn (6)	
Formula weight	2078.51	2109.14	2113.13	2112.91	2117.74	2119.57	
Crystal system	Trigonal						
Space group, Z			P <u>3</u>	c1, 2			
a = b, Å	10.02260(10)	10.09220(10)	10.0514(2)	10.02760(10)	10.0370(2)	10.0455(2)	
c, Å	13.2493(3)	13.2654(3)	13.2465(5)	13.2392(3)	13.2442(3)	13.2479(3)	
V, Å ³	1152.61(3)	1170.10(4)	1159.00(6)	1152.89(3)	1155.48(5)	1157.77(5)	
$\rho_{calcd}, g/cm^3$	5.989	5.986	6.055	6.087	6.087	6.080	
Radiation (λ, Å)	$MoK_{\alpha}(0.71073)$						
μ , mm ⁻¹	38.898	38.805	39.347	39.653	39.670	39.709	
Т, К	300(2)	300(2)	301(2)	300(2)	303(2)	301(2)	
Crystal dim., mm ³	0.03×0.02×0.02	0.03×0.02×0.02	0.03×0.02×0.02	0.05×0.02×0.02	0.04×0.02×0.02	0.03×0.02×0.02	
2θ range, deg.	3.08-27.49	3.07-27.47	3.08-27.50	3.08-27.47	3.08-27.49	3.08-27.50	
Reflections collected	21355	21815	21974	44358	26883	22458	
Data/paramet ers/restraints	888/66/0	908/66/0	900/66/0	884/67/0	892/66/0	896/66/0	
R _{int}	0.0281	0.0362	0.0302	0.0288	0.0284	0.0150	
Goodness of fit	1.099	1.113	1.049	1.046	1.073	1.161	
$R_1(I > 2\sigma(I))$	0.0128	0.0202	0.0137	0.0085	0.0127	0.0150	
wR_2 (all data)	0.0407	0.0571	0.0440	0.0186	0.0421	0.0394	

Table 2. Crystallographic data for $Na_4M^{II}Th_6F_{30}$ ($M^{II} = Mg$, Mn, Co, Ni, Cu, Zn).

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Table 3	5. Crystanograp	onic data for Mag	$101^{11} 1 1_6 F_{30}$ (101^{11}	$^{n} - AI, SC, II, T$	v, Cr, Fe, Ga, I	n).		
Chemical formula	Al (7)	Sc (8)	Ti (9)	V (10)	Cr (11)	Fe (12)	Ga (13)	In (14)
Formula weight	2058.19	2076.17	2079.11	2082.15	2083.21	2087.06	2100.93	2146.03
Crystal system				Trig	onal			
Space group, Z				P 3 c	1, 2			
a = b, Å	9.9301(3)	10.04900(10)	10.0250(2)	9.99120(10)	9.9670(10)	10.00820(10)	9.9528(2)	10.0575(2)
c, Å	13.1454(4)	13.2473(3)	13.2121(2)	13.1872(3)	13.1707(14)	13.1973(3)	13.1756(3)	13.2300(3)
V, Å ³	1122.56(8)	1158.52(3)	1149.93(5)	1140.04(3)	1133.1(3)	1144.79(3)	1130.29(5)	1158.97(5)
ρ_{calcd} , g/cm ³	6.089	5.952	6.005	6.066	6.106	6.055	6.173	6.150
Radiation (λ, Å)		ΜοΚ _α (0.71073)						
μ , mm ⁻¹	39.930	38.921	39.264	39.664	39.974	39.725	40.785	39.608
Т, К	301(2)	301(2)	300(2)	300(2)	299(2)	300(2)	300(2)	300(2)
Crystal dim., mm ³	$\frac{Crystal \text{ dim.,}}{mm^3} = 0.04 \times 0.03 \times 0.02 = 0.03 \times 0.02 \times 0.02 = 0.03 \times 0.02 \times 0.02 = 0.04 \times 0.04 \times 0.03 = 0.06 \times 0.04 \times 0.04 \times 0.02 \times 0.02 = 0.04 \times 0.02 \times 0.02 \times 0.02 = 0.04 \times 0.02 \times$					0.04×0.02×0.02		
2θ range, deg.	3.10-27.49	3.08-27.49	3.08-27.50	3.09-26.48	3.09-27.50	3.09-27.46	2.36-24.99	3.08-27.48
Reflections collected	26737	27449	17887	25553	13336	26858	13845	32529
Data/parameters /restraints	869/62/0	896/61/0	885/62/0	789/62/0	875/62/0	881/62/0	672/62/0	899/62/0
R _{int}	0.0286	0.0462	0.0369	0.0259	0.0308	0.0305	0.0249	0.0292
Goodness of fit	1.135	1.167	1.124	1.151	1.163	1.076	1.162	1.257
$R_1(I > 2\sigma(I))$	0.0182	0.0248	0.0105	0.0106	0.0176	0.0124	0.0219	0.0128
wR_2 (all data)	0.0547	0.0532	0.0222	0.0326	0.0443	0.0387	0.0547	0.0272

N. MIITLE (MIII. Table 2 C Al Co Ti V Cr Eo (C_{n}, I_{n}) 4 - 11 1-4- 6-

Chemical formula	Na _{3.87} Y _{0.71} (15)	Na _{4.39} Lu _{0.54} (16)	Na _{4.11} Tm _{0.63} (17)	Na ₃ ScU ₆ F ₃₀ (18)	Na _{3.84} In _{0.72} U ₆ F ₃₀ (19)		
Formula weight	2114.22	2156.89	2163.27	2112.11	2169.02		
Crystal system		Trigonal					
Space group, Z			P 3 c1, 2				
a = b, Å	10.16370(10)	10.1432(2)	10.1578(2)	9.91740(10)	9.9423(2)		
c, Å	13.1698(3)	13.2023(3)	13.1864(3)	13.0232(3)	12.9997(2)		
V, Å ³	1178.18(4)	1176.33(5)	1178.30(5)	1109.29(3)	1112.85(5)		
$\rho_{calcd}, g/cm^3$	5.960	6.089	6.097	6.323	6.473		
Radiation $(\lambda, \text{\AA})$							
μ, mm ⁻¹	39.747	40.313	40.367	44.218	44.542		
Т, К	300(2)	300(2)	300(2)	301(2)	300(2)		
Crystal dim., mm ³	0.06×0.06×0.04	0.03×0.02×0.02	0.04×0.03×0.02	0.03×0.02×0.02	0.06×0.02×0.02		
2θ range, deg.	3.09-27.50	3.09-27.44	3.09-27.45	3.13-27.49	3.13-27.49		
Reflections collected	29091	24889	24226	26898	25618		
Data/parameter s/restraints	911/68/0	909/72/0	909/72/0	856/62/0	858/68/0		
R _{int}	0.0260	0.0306	0.0258	0.0399	0.0346		
Goodness of fit	1.072	1.112	1.109	1.189	1.090		
$R_1(I > 2\sigma(I))$	0.0116	0.0181	0.0144	0.0164	0.0106		
wR_2 (all data)	0.0304	0.0384	0.0316	0.0380	0.0251		

Table 4. Crystallographic data for $Na_{6-3x}M_xTh_6F_{30}$ (M = Y, Lu, and Tm), $Na_3ScU_6F_{30}$, $Na_{3.84}In_{0.72}U_6F_{30}$.

Results and discussion

Synthesis

Unlike uranium(IV) compounds, which can be readily obtained via an *in situ* reduction route from uranyl acetate or other uranyl salts with a reducing anion, the most convenient way to obtain thorium(IV) compound appears to be the direct reaction using a thorium salt, e.g. $Th(NO_3)_4 \cdot 4H_2O$ or ThF_4 . Thorium nitrate is hygroscopic and therefore is a less convenient starting reagent compared to thorium fluoride. Using an excess of a hydrofluoric acid solution, thorium nitrate can be readily converted to thorium fluoride in nearly quantitative yield as ThF_4 is practically insoluble. The low solubility however can also be a disadvantage when using ThF_4 as a precursor, because unreacted ThF_4 cannot be dissolved in any solvent and will be present in the product. However, unlike the resulting phase, which is usually crystalline, unreacted thorium fluoride is present in the form of a very fine powder that can be easily separated from the reaction mixture by decanting or sieving.

Another important feature of this synthesis approach using hydrofluoric acid is that the presence of an excess of fluoride anions allows for the use of metal oxide reagents that are typically insoluble and often quite inert. A good example of this feature is the syntheses of Na₃ScTh₆F₃₀ and Na₃ScU₆F₃₀ compounds, which both employ the inert Sc₂O₃ as the scandium source.

Recently we pointed out the difference in the reaction products that are obtained from the use of either uranyl acetate or uranium(IV) fluoride as the uranium source in hydrothermal reactions.²³ We have shown that these two different sources of uranium result in different crystalline products, although in both cases the resulting product contains uranium in its +4 oxidation state. Similar behavior can be observed in the quaternary uranium fluoride system. The use of uranyl acetate in the presence of Sc_2O_3 under highly fluorinating hydrothermal conditions produces no scandium-containing quaternary phase;³¹ on the other hand, the desired quaternary scandium phase can readily be obtained if uranium fluoride is utilized instead of uranyl acetate, avoiding the *in situ* reduction step. Given the fact that the scandium cation has a larger volume than all the other cations in the uranium quaternary series, one could speculate that the scandium phase is not as thermodynamically favored as the other reported quaternary uranium fluorides. This might explain why this phase does not form from uranyl acetate if a kinetic energy barrier

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needs to be overcome during the *in situ* reduction step. By contrast, the direct reaction between UF_4 and Sc_2O_3 in HF proceeds without this intermediate step and involves a different reaction path, which apparently has less of an activation barrier to produce $Na_3ScU_6F_{30}$ phase. A larger M cation in the uranium series results in the compound $Na_{3.84}In_{0.72}U_6F_{30}$ with partial occupancy of the M site by the indium cation. This compound also could not be obtained via a mild hydrothermal reaction that relies on the *in situ* reduction step.

Using an analogous approach, the reactions between rare-earth oxides and thorium fluoride all resulted in a mixture of phases that include the targeted quaternary fluoride along with some ternary sodium thorium fluorides. The presence of the targeted phase in the products can be confirmed by PXRD patterns (Figures S9-S14), but only the single crystals of 15-17 containing M = Y, Lu, or Tm were picked and studied by single crystal X-ray diffraction. We were unable to obtain a satisfactory structure model for the other rare earth containing compounds because of the small size and low quality of their crystals. Although PXRD patterns indicate the presence of the targeted phase, Chemey at. al. recently reported on a new polymorphic modification of NaUF₅ that crystallizes in P $\overline{3}$ cl space group with unit cell parameters a = b = 10.0029(12) and c = 13.0457(16) Å, highly reminiscent of those of the quaternary phases $Na_xMU_6F_{31}$ reported by Yeon et.al. that also crystallize in the P3c1 space group.²⁹⁻³¹ Given the striking similarity of PXRD patterns of β-NaUF₅ and Na_{3 84}In_{0.72}U₆F₃₀ (Figure 1), the potential existence of a hypothetical isostructural NaThF₅ greatly complicates the product identification if only PXRD data are available. Therefore, while we can be certain that the thorium compounds with Y, Lu, and Tm were successfully obtained, because their compositions were confirmed by both single crystal XRD and by EDS analysis using the same single crystals for both single crystal XRD and by EDS analyses, the same certainly does not exist for the remaining rare earth compositions, where we only have powder X-ray diffraction data. While it is likely that the other rare earth quaternary thorium fluoride compounds were indeed obtained by the identical synthetic procedure, the similarity of the diffraction patterns of the hypothetical NaThF₅ and the expected quaternary phases prevents us from stating this with confidence.



Figure 1. Comparison of the calculated PXRD patterns of $NaUF_5$ (black) and $Na_{3.84}In_{0.72}U_6F_{30}$ (green).

Structure description

All the compounds reported herein belong to the same structure type that was described in detail previously.^{30–32} **1-17** crystallize in the trigonal space group $P\overline{3}c1$ and are based on a framework built from vertex- and corner-sharing ThF₉ and MF₆ polyhedra (Figure 2). The uninodal 6-coordinated simplified net of the $[Th_6F_{30}]^{6-}$ framework has the **wmo** topology, which is decorated by M nodes.⁴² Noteworthy, the framework has the highest symmetry, $P\overline{3}c1$, allowed by its underlying net.

The single crystallographic thorium atom forms a ThF₉ polyhedron in the shape of a distorted tricapped trigonal prism with Th-F bond lengths spanning the range from 2.264(4) to 2.460(4) Å. The M site adopts an almost regular octahedral coordination environment with six equivalent bonds. The M-F distances vary over a wide range, from 1.807(4) for M = Al to 2.119(4) Å for M = Tm. The Na_{6-3x}M_xTh₆F₃₀ structure type exhibits either two or three crystallographically unique sodium sites. Both fully occupied Na1 and Na2 sites are present in all the structures, and are located at special positions with C₃ and C_{3i} site-symmetry, respectively; the third Na3 atom, on the other hand, occupies a general position and is partially occupied depending on the valence and the site occupancy of the M metal. In the case of M = Mg, Mn, Co, Ni, Cu, or Zn the Na3 site occupancy equals 0.167 and increases when the M site is partially occupied; e.g. the highest Na3 site occupancy of 0.233(2) is observed in Na_{4.39}Lu_{0.54}Th₆F₃₀. The Na1 atoms adopt an irregular octahedral environment with Na-F bond

lengths of 2.281(5) - 2.386(4) Å, whereas the twelve-coordinated Na2 atoms form polyhedra in the shape of an icosahedron with slightly elongated bonds of 2.633(4) - 2.810(3) Å. The Na3 atoms are located in a larger pore than those in which the Na1 and Na2 atoms are located and is disordered over two positions with Na-F bond distances of 2.31(3) - 2.97(3) Å.



Figure 2. (a and b) A view of the $Na_4ZnTh_6F_{30}$ structure and (c and d) of the simplified net of the $[Th_6F_{30}]^{6-}$ framework with **wmo** topology.⁴² Thorium and zinc polyhedra are gray and violet, respectively, and fluorine atoms are light green.

The two quaternary uranium fluorides reported here, $Na_3ScU_6F_{30}$ and $Na_{3.84}In_{0.72}U_6F_{30}$, share the same structure type with the thorium series. The actinide contraction slightly affects the U-F distances, which range from 2.268(2) to 2.420(2) Å

Previously a quaternary thorium fluoride with a formula Na₃ZnTh₆F₂₉ has been reported.⁴³ The unit cell parameters of this phase, a = b = 10.116(2) and c = 13.255 Å, space group *P*321, are reminiscent of those of Na₄ZnTh₆F₃₀, a = b = 10.0455(2) and c = 13.2479(3) Å, space group *P*3*c*1, suggesting that these two compounds are likely the same one. Indeed, the *P*321 space group is a subgroup of the *P*3*c*1 space group, and for a direct comparison of the atomic coordinates in both models, new positions of the atoms were calculated by reducing the symmetry from $P\overline{3}c1$ to P321 (Table S2). Two symmetrically equivalent atoms were generated for all except the Na2 atoms according to the symmetry operations listed in Table 5 and the origin was shifted by a $(0 \ 0 \ \frac{1}{4})$ vector. The resulting set of coordinates virtually coincides with the coordinates reported by Cousson et al.⁴³ In the $P\overline{3}c1$ space group model all the fluorine sites are fully occupied and there is an additional Na site, whereas in the P321 space group the absence of the Na site leads to a charge misbalance, which was resolved by introducing a partial occupancy on one of the F sites. As a result, the single crystal structures result in the compositions Na₄ZnTh₆F₃₀ and Na₃ZnTh₆F₂₉, respectively. For further comparison, the previously reported model was refined against the new single crystal X-ray diffraction dataset. To compensate for the lack of an inversion center in the P321 space group, a (-1 0 0 0 - 1 0 0 0 -1) twin law was introduced to the model, which was subsequently refined as a 50:50 twocomponent twin. The resulting R_1 value was found to be 1.92% for all reflections with I>4 σ (I), which is considerably higher than $R_1 = 1.50\%$ found for the model in the $P\overline{3}c1$ space group. The main disadvantages of the low symmetry model, however, is that one sodium and 7 fluorine atoms were found to be non-positive definite after anisotropic refinement and two prominent electron density peaks, 3.57 and 3.34 \overline{e} , corresponding to the potential partially occupied Na sites. The R_1 value decreases down to 1.49% after introducing these two partially occupied sodium sites into the model, but there still remain 7 non-positive definite fluorine atoms, indicating the missing symmetry in the structure. This allows us to conclude that although both structure determinations for quaternary sodium zinc thorium fluoride correspond to the same compound, the structural model with the formula Na₄ZnTh₆F₃₀ and the $P\overline{3}c1$ space group provides a better description of the structure of this compound.

Crystal chemical analysis of the Na_nMTh₆F₃₀ family

The Na_nMTh₆F₃₀ structure type accommodates di- and trivalent metals with their ionic radii varying over a wide range from 0.535 (Al) to 0.900 Å (Y). To estimate the volume of the M site, we built Voronoi polyhedra of the M atoms in the title compounds and calculated their R_{SD}, which show the radius of a sphere that has the same volume as the Voronoi polyhedron of a selected atom (Figure 3). As expected, the Al site in Na₃AlTh₆F₃₀ exhibits the smallest M site size with an R_{SD} of 1.123 Å, whereas the largest R_{SD}'s of 1.309–1.315 Å are observed in the case of M = Y, Lu, and Tm. It is noteworthy that there is no direct correlation between the

radius of the M^{3+} cation and the M-F bond length in the Na_nMTh₆F₃₀ (M = Y, Lu and Tm) structures. Our numerous attempts to obtain a lanthanide-containing compound with a full M site occupancy were unsuccessful, which leads us to suggest that the structure type reaches a certain size limit, after which only a partial site occupancy is possible. The value of R_{SD} of ~1.32 Å, therefore, reflects the maximum M site size capacity in the Na_xMTh₆F₃₀ family, and the maximum radius of the M metal falls into the range between 0.80 (In) and 0.861 Å (Lu), which corresponds to the transition from a fully to a partially occupied M site. A similar trend is observed in the uranium quaternary fluoride series, where the transition to partial occupancy of the M site occurs between 0.745 (Sc) and 0.80 Å (In), reflecting the smaller size of U(IV) as compared to Th(IV).



Figure 3. The coordination (left) and Voronoi polyhedra (right) of the thorium atoms in the structure of $Na_4ZnTh_6F_{30}$.

To establish the influence of the varying M site size on the thorium site, we calculated R_{SD} values for the thorium sites. The thorium R_{SD} vary in a narrow range of 1.354–1.358 Å with an average of 1.357(1) Å. Given the fact that the framework in the Na_nMTh₆F₃₀ structure type is built of corner- and edge-sharing ThF₉ polyhedra, the constant size of the thorium atoms indicates the extreme rigidness of the framework and suggests that the accommodation of the different M cations occurs via a distortion of the bond angles rather than via Th-F bond elongation. Noteworthy, the R_{SD} values of the U sites in the previously reported Na_xMU₆F₃₀ series lie within a range of 1.329–1.336 Å with an average of 1.333(1) Å, which is only slightly less than that of the thorium sites in Na_xMTh₆F₃₀. However, coupled with the large number of

the actinide atoms per one M site, this slight difference allows the thorium family to accommodate significantly larger cations, such as the lanthanides.

Magnetism

The magnetic susceptibility data were collected over a temperature range of 2–300 K for the quaternary thorium fluorides that contain the magnetic Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ti^{3+} , V^{3+} , Cr^{3+} , and Fe³⁺ ions (Figure 4, Figures S15–S20). All the compounds, except Na₃TiTh₆F₃₀, exhibit paramagnetic behavior similar to that of Na₄MnTh₆F₃₀ (Figure 4) and follow the Curie-Weiss law over a wide temperature range. As shown in Figure 4, the inverse susceptibility plot of Na₃TiTh₆F₃₀ starts to deviate from the Curie-Weiss law at approximately 240 K; therefore, the temperature range of 240–300 K was used to calculate the Weiss constant and the effective magnetic moment. The inverse susceptibility plots for the other compounds can be fitted to the Curie-Weiss law almost across the entire measured temperature range and were used to calculate the Weiss constants and effective magnetic moments, which are summarized in Table 5 along with the calculated expected values.

The effective magnetic moments for the compounds with Mn and Ni are in reasonable agreement with the expected magnetic moments for the respective cations. All the other compounds, except Na₃VTh₆F₃₀, show magnetic moments noticeably higher than the expected values. Magnetic measurements are well-known for the sensitivity to the presence of any magnetic impurity; especially, a significant deviation from the expected values can be observed when a compound with a high molar mass and a small number of magnetic atoms per formula unit contains an impurity with a low molar mass and high magnetic atom content. In this case even a small and effectively undetectable amount of an impurity would significantly affect the μ_{eff} value. To illustrate this, we studied a sample of Na₃CrTh₆F₃₀ with both PXRD and ICP MS. According to the PXRD data, the sample contained only the target phase. However, the diffraction peaks of CrF₃, which could be present as an impurity and as the source of the discrepancy between the calculated magnetic moment and the expected value, are perfectly overlapping with the peaks of the target phase. The ICP MS shows a higher than expected chromium content, however the expected 1 : 6 molar ratio is within the 3 sigma range of the ICP data, making quantitative estimations unreasonable. Considering that all the compounds

exhibit only simple paramagnetic behavior, we did not undertake further attempts to improve the purity of the samples.

Table 5. Curie-Weiss constants and effective magnetic moments for the quaternary thorium fluorides. Expected values for

Compound	$\theta(\mathbf{K})$	$\mu_{\rm eff}/\mu_{\rm B}$	$\mu_{ m calc}/\mu_{ m B}$
Na ₄ MnTh ₆ F ₃₀	-1.4	6.20	5.92
Na ₄ CoTh ₆ F ₃₀	-8.0	5.23	3.88
Na ₄ NiTh ₆ F ₃₀	0.4	3.25	2.83
Na ₄ CuTh ₆ F ₃₀	9.7	1.93	1.73
Na ₃ TiTh ₆ F ₃₀	-175	2.68	1.73
Na ₃ VTh ₆ F ₃₀	-24.2	2.01	2.83
Na ₃ CrTh ₆ F ₃₀	-1.9	4.54	3.88
Na ₃ FeTh ₆ F ₃₀	-13.6	6.78	5.92



Figure 4. Temperature dependence of the molar and inverse molar susceptibilities of $Na_4MnTh_6F_{30}$ (left) and $Na_3TiTh_6F_{30}$ (right).

Conclusion

A large family of new quaternary thorium fluorides, $Na_nMTh_6F_{30}$, containing various diand trivalent cations was obtained and structurally characterized. The $Na_nMTh_6F_{30}$ structure type can accommodate a cation as small as Al^{3+} and as large as Y^{3+} , spanning a range of ionic radii from 0.535 to 0.900 Å. Further increase of the cation size significantly decreases the yield of the target phase and deteriorates the quality of the crystals. It was shown that a compound, which has been reported as $Na_3ZnTh_6F_{29}$, has similar unit cell parameters as $Na_4ZnTh_6F_{30}$ and most likely corresponds to the same composition. It was found that changes in the di- and trivalent cation sizes do not significantly affect the size of the Th coordination polyhedra.

Magnetic susceptibility measurements for the compounds containing Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ti^{3+} , V^{3+} , Cr^{3+} , and Fe^{3+} ions all exhibit simple paramagnetic behavior with, in most cases, moments higher than are expected. A possible explanation for this is the potential presence of an impurity that falls below the detection limit of PXRD and/or cannot be detected due to overlap of the diffraction peaks with those of the target phase. This hypothesis is supported by an ICP MS analysis of the Na₃CrTh₆F₃₀ sample showing a slightly elevated Cr content versus what is expected from the formula.

Supporting Information

PXRD patterns and magnetic susceptibility versus temperature plots for 2–5 and 9–12. CSD 1879489-1879507 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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Na_nMTh₆F₃₀ – a Large Family of Quaternary Thorium Fluorides

Vladislav V. Klepov, Gregory Morrison, and Hans-Conrad zur Loye



A slight increase in the $An_6F_{30}^{6-}$ framework size allows for the incorporation of much larger cations, such as the rare-earths, into the $Na_nMTh_6F_{30}$ structure. The result is a large family of compounds encompassing 17 elements, which exhibit paramagnetic behavior for the compositions containing magnetic 3*d* cations.