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Chromium Chains as Polydentate Fluoride Ligands for Actinides and Group IV Metals

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The reactions of {Cr₆} horseshoe chains {[ⁿPr₂NH₂]₃[Cr₆F₁₁(O₂C^tBu)₁₀]}₂, **1** and precursors of actinides and group IV metals led to a series of ring complexes [ⁿPr₂NH₂][Cr₇TiF₆O₂(O₂C^tBu)₁₆], **2**, [ⁿPr₂NH₂][Cr₆Ti₂F₅O₃(O₂C^tBu)₁₆], **3**, [Cr₆ThF₇(O₂C^tBu)₁₅(Me₂SO)], **4**, [ⁿPr₂NH₂]₂(Cr₆Th₂F₁₂(O₂C^tBu)₁₆), **5** and [ⁿPr₂NH₂][Cr₆U₂O₂F₈(O₂C^tBu)₁₆(Me₂SO)], **6**. X-ray structure studies indicate that the {Cr₆} chains maintain their structures in these complexes, acting as polydentate fluoride ligands. Their static magnetic properties were measured and fitted by isotropic exchange Hamiltonian. In accordance with **1**, the magnetic exchanges between Cr^{III} are antiferromagnetic, while the exchange interactions can be modified by the tetravalent metals. For compound **6**, ferromagnetic exchanges *J*_{Cr-U} and *J*_{U-U} are obtained. EPR spectra of compounds **2-5** were measured at Q band and were simulated. The spectrum of **2** has the same profile as {Cr₇Cd} and {Cr₇Zn} rings with a ground state *S* = 3/2. **3**, **4** and **5** give similar EPR spectra with *S* = 0 ground states.

Introduction

We have been focusing on anti-ferromagnetically coupled heterometallic rings because of their interesting magnetic frustration behaviour and potential application in quantum information processing.¹ A series of {Cr₇M} rings and supramolecular architectures derived from them have been synthesized and investigated.² The {Cr₇M} rings are obtained by one-pot reaction of CrF₃·4H₂O an appropriate carboxylic acid, a secondary amine and corresponding metal (II) salts.

An alternative route uses anionic {Cr₆} chains as ligands to bind metal ions. The {Cr₆} chains {[ⁿPr₂NH₂]₃[Cr₆F₁₁(O₂C^tBu)₁₀]}₂, **1**, and [(Et₂NH₂)₃{Cr₆F₁₁(O₂C^tBu)₁₀}]₂ adopt a “horseshoe” motif of chromium centres, each with six terminal fluoride ligands. Reactions between {Cr₆} chains and precursors of sodium³ and lanthanides⁴ lead to a series of {(Cr₆)M_x]_n (M = Na, Y, Ce, Gd) clusters including cage, ring and bicycle motifs. In the obtained clusters, the {Cr₆} horseshoe chains maintain their characteristic structures and bind the metal ions with the terminal fluoride ions. These results have shown that {Cr₆} chains can act as fairly robust polydentate fluoride ligands for hard metals.

Fluoride is widely used to extract actinides because the resultant compounds are insoluble in water and can be

separated with redox reactions.⁵ The monovalency and high electronegativity of fluorides lead to a very limited number of polydentate fluoride donor ligands (i.e. SiF₆²⁻ can as a bridging ligand, but this is quite rare⁶). As these chains bind electropositive elements, we reasoned they would bind strongly to the actinides and prevent the precipitation of extremely insoluble AnF₄ salts. The development of new ligands for actinide binding is a very important field of chemistry, especially in the context of nuclear fuel processing and recycling.

In addition, the clusters combining paramagnetic transition-metal and actinide ions may exhibit interesting single-molecule magnets (SMMs) behaviours. For example, M. Mazzanti et al. have reported a ring-shaped {[UO₂(salen)]₂Mn(Py)₃]₆ as an SMM with a *U*_{eff} = 99 cm⁻¹.⁷

The aim of this work was to investigate whether we could make {Cr₆} chains bind to tetravalent actinides Th^{IV} and U^{IV}. Prior to experiments involving radioactive materials, we studied the binding of {Cr₆} chains to titanium(IV). The reactions of **1** with Ti^{IV} precursors led to the isolation of two eight membered rings [ⁿPr₂NH₂][Cr₇TiF₆O₂(O₂C^tBu)₁₆] **2** and [ⁿPr₂NH₂][Cr₆Ti₂F₅O₃(O₂C^tBu)₁₆] **3**. Similar reactions of **1** with Th^{IV} and U^{IV} precursors led to ring structures [Cr₆ThF₇(O₂C^tBu)₁₅(Me₂SO)] **4**, [ⁿPr₂NH₂]₂(Cr₆Th₂F₁₂(O₂C^tBu)₁₆) **5** and [ⁿPr₂NH₂][Cr₆U₂O₂F₈(O₂C^tBu)₁₆(Me₂SO)] **6**. Herein we report their syntheses, structures and magnetic properties.

Experimental section

General information

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Unless stated otherwise, all reagents and solvents were purchased from commercial sources and used without further purification.

For U^{IV} reactions, all manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and degassed before use. All solvents were stored over potassium mirrors. Most solid reagents were dried under vacuum for four hours and most liquid reagents were dried over 4 Å molecular sieves and distilled before use.

Analytical data were obtained by the microanalysis laboratory at the University of Manchester—carbon, hydrogen, nitrogen analysis (CHN) by a Flash 2000 elemental analyser and metals analysis by Thermo iCap 6300 inductively coupled plasma optical emission spectroscopy (ICP-OES).

Thermo Fisher Scientific "Exactive Plus EMR Orbitrap" mass spectrometer was used for mass spectrometry analysis. The samples were ionised in the electrospray ion source operated in both positive and negative modes, ~3.5 kV was applied to the capillary. The ions were detected using electrostatic trap with mass resolution of ~140000 and stability sufficient to achieve a precision of <5 ppm for mass measurements.

Starting materials

The starting materials $\{[{}^n\text{Pr}_2\text{NH}_2]_3[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}]\}_2$, **1**, and $[(\text{Et}_2\text{NH})_3[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}]]_2$ were prepared according to literature procedures.³ The preparation of $\text{Ti}_8\text{O}_8(\text{O}_2\text{C}^t\text{Bu})_{16} \cdot (\text{MeCN})_2$ was adapted from literature.⁸

Synthesis of compounds

$[{}^n\text{Pr}_2\text{NH}_2][\text{Cr}_7\text{TiF}_6\text{O}_2(\text{O}_2\text{C}^t\text{Bu})_{16}]$, **2**

$\{[{}^n\text{Pr}_2\text{NH}_2]_3[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}]\}_2$ (3.0g, 0.80 mmol), titanyl acetylacetonate (0.833g, 3.18 mmol) and pivalic acid (14.0g, 137 mmol) were placed in a 150 mL Teflon® Erlenmeyer flask. The flask was placed in a silicone oil bath at 140 °C for 20 hrs and stirred continuously. After heating, the reaction mixture had dried to a green powder due to the evaporation of excess pivalic acid. Upon cooling to ambient temperature, acetone:MeCN (1:1, 50 mL) was added to the flask and stirred for 4 hr. A green solid was obtained via vacuum filtration, washed with Et_2O :MeCN (1:1, 25 mL) and dried in air. TLC shows movement of the least polar species, **2**, from baseline using toluene, further isolable species show movement using EtOAc and Et_2O . Separation of **2** on silica column (length = 25 cm) is achieved using toluene as the eluent. Rotary evaporation of the toluene fraction under reduced pressure yields **2** as a green powder. Single crystals were grown after dissolution in a Et_2O :MeCN mixture (7:3).

Yield: 1.95 g (62.4 % based on Cr). Elemental analysis calculated (%) for $\text{C}_{86}\text{H}_{160}\text{O}_{34}\text{N}_1\text{Cr}_7\text{Ti}_1\text{F}_6$: Cr 15.97, Ti 2.10, C 45.34, H 7.08, N 0.61; Found (%) Cr 15.15, Ti 2.30, C 46.54, H 7.52, N 0.36. ES-MS (THF, m/z): +2278 $[\text{M}+\text{H}]^+$; +2300 $[\text{M}+\text{Na}]^+$.

$\text{Ti}_8\text{O}_8(\text{O}_2\text{C}^t\text{Bu})_{16} \cdot (\text{MeCN})_2$

Pivalic acid was distilled prior to use by hydrolysis of trimethyl acetic anhydride. Standard distillation apparatus was used to reflux trimethyl acetic anhydride at 165 °C. Anhydrous pivalic

acid (17.5 g, 170 mmol) dissolved in dry MeCN (40 g, 970 mmol) was added to a 2-necked round bottomed flask, flushed with N_2 . Titanium (IV) isopropoxide (5 g, 17 mmol) and dry MeCN (8 g, 195 mmol) were added dropwise to the flask, through a suba seal, using a syringe. After stirring at room temperature for a few minutes, all reactants were visibly solvated. Following this, the reaction mixture was refluxed at 100 °C for 4 hr. White translucent crystals formed at the base of the flask. The remaining MeCN was evaporated under reduced pressure and the white crystals of $\text{Ti}_8\text{O}_8(\text{O}_2\text{C}^t\text{Bu})_{16} \cdot (\text{MeCN})_2$ were used in further synthetic transformations without further purification. Yield: 4.19 g (89.2 % based on Ti) Elemental analysis calculated (%) for $\text{C}_{84}\text{H}_{150}\text{O}_{40}\text{Ti}_8\text{N}_2$: C 45.63, H 6.84, N 1.27, Ti 17.32; Found (%) C 46.25, H 6.91, N 0.77, Ti 16.75. ES-MS (MeOH, m/z) +2026 $[\text{M} - (\text{MeCN})_2 - \text{O}_2\text{C}^t\text{Bu}]^+$; +2153 $[\text{M} - (\text{MeCN})_2 + \text{Na}]^+$.

Synthesis of $[{}^n\text{Pr}_2\text{NH}_2][\text{Cr}_6\text{F}_5\text{Ti}_2\text{O}_3(\text{O}_2\text{C}^t\text{Bu})_{16}]$, **3**

$\{[{}^n\text{Pr}_2\text{NH}_2]_3[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}]\}_2$ (3.0g, 0.80 mmol), $\text{Ti}_8\text{O}_8(\text{O}_2\text{C}^t\text{Bu})_{16} \cdot (\text{MeCN})_2$ (1.70 g, 0.8 mmol) and pivalic acid (14.0g, 137 mmol) were added to a 150 mL Teflon® Erlenmeyer flask. The flask was placed in a silicone oil bath at 140 °C for 3 hrs and stirred continuously. After cooling to room temperature, acetone:MeCN (1:1, 50 mL) was added with continued stirring for 5 hr. A green microcrystalline solid was obtained via vacuum filtration. The product, **3**, was extracted using Et_2O (30 mL) and precipitated out of solution after addition of MeCN (30 mL). Finally, the product is filtered and washed with Et_2O and acetonitrile (1:1, 25 mL). TLC shows movement of least polar species, **3**, from baseline using toluene, a further compound shows movement in Et_2O . Separation of **3** on silica column (length = 25 cm) was achieved using toluene:EtOAc (3:1) as the eluent. The solvent mixture was then evaporated under reduced pressure. Et_2O was used to produce single crystals of **3** for XRD measurements.

Yield: 2.89 g, 79.5 % based on Cr. Elemental analysis calculated (%) for $\text{C}_{86}\text{H}_{160}\text{O}_{35}\text{N}_1\text{Cr}_6\text{Ti}_2\text{F}_5$: Cr 13.74, Ti 4.21, C 45.48, H 7.10, N 0.62; Found Cr 14.11, Ti 4.05, C 45.98, H 7.26, N 0.66. ES-MS (THF, m/z): +2169 $[\text{M} - \text{O}_2\text{C}^t\text{Bu}]^+$; +2271 $[\text{M}+\text{H}]^+$; +2293 $[\text{M}+\text{Na}]^+$; +2311 $[\text{M}+\text{K}]^+$.

$[\text{Th}(\text{O}_2\text{C}^t\text{Bu})_4]_n$

$\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$ (2.49 g, 4.51 mmol) was refluxed in $\text{HO}_2\text{C}^t\text{Bu}$ (100 g) with stirring for 12h at 120 °C with slow N_2 flow to remove the NO_2 . Then the reaction mixture was allowed to cool to room temperature. The product was then collected by filtration and washed with further Et_2O and dried in air. Yield: 0.58g, 20% based on Th. Elemental analysis calculated (%) for $\text{ThC}_{20}\text{H}_{36}\text{O}_8$: C 37.74, H 5.70; found (%) C 37.72, H 5.66.

$[\text{U}_4\text{O}_2(\text{O}_2\text{C}^t\text{Bu})_{12}] (\text{Toluene})_{1.5}$

UCl_4 (0.38 g, 1 mmol) and $\text{KO}_2\text{C}^t\text{Bu}$ (0.56 g, 4 mmol) were refluxed with stirring in toluene for 12h at 120 °C. Then the reaction mixture was allowed to cool to room temperature. The solution was filtered and the filtrate was concentrated and stored at 5 °C to give the crystalline product as green needles. Crystalline product yield: 0.224 g, 38% based on U.

[Cr₆ThF₇(O₂C^tBu)₁₅(Me₂SO)](HO₂C^tBu)(MeCN)(THF)_{0.5}, **4**

[Th(O₂C^tBu)₄]_n (0.127 g, 0.2 mmol), pivalic acid (1 g, 9.8 mmol), DMSO (0.8 g) and [(ⁿPr₂NH₂)₃[Cr₆F₁₁(O₂C^tBu)₁₀]]₂ (0.53 g, 0.15 mmol) were stirred at room temperature with THF (35 ml) for 15 min, then MeCN (20 ml) added and stirring continued for 18 hours at room temperature. The solution was then filtered and the filtrate was left undisturbed for slow evaporation in a partially open flask. After 1 week a small amount of crystalline product including crystals suitable for X-ray structure studies were collected by filtration and washed with MeCN.

Yield: 0.096 g, 19.5% based on Th. Elemental analysis calculated (%) for ThCr₆F₇C₈₆H₁₅₈O_{33.5}NS: Th 9.61, Cr 12.93, C 41.80, H 6.43, N 0.58; found (%) Th 9.70, Cr 12.44, C 40.40, H 6.4, N 0.64.

[(ⁿPr₂NH₂)₂(Cr₆Th₂F₁₂(O₂C^tBu)₁₆)](ⁿPr₂NH)₂(Et₂O), **5**

[Th(O₂C^tBu)₄]_n (0.255 g, 0.4 mmol), pivalic acid (1 g, 9.8 mmol), DMSO (0.8 g) and [(ⁿPr₂NH₂)₃[Cr₆F₁₁(O₂C^tBu)₁₀]]₂ (0.35 g, 0.1 mmol) were dissolved in toluene (80 mL) and refluxed with stirring for 30 min at 120°C. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Then MeCN (30 mL) was added to the residue and stirred for 0.5 h. The solid was collected by filtration, washed with further MeCN and dried in air. Crystals suitable for X-ray structure studies were obtained by slow evaporation from a mixture of Et₂O-MeCN.

Yield: 0.38 g, 66% based on Th. Elemental analysis calculated (%) for Th₂Cr₆F₁₂C₉₆H₁₈₆O₃₃N₂: Th 15.77, Cr 10.60, C 39.75, H 6.46, N 0.97; found (%) Th 16.15, Cr 10.57, C 39.08, H 6.26, N 0.85.

[ⁿPr₂NH₂][Cr₆U₂O₂F₈(O₂C^tBu)₁₆(Me₂SO)], **6**

[U₄O₂(O₂C^tBu)₁₂] (0.234 g, 0.1 mmol), pivalic acid (0.2 g, 2.0 mmol), DMSO (1.0 g) and [(ⁿPr₂NH₂)₃[Cr₆F₁₁(O₂C^tBu)₁₀]]₂ (0.268 g, 0.075 mmol) were dissolved in toluene (20 mL) and refluxed with stirring for 30 min at 120°C. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Then MeCN (30 mL) was added to the residue and stirred for 0.5 h. The green solid was collected by filtration, washed with further MeCN and dried *in vacuo*. The solid was then extracted with a mixture of Et₂O-MeCN (1:1, 5 mL), reduced in volume to ca. 2 mL, and stored at -10 °C to give **3** as green blocks.

Yield: 0.51 g, 36% based on U. Elemental analysis calculated (%) for U₂Cr₆F₈C₈₈H₁₆₆O₃₅N₁: U 17.18, Cr 11.26, C 38.15, H 6.04, N 0.51; found (%) U 17.45, Cr 11.26, C, 38.92, H 6.09, N 0.91.

Crystallography

Data Collection

Single crystal X-ray diffraction data were collected for the crystal structures **2** and **3** at a temperature of 150 K using MoK α radiation, (λ = 0.71073 Å) on an Oxford X'calibur diffractometer, equipped with an Atlas CCD detector and an Oxford Cryojet nitrogen flow gas system. Data was measured using CrysAlisPro suite of programs. X-ray data for compound **4** were collected at a temperature of 150 K using MoK α radiation,

(λ = 0.71073 Å) on an Agilent Technologies Supernova diffractometer equipped with an Eos CCD detector and an Oxford Cryostream 700 nitrogen flow gas system. X-ray data for compounds **5** and **6** were collected at a temperature of 150 K using CuK α radiation (λ = 1.54184 Å) on a Bruker X8 prospector diffractometer equipped with an Apex II CCD detector and an Oxford Cryostream 700 nitrogen flow gas system.

Crystal structure determinations and refinements.

X-ray data for crystals **2**, **3**, **4** and **5** were processed and reduced using CrysAlisPro suite of programs. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles using SCALE3 ABSPACK. X-ray data for crystal **6** were processed using Bruker SAINT and absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles using Bruker SADABS. The crystal structures for all were solved and refined against all F^2 values using SHELX-2016 implemented through Olex2 v1.2.8.⁹ All non-H atoms were refined anisotropically, with the exceptions of the carbon atoms corresponding to disordered solvent toluene molecules. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Occupancies of the Chromium and Titanium atoms were fixed to a 7:1 and 3:1 ratio in crystals **2** and **3**, respectively. The position and atomic displacement parameters were constrained to be equal using EXYZ and EADP commands. Occupancy of the bridging fluorides and oxides were set to have 3:1 and 5:3 proportions in crystals **2** and **3**, respectively. The atomic displacement parameters were constrained to be equal using EADP command. Pivalate ligands in all the crystal structures were disordered and modelled over two positions where possible. Same distance and fixed distance restraints were applied to restrain some of the C-C bonds. Similar neighbouring atomic displacement parameter (apd) and rigid bond restraints, and in some cases isotropic adp restraints were used to restrain the apds.

Physical measurements

Variable temperature and field-dependent magnetic moment data were recorded on a Quantum Design MPMS XL7 SQUID magnetometer. To avoid sample reorientation during measurements, ground samples were fixed with a known amount of eicosane. Diamagnetic corrections were applied using tabulated Pascal constants and measurements were corrected for the effect of the blank sample holders (straw or flame sealed Wilmad NMR tube) and eicosane.

Continuous wave EPR spectra were recorded at Q-band (ca. 34 GHz) using a spectrometer equipped with a Bruker EMX EPR console, a 1.8 T magnet and a Bruker ER051 QG microwave bridge with an ER 5106 QT (Q band) resonator. The data were collected on polycrystalline powders grounded with eicosane at variable low temperatures (using a liquid He Oxford Cryostat).

Table 1. Crystallographic information for compounds **2** - **6**.

	2	3	4	5	6
Identification code	orepw1860_Cr7Ti	orepw1883_Cr6Ti2	adpm291_Cr6Th	xadpm45_Cr6Th2	Xrepw772_Cr6U2
Empirical formula	C ₈₈ H ₁₆₅ Cr ₇ F ₆ NO _{34.5} Ti	C ₉₃ H ₁₆₈ Cr ₆ F ₅ NO ₃₅ Ti ₂	C ₉₀ H ₁₆₅ Cr ₆ F ₇ N ₂ O ₃₄ STh	C ₉₆ H ₁₈₆ Cr ₆ F ₁₂ N ₂ O ₃₃ Th ₂	C ₁₀₂ H ₁₈₂ Cr ₆ F ₈ NO ₃₅ SU ₂
Mr	2315.10	2363.07	2528.33	2900.54	2954.60
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /n	P2 ₁ 2 ₁ 2
a/Å	25.3319(14)	25.0563(18)	35.4782(4)	17.7566(3)	33.1772(7)
b/Å	16.6836(8)	16.9637(14)	29.7042(3)	42.1752(6)	32.7339(8)
c/Å	31.1000(14)	31.2329(18)	24.7842(4)	18.6391(3)	13.1235(3)
α/°	90	90	90	90	90
β/°	99.847(5)	99.553(5)	105.4775(14)	103.033(2)	90
γ/°	90	90	90	90	90
Volume/Å ³	12950.0(11)	13091.3(16)	25171.6(6)	13599.0(4)	14252.4(6)
Z	4	4	8	4	P2 ₁ 2 ₁ 2
ρ _{calc} /cm ³	1.187	1.199	1.334	1.417	33.1772(7)
Temperature/K	150.15	150.15	150.02(10)	150.00(2)	150.00(2)
μ/mm ⁻¹	0.695	0.666	1.769	11.429	10.689
Goodness-of-fit on F ²	1.028	1.086	1.014	1.110	1.039
Final R indexes [I>2σ(I)]	R ₁ = 0.0960, wR ₂ = 0.2603	R ₁ = 0.1253, wR ₂ = 0.2418	R ₁ = 0.0578, wR ₂ = 0.1122	R ₁ = 0.0792, wR ₂ = 0.1818	R ₁ = 0.0876, wR ₂ = 0.2226
Final R indexes [all data]	R ₁ = 0.1757, wR ₂ = 0.3268	R ₁ = 0.2125, wR ₂ = 0.2837	R ₁ = 0.1093, wR ₂ = 0.1343	R ₁ = 0.0904, wR ₂ = 0.1888	R ₁ = 0.1202, wR ₂ = 0.2549
F(000)	4880.0	4984.0	10432.0	5888.0	5988.0
Crystal size/mm ³	0.65 × 0.3 × 0.3	0.65 × 0.3 × 0.2	0.303 × 0.245 × 0.109	0.04 × 0.03 × 0.02	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/°	6.884 to 52.744	6.938 to 50.7	4.812 to 52.744	5.298 to 150.118	2.662 to 139.384
Index ranges	-31 ≤ h ≤ 31, -18 ≤ k ≤ 20, -33 ≤ l ≤ 38	-24 ≤ h ≤ 30, -17 ≤ k ≤ 20, -37 ≤ l ≤ 27	-29 ≤ h ≤ 44, -37 ≤ k ≤ 34, -30 ≤ l ≤ 28	-22 ≤ h ≤ 20, -49 ≤ k ≤ 52, -22 ≤ l ≤ 22	-39 ≤ h ≤ 39, -39 ≤ k ≤ 37, -15 ≤ l ≤ 15
Reflections collected	61269	49742	88604	117174	105200
Independent reflections	26204 [R _{int} = 0.0591, R _{sigma} = 0.1017]	23853 [R _{int} = 0.0641, R _{sigma} = 0.1319]	51081 [R _{int} = 0.0387, R _{sigma} = 0.0846]	27102 [R _{int} = 0.0976, R _{sigma} = 0.0557]	25941 [R _{int} = 0.1236, R _{sigma} = 0.1132]
Data/restraints/ parameters	26204/2263/1280	23853/904/1470	51081/8175/3186	27102/4655/2020	25941/4230/1557

$$^a R_1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|; [b] wR^2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}; [c] S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]$$

Results and discussion

Syntheses and structures

Initially, we studied the binding of $[(^n\text{Pr}_2\text{NH}_2)_3\{\text{Cr}_6\text{F}_{11}(\text{O}_2\text{C}^t\text{Bu})_{10}\}]_2$, **1**, to group (IV) transition metal metals, reasoning that these analogues would mimic thorium(IV) chemistry, as the +4 oxidation state predominates for thorium. The reaction of **1** with $\text{Ti}(\text{acac})_4$ resulted in the formation of $[(^n\text{Pr}_2\text{NH}_2)[\text{Cr}_7\text{TiF}_6\text{O}_2(\text{O}_2\text{C}^t\text{Bu})_{16}]]$ **2** (Figure 1).

Figure 1. The crystal structure of (a) **2**, (b) **3**. Methyl groups of pivalates and solvent molecules omitted for clarity. Colours: Cr, green; Ti, light green; O, red; F, turquoise; N, blue; C, grey.

The structure of **2** consists of an octametallic ring, bridged internally by two μ_2 -oxide and six μ_2 -fluoride anions, with each M...M edge further bridged on the periphery by two pivalate ligands (Figure 1). The Ti^{IV} ion cannot be localised within the structure and is modelled as disordered over eight metal sites. This is a common feature for $\{\text{Cr}_7\text{M}\}$ rings, where M adopts an octahedral geometry.² As the Ti^{IV} sites are disordered, so are the bridging anions; charge balance require two oxides to be present as μ_2 -bridges, which are probably localised on the Cr...Ti edges, while the fluorides bridge the Cr...Cr edges. If a $\{\text{Ti}_8\}$ ring⁹ is used as the starting material, we form $[(^n\text{Pr}_2\text{NH}_2)[\text{Cr}_6\text{F}_5\text{Ti}_2\text{O}_3(\text{O}_2\text{C}^t\text{Bu})_{16}]]$ **3**. Again it is not possible to localize the Ti^{IV} sites in the crystal structure of **3**, which

generates the possibility of structural isomers. Given the other chemistry we have seen starting with **1** we believe it most likely that the two Ti^{IV} ions neighbour each other in the structure. Electrospray mass spectrometry confirms the constitution of these structurally analogous clusters, with **2** and **3** giving distinct positive ion peaks by electrospray mass spectrometry (Figures S1 and S2, $[(\text{Cr}_7\text{Ti})+\text{Na}]^+$: +2300 and $[(\text{Cr}_6\text{Ti}_2)+\text{Na}]^+$: +2293).

The severe positional disorder in these structures makes any analysis of metric parameters impossible; the necessary restraints imposed on the crystallographic model preclude this. Attempts were also made to combine **1** and precursors of Zr^{IV} and Hf^{IV} , but no crystalline product was obtained.

The reaction of **1** with $[\text{Th}(\text{O}_2\text{C}^t\text{Bu})_4]$ in THF/MeCN at room temperature with the presence of DMSO resulted in the formation of a $\{\text{Cr}_6\text{Th}\}$ ring $[\text{Cr}_6\text{ThF}_7(\text{O}_2\text{C}^t\text{Bu})_{15}(\text{Me}_2\text{SO})]$ **4** (Figure 2a). Complex **4** crystallizes with two heptametallic rings in the asymmetric unit. Each ring contains one Th^{IV} and six Cr^{III} ions with each edge of the ring bridged by a fluoride and two pivalates. The Th^{IV} site is nine-coordinate with a terminal coordinated DMSO and a chelating pivalate. Two MeCN molecules lie on each side of the ring forming C-H...F hydrogen bonds with the fluorides in the cavity of the ring. The C...F distances are between 3.076(4) - 3.573(2) Å and are thus in the range as many other reported C-H...F hydrogen bonds.¹⁰ Performing the reaction with the same reaction mixture in refluxing toluene results in a $\{\text{Cr}_6\text{Th}_2\}$ ring $[(^n\text{Pr}_2\text{NH}_2)_2(\text{Cr}_6\text{Th}_2\text{F}_{12}(\text{O}_2\text{C}^t\text{Bu})_{16})]$ **5** (Figure 2b). Complex **5** contains an octametallic ring $\{\text{Cr}^{\text{III}}_6\text{Th}^{\text{IV}}_2\}$. Each Cr...Cr and Cr...Th edge is bridged by a fluoride and two pivalates. The unique Th...Th edge is bridged by three fluorides. Each Th site is nine-coordinate with a terminal fluoride and a chelating pivalate complementing the bridging ligands. The Th-F bond lengths (with an average value of 2.393 Å for bridging fluorides and 2.210 Å for terminal ones) are relatively shorter than the Th-O bond lengths (with an average value of 2.481 Å). There are two protonated amide counteranions ($^n\text{Pr}_2\text{NH}_2$) in the asymmetric unit. One of lies within the ring, forming many N-H...F and C-

Figure 2. The crystal structure of (a) **4**, (b) **5**, and (c) **6**. Methyl groups of pivalates and solvent molecules omitted for clarity. Colours: Cr, green; O, red; F, turquoise; N, blue; Th, pink; U, violet; S, yellow; C, grey.

H...F hydrogen bonds with the fluorides. The second is outside the ring, forming N-H...F hydrogen bonds to terminal fluorides. The structures of **4** and **5** are similar to those previously reported in reactions between {Cr₆} horseshoes and lanthanides. **4** is similar to the [(Cr₆CeF₇(O^tBu)₁₄(THF)₂] ring,⁴ and is a rare example of a heptametallic ring.¹¹ The Th^{IV} ring differs from the Ce^{III} ring in the ligands attached to the f-block metal; for Th^{IV} a chelating pivalate and a DMSO occupy positions taken by two THF molecules on the Ce^{III} site. **5** is similar to the previously reported [(Et₂NH₂)(Cr₆Y₂F₈(O₂CtBu)₁₇(H₂O))].⁴ The differences between these eight membered rings are in the f-block metals; for {Cr₆Y₂} the two Y^{III} are bridged by a fluoride and three pivalates and Y sites are eight-coordinate.

The change in the number of f-block metal ions incorporated in the structures of **4** and **5** mirrors results previously observed in the synthesis of {(Cr₆)₂Gd_x} (x = 2 or 4) compounds.⁴ In that case, the reaction of {Cr₆}₂ and [Gd(O₂C^tBu)₃(HO₂C^tBu)₃]₂ in THF/MeCN with the presence of DMSO at room temperature led to {(Cr₆)₂Gd₂} and produced {(Cr₆)₂Gd₄} in refluxing toluene. In both cases the reactions at higher temperatures results in the {Cr₆} chains binding a greater number of metal ions.

Attempts to make an analogous starting material with U(IV), [U(O₂C^tBu)₄], resulted instead in the formation of a tetrametallic U^{IV} cage, [U₄O₂(O₂C^tBu)₁₂] and a direct analogue could not be produced. Therefore, we used this cage as a starting material. These resulted in the formation of [Pr₂NH₂][Cr₆U₂F₈O₂(O₂C^tBu)₁₆](Me₂SO)], **6**. The structure differs significantly from **5** (Figure 2c). A complication in preparing the crystallographic model arises from the potential presence of two monoatomic ligands – fluoride and oxide with a metal that can vary oxidation state. Here we report the result we believe most likely based on metric parameters and refined thermal parameters, but clearly other alternatives are possible which would then change the oxidation states of the uranium centres.

The U...U edge is bridged by two fluorides (average U-F bond length 2.330 Å) and two pivalates. This implies there two eight-coordinated U sites with differing oxidation states, based on the charge balance of the complex, one being a U^V ion and the other a U^{IV} ion. Both U sites are bridged to Cr through oxides (2.200 Å average U-O_{bridging} bond length). These U-O bond are significantly shorter than the average U-O-M bridging oxide distances found in the CSD (mean U-O distances for μ₂-oxide bridging to other metals = 2.32(16) Å). There are no U-F-M distances in the CSD with which to compare.

Structurally characterised examples of actinides bridged by three μ-fluorides have been reported previously,^{12–14} mainly in coordination polymers. The two zero-dimensional examples are (C₅N₂H₁₄)₂(H₃O)[U₂F₁₃]¹³ with a dimeric [U₂F₁₃]⁵⁻ unit reported by the O'Hare group and an organometallic complex [Th₂F₅(1,3-(Me₃C)₂C₅H₃)₂(bipy)]¹⁴ reported by Zi and Walter. There is some analogy between **5** and the structures found when **1** is reacted with lanthanides; instead of the formation of the An₂F₃ unit the lanthanides tend to form a dimer of the structure of **5** with a central Ln₄F₇ cage.⁴

In complexes **2–5**, the {Cr₆} chain binds with the same mode as previously seen in other compounds formed by reaction of

horseshoes, with one fluoride and two pivalates binding to the heterometal at each edge of the chain. Two of the three terminal fluorides on each terminal Cr^{III} site are displaced by pivalates, while the other one is retained. The Cr...Cr distances and Cr-F-Cr angles in complexes **4–5** are comparable to those in the chain **1**, indicating the chain's robustness. The chains are further stabilized by metal-bonded fluorides which are good acceptors and can form strong hydrogen bondings.¹² Compound **6** is an anomaly in these systems with the potential oxide bridging, assuming the oxidation states of the uranium sites are correct.

SQUID Magnetometry

Variable-temperature magnetic susceptibilities were recorded in an applied dc field of 0.1 T and 0.5 T for compounds **2–6** to study the effect of the M^{IV} ions to the magnetic exchange pathways of the Cr_x chains.

The plots of molar magnetic susceptibility (χ_M and χ_MT) of the five compounds are similar, indicating antiferromagnetic intra-molecule exchanges. All the data for **2–5** were fitted¹⁵ with a simple isotropic exchange Hamiltonian, where J₁ and J₂ are the terminal and internal Cr-Cr exchange coupling constants within the (n + m) - membered rings, with n = number of paramagnetic metal ions:

$$\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_{n-1} \cdot \hat{S}_n) - 2J_2 \sum_{i=2}^{n-1} \hat{S}_i \cdot \hat{S}_{i+1} + \mu_B \cdot \vec{B} \sum_{i=1}^n g_i \cdot \hat{S}_i$$

Figure 3. (a) Susceptibility vs. Temperature (χ_MT vs. T, black circles and χ_M vs. T, blue circles) and (b) Magnetization plots for **4**. Solid lines represent fittings, where $g_{\text{eff}} = 1.98$, $J_1 = -4.8 \text{ cm}^{-1}$ and $J_2 = -6.8 \text{ cm}^{-1}$. An inset of the magnetic coupling model is included.

In **2** - **5**, the only paramagnetic centres present are within the $\{\text{Cr}_6\}$ chain and the data can be fitted with g_{Cr} fixed at 1.98 allowing the exchange interactions to vary. The best fit parameters (in cm^{-1}) are: for **2**, $J_1 = J_2 = -5.7$; for **3**, $J_1 = -5.8$, $J_2 = -5.3$; for **4**, $J_1 = -4.8$, $J_2 = -6.8$; for **5**, $J_1 = -5.3$, $J_2 = -6.2$ cm^{-1} . (Figure 3a and Figure S3). We have previously observed variations of the two exchange interactions in Cr-chains;¹⁶ here the variation seems to be dependent on the tetravalent metal present and the bridging atoms at the terminal Cr^{III} . For the two Ti^{IV} rings the two exchange interactions are very similar. For the two Th^{IV} rings, the internal Cr...Cr exchange (J_2) is larger than the terminal exchange.

The temperature dependence of χ_M for **6** is markedly different to that observed for **3-5** as might be expected as both U^{V} and U^{IV} are paramagnetic (Figure 4). Quantifying the contribution of these ions is very difficult due to very large spin-orbit coupling for actinides.¹⁷⁻¹⁹ It is possible to fit the magnetic data measured on **6** assuming a spin-only approximation and four different J-couplings accounting for the different metal pairs present in the ring (Cr...Cr, Cr...U and U...U) giving $J_{\text{Cr-Cr}} = -5.2$ cm^{-1} , $J_{\text{1Cr-U}} = -4.0$ cm^{-1} , $J_{\text{2Cr-U}} = +4.0$ cm^{-1} and $J_{\text{U-U}} = +0.8$ cm^{-1} . (Figure S5). The "spin-only" approximation associated with most 3d transition metals cannot be widely used and can act only as an estimation of the lower limit of exchange coupling between such ions. Whether the derived parameters have any physical meaning is doubtful.

Magnetization (M) as a function of field (H) was measured for **2**, **4**, **5** and **6** at 2.0 and 4.0 K (Figure 3b, 4b and Figure S4).

Figure 4. (a) Susceptibility vs. Temperature ($\chi_M T$ vs. T , black circles and χ_M vs. T , blue circles) and (b) Magnetization plots for **6**. For the MVH, lines are guides to the eye.

For **2**, the magnetization saturates in accordance with a $S = 3/2$ ground state at low temperature. For **4** and **5**, the slow-increase in isothermal magnetization confirms the intramolecular antiferromagnetic coupling and $S = 0$ ground state. The magnetization of **6** increases faster at low field than **4** and **5**. This suggests **6** has a paramagnetic ground state.

EPR Spectroscopy

Variable temperature EPR spectra of compounds **2-5** were measured at Q-band (ca. 34 GHz). All compounds give rich and temperature-dependent EPR spectra below 20 K. EPR simulations were performed with Easyspin²⁰ using a strong exchange limit approximation where the EPR transitions occur within the thermally populated S levels of the metal chain at a given temperature.²¹ Simulation of these individual states separately using axial (D) and rhombic (E) zero field splitting parameters followed by addition give a good agreement with the observed spectra (Figure 6 and 7). The spectrum of **2** (Figure 6a) has the same profile as $\{\text{Cr}_7\text{Cd}\}$ ²² and $\{\text{Cr}_7\text{Zn}\}$ ²³ rings, with over 90% of the rings in the ground state $S = 3/2$ at 5 K and the

Figure 7. Experimental Q-band (ca. 34 GHz) EPR spectra and simulations (see main text and SI) for (a) **2** at 34.0720 GHz and (b) **3** at 33.9705 GHz for powdered samples suspended in eicosane at 5 K. Simulation parameters (with $g = 1.98$ and Gaussian linewidth): for **2**, $D_{S=3/2} = -0.419$ cm^{-1} , $E_{S=3/2} = 0.0489$ cm^{-1} ($E/D = 0.12$), $D_{S=5/2} = 0.066$ cm^{-1} , $E_{S=5/2} = 0.0034$ cm^{-1} ($E/D = 0.05$) and 15mT linewidth; for **3**, $D_{S=1} = -0.95$ cm^{-1} , $E_{S=1} = 0.171$ cm^{-1} ($E/D = 0.18$, 60mT linewidth), $D_{S=2} = 0.130$ cm^{-1} , $E_{S=2} = 0.013$ cm^{-1} , $B_4^0 = 4 \times 10^{-4}$ cm^{-1} ($E/D = 0.10$, 20mT linewidth).

Figure 7. Experimental Q-band (ca. 34 GHz) EPR spectra and simulations (see main text) for (a) **4** at 34.1771 GHz and (b) **5** at 34.1434 GHz for powdered samples suspended in eicosane at 5 K. Simulation parameters (with $g = 1.98$ and Gaussian linewidth): for **4**, $D_{S=1} = -0.81 \text{ cm}^{-1}$, $E_{S=1} = 0.186 \text{ cm}^{-1}$ ($E/D = 0.23$, 60 mT linewidth), $D_{S=2} = 0.129 \text{ cm}^{-1}$, $E_{S=2} = 0.012 \text{ cm}^{-1}$, $B_4^0 = 4 \times 10^{-4} \text{ cm}^{-1}$ ($E/D = 0.09$, 20 mT linewidth); for **5**, $g = 1.98$, $D_{S=1} = -1.675 \text{ cm}^{-1}$, $E_{S=1} = 0.553 \text{ cm}^{-1}$ ($E/D = 0.33$), $D_{S=2} = 0.134 \text{ cm}^{-1}$, $E_{S=2} = 0.0131 \text{ cm}^{-1}$, $B_4^0 = 2.7 \times 10^{-4} \text{ cm}^{-1}$ ($E/D = 0.10$, 5% D -strain) with a 60 mT and 15 mT linewidth respectively.

remaining features attributed to the first two excited states ($S = 1/2$ and $5/2$), thus it was simulated with similar parameters (Figure S7a).

Compounds **3**, **4** and **5** (Figure 6 and 7) have $S = 0$ ground states, and give similar EPR spectra. For all three compounds the majority of the observed resonances can be assigned to $S = 1$ and $S = 2$ excited states. The intensity of the low field peak is increased with lowering the temperature and this is assigned as the $\Delta m_s = \pm 2$ transition of a spin triplet state. The majority of the remaining features can be attributed to the $S = 2$, the simulation of which required the addition of an axial fourth-order term B_4^0 for all compounds.

Some features around 1230 mT in the spectra of **3** and **5** are not accounted for in the simulation and can be attributed to either the $S = 3$ next excited state or, in the case of **3**, to the presence of other linkage isomers that would generate a single Cr^{III} or Cr_5 chains. The former explanation seems more likely given their magnetic behaviour and the temperature dependence of their EPR spectra (Figure S6). The spectrum of compound **6** has a very broad feature at $g_{\text{eff}} = 1.98$ and some

very weak features appearing at higher temperatures (Figure S6d). Thus it is not possible to assign any spin states in the spectrum.

Conclusions

The chemistry of $\{\text{Cr}_6\}$ horseshoe chains as ligands has been extended to actinides and Ti^{IV} . The reactions of the $\{\text{Cr}_6\}$ chains **1** and precursors of actinides and group IV metals led to a series of rings $\{\text{Cr}_7\text{Ti}\}$, **2**, $\{\text{Cr}_6\text{Ti}_2\}$, **3**, $\{\text{Cr}_6\text{Th}\}$, **4**, $\{\text{Cr}_6\text{Th}_2\}$, **5** and $\{\text{Cr}_6\text{U}_2\}$, **6**. Complex **4** is a rare example of a heptametallic ring and is similar to $\{\text{Cr}_6\text{Ce}\}$. **5** and **6** are eight membered rings similar to $\{\text{Cr}_6\text{Y}_2\}$. The $\{\text{Cr}_6\}$ chains maintain their structures in these complexes and bind the tetravalent metals with same mode. This indicates that $\{\text{Cr}_6\}$ chains can act as polydentate fluoride ligands for actinides and Ti^{IV} to construct antiferromagnetic coupled heterometallic rings.

Their static magnetic properties were measured and fitted by isotropic exchange Hamiltonian. In accordance with **1**, the magnetic exchanges between Cr^{III} are antiferromagnetic, while the exchange interactions can be modified by the tetravalent metals. For complex **6**, ferromagnetic exchanges $J_{\text{Cr-U}}$ and $J_{\text{U-U}}$ are obtained. EPR spectra of compounds **2-5** were measured at Q-band and were simulated. The spectrum of **2** has the same profile as $\{\text{Cr}_7\text{Cd}\}$ and $\{\text{Cr}_7\text{Zn}\}$ rings with a ground state $S = 3/2$. **3**, **4** and **5** give similar EPR spectra with $S = 0$ ground states.

Conflicts of interest

In accordance with our policy on [Conflicts of interest](#) please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

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Notes and references

‡ CCDC 1569554, 1569555, 1569557, 1813191 and 1813192 contain the supplementary crystallographic data for compounds **1-6**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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