NEW HOMOMETALLIC OCTANUCLEAR CHROMIUM(III) RINGS

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Abstract. Four new {Cr$_8$} rings have been synthesized and characterized; they are all based on the classic $[CrF(O_2C^tBu)_2]_8$ ring **1**. Three routes have been studied. The first is direct synthesis, by reacting hydrated chromium(III) fluorides with the acid; this has been used to produce $[CrF(O_2CEt)_2]_8$ **3**. The second route uses **3** as a precursor and substitute with an incoming carboxylate. This has been used to make $[CrF(O_2CCCl_3)_2]_8$ **4** and $[CrF(O_2CC_6F_5)_2]_8$ **5**. The third route uses *N*-ethyl-*D*-glucamine (H$_5$Etglu) as a template and produces chiral rings $[Cr_8F_4(Etglu)(O_2C^tBu)_{15}]$ **6**. The single crystal X-ray structures of these new compounds are reported.

Introduction

Studies of cyclic anti-ferromagnetically coupled metallic complexes start with two complexes. One is the decanuclear iron(III) complex, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ **2** first reported by the Lippard group, and later studied in collaboration with Gatteschi, D. *et al.* [1]. The second is the octanuclear chromium(III) complex $[CrF(O_2C^tBu)_2]_8$ **1**, reported by Gerbeleu, N.V. *et al.* [2]. While much initial attention was paid to **2** there has been little work derived from this initial work. Benelli, C. *et al.* reported [3] another derivative $[Fe(OMe)_2(O_2CCH_3)]_{10}$ and McInnes, E.J.L. *et al.* reported the chromium(III) versions, made by solvothermal synthesis [4]. Later the McInnes group reported the vanadium(III) rings [5]. By contrast, the {Cr$_8$} ring **1** has generated a very large body of work. It has been studied by crystallography as a host for organic molecules [6], and more recently as a host for small molecules such as CO$_2$ [7], halogens [8] or SO$_2$ [9]. The magnetic properties of **1** have been studied by torque magnetometry [10], heat capacity [11] and by inelastic neutron scattering [12,13]. This includes a single crystal study that allowed the magnetic dynamics to be understood directly [14]. Based on this structure a very large family of heterometallic rings has been synthesized [15,16] and studied for their unusual quantum behavior [17], and as possibly as qubits for quantum information processing [18]. This work has been reviewed several times [19-22]. Relevant to this paper, the knowledge learnt from the heterometallic rings allowed the first homometallic nine-metal ring to be made: $[CrF(O_2C^tBu)_2]_9$ [23]. This last compound is unusual as it is a very rare new derivative based on the $[CrF(O_2CR)_2]_n$ archetype. Here we report our initial studies making new versions of **1**.

The first octanuclear {Cr$_8$} ring $[Cr_8F_8(O_2C^tBu)_{16}]$ **1** was synthesised by one of us during his PhD studies under supervision of Prof. Gerbeleu, Nicolae V., Timco, Grigore was his 13th PhD student in the early eighties of the last century.

The project selected by Prof. Gerbeleu, N.V. for his 13th PhD student was synthesis and investigation of new 3*d*- metal carboxylates, with an ambitious aim of making of new type of metal carboxylates complexes. This was achieved with synthesis of {Fe$_6$} and {Cr$_{12}$} oxo- and hydroxo- bridged carboxylate complexes starting from simple M$_3$O carboxylates (M= Fe, Cr). We were intrigued if this could be extended to fluoride bridged metal carboxylates. The first targets were planned to be a fluoro-centred {Cr$_3$} triangle or a triangle with terminal coordinated fluorides. Timco, Grigore decided to use hydrated chromium(III) fluoride, pivalic acid and dimethylformamide (DMF) as a solvent and found that chromium(III) fluoride dissolved only in a mixture of pivalic acid and DMF; some of the expected products were probably formed but they were not characterised at the time because they were eclipsed by **1**, which was an unexpected new compound, first identified as a high molecular mass compound and a very stable under e-impact mass spectrometry

by Indrichan, K.M., then by structural characterisation by Batsanov, A.S. (the names are cited as in the patent [24] and in the first paper [2]). Serendipity had played its role and it was for Timco, Grigore and his colleagues to understand and explore this reaction, which was continued in the group of Prof. Richard, E.P. Winpenny.

Prof. Gerbeleu, N.V. and Prof. Winpenny, R.E.P. had a scientific collaboration involving two INTAS projects and several individual visits between the laboratories. In 2006 Prof. Gerbeleu, N.V., Dr. Timco, G. and Prof. Winpenny, R.E.P. met in Chisinau. Unfortunately, that was the last meeting of the three of them.

This paper is devoted to the memory of professor, academician of the Academy of Sciences of Moldova Nicolae Gerbeleu.

Background

The synthesis of **1** proceeds in 30% yield from reaction of hydrated chromium fluoride with pivalic acid, in DMF in molar ratio 1:4:4 at 135–140ºC. It is important to stress here that hydrated chromium fluoride does not dissolve alone in pivalic acid or in DMF, this suggested that an amine was involved in this reaction. Strong acids and bases, especially at elevated temperatures, hydrolyze DMF, and DMF undergoes decarbonylation at high temperatures to give dimethylamine (Me$_2$NH). Compound **1** was patented as a new type of chromium coordination compound with potential application as a catalyst [24]. Although this procedure was reproducible for pivalate, it was not extended to make equivalent [CrF(O$_2$CR)$_2$]$_8$ rings with other carboxylates because it was difficult to control the quantity of amine formed from DMF.

The formation of Me$_2$NH from DMF in acidic condition leads to formation of [Me$_2$NH$_2$]$^+$ ion later found in heterometallic rings [Me$_2$NH$_2$][Cr$_7$MF$_8$(O$_2$C^{t}Bu)$_{16}$] [15]. Further evidence that formation of [CrF(O$_2$C^{t}Bu)$_2$]$_8$ is facilitated by an alkyl ammonium cation is the synthesis of {Cr$_6$} horseshoes [(R$_2$NH$_2$)$_3${Cr$_6$F$_{11}$(O$_2$C^{t}Bu)$_{10}$}]$_2$, first reported for R= ^{n}Pr, by reacting hydrated chromium fluoride, *n*-dipropylamine (^{n}Pr$_2$NH) and pivalic acid, in molar ratio 1.06:1:5.5 at 115ºC, where the [^{n}Pr$_2$NH$_2$]$^+$ stabilized formation of the {Cr$_6$} horseshoe [25].

Here it was explore the formation of [CrF(O$_2$CEt)$_2$]$_8$ ring from reaction of hydrated chromium fluoride, with a small amount of ^{n}Pr$_2$NH and propionic acid acting as the solvent in molar ratio 17.5:1:68.4 at 140ºC which gives [CrF(O$_2$CEt)$_2$]$_8$ **3**. It was found that adding a small

amount of ammonium trifluoromethanesulfonate increases the yield of **3**, although the procedure works without trifluoromethanesulfonate anion. Previously the trifluoromethanesulfonate additive was used in the synthesis of [CrF(O$_2$C^{t}Bu)$_2$]$_9$ [23].

Synthesis of [CrF(O$_2$CEt)$_2$]$_8$·(Et$_2$O) 3

Propionic acid (40 mL, 540 mmol), ^{n}Pr$_2$NH (0.8 g, 7.9 mmol), chromium(III) fluoride tetrahydrate (10.0 g, 138.08 mmol) and ammonium trifluoromethanesulfonate (0.8 g, 4.88 mmol) were combined in a Teflon flask and stirred for 52 hours at 140ºC. During this time, chromium fluoride dissolved and a green crystalline product formed. The flask was then allowed to cool to room temperature, after which hexane (50 mL) was added to complete precipitation and stirred for 1 hour. The solid was filtered, washed with hexane (100 mL), then dissolved in diethyl ether (100 mL) and the solution filtered. A chromatographic separation was then performed on silica with diethyl ether as eluant; **3** elutes as the first green band. To the eluted solution was added hexane (50 mL) and the solvents removed under vacuum, leaving a green residue, which was washed with hexane (100 mL) and dried in air. Yield: 10.4 g (73% based on Cr). Elemental analysis (%) calc. for Cr$_8$F$_8$(O$_2$CC$_2$H$_5$)$_{16}$·Et$_2$O: C$_{52}$H$_{90}$Cr$_8$F$_8$O$_{33}$: C 34.48, H 5.01, Cr 22.97; found: C 34.57, H .93, Cr 22.02. ES-MS (sample dissolved in THF, run in MeOH): 1759 [M+Na]$^+$, 1777 [M+Na+H$_2$O]$^+$ (100%). X-Ray quality crystals were formed from crystallization of **3** from a saturated solution in 2-propanol. The structural study shows the formation of an octagon of chromium sites, with each internal edge of the ring bridged by a fluoride and each external edge bridged by propionate (Figure 1).

The propionate was selected from other carboxylate ligands because it was expected that the **3** will be soluble in polar solvents, and therefore it would be possible for the propionate ligands to be exchanged with further carboxylates in substitution reactions. This was explored in second route for making [CrF(O$_2$CR)$_2$]$_8$ rings; **1** has very low solubility in polar solvents and therefore substitution reactions do not lead to full replacement of pivalate ligands. This second route allows access to new {Cr$_8$} rings that cannot be made by direct synthesis. This was previously demonstrated by synthesis of heterometallic {Cr$_7$Ni} rings with carboxylates containing halogens [26].

To use **3** as a starting material typically involves heating **3** with an excess of the incoming

acid in a high boiling polar solvent such as 1,2-dichlorobenzene. Here we report two such reactions: with trichloroacetic acid, which produces [CrF(O$_2$CCCl$_3$)$_2$]$_8$ **4** in 23% yield, and with 2,3,4,5,6-pentafluorobenzoic acid, which gives [CrF(O$_2$CC$_6$F$_5$)$_2$]$_8$ **5** in 31% yield.

Synthesis of [Cr$_8$F$_8$(O$_2$CCCl$_3$)$_{16}$] 4

Compound **3** (2.15 g, 1.18 mmol), trichloroacetic acid (5.0 g, 30.60 mmol), 1,2-dichlorobenzene (10 mL) were stirred for 17 hours at 160ºC. The flask was then allowed to cool to room temperature and nitromethane (25 mL) was added while stirring for 1 hour during which a solid precipitated. The solid was collected by filtration, washed with nitromethane (30 mL) and dried *in vacuo*. Then the solid was extracted while stirring with hexane (300 mL) under reflux. The solution obtained was filtered and concentrated by distillation to *ca*.50 mL, and was kept at room temperature for 2 days. During this time a microcrystalline green product precipitated, which included X-ray quality crystals. Product was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.87 g (23%). Elemental analysis calculated (%) for C$_{32}$Cl$_{48}$Cr$_8$F$_8$O$_{32}$: C 12.14, Cr 13.14; found: C 12.57, Cr 13.51. The structure of **4** is shown in Figure 2.
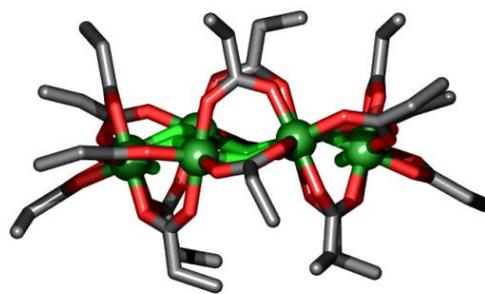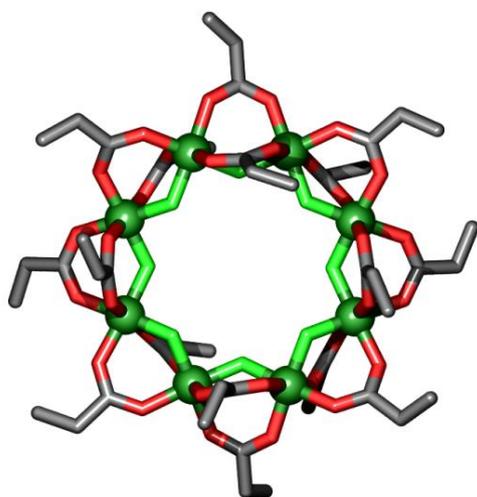

Figure 1. Structure of 3 in the crystal. (Green = chromium, light green = fluorine, red = oxygen, grey = carbon. Hydrogens omitted for clarity).
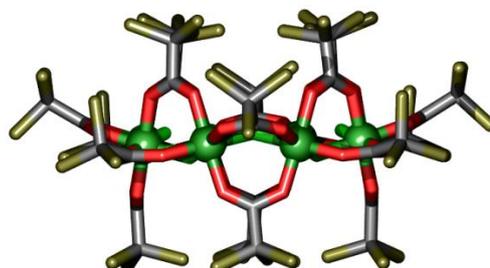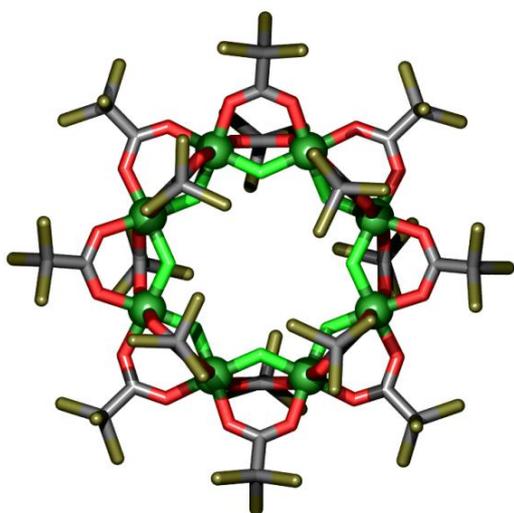

Figure 2. Structure of 4 in the crystal. (Green = chromium, light green = fluorine, mustard yellow = chlorine, red = oxygen, grey = carbon).

Synthesis of [Cr₈F₈(O₂CCC₆F₅)₁₆]·2C₆H₅CH₃ 5

Compound **3** (2.15 g, 1.24 mmol), 2,3,4,5,6-pentafluorobenzoic acid (10.0 g, 47.15 mmol), 1,2-dichlorobenzene (10 mL) were stirred for 24 hours at 160°C. Then the flask was cooled to room temperature and acetonitrile (30 mL) was added while stirring for 24 hours. The solid was filtered, washed with acetonitrile (45 mL). After this the solid was stirred diethyl ether (100 mL) and the solution obtained was filtered and to filtrate toluene (50 mL) added. Then the solvents removed under reduced pressure leaving a green residue, which was washed with toluene, then pentane and dried at 55°C for 2 hours. Yield: 1.5 g (31%). Elemental analysis calculated (%) for $C_{126}H_{16}Cr_8F_{88}O_{32}$: C 36.65, H 0.39, Cr 10.07; found: C 36.03, H 0.1, Cr 10.60.
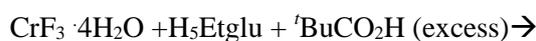
X-Ray quality crystals were obtained from the recrystallization of **5** from a mixture of ethyl acetate/toluene. ES-MS (sample dissolved in THF, run in MeOH): +3967 [M+Na]+ (100%).

The yields of **4** and **5** have not been optimized, as we were looking first at feasibility of full substitution of sixteen propionate ligands from **3** while keeping the {Cr₈} ring intact.

The bond lengths in **3–5** are unremarkable; bond length ranges and averages are given in Table 1, and all are very similar to the bond lengths found in **1**. The Cr-F bonds in **5** appear to be very slightly shorter than in **3** and **4**; this could be explained as due to the electron withdrawing C₆F₅ groups attached to the carboxylates, making the O-donors less strong leading to stronger Cr-F interactions. However, there is no noticeable increase in the Cr-O bond lengths.

We were interested in whether a further {Cr₈} ring could be made, based on chiral {Cr₇Ni} rings we have previously reported [27,28]. This involves adding the penta-alcohol pro-ligand *N*-ethyl-*D*-glucamine (H₅Etglu) to the reaction; during reaction this is deprotonated five times to give a penta-anionic ligand. The reaction is according to Eq.(1).

$$CrF_3 \cdot 4H_2O + H_5Etglu + {}^tBuCO_2H \text{ (excess)} \rightarrow$$

$$[Cr_8F_4(Etglu)(O_2C^tBu)_{15}] \textbf{ 6} \quad (1)$$

In the presence of a divalent metal such as nickel(II), this is incorporated into the reaction and the site of the divalent metal is found with a neutral ligand such as water attached [27]. Here we have no source of a divalent metal and as a result this site is occupied by chromium(III) giving: $[Cr_8F_4(Etglu)(O_2C^tBu)_{15}]$ **6**.

Table 1

Bond length averages and ranges Å for compounds 3, 4 and 5 (standard uncertainties in brackets).

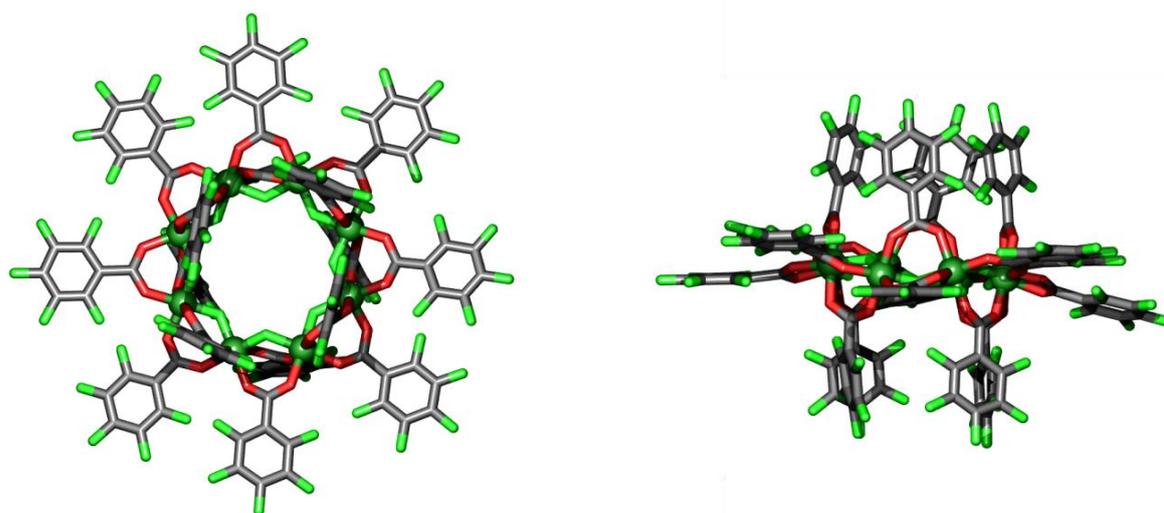|	*3*	*4*	*5*
Range Cr-F	1.908(2)-1.928(2)	1.904(5)-1.924(6)	1.892(5)-1.919(5)
Average Cr-F	1.918(2)	1.919(6)	1.908(5)
Range Cr-O	1.942(2)-1.967(2)	1.937(7)-1.974(8)	1.940(6)-1.986(6)
Average Cr-O	1.956(2)	1.949(8)	1.953(6)

Figure 3. Structure of 5 in the crystal. (Green = chromium, light green = fluorine, red = oxygen, grey = carbon).

Synthesis of [Cr₈F₄(Etglu)(O₂CᵗBu)₁₆] 6

Chromium(III) fluoride tetrahydrate (6.0 g, 33 mmol), H₅Etglu (3.6 g, 17 mmol), pivalic acid (30.0 g, 294 mmol) were heated together with constant moderate stirring in a Teflon flask at 160°C for 24 hours. The reaction is cooled to room temperature and diethyl ether (100 mL) was added with stirring and the resulting solution was filtered. The filtrate was diluted slowly with stirring with acetonitrile (~250 mL) and a purple product started to precipitate during this time. The product was collected next day, washed with a mixture of acetone (25 mL) and acetonitrile (50 mL) and then recrystallized from acetone. The crystals (including X-ray quality) were collected by filtration next day, washed with a mixture of acetone acetonitrile (1:2) and dried in air. Yield 4.1 g (31%, based on Cr). Elemental analysis calcd (45%) for $C_{83}H_{149}Cr_8F_4N_1O_{35}$: C 45.05, H 6.79, N 0.63, Cr 18.80; found: C 44.92, H 6.90, N 0.66, Cr 17.96. ES-MS (sample dissolved in Et₂O, run in MeOH): +2234 [M+Na]⁺ (100%).

Charge neutrality is achieved by a having a terminal fluoride attached to this chromium site (Figure 4); in the heterometallic rings this is a neutral ligand.

The internal edges of the octagon in **6** are bridged by three fluorides and five alkoxides derived from Etglu⁵⁻. The eight Cr(III) sites have five distinct coordination environments. One site (Cr1) is bound to two bridging fluorides, three bridging pivalate ligands and a terminal fluoride. A second site (Cr8) adjacent to the first has an *N*-donor from Etglu⁵⁻ coordinated to it, one bridging fluoride, one bridging alkoxide and three bridging pivalates. The other site adjacent to the first site (Cr2) is bound to two μ-fluorides and

four oxygens from pivalates. The next site around the ring (Cr3) is also bound to two μ-fluorides and four oxygens from pivalates. The final coordination geometries are: a single site (Cr4) bound to a single μ-fluoride, a single μ-alkoxide and four pivalates, and three further Cr(III) sites (Cr5, Cr6 and Cr7) bound to two μ-alkoxides and four pivalates. The bond lengths at these metal sites is given in Table 2. They are in general very similar to equivalent bond lengths in chiral {Cr₇M} rings (M= Ni(II), Mn(II), Zn(II)) [28].

Table 2

Bond lengths (Å) for metal sites in compound 6.

| Bond	d, (Å)	Bond	d, (Å)
Cr1-F1	1.853(9)	Cr5-O31	1.972(9)
Cr1-F2	1.914(8)	Cr5-O32	1.935(10)
Cr1-O35	2.016(11)	Cr5-O13	1.960(10)
Cr1-O1	1.989(11)	Cr5-O15	1.960(9)
Cr1-O4	1.967(10)	Cr5-O18	1.976(10)
Cr1-O29	1.956(10)	Cr5-O20	1.952(10)
Cr2-F2	1.918(8)	Cr6-O32	1.952(9)
Cr2-F3	1.904(7)	Cr6-O33	1.953(11)
Cr2-O2	1.948(10)	Cr6-O17	1.971(11)
Cr2-O3	1.949(9)	Cr6-O19	1.988(10)
Cr2-O6	1.952(10)	Cr6-O22	1.960(10)
Cr2-O8	1.957(10)	Cr6-O24	1.973(10)
Cr3-F3	1.883(8)	Cr7-O33	1.931(10)
Cr3-F4	1.895(8)	Cr7-O34	1.949(11)
Cr3-O5	1.945(13)	Cr7-O21	1.975(11)
Cr3-O7	1.942(13)	Cr7-O23	1.965(11)
Cr3-O10	1.889(13)	Cr7-O26	2.006(11)
Cr3-O12	1.944(15)	Cr7-O28	1.972(11)
Cr4-F4	1.913(8)	Cr8-O34	1.941(11)
Cr4-O31	1.963(9)	Cr8-O35	1.966(10)
Cr4-O9	1.957(9)	Cr8-N1	2.072(13)
Cr4-O11	1.935(10)	Cr8-O25	1.987(10)
Cr4-O14	1.945(10)	Cr8-O27	1.967(10)
Cr4-O16	1.964(9)	Cr8-O30	1.984(11)
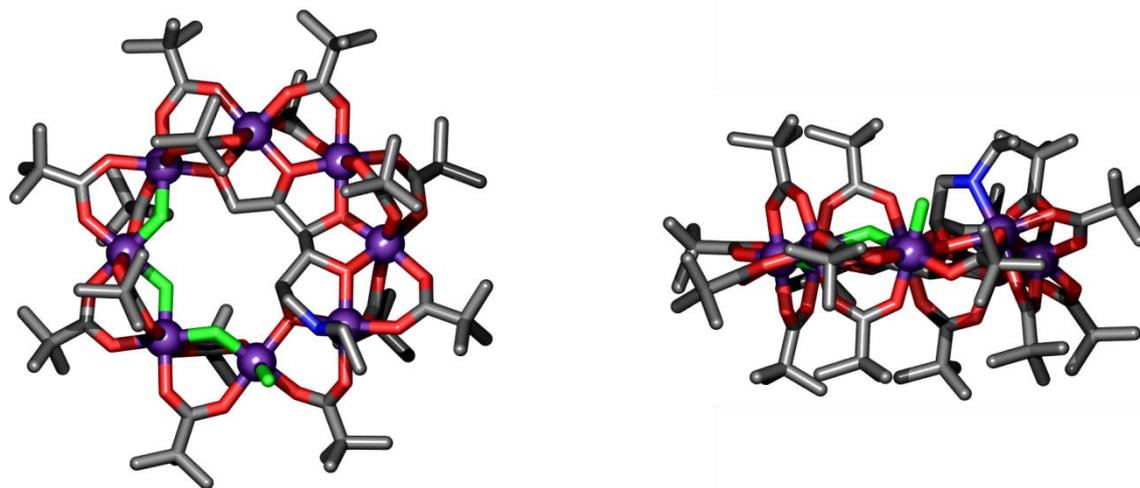
Figure 4. Structure of 6 in the crystal. (Purple = chromium, light green = fluorine, red = oxygen, grey = carbon, blue = nitrogen. Hydrogens omitted for clarity).

Crystallographic information for compounds 3, 4, 5 and 6.

Identification code	3	4	5	6
Empirical formula	$C_{52.5}Cr_8F_8H_{92}O_{33.5}$	$C_{32}Cl_{48}Cr_8F_8O_{32}$	$C_{191}H_{93}Cr_8F_{88}O_{32.5}$	$C_{83}H_{149}Cr_8F_4NO_{35}$
Formula weight	1827.26	3165.92	4995.65	2213.02
Temperature/K	150.00(10)	150.00(10)	150.00(10)	100.02(10)
Crystal system	monoclinic	tetragonal	triclinic	monoclinic
Space group	$P2_1/c$	$P42_12$	$P\text{-}1$	$P2_1$
a (Å)	20.6280(11)	19.1913(6)	18.4248(9)	16.7090(3)
b (Å)	15.4513(8)	19.1913(6)	19.0875(11)	60.2871(9)
c (Å)	26.5459(12)	15.9077(11)	29.3393(14)	24.0252(4)
α (°)	90	90	98.712(5)	90
β (°)	111.512(6)	90	108.098(4)	90.0972(13)
γ (°)	90	90	100.031(4)	90
Volume, (Å^3)	7871.6(7)	5858.9(5)	9421.9(9)	24201.5(6)
Z	4	2	2	8
ρ_{calc} (g/cm^3)	1.542	1.795	1.761	1.215
μ (mm^{-1})	1.159	1.878	0.605	6.306
$F(000)$	3756	3056	4966	9296
Crystal size (mm^3)	0.458×0.325×0.253	0.598×0.417×0.333	0.484×0.396×0.211	0.249×0.111×0.058
Radiation	MoKα (λ= 0.71073)	MoKα (λ= 0.71073)	MoKα (λ= 0.71073)	CuKα (λ= 1.54184)
2Θ range for data collection/°	6.522 to 59.272	4.746 to 57.064	4.492 to 57.178	3.678 to 136.498
Reflections collected	47794	14105	45107	272089
Independent reflections	18472 [R_{int}= 0.0483, R_{sigma}= 0.0755]	6613 [R_{int}= 0.0435, R_{sigma}= 0.0733]	45107 [R_{int}= 0.0676, R_{sigma}= 0.1739]	86747 [R_{int}= 0.1010, R_{sigma}= 0.0878]
Data/restraints/ parameters	18472/0/911	6613/1119/418	45107/6494/3033	86747/35419/4718
Goodness-of-fit on F^2	1.017	1.016	0.994	1.034
Final R indexes [$I>=2\sigma\,(I)$]	R_1= 0.0503, wR_2= 0.0979	R_1= 0.0734, wR_2= 0.1718	R_1= 0.0868, wR_2= 0.1938	R_1= 0.0889, wR_2= 0.2341
Final R indexes [all data]	R_1= 0.0849, wR_2= 0.1117	R_1= 0.1406, wR_2= 0.2091	R_1= 0.1882, wR_2= 0.2215	R_1= 0.1066, wR_2= 0.2539
Largest diff. peak/hole / e Å^{-3}	0.61/-0.43	0.53/-0.46	1.00/-0.56	0.72/-1.08
Flack parameter		-0.050(17)		0.0545(18)

*Note: X-ray crystallography data for **3**, **4** and **5** were collected on an Oxford X'Calibur2 4-circle diffractometer with a fine focus MoKα source and a Sapphire CCD detector at a temperature of 150 K. Data for **6** were collected using a dual source Rigaku FR-X rotating anode diffractometer using CuK$_\alpha$, at a temperature of 100 K. All data were and reduced using CrysAlisPro v41 [29]. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles [29]. The structures were solved using ShelXT and refined against all F^2 values using ShelXL implemented through Olex2 v1.5 [30,31].*

The crystallographic data and experimental details of the structural refinement for the X-ray crystal structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2122949-2122952. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/data_request/cif).

Concluding remarks

{Cr$_8$} rings are more difficult to make than the heterometallic octanuclear rings. In the {Cr$_7$M} series the presence of a templating cation, typically a secondary ammonium, drives formation of the cyclic structure. For {Cr$_8$} rings there is no template and therefore cyclisation is less preferred.

Here we solve this problem by having either a small amount of a secondary ammonium present, as in the direct synthesis of **3**, or we pre-form the ring and then replace the carboxylates, as in the synthesis of **4** and **5**. Finally, we show that the chiral template *N*-ethyl-*D*-glucamine can be used to form a homometallic chiral {Cr$_8$} ring **6**.

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Richard E. P. Winpenny obtained both his degrees from Imperial College, London; his Ph.D. studies with Prof. David Goodgame involved synthesis of coordination polymers. After a period at Texas A&M University, working as a postdoctoral fellow with Prof. John Fackler, Jr., he moved to a lectureship at the University of Edinburgh. In 2000, after ten years in the frozen wastes of Northern Britain, he was appointed to the Chair of Inorganic Chemistry at the University of Manchester. Since 2018 he has held an EPSRC Established Career Fellowship and an ERC Advanced Grant. He won the Royal Society of Chemistry Tilden Prize in 2011 and Ludwig-Mond Prize in 2016, and led the team that won the RSC 2021 Dalton Division Horizon Prize. He is a Fellow of the Learned Society of Wales and a Member of the Academia Europaea. He has published over 400 research papers.

George Whitehead obtained his Ph.D. at the University of Manchester in 2013 under the supervision of Prof. Richard Winpenny as part of the North West Nanoscience doctoral training centre focusing on the synthesis, functionalization, and structural characterization of large $\{Cr_7Ni\}$ heterometallic pseudo-rotaxane assemblies. He was awarded an EPSRC Doctoral Prize and remained at the University of Manchester for a further 10 months before joining the group of Prof. Matt Rosseinsky as a Research Associate at the University of Liverpool in 2014. After 2 ½ years he returned to the University of Manchester in 2017 as an Experimental Officer in the X-ray Crystallography Facility

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