

Octa-, Deca-, Trideca-, and Tetradecanuclear Heterometallic Cyclic Chromium–Copper Cages**

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We have made a series of compounds featuring a divalent metal ions (Ni^{II} , Co^{II} , Zn^{II} , Mn^{II} , Fe^{II}) doped into an octanuclear ring of trivalent ions (Cr^{III} , Fe^{III} , V^{III} , Ga^{III} , Al^{III} , In^{III}), with the $\text{M}\cdots\text{M}$ vectors bridged by a fluoride and two carboxylate ligands.^[1] The work builds on and extends ideas from the groups of Saalfrank^[2] and Pecoraro.^[3] The control we have achieved has allowed us to begin detailed studies of the physics of these rings^[1,4] and to make the proposal that they could be used as quantum bits (or “qubits”).^[5,6] This chemistry relies on the divalent metal ion adopting an octahedral coordination geometry; when Cu^{II} was used, a different structure resulted—a $\{\text{Cr}_{10}\text{Cu}_2\}$ “hourglass”.^[7] We also found that in the $\text{Cr}_{10}\text{Cu}_2$ system the size of the templating amine did not have the same controlling influence we had found with Cr-Ni rings. These observations suggested a different family of structures might result from control of reaction conditions.

$[\text{R}_2\text{NH}_2]_2[\text{Cr}_{10}\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{22}]$ cages ($\text{R} = \text{Me}$ **1a**, *i*Pr **1b**) can be made by reaction of hydrated chromium trifluoride, basic copper carbonate, and the secondary amine in hot pivalic acid. Originally the reaction time was five hours. If the heating time is extended to longer than one day, the reaction produces a green precipitate and a filtrate that contains several different $\{\text{Cr}_x\text{Cu}_y\}$ rings. The precipitate contains $[\text{iPr}_2\text{NH}_2]_2[\text{Cr}_{12}\text{Cu}_2\text{F}_{16}(\text{O}_2\text{CCMe}_3)_{26}]$ (**2**), which we can isolate in pure form in 20% yield. The structure^[8] resembles an hourglass, with the five-coordinate Cu^{II} sites linked by $\{\text{Cr}_6\}$ chains (Figure 1); in **1** the sites were linked by $\{\text{Cr}_3\}$ chains. The copper(II) centers are five-coordinate, bridged to one Cr^{III} center through one fluoride and two pivalate ligands and to a second Cr^{III} center through only one fluoride and one

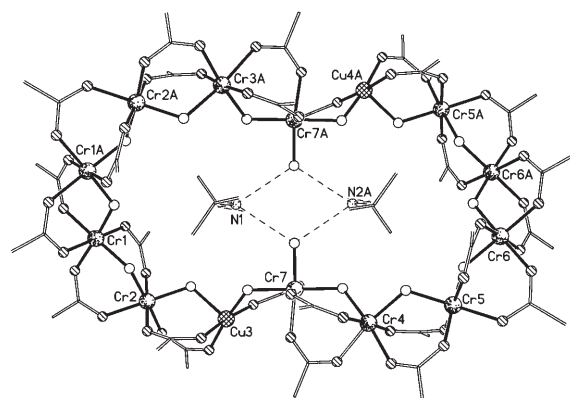


Figure 1. The crystal structure of **2**. Methyl groups of ligands excluded for clarity. Atom shading: F open circles, O diagonal lines, N regular dots, Cr heavy irregular shading, Cu crosshatched; C lines.

pivalate. This second Cr^{III} center is found at the waist of the hourglass with a terminal fluoride ligand attached. The $\text{Cr}\cdots\text{Cr}$ vectors are all bridged by one fluoride and two pivalate ligands. Two secondary ammonium cations are found at the center of the structure. They form H-bonds to the terminal fluorides ($\text{N}\cdots\text{F}$ 2.65 Å). The structure is disordered, and the two Cu^{II} ions are disordered over the four metal sites adjacent to the Cr centers at the waist of the hourglass. This disorder makes it possible, but less likely, that in some molecules the Cu centers are linked by $\{\text{Cr}_4\}$ and $\{\text{Cr}_8\}$ chains. Although dodeca-,^[12] hexadeca-,^[13] and octadecanuclear rings^[14] are known, this is, to our knowledge, the first tetradecanuclear ring to be isolated.

The filtrate from which **2** precipitated can be manipulated to produce green crystals of $[\text{iPr}_2\text{NH}_2]_2[\text{Cr}_{11}\text{Cu}_2\text{F}_{15}(\text{O}_2\text{CCMe}_3)_{24}]$ (**3**), formed in 5% yield. Structure determination^[8] shows the formation of a tridecanuclear ring, with the two Cu^{II} sites linked by $\{\text{Cr}_5\}$ and $\{\text{Cr}_6\}$ chains (Figure 2). The structure is disordered, with the two Cu^{II} ions disordered over the four sites which are adjacent to the waist of the distorted hourglass. As in **2**, this disorder makes it possible that the two copper sites are linked through $\{\text{Cr}_3\}$ and $\{\text{Cr}_8\}$ chains or through $\{\text{Cr}_4\}$ and $\{\text{Cr}_7\}$ chains. Given the structures of **1** and **2**, the model proposed herein looks the most plausible. This compound is a very rare example of a large polymetallic cycle with an odd number of metal centers^[15,16] and the first tridecanuclear ring. The two ammonium cations H-bond to fluorides in very different ways; N1A H-bonds in a similar manner to the templates in **2**, while N2A H-bonds to only one terminal and two bridging fluoride ions (Figure 2).

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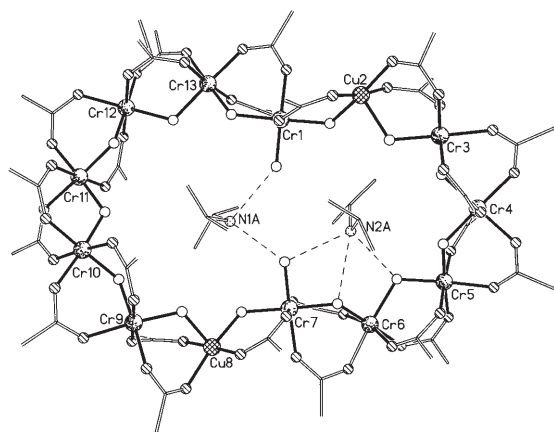


Figure 2. The crystal structure of **3**. Methyl groups of ligands excluded. Shading as Figure 1.

We were also able to crystallize **1b** from the pentane washings produced during the isolation of **2**. The formation of **1b**, **2**, and **3** from the same reaction, separable by fractional crystallization, suggests that the reaction contains a mixture of $\{\text{Cr}_x\}$ chains. The preference of Cu^{II} for non-octahedral coordination geometry leads to a series of structures of comparable stability; with an ion such as Ni^{II} , the overwhelming preference is for a $\{\text{Cr}_7\text{Ni}\}$ ring.

This reasoning suggested that a $\{\text{Cr}_7\text{Cu}\}$ ring could be made if the right conditions were employed. These conditions (see the Supporting Information) involve using diethylammonium as the templating cation and heating the reaction for 7 h before addition of copper; this protocol produces a mixture of $\{\text{Cr}_6\}$ and $\{\text{Cr}_7\}$ “horseshoes” in the solution. After addition of copper(II) carbonate, the reaction was heated for 10 h. Under these conditions, $[\text{NEt}_2\text{H}_2][\text{Cr}_7\text{CuF}_8(\text{O}_2\text{CtBu})_{16}]$ (**4**) could be made in 65 % yield (Figure 3). The structure is an octagon of metal sites, and the Cu^{II} ion is disordered over all eight sites. The identity of **4** is confirmed by elemental

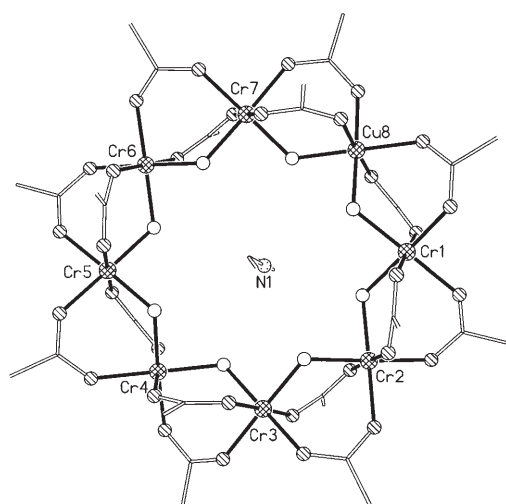


Figure 3. The crystal structure of **4**. The Cu site is disordered over all eight sites (see text). Methyl groups of ligands excluded. Shading as Figure 1, except all metal sites are cross-hatched.

analysis and ES-MS. $[\text{NEt}_2\text{H}_2][\text{Cr}_{10}\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{22}]$ (**1c**) is formed as a by-product in this reaction and can be made as the major product (55 %) if the copper salt is added at the beginning of the reaction and heating is restricted to 3 h.

If benzimidazole (Bz) is used as the templating amine, a further related cycle can be formed: $[\text{HBz}]_2[\text{Cr}_8\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{16}(\text{Bz})_2]$ (**5**).^[8] In this case, $\{\text{Cr}_4\}$ chains link the copper sites, which are found at the waist of the hourglass (Figure 4). Each $\text{Cu}\cdots\text{Cr}$ edge is bridged by a fluoride ion and

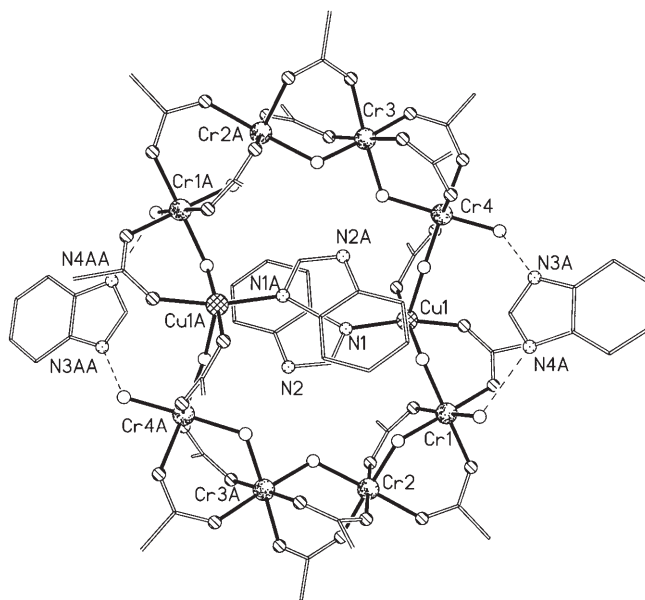


Figure 4. The crystal structure of **5**. Methyl groups of ligands excluded. Shading as Figure 1.

a pivalate ligand, with the coordination sphere of the copper center completed by an N donor from the benzimidazole. Each $\text{Cr}\cdots\text{Cr}$ edge is bridged by one fluoride and two carboxylate ligands; the result is that the Cr^{III} ions adjacent to the copper sites (Cr1 and Cr4 and symmetry equivalents) have terminal fluoride ions attached to them. Two protonated benzimidazolium cations are found H-bonded to these terminal fluoride ions. The structure of **5** is very different from other heterometallic rings found with imidazolium templates,^[17] in which no bonds are formed between the N atoms of the imidazole and the metal centers.

Magnetic studies of **2–5** show room-temperature values of $\chi_m T$ that are correct for the appropriate number of non-interacting chromium and copper centers (see Figure S1 in the Supporting Information); in all cases, $\chi_m T$ falls with decreasing temperature but does not reach zero. Studying the magnetization against field behavior (see Figure S2 in the Supporting Information) suggests a spin ground state of $S = 1$ for **2**, **4**, and **5**. For **1**, the ground state is $S = 0$.^[7] For **3**, the results are more complex, suggesting that the lowest energy levels are $S = 1/2$ and $S = 3/2$ and that these are very close in energy.^[18]

The largest of these rings are too big to use matrix-diagonalization techniques to fit the magnetic data; therefore we have used quantum Monte Carlo (QMC) methods using

$g_{\text{Cr}} = 1.98$ and $g_{\text{Cu}} = 2.10$ and a Hamiltonian of the form $\hat{H} = JS_a S_b$ (Figure 5). We have refitted the data for **1** for comparison. For **4**, we only require antiferromagnetic (AF)

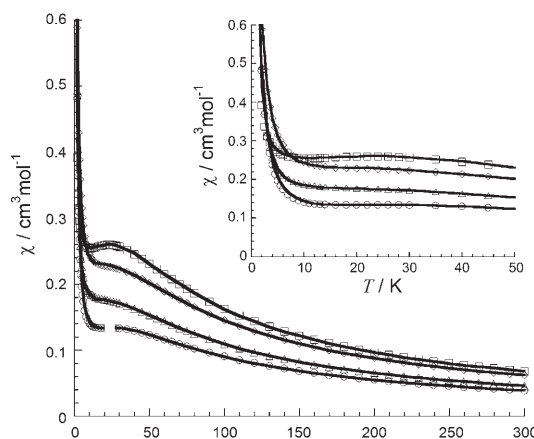


Figure 5. Variable-temperature behavior of χ_{m} for **2** ($\square$), **3** ($\diamond$), **4** ($\circ$), and **5** ($\triangle$). All compounds were measured in a 0.1-T field. Solid lines: fit of data using set A parameters from Table 1. The inset shows an expansion of the curves for the low-temperature region.

Cr–Cr (J_1) and Cr–Cu (J_2) exchange, while for **2**, **3**, and **5**, we require three exchange interactions: a Cr–Cr exchange, J_1 , which is AF; a Cr–Cu exchange, J_2 , which is AF; and a second Cr–Cu exchange, J_3 , which is ferromagnetic (F). For **2**, **3**, and **5**, two sets of parameters fit the data (Table 1), with set A

Table 1: Exchange parameters used to fit magnetic data for **1–5**.

Set	Compound	J_1 [K]	J_2 [K]	J_3 [K]	Diamagnetic correction [$\times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$]
	4	16.9 ± 1	18.0 ± 5	–	0.5 ± 0.1
A	1	14.8 ± 0.5	52.9 ± 6	-11.8 ± 2	2.2 ± 0.2
	2	15.0 ± 0.5	65.0 ± 8	-5.0 ± 5	2.4 ± 0.4
	3	14.5 ± 0.5	43.5 ± 10	-2.4 ± 2	3.5 ± 0.5
	5	15.1 ± 0.5	55.5 ± 10	-10.1 ± 5	2.4 ± 0.5
B	1	16.9 ± 1	27.2 ± 5	-13.1 ± 2	2.6 ± 0.5
	2	17.6 ± 1	22.0 ± 4	-4.4 ± 4	2.7 ± 0.5
	3	15.5 ± 0.5	24.2 ± 5	-1.9 ± 2	3.6 ± 0.5
	5	18.4 ± 1	24.5 ± 5	-18.4 ± 8	2.5 ± 0.5

yielding better results. Set A therefore represents the global minimum in each case. The sensitivity of the quality of fit varies between parameters; thus, the fit gets markedly worse if J_1 varies from a narrow range, while the fit is less sensitive to J_3 and almost insensitive to variation in J_2 . The diamagnetic correction, which includes any temperature-independent paramagnetism and any error in estimating the g values, was also allowed to vary. The quality of fit is not very sensitive to this parameter, except for set A for **1**, where a large value is required.

The results show that both F and AF Cr–Cu exchange is present in **2**, **3**, and **5**; the observed ground states could not be

achieved if this were not the case. Examining the structures, we can see two Cr–Cu exchange paths; in one, the bridging ligands are only attached at the basal sites of the Cu square pyramid (e.g. exchange between Cu3 and Cr7 in Figure 1), while the other exchange also involves the fluoride in the apical site of the Cu ion. One of these paths is the AF and the other F exchange. For **3**, the $S = 1/2$ and $S = 3/2$ states are very close in energy; on the basis of low-temperature data, we estimate that these levels are separated by around 0.7 cm^{-1} ; therefore, we are approaching the degeneracy predicted for odd-electron, odd-numbered rings.^[19]

The QMC method allows the low-temperature increase in χ to be modeled in all cases, without invoking the presence of a paramagnetic impurity. This result leads to the thought that the frequent use in the literature of paramagnetic impurities to explain low-temperature rises in χ may be incorrect—they may often be due to low-lying paramagnetic excited states. It is also likely that as structures get more complex, both the possibility of false minima in fitting data and of parameters being used which only weakly influence the quality of fit must increase.

Experimental Section

Detailed synthetic procedures are given in the Supporting Information. The synthesis of **2** is given as a representative example.

2: $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ (5.0 g, 27.6 mmol), diisopropylamine (1.26 g, 12.5 mmol), and pivalic acid (20.5 g, 201 mmol) were stirred together at 140°C for 4 h in a teflon flask. Basic copper carbonate (0.37 g, 1.7 mmol) was added and the temperature was increased to 160°C for 26 h. The flask was cooled to room temperature, and acetone (30 mL) was added with stirring. A green microcrystalline product formed. The product was filtered, washed with acetone, and dried in air (yield: 4.8 g). It was then washed with pentane ($3 \times 25 \text{ mL}$), removing a mixture of $[(i\text{C}_3\text{H}_7)_2\text{NH}_2][\text{Cr}_8\text{CuF}_9(\text{O}_2\text{CCMe}_3)_{18}]$ (identified by ES-MS: $m/z + 2572$, $[M]^+$, 100%), **1b** (identified by X-ray cell parameters^[7]), and some **3**. The remaining product (3.6 g) was extracted with boiling toluene (ca. 300 mL) and filtered, and the solution was cooled to room temperature. A crystalline product (including X-ray quality crystals) was collected after two weeks, washed with toluene, and dried in air. Yield 1.9 g (20%). Elemental analysis (%) calcd for $\text{C}_{156}\text{H}_{282}\text{Cr}_{12}\text{Cu}_2\text{F}_{16}\text{N}_2\text{O}_{52}$: Cr 15.32, Cu 3.12, C 46.00, H 6.98, N 0.69; found: Cr 14.94, Cu 3.18, C 45.71, H 7.07, N 0.66.

3: Yield 0.44 g (5%). Elemental analysis (%) calcd for $\text{C}_{130}\text{H}_{256}\text{Cr}_{11}\text{Cu}_2\text{F}_{15}\text{N}_2\text{O}_{48}$: Cr 15.43, Cu 3.43, C 45.03, H 6.96, N 0.76; found: Cr 15.11, Cu 3.35, C 45.67, H 6.96, N 0.71.

4: Yield 3.5 g (65%). Elemental analysis (%) calcd for $\text{C}_{84}\text{H}_{156}\text{Cr}_7\text{Cu}_8\text{F}_8\text{N}_2\text{O}_{32}$: Cr 16.02, Cu 2.80, C 44.41, H 6.92, N 0.62; found: Cr 16.44, Cu 2.73, C 44.04, H 7.18, N 0.59. ES-MS (toluene/MeOH): $m/z + 2272$ $[M+H]^+$ (100%), $+ 2294$ $[M+Na]^+$, -2197 $[\text{Cr}_7\text{CuF}_8(\text{O}_2\text{CCMe}_3)_{16}]^-$ (100%).

1c: Yield 3.0 g (55%). Elemental analysis (%) calcd for $\text{C}_{118}\text{H}_{222}\text{Cr}_{10}\text{Cu}_2\text{F}_{14}\text{N}_2\text{O}_{44}$: Cr 13.82, Cu 3.87, C 43.13, H 6.81, N 0.85; found: Cr 15.38, Cu 3.75, C 42.94, H 6.62, N 0.80.

5: Yield from reaction 0.38 g (6%). Elemental analysis (%) calcd for $\text{C}_{118}\text{H}_{190}\text{Cr}_8\text{Cu}_2\text{F}_{14}\text{N}_8\text{O}_{36}$: Cr 13.39, Cu 4.09, C 45.63, H 6.17, N 3.61; found: Cr 13.27, Cu 3.99, C 45.57, H 6.23, N 3.52.

A second batch was obtained from toluene. Yield 0.43 g (6%). Elemental analysis (%) calcd for $\text{C}_{146}\text{H}_{222}\text{Cr}_8\text{Cu}_2\text{F}_{14}\text{N}_8\text{O}_{36}$ (**5-4C₇H₈**): Cr 11.97, Cu 3.66, C 50.47, H 6.44, N 3.23; found: Cr 10.94, Cu 3.64, C 49.24, H 6.45, N 3.17.

Magnetic susceptibility measurements were performed on polycrystalline samples in the temperature range 2.0–298 K in applied

fields of 0.1 and 1 T using a Quantum Design MPMS SQUID magnetometer. Corrections for diamagnetic contributions were applied using the Pascal constants. The sample holder diamagnetism was measured and subtracted from the raw data.

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- [8] Crystal data for **2** ($C_{149}H_{271}Cr_{12}Cu_7F_{16}N_2O_{52}$; $M_r = 3977.8 \text{ g mol}^{-1}$): dark green block, monoclinic, space group $C2/c$, $a = 31.710(4) \text{ \AA}$, $b = 26.311(5) \text{ \AA}$, $c = 28.183(4) \text{ \AA}$, $\beta = 116.584(10)^\circ$, $V = 21027.8(5) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\rho = 1.256 \text{ g cm}^{-3}$, $F(000) = 8340$, $\mu(\text{Mo}_{K\alpha}) = 0.87 \text{ mm}^{-1}$. Crystal data for **3** ($C_{146}H_{264}Cr_{11}Cu_2F_{15}N_2O_{48}$; $M_r = 3799.7 \text{ g mol}^{-1}$): green plate, monoclinic, space group $P2_1/c$, $a = 20.2730(3) \text{ \AA}$, $b = 41.3517(8) \text{ \AA}$, $c = 25.2874(6) \text{ \AA}$, $\beta = 105.5320(10)^\circ$, $V = 20424.8(7) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\rho = 1.2367 \text{ g cm}^{-3}$, $F(000) = 7980$, $\mu(\text{Mo}_{K\alpha}) = 0.841 \text{ mm}^{-1}$. Crystal data for **4** ($C_{96}H_{160}Cr_7CuF_8NO_{33}$; $M_r = 2315.7 \text{ g mol}^{-1}$): dark green plate, monoclinic, space group $P2_1/c$, $a = 25.0974(4) \text{ \AA}$, $b = 16.6749(3) \text{ \AA}$, $c = 30.9582(7) \text{ \AA}$, $\beta = 110.2050(10)^\circ$, $V = 12158.6(4) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\rho = 1.265 \text{ g cm}^{-3}$, $F(000) = 4864$, $\mu(\text{Mo}_{K\alpha}) = 0.85 \text{ mm}^{-1}$. Crystal data for **5** ($C_{143}H_{220}Cr_8Cu_2F_{14}N_8O_{38}$; $M_r = 3468.4 \text{ g mol}^{-1}$): dark green plate, monoclinic, space group $P2_1/n$, $a = 18.3950(2) \text{ \AA}$, $b = 23.8470(3) \text{ \AA}$, $c = 21.0320(3) \text{ \AA}$, $\beta = 105.51(3)^\circ$, $V = 8889.99(19) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, $\rho = 1.296 \text{ g cm}^{-3}$, $F(000) = 3628$, $\mu(\text{Mo}_{K\alpha}) = 0.785 \text{ mm}^{-1}$. Data were collected on a Bruker Nonius Kappa CCD diffractometer ($\text{Mo}_{K\alpha}$, $\lambda = 0.71073 \text{ \AA}$). In all cases the selected crystals were mounted on the tip of a glass pin using Paratone-N oil and placed in the cold flow (150 K) produced with an Oxford Cryosystems cryostream. Data was collected using ϕ and ω scans chosen to give a complete asymmetric unit. Integrated intensities were obtained with HKL DENZO and SCALEPACK^[9] and were corrected for absorption using SORTAV.^[10] Structure solution and refinement was performed with the SHELX package.^[11] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 to give: for **2** using 1039 parameters, $wR_2 = 0.2874$ (18428 unique reflections), $R_1 = 0.0923$ (10028 reflections with $I > 2\sigma(I)$); for **3** using 1918 parameters and 3571 restraints, $wR_2 = 0.3134$ (20784 unique reflections), $R_1 = 0.1152$ (7210 reflections with $I > 3\sigma(I)$); for **4** using 1215 parameters, $wR_2 = 0.2261$ (19834 unique reflections), $R_1 = 0.0720$ (11544 reflections with $I > 3\sigma(I)$); for **5**: 994 parameters and 64 restraints, $wR_2 = 0.2022$ (15579 unique reflections), $R_1 = 0.0676$ (10300 reflections with $I > 3\sigma(I)$). CCDC-659843 (**2**), 659844 (**3**), 659845 (**4**), and 659846 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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