A family of heterometallic wheels containing potentially fourteen hundred siblings†

Rebecca H. Laye,[a] Finn K. Larsen,[b] Jacob Overgaard,[b] Christopher A. Muryn,[a] Eric J. L. McInnes,*[a] Eva Rentschler,*[c] Veronica Sanchez,[a] Simon J. Teat,[e] Hans U. Güdel,[f] Oliver Waldmann,[f] Grigore A. Timco*[ad] and Richard E. P. Winpenny*[a]

Received (in Cambridge, UK) 4th November 2004, Accepted 16th December 2004
First published as an Advance Article on the web 13th January 2005
DOI: 10.1039/b416770h

The synthesis and structure of new heterometallic wheels are reported, with preliminary studies of selected compounds.

The oxo-centered carboxylate-bridged trinuclear complexes of general formula $[M_2M'O(O_2CR)_6L_3]^Z$ have been studied since 1908 when their trinuclear nature was first proposed by Weinlund[1,2] and Werner.[3] This literature has been reviewed by Cannon and White.[4] In the intervening century, no other polymetallic structural type has been found which can be made for a range of metals, made as homo- and hetero-valent, made in a heterometallic form and with a range of carboxylates and terminal ligands. Our recent report[5] of a series of octanuclear $\{Cr_7M\}$ rings is the first report of anti-ferromagnetically coupled cyclic molecules that have a non-diamagnetic ground state. There has been considerable interest in such molecules for applications as diverse as olefin polymerisation catalysis,[6] magnetic cooling[7] and quantum computing.[8] The latter application depends on the quantum coherence displayed by the spin ground state, which can be adversely affected by interactions including dipolar coupling between molecules in a lattice, and by hyperfine interactions between the electron and nuclear spins within the molecule. In other cases new phenomena are being discovered, *e.g.* tunnelling of the Néel vector in anti-ferromagnetic rings,[9] when systems display precise combinations of spin Hamiltonian parameters. Therefore, partly to study such new physics systematically, we have extended the family of heterometallic rings to include other metals and other carboxylates. Here we show that complexes of the general formula $[NR_2H_2][M_7M'F_8(O_2CR')_{16}]$ can be made straightforwardly and in good yield for a range of R, M, M′ and R′. This creates a huge potential for studying the physics of such systems. The compounds form a vast family of polynuclear cages; the biggest reported since the oxo-centred triangles.

The synthetic procedure is remarkably simple, and based on that established for M = Cr(III).[5] The M(III) fluoride is added to a mixture of the secondary amine and a large excess of carboxylic acid, which is then heated to 160 °C, before a source of the M′ metal is added (typically the carbonate or chloride salt). The products can be precipitated by addition of acetone or MeCN and can be crystallized from a range of solvents including hexane, ethylacetate, toluene or mixtures of solvents. For M = Fe(III) or V(III) the operations have to be performed under anaerobic conditions. By this method we can make the range of compounds given in Table 1.‡ For most of these compounds a range of solvates has been characterised, depending on the solvents used for crystallisation.

In each case the structure of the anion (Fig. 1) consists of an octagon of metal centres, with each edge of the octagon bridged by a single fluoride and two carboxylates. In no case is the position of M′ within the ring unequivocally established; normally it appears to be disordered about the eight metal sites. In some cases one site does appear to have subtly different metric parameters, but in no case does this establish that the structure is ordered. The

Table 1 Range of heterometallic rings prepared

M[a]	M′[b]	R	R′
Cr	Mn, Fe, Co, Ni, Zn, Cd, Mg	Et, ^{n}Pr	*ca.* 14 carboxylates
V	Zn, Ni	^{n}Pr	CMe_3
Fe	Mn, Fe, Co, Ni, Zn, Cd	Et, ^{n}Pr	CMe_3, CMe_2Et, CH_2CMe_3

[a] All M(III) ions. [b] All M(II) ions.

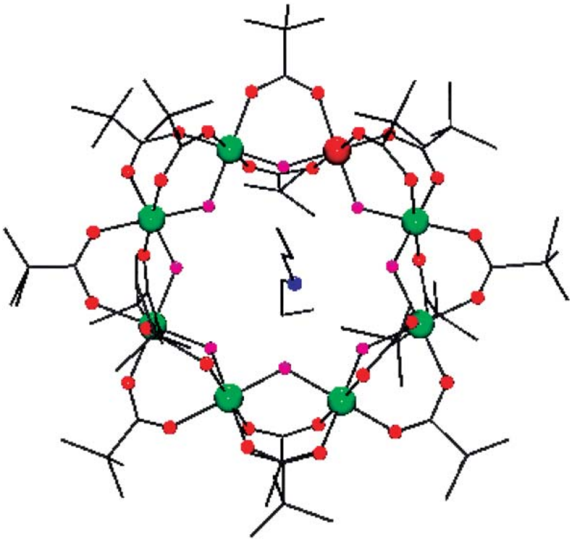

Fig. 1 Structure of $[N^nPr_2H_2][V_7ZnF_8(O_2CCMe_3)_{16}]$. Colours: V, green; Zn, orange; F, pink; O, red; N, blue; C, black lines.

---

† Electronic supplementary information (ESI) available: synthetic details and unit cell parameters for representative wheels. See http://www.rsc.org/suppdata/cc/b4/b416770h/

*richard.winpenny@manchester.ac.uk (Richard E. P. Winpenny)
eric.mcinnes@manchester.ac.uk (Eric J. L. McInnes)
grigore.timco@manchester.ac.uk (Grigore A. Timco)

protonated amine is in each case found H-bonded at the centre of the metal ring.

The formation of the rings requires a linear alkyl-chain R on the secondary amine used, but other than this requirement the synthesis is remarkably general. Packing of the rings in the crystal lattice can be influenced by the choice of R, *e.g.* for R′ = CMe_3 both short and very long R chains lead to packing where the octanuclear wheels are co-planar (generally tetragonal or orthorhombic crystals), but for intermediate chain lengths (Et, Pr) monoclinic crystals are found where the rings pack with an angle of *ca.* 50° between the mean planes of neighbouring rings.

Both M = Fe(III) and V(III) rings are susceptible to decomposition either by hydrolysis for the former or oxidation for the latter while the M = Cr(III) rings are the most stable. We have therefore used the $\{Cr_7M'\}$ family to examine how wide a range of carboxylates can be used in this chemistry. We have made $\{Cr_7Ni\}$ rings for the carboxylates: 2,2-dimethylbutyrate, *tert*-butylacetate, diethylacetate, 3-methylbenzoate, 2-methylbenzoate, 1-methyl-1-cyclohexanecarboxylate, 3,3-dimethylacrylate, chloroacetate, furan-2-carboxylate, hydroxypivalate, 2-thiophenecarboxylate, 3-thiophenecarboxylate (3-tpc), 2,3,4-trimethoxybenzoate and *trans*-2,3-dimethylacrylate. The structure of $[NEt_2H_2][Cr_7NiF_8(3\text{-tpc})_{16}]$ is shown in Fig. 2. There seems to be no restriction on the size of the R′ group in these molecules, which could also be used for other combinations of M and M′. The inclusion of further functional groups in R′ opens up new ideas for multifunctional materials or for forming ordered arrays. For example, with R′ = thiophene we can envisage incorporating the rings in conducting polymers by redox-induced polymerisation,[10] or we could use the S-atoms to attach the wheels to Au-surfaces.

The existence of so many structurally identical rings gives unique opportunities for tuning the magnetic properties. In all the cases we have studied by variable temperature magnetic susceptibility measurements,§ the nearest neighbour exchange interaction is anti-ferromagnetic, leading to low spin, but not diamagnetic ground states. Thus for M = Cr(III), M′ = Ni(II) the ground state is S = 1/2—giving an effective two-level ground state believed to have some suitability for quantum computing.[8] For M = Fe(III), M′ = Zn(II), the ground state is S = 5/2. Other combinations give S = 1 and 3/2 ground states, which can be confirmed by EPR spectroscopy. Furthermore, we can tune the zero-field splitting (D) for a given value of the ground state S. For example, both $\{V_7Zn\}$ and $\{Cr_7Mn\}$ have S = 1 ground states but D is much larger in the former since it is derived from much more anisotropic ions. This ability to tune S and D in isostructural polymetallic compounds is unique.

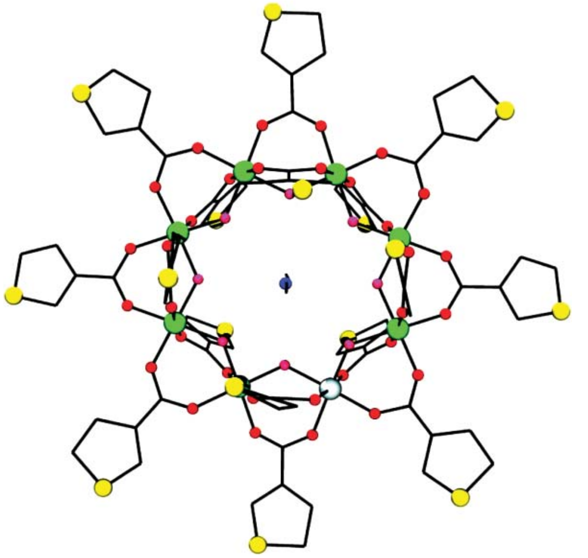

Fig. 2 Structure of $[NEt_2H_2][Cr_7NiF_8(3\text{-tpc}_3)_{16}]$. Colours as Fig. 1: Cr, green; S, yellow.

A particularly intriguing complex is $[N^nPr_2H_2][Fe^{III}{}_7Fe^{II}F_8(O_2CCMe_3)_{16}]$ **1**, which is homometallic but heterovalent. Mössbauer spectroscopy confirms the presence of both oxidation states, with two doublets with the parameters QS = 0.525 and IS = 0.439 mm s^{-1}—typical of Fe(III), and QS = 1.493 and IS = 2.080 mm s^{-1}—typical of Fe(II); the ratio of intensities is as expected 7 : 1. The electronic spectra (recorded in toluene and hexane) show significant bands at 290 nm (ε_{max} 1000 M cm^{-1}) and a very broad band (peak-width at half-height *ca.* 600 nm) centred at 932 nm (ε_{max} 94 M cm^{-1}); we assign the bands, provisionally, as F → Fe charge transfer and an IVCT band respectively. Further work is needed to decide whether **1** is a class-II or, much less likely, class-IIIb mixed-valence compound using the Robin–Day classification.[11] Electrochemical studies§ of **1** show a quasi-reversible oxidation at +0.27 V. The family of $\{Cr_7Fe^{II}\}$ wheels also undergoes quasi-reversible oxidation, with the $E_{1/2}$ value sensitive to the secondary ammonium ion present at the centre of the ring (*e.g.* for R = Me, $E_{1/2}$ = +0.14 V while for R = *n*-octyl $E_{1/2}$ = +0.06 V). We have crystallised the oxidised version of this compound, the neutral wheel $[Cr_7Fe^{III}F_8(O_2CCMe_3)_{16}]$, where a molecule of solvent (EtOAc) is found within the cavity.

There has been some progress in synthesising isostructural homometallic compounds with different metals, *e.g.* $[M(OMe)_2(O_2CMe)]_{10}$ rings have been reported for M = Fe,[12] Cr[13] and V.[14] This family of heterometallic wheels—based on variation of M, M′, R and R′—could have more than fourteen hundred members, of which we have made around one hundred so far. The ability to tune properties—both molecular *via* choice of M and M′ and inter-molecular *via* choice of R and R′—creates great scope for future physical studies. They are also excellent starting materials for the synthesis of further cage complexes.

This work was supported by the EPSRC (UK), the Leverhulme Trust, the EC programme "QuEMolNa" (MRTN-CT 2003-504880) and INTAS (03-51-4532).

Rebecca H. Laye,[a] Finn K. Larsen,[b] Jacob Overgaard,[b] Christopher A. Muryn,[a] Eric J. L. McInnes,*[a] Eva Rentschler,*[c] Veronica Sanchez,[a] Simon J. Teat,[e] Hans U. Güdel,[f] Oliver Waldmann,[f] Grigore A. Timco*[ad] and Richard E. P. Winpenny*[a]
[a]*Department of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL.*
E-mail: richard.winpenny@manchester.ac.uk; eric.mcinnes@manchester.ac.uk; grigore.timco@manchester.ac.uk
[b]*Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark*
[c]*Johannes Gutenberg-Universität, Institut für Anorganische Chemie und Analytische Chemie, Duesbergweg 10-14, 55099 Mainz*
[d]*Institute of Chemistry, Academy of Sciences of Moldova, Academy Str. 3, Chisinau, MD-2028 Republic of Moldova*
[e]*CCLRC Daresbury Laboratory, Warrington, Cheshire, UK WA4 4AD*
[f]*Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland*

Notes and references

‡ Elemental analysis (C, H, N, F and both metals) and mass spectroscopy, and X-ray structural determinations confirm the identity of all the compounds discussed explicitly here. CCDC 257789 and 257790. See http://www.rsc.org/suppdata/cc/b4/b416770h/ for crystallographic data in .cif or other electronic format. Full details will be published later.†

§ Variable temperature magnetic measurements in the region 1.8–325 K were made using SQUID magnetometers (Quantum Design) with samples sealed in gelatine capsules in fields of 100 or 1000 G. Redox potentials were measured with Pt working and counter electrodes and are quoted *vs.* Ag/AgCl reference (Fc/Fc$^+$ measured at +0.54 V).

1 R. F. Weinland, *Chem.–Ztg.*, 1908, **32**, 812.
2 R. F. Weinland, *Ber. Dtsch. Chem. Ges.*, 1908, **41**, 3236.
3 A. Werner, *Ber. Dtsch. Chem. Ges.*, 1908, **41**, 3447.
4 R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195.
5 F. K. Larsen, E. J. L. McInnes, H. El Mkami, J. Overgaard, S. Piligkos, G. Rajaraman, E. Rentschler, A. A. Smith, G. M. Smith, V. Boote, M. Jennings, G. A. Timco and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2003, **42**, 101.
6 P.-G. Lassahn, V. Lozan, G. A. Timco, P. Christian, C. Janiak and R. E. P. Winpenny, *J. Catal.*, 2004, **222**, 260.
7 M. Affronte, A. Ghirri, S. Carretta, G. Amoretti, S. Piligkos, G. A. Timco and R. E. P. Winpenny, *Appl. Phys. Lett.*, 2004, **84**, 3468.
8 (*a*) F. Meier, J. Levy and D. Loss, *Phys. Rev. Lett.*, 2003, **90**, 47901–1; (*b*) F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.*, DOI: condmat/0405507.
9 O. Waldmann, C. Dobe, H. Mutka, A. Furrer and H. U. Güdel, *Phys. Rev. Lett.*, DOI: condmat/0410447.
10 P. Bäuerle, in *Handbook of Oligo- and Polythiophenes*, ed. D. Fichou, Wiley-VCH, Weinheim, Germany, 1999, p. 89.
11 M. B. Robin and P. Day, *Adv. Inorg. Chem.*, 1967, **10**, 247.
12 K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823.
13 E. J. L. McInnes, C. Anson, A. K. Powell, A. J. Thomson, S. Poussereau and R. Sessoli, *Chem. Commun.*, 2001, 85.
14 R. H. Laye, M. Murrie, S. Ochsenbein, A. R. Bell, S. J. Teat, J. Raftery, H. U. Güdel and E. J. L. McInnes, *Chem.–Eur. J.*, 2003, **9**, 6.