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Synthesis and reactions of N-heterocycle functionalised variants of heterometallic {Cr_7Ni} rings†

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Here we present a series of linked cage complexes of functionalised variants of the octametallic ring {Cr_7Ni} with the general formula [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CR)$], where HO_2CR is a N-heterocycle containing carboxylic acid. These compounds are made by reacting [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CR)$] with a variety of simple metal salts and metal dimers. The carboxylic acids studied include iso-nicotinic acid, 3-(4-pyridyl)acrylic acid and 4-pyridazine carboxylic acid. These new linked cage complexes have been studied structurally and the study highlights the versatility of functionalised {Cr_7Ni} as a Lewis base ligand. As {Cr_7Ni} is a putative molecular electron spin qubit this work contributes to our understanding of the chemistry that might be required to assemble molecular spin qubits.

Introduction

Several strategies have been proposed to create qubits that could act as the fundamental unit of a quantum computer; these include quantum dots,[1] semiconductor nanowires,[2] large atomic ensembles,[3] ion traps,[4] defects in solids,[5] carbon nanotubes,[6] nuclear spin[7] and molecular nanomagnets.[8] Molecular nanomagnets have one major advantage over most other strategies, which is that through chemistry it is possible to engineer the interaction between individual qubits. We have been studying heterometallic rings as possible qubits and have shown they have reasonable coherence times, and that they can be linked so that spin on individual rings entangle with neighbours.[9] Here we report coordination chemistry to produce a series of functionalised rings.

Functionalisation of [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{16}$)] (hereafter {$Cr_7Ni$}, Fig. 1) rings with N-heterocycle functional groups allows the ring to act as a Lewis base towards metal sites, essentially acting as a bulky N-donor ligand.[10] By synthesising the functionalised {Cr_7Ni} rings prior to binding to another metal or simple dimer, we produce a controlled approach to synthesis of linked systems. This should allow the design of appropriate linkers with the capability of providing switchable communication between qubits. The functionalised rings have the general formula [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^{t}Bu)_{15}(O_2CR)$], herein {$Cr_7Ni(O_2CR)$}, where HO_2CR is either iso-nicotinic acid ($HO_2C_5H_4N$, herein HO_2C-py), 3-(4-pyridyl)acrylic acid ($HO_2C_2H_2C_5H_4N$, herein HO_2C-4pyac) or 4-pyridazine carboxylic acid ($HO_2C_4H_3N_2$, herein HO_2C-pyd). These complex N-donor ligands have remarkable solubility in non-polar solvents and are very sterically demanding. In the following we discuss the diversity of structures that can be formed from reactions with simple metal salts and metal dimers. The range of metal used represents a wide selection from across the periodic table including 3d, 4d and 5d transition metals with a range of anions, including chelating and bridging ligands. The resulting complexes are discussed in terms of their structure and crystal packing.

Experimental

Column chromatography was carried out using Silica 60A (particle size 35–70 μm, Fisher, UK) as the stationary phase, and TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany). Elemental analyses were performed by departmental services at The University of Manchester. Carbon, nitrogen and hydrogen analysis was performed using a Flash 200 elemental analyser. Metal analysis was performed by Thermo iCap 6300 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Starting materials

All reagents and solvents used to synthesise the functionalised rings and linkers were commercially available and used as

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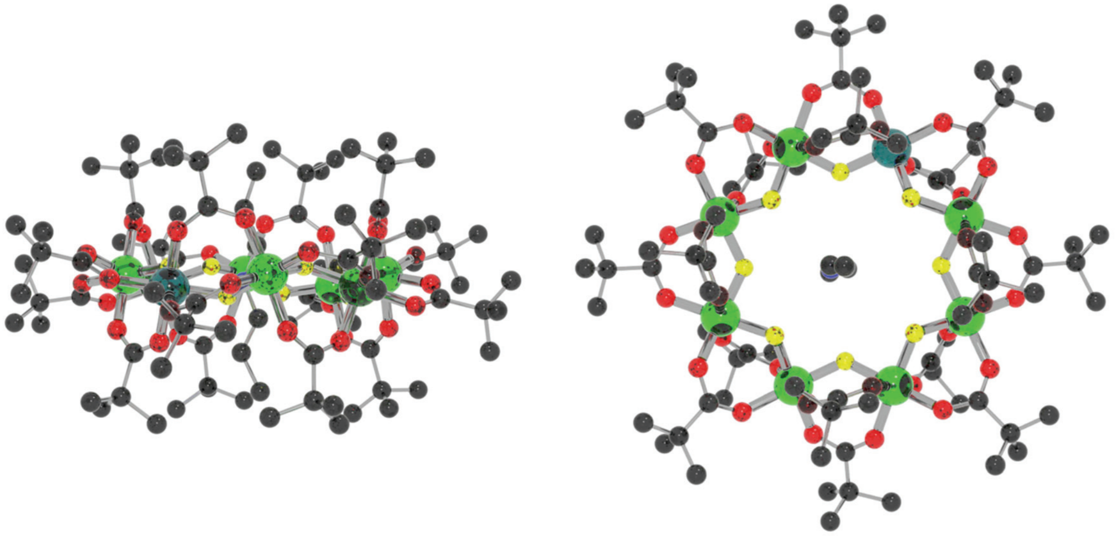

Fig. 1 Side and top views of {Cr_7Ni} in the crystal. Cr = green, Ni = turquoise, C = black, O = red, N = blue, F = yellow. H-atoms omitted for clarity.

received. $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{16}]$,[11] $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]$, **1**,[9c] $[Ni_2(\mu\text{-}OH_2)(O_2C^tBu)_4(HO_2C^tBu)_4]$[12] and $[Co_2(\mu\text{-}OH_2)(O_2C^tBu)_4(HO_2C^tBu)_4]$[13] were prepared by published methods. Copper(II) pivalate, $[Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2]$, was synthesised in an analogous procedure to $[Ni_2(\mu\text{-}OH_2)(O_2C^tBu)_4(HO_2C^tBu)_4]$. $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_2H_2C_5H_4N)]$, **2**, and $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_3N_2)]$, **3**, were synthesised by an analogous procedure to **1**, the details of which are in the ESI.†

Coordination compounds with rings as ligands

The linked ring systems are obtained from the reaction of the corresponding N-heterocycle functionalized {Cr_7Ni} ring, in slight excess, and the link of choice in an appropriate solvent, usually hot acetone or toluene. The reaction mixture is then stirred for anywhere between 5 and 20 minutes (with the exception of $ReCl(CO)_5$ and $Rh_2(O_2CCH_3)_4$ due to their inertness) during which time a precipitate may have formed. If a precipitate forms, the solution is cooled, the precipitate collected, washed with the same solvent used in the reaction and recrystallized from an appropriate solvent mix. If no precipitate forms the reaction solution is left to cool and in most cases the desired product will crystallise in 24–48 hours. An example is given for compound **4** below and in detail for all compounds in the ESI.† The reagents involved, yield and elemental analysis are listed in Table 1.

$\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Cu(NO_3)_2(OH_2)]$ 4. $Cu(NO_3)_2\cdot 2.5H_2O$ (0.011 g, 0.049 mmol) was added to a solution of **2** (0.3 g, 0.13 mmol) in hot acetone (30 mL) with stirring. The solution was refluxed for 5 minutes before cooling and left undisturbed in a sealed flask at room temperature. Dark green crystals suitable for single crystal XRD formed after 1 week and were collected by filtration and washed with acetone.

X-ray crystallography

Structures **2**, **3**, **6**, and **17** were collected on a Bruker X8 Prospector 3-circle diffractometer with a copper microfocus source and an APEX II CCD detector. Structure **21** were collected on an Enraf Nonius FR590 4-circle diffractometer with a molybdenum sealed-tube, fine focus molybdenum source, structures **1**, **5**, **10**, **11**, **12**, **14**, **16**, **18**, **19** and **20** were collected on Advanced Light Source station 11.3.1. Structures were solved and refined using SHELX97 and SHELX-2013. Structures **4**, **7**, **8**, **9**, **12** and **15** have already been communicated previously.[9c,10d] Full crystallographic details for all crystal structures are included in Table S1.† CCDC numbers 1424323–1424336 contain the supplementary crystallographic data for the new structures reported in this paper.

Results and discussion

In all the structures discussed here the heterometallic ring is unchanged from the parent unsubstituted {Cr_7Ni} ring.[11] The ring contains an octagon of metal sites, with each edge bridged internally by a fluoride and by two carboxylates. On each edge, one carboxylate lies close to the plane of the metal ring while the second carboxylate is perpendicular to the plane of eight metals; this site is labelled as the axial carboxylate, with the in-plane carboxylates described as equatorial.

In the functionalised derivatives the nickel(II) site is always found in the edge that is substituted and is disordered between the two sites in that edge. The incoming carboxylate (*e.g.* iso-nicotinate) is found in an axial site in the molecules described below and this is always the more common isomer.

Functionalised {Cr_7Ni} derivatives

Iso-nicotinate {Cr_7Ni}, $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]$, 1 (Fig. 2). Functionalising {Cr_7Ni} with iso-

Table 1 Reactants, yields and elemental analyses for compounds **4–21**

Linker	Ring	Product	Yield/%[a]	Elemental analysis/% Calculated (found)
$Cu(NO_3)_2\cdot 2.5H_2O$	**1**	**4**	71.7	Calc. for: $C_{174}H_{312}Cr_{14}Cu_1F_{16}N_6Ni_2O_{71}$ C43.20 H6.50 N1.74 Cr15.05 Ni2.43 Cu1.31 (C43.05 H6.54 N1.66 Cr15.25 Ni2.42 Cu1.26)
$AgNO_3$	**1**	**5**	6.7	Calc. for: $C_{174}H_{310}AgCr_{14}F_{16}N_5Ni_2O_{67}$ C43.59 H6.52 N1.46 (C43.65 H6.63 N1.40)
$Cu(NO_3)_2\cdot 2.5H_2O$	**2**	**6**	52.0	Calc. for: $C_{178}H_{316}Cr_{14}CuF_{16}N_6Ni_2O_{71}$ C43.73 H6.51 N1.72 Cr14.89 Ni2.40 Cu1.30 (C43.51 H6.55 N1.71 Cr14.94 Ni2.35 Cu1.23)
$Ni(acac)_2(H_2O)_2$	**1**	**7**	38.0	Calc. for: $C_{184}H_{324}Cr_{14}F_{16}N_4Ni_3O_{68}$ C45.21 H6.68 N1.15 Cr14.89 Ni3.60 (C44.92 H6.86 N1.21 Cr14.77 Ni3.53)
$Ni(F_3acac)_2(H_2O)_2$	**1**	**8**	45.7	Calc. for: $C_{184}H_{318}Cr_{14}F_{22}N_4Ni_3O_{68}$ C44.23 H6.42 N1.12 Cr14.57 Ni3.52 (C43.95 H6.57 N1.18 Cr14.52 Ni3.62)
$Ni(Hfac)_2(H_2O)_2$	**1**	**9**	42.0	Calc. for: $C_{184}H_{312}Cr_{14}F_{28}N_4Ni_3O_{68}$ C43.30 H6.16 N1.09 Cr14.26 Ni3.45 (C43.02 H6.37 N1.08 Cr14.02 Ni3.36)
$Cu(Hfac)_2(H_2O)_2$	**1**	**10**	42.9	Calc. for: $C_{184}H_{312}Cr_{14}CuF_{28}N_4Ni_2O_{68}$ C43.25 H6.15 N1.10 Cr14.25 Ni2.30 Cu 1.24 (C43.15 H6.18 N1.11 Cr13.92 Ni2.29 Cu 1.23)
$Mn(Hfac)_2(H_2O)_2$	**1**	**11**	48.6	Calc. for: $C_{184}H_{312}Cr_{14}F_{28}MnN_4Ni_2O_{68}$ C43.33 H6.17 N1.10 Cr14.27 Ni2.30 Mn1.08 (C43.12 H6.23 N1.09 Cr14.08 Ni2.33 Mn1.02)
$Ni(Hfac)_2(H_2O)_2$	**3**	**12**	39.0	Calc. for: $C_{182}H_{310}Cr_{14}F_{28}N_6Ni_3O_{68}$ C42.81 H6.12 N1.65 Cr14.26 Ni3.45 (C42.47 H6.00 N1.59 Cr13.95 Ni3.46)
$Mn(Hfac)_2(H_2O)_2$	**3**	**13**	47.0	Calc. for: $C_{182}H_{310}Cr_{14}MnF_{28}N_6Ni_2O_{68}$ C43.27 H6.22 N1.61 Cr13.95 Mn1.05 (C43.15 H6.19 N1.66 Cr13.64 Mn0.80)
$ReCl(CO)_5$	**1**	**14**	62.7	Calc. for: $C_{177}H_{310}ClCr_{14}F_{16}N_4Ni_2O_{67}Re$ C43.06 H6.33 N1.13 Cr14.74 Re3.77 (C42.77 H6.32 N1.07 Cr14.46 Re3.85)
$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$	**1**	**15**	89.9	Calc. for: $C_{194}H_{346}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$ C45.13 H6.75 N1.09 Cr14.10 Ni2.27 Cu2.46 (C44.98 H6.87 N1.07 Cr14.39 Ni2.23 Cu2.43)
$[Ni_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$	**1**	**16**	38.5	Calc. for: $C_{196}H_{336}Cr_{14}F_{16}N_6Ni_4O_{72}$ C45.21 H6.77 N1.09 Cr14.13 Ni4.56 (C44.99 H6.67 N1.01 Cr13.71 Ni4.78)
$[Co_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$	**1**	**17**	89.6	Calc. for: $C_{196}H_{336}CoCr_{14}F_{16}N_6Ni_2O_{72}$ C45.21 H6.77 N1.08 Cr14.12 Ni2.28 Co2.29 (C45.15 H6.74 N1.11 Cr14.03 Ni2.17 Co2.42)
$[Ru_2(O_2C^tBu)_4]BF_4$	**1**	**18**	65.4	Calc. for: $C_{194}H_{346}B_1Cr_{14}F_{20}N_4Ni_2O_{72}Ru_2$ C43.76 H6.55 Cr13.67 Ni2.20 (C43.75 H6.60 Cr13.40 Ni2.12)
$Rh_2(O_2CCH_3)_4$	**1**	**19**	89.9	Calc. for: $C_{182}H_{322}Cr_{14}F_{16}N_4Ni_2O_{72}Rh_2$ C43.08 H6.40 N1.10 Cr14.35 Ni2.31 Rh4.06 (C43.43 H6.56 N1.09 Cr14.38 Ni2.25 Rh3.96)
$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$	**2**	**20**	14.0	Calc. for: $C_{198}H_{350}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$ C45.60 H6.76 N1.07 Cr13.96 Cu2.44 (C45.70 H6.85 N1.02 Cr13.59 Cu2.48)
$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$	**3**	**21**	44.0	Calc. for: $C_{192}H_{344}Cr_{14}Cu_2F_{16}N_6Ni_2O_{72}$ C44.65 H6.71 N1.63 Cr14.09 Cu2.46 (C44.78 H6.84 N1.51 Cr13.27 Cu2.47)

[a] All yields based on linker.

nicotinic acid provides the ring with a very sterically congested pyridyl moiety, with the nitrogen of the pyridyl barely protruding beyond the neighbouring pivalate groups. This provides a pathway for spin propagation from the ring to whatever it may bind through the conjugated π-system.

3-(4-Pyridyl)acrylate {Cr_7Ni}, $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_2H_2C_5H_4N)]$, 2 (Fig. 3). The introduction of the 3-(4-pyridyl)acrylate group provides a longer, less sterically demanding linker whilst still maintaining the potential for spin propagation from the ring to whatever it may bind to through the conjugated π-system.

4-Pyridazine carboxylate {Cr_7Ni}, $[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_3N_2)]$, 3 (Fig. 4). The 4-pyridazine carboxylate group provides a very sterically congested pyridazine

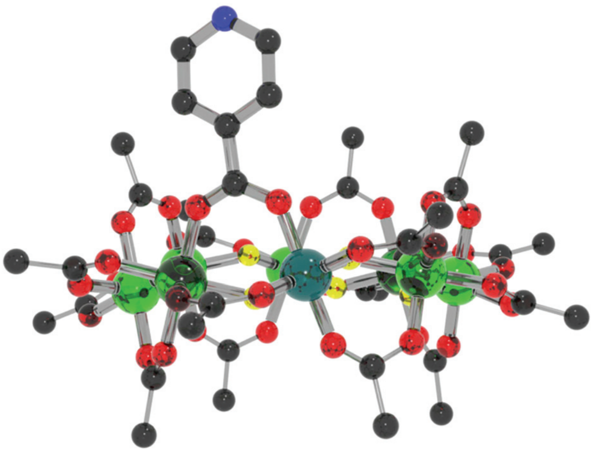

Fig. 2 Structure of **1** in the crystal viewed into the plane of the {Cr$_7$Ni} ring. Colour code: Cr = green, Ni = turquoise, C = black, O = red, N = blue, F = yellow. H-atoms, methyl groups of {Cr$_7$Ni} pivalates and central cation omitted for clarity.

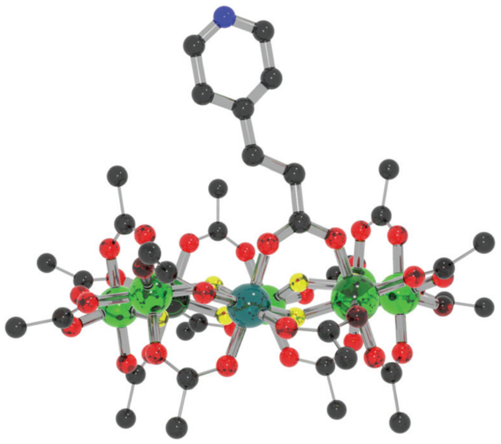

Fig. 3 Structure of **2** in the crystal. Colours and omissions as Fig. 2.

moiety thorough which spin propagation can occur with the potential for different coordination modes and strength of coupling compared to **1**.

Linked {Cr$_7$Ni} systems

The following structures are described using three metric parameters; the torsion angle between the centre of the Cr–Ni edges and the centre of each ring, the N–M–N bond angle (in the case of dimetallic linkers the centroid between the metals is used) and the deviation from co-planar of the two rings. Schematics for the torsion and deviation from co-planar metrics are shown in Fig. 5. If the torsion angle is 180°, the rings are considered staggered and if the angle is 0° they are considered eclipsed and co-planar if there is 0° deviation between the planes.

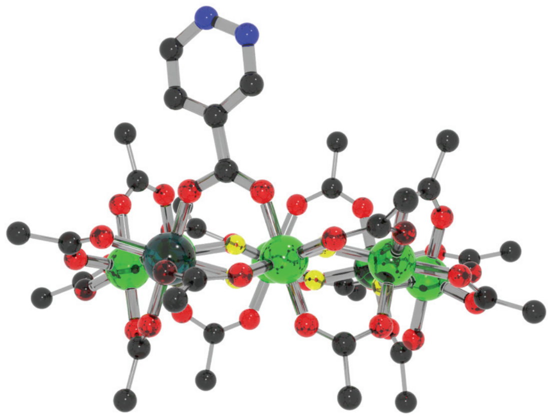

Fig. 4 Structure of **3** in the crystal. Colours and omissions as Fig. 2.

Simple metal salt linked structures

Reactions with group 11 metal nitrates. The reaction of **1** in a 2.6 : 1 ratio (to provide a slight excess of **1**) with Cu(NO$_3$)$_2$·2.5H$_2$O, refluxing in hot acetone for a few minutes and allowing to cool produces {[^{n}Pr$_2$NH$_2$][Cr$_7$NiF$_8$(O$_2$C^{t}Bu)$_{15}$(O$_2$C-Py)]}$_2$[Cu(NO$_3$)$_2$(H$_2$O)] **4** with a 72% yield (Fig. 6). The central copper(II) adopts a 7-coordinated geometry that could be described like a distorted pentagonal bipyramid, with two pyridine nitrogen atoms from two different iso-nicotinic groups of two **1** in a *trans* arrangement and two bidentate nitrate counter ions in a trans disposition and a water molecule completing the pentagonal basal plane. Similar coordination geometries have been seen previously, chiefly in coordination polymers.[14] The rings themselves adopt a staggered geometry with a torsion angle of 176.7(2)°. This is most likely due to the short distance between the rings binding through a single metal ion with an eclipsed geometry *i.e.* with 0° rotation resulting in a steric clash. The rings lie almost parallel with a deviation of 7.2(2)° from co-planarity, with the N–Cu–N angle being 176.3(10)°.

Reacting **1** with silver nitrate gives {[^{n}Pr$_2$NH$_2$]-[Cr$_7$NiF$_8$(O$_2$C^{t}Bu)$_{15}$(O$_2$C-Py)]}$_2$[AgNO$_3$], **5**, with the silver adopting a distorted four-coordinate geometry, similar to other examples of N-donor groups bound to silver nitrate (Fig. 7).[15] Unlike **4**, the rings adopt an eclipsed geometry with a torsion angle of 8.3(2)°. However, the rings as are not parallel with an angle of 49.8(2)° from planar between the plane of the rings. The iso-nicotinates bind to the silver(I) with an N–Ag–N angle of 145.1(6)° and N–Ag distances of N–Ag 2.246(15) Å and 2.284(15) Å.

The reaction of **2** with hydrated copper(II) nitrate gives [{Cr$_7$Ni(O2C-4pyac)}$_2$Cu(NO$_3$)$_2$(OC$_3$H$_6$)] **6** (Fig. 8). The ethene-link to the pyridyl group in **2** leads to different crystal packing in **6** compared with **4**; the rings adopt an eclipsed, rather than staggered geometry with a torsion angle of 19.49(2)° and with a 34.65(2)° deviation from co-planarity. The Cu–N bond distances of 2.146(6) Å for **6** are slightly longer than literature examples of similar motifs (the CSD average is 1.978(4) Å for

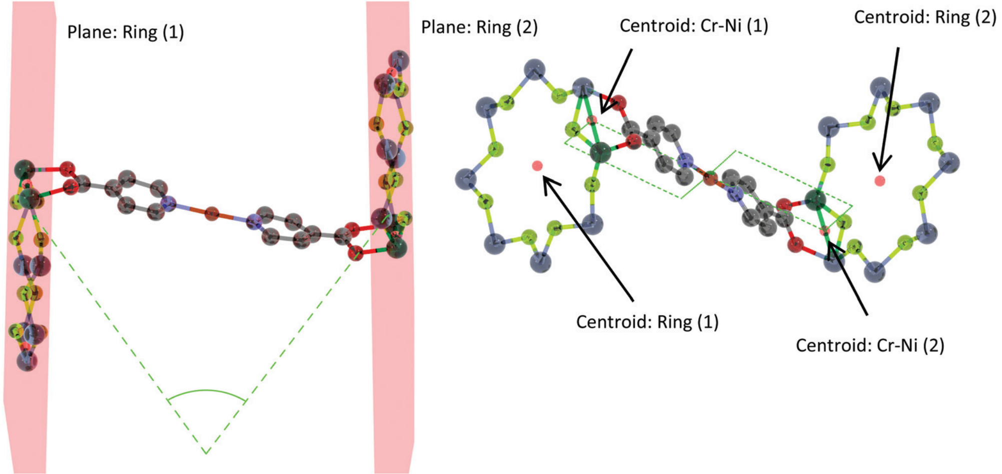

Fig. 5 Schematics for the deviation from co-planar and torsion metrics of the rings.

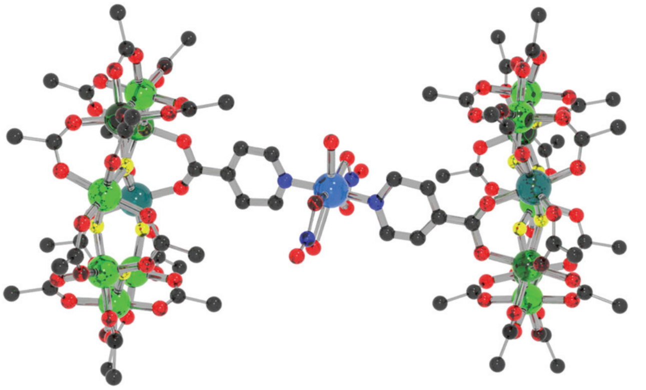

Fig. 6 Structure of **4** in the crystal. Colours and omissions as Fig. 2, Cu = light blue.

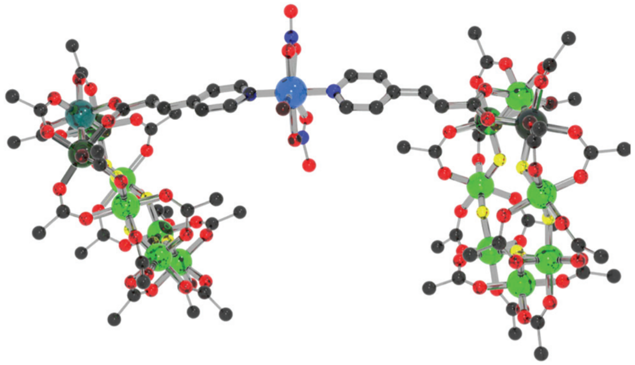

Fig. 8 Structure of **6** in the crystal. Colours and omissions as Fig. 2, Cu = light blue.

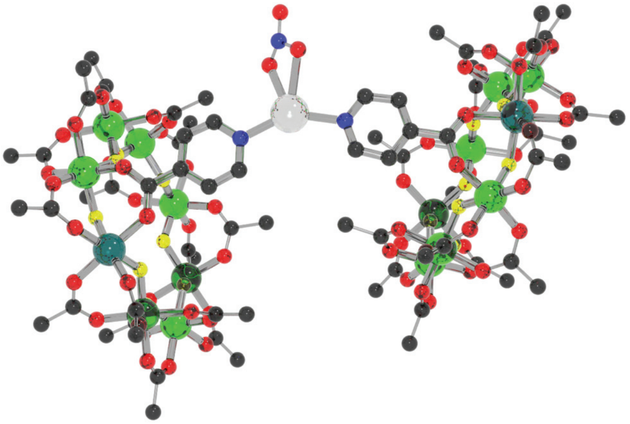

Fig. 7 Structure of **5** in the crystal. Colours and omissions as Fig. 2, Ag = white.

3-(4-pyridyl) acrylic moieties bound to $\{Cu(NO_3)_2\}$).[14] As with **4**, the central copper adopts a 7-coordinate geometry, with the rings binding in a *trans* disposition with two nitrates and a water molecule in the pentagonal basal plane.

The reaction of **3** with copper(II) nitrate proved unsuccessful, which was unexpected as 4-pyradizine has previously been shown to coordinate to copper(II) nitrate.[16]

Reactions of with M(II) acetylacetonate derivatives. Compound **1** reacts with M(II) acetylacetonate derivatives, including acetylacetonate ($[M(II)(acac)_2]$), 1,1,1-trifluoroacetylacetonate ($[M(II)(F_3acac)_2]$) and 1,1,1,6,6,6-hexafluoroacetylacetonate ($[M(II)(Hfac)_2]$) salts. This produces compounds $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2C\text{-}Py)]\}_2[ML_2]$, (L = acac, M = Ni **7**; L = F$_3$acac, M = Ni **8**; L = Hfac, M = Ni **9**; L = Hfac, M = Cu **10**; L = Hfac, M = Mn **11**) (**9** is shown in Fig. 9). In all cases the central metal lies on an inversion centre with a *trans* disposition of the ligands. The presence of electron withdrawing F atoms in the acac ligand leads to a shortening of the N–M bond distances from 2.104(7) and 2.122(7) in **7** to 2.075(9) in **8** and 2.074(9) Å in **8** and **9** respectively. In **7**, the rings are not

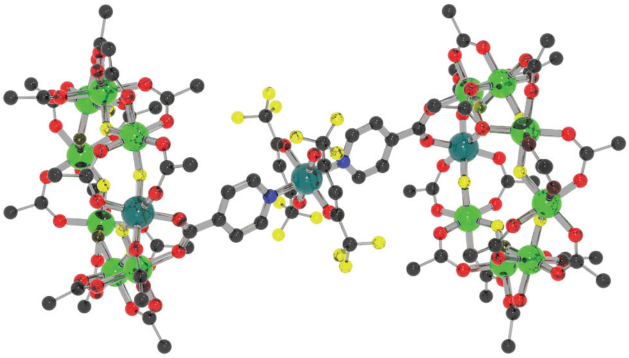

Fig. 9 Structure of **9** in the crystal. Colours and omissions as Fig. 2.

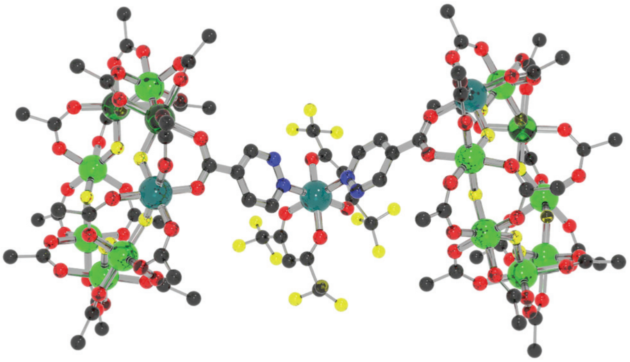

Fig. 10 Structure of **12** in the crystal. Colours and omissions as Fig. 2.

co-planar with a deviation of 9.8(2)°, with a torsion angle of 178.9(2)° and a N–Ni–N bond angle of 177.5(3). In contrast, **8** and **9** exhibit perfect co-planarity of the rings, a torsion angle of 180° and an N–M–N bond angle of 180.0°.

The other examples of M(Hfac)$_2$ linked rings (**10** and **11**) crystallise in a triclinic $P\bar{1}$ rather than monoclinic $C2/c$. They have the same disposition of rings as **9**, with a torsion angle of 180° with 0° deviation from co-planar, and a N–M–N bond angle of 180. Interestingly, **10** does not appear to display a significant Jahn–Teller elongation, as might be expected from copper(II). However, this could be due to its position on an inversion centre averaging the Cu–O bond lengths. In any case, the Cu–N bond distance from the centre to the ring is shorter than the two Cu–O bond lengths, which could imply that the rings coordinate in the x–y plane of the central copper (Cu–N = 1.993(3) Å, Cu–O1 = 2.065(4) Å and Cu–O2 = 2.178(3) Å). In the case of **11**, the central manganese adopts a slightly distorted octahedral geometry with the coordinating nitrogen atoms exhibiting a slightly longer bond length to the oxygen atoms of the Hfac (2.150(3) Å *vs.* 2.085(3) and 2.089(3) Å).

While **3** did not coordinate to copper(II) nitrate, it acts as a ligand towards M(Hfac)$_2$ derivatives (M = Ni and Mn); again there was no reaction with Cu(Hfac)$_2$. $\{[^n\text{Pr}_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}^t\text{Bu})_{15}(\text{O}_2\text{C-pyd})]\}_2[\text{M(Hfac)}_2]$, (M = Ni **12**; M = Mn **13**) form in decent yields; unfortunately **13** does not crystallise, therefore we are unsure which isomer forms. The structure of **12** shows the Ni(Hfac)$_2$ adopting the *cis* conformation (Fig. 10), contrasting with the *trans*-geometry of **9**. The rings are eclipsed, with a torsion angle of 26.93(3)° and the rings lie with a 53.73(3)° deviation from co-planar. The Ni–N distance is 2.073(6) Å and the N–Ni–N bond angle is 90.0(3)°. It is unclear why the 4-pyridazinecarboxylate favours a *cis*-geometry, which seems more sterically demanding. It is also intriguing that **3** seems to bind to Ni(II) but not Cu(II).

Reactions with 5d metals. We have also fully characterised one example of {Cr$_7$Ni} bound to rhenium by reacting **2** with ReCl(CO)$_5$ to give $\{[^n\text{Pr}_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}^t\text{Bu})_{15}(\text{O}_2\text{C-Py})]\}_2[\text{ReCl(CO)}_3]$, **14** (Fig. 11). The rings are half eclipsed with a torsion angle of 72.3(2)° with an angle of 55.2(2)° from co-planarity. The Re–N are 2.13(3) Å and 2.16(3) Å, shorter than the average of 2.23(3) Å found in the CSD for similar ReCl(CO)$_3$(py)$_2$ complexes.[17]

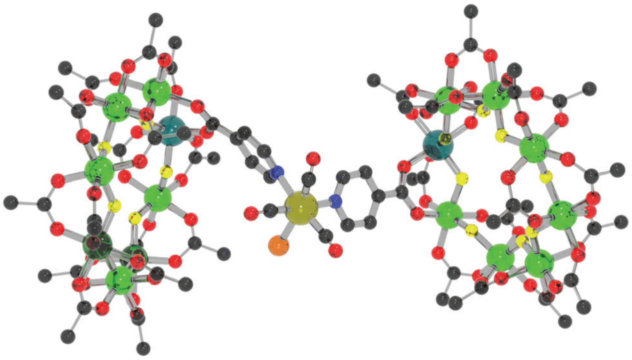

Fig. 11 Structure of **14** in the crystal. Colours and omissions as Fig. 2, Re = dark yellow, Cl = orange.

Dimetallic tetracarboxylates

Compound **2** was reacted with a range of dimetallic tetracarboxylates; [Cu$_2$(O$_2$C^{t}Bu)$_4$(HO$_2$C^{t}Bu)$_2$], [Rh(O$_2$CMe)$_4$] and [Ru$_2$(O$_2$CC^{t}Bu)$_4$]BF$_4$, and water-bridged metal carboxylate dimers [M$_2$(μ-OH$_2$)(O$_2$C^{t}Bu)$_4$(HO$_2$C^{t}Bu)$_4$] (M = Ni or Co). Similar results are found in each case with compounds $\{[^n\text{Pr}_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}^t\text{Bu})_{15}(\text{O}_2\text{C-Py})]\}_2[\text{M}_2(\text{O}_2\text{C}^t\text{Bu})_4]$, (M = Cu **15**; M = Ni, **16**; M = Co, **17**; M = Ru **18**) and $\{[^n\text{Pr}_2\text{NH}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}^t\text{Bu})_{15}(\text{O}_2\text{C-Py})]\}_2[\text{Rh}_2(\text{O}_2\text{CMe})_4]$M = Rh **19**) forming in good yields (see Table 2). The water is displaced from the two water-bridged dimers. In all these compounds the N-donor from iso-nicotinate binds to the apical sites of the metal dimers. In the five crystal structures, three crystallise in monoclinic settings (**15**, **18** and **19**) with similar unit cells and with half the assembly in the asymmetric unit. Compound **16**, has the highest molecular symmetry with 1/4 of the assembly present in the asymmetric unit in the orthorhombic *Pnnm* space group. Compound **17**, crystallises in tetragonal $I4_{1/a}$ and features half the assembly in the asymmetric unit. The crystal

Table 2 Selected metric parameters for compounds **15–19**

Compound	**15**	**16**	**17**	**18**	**19**
M–M bond length/Å	2.606(2)	2.542(5)	2.607(3)	2.2657(14)	2.4038(10)
CSD average M–M bond lengths for similar/Å	2.604(20)	2.596(11)	2.72(4)	2.279(3)	2.398(4)
M–N bond distance/Å	2.146(6)	1.97(2)	2.061(12)	2.285(9)	2.223(7)
CSD average M–N bond lengths for similar/Å	2.165(16)	1.993(20)	2.066(9)	2.276(6)	2.231(15)

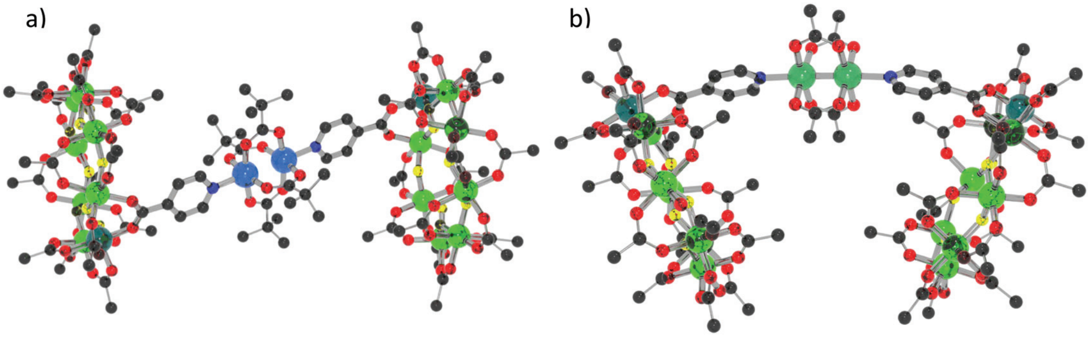

Fig. 12 (a) Structure of **15** in the crystal. (b) Structure of **19** in the crystal. Colours and omissions as Fig. 2 (a) Cu = light blue, (b) Rh = emerald.

for **16** contains huge solvent channels throughout the crystal with total solvent accessible voids of 8579.4 Å^3, making the crystal 41.3% solvent accessible voids with a unit cell of volume of 20795 Å^3. PLATON calculates the largest nine cavities to have radii ranging from 7.4–5.2 Å. It is unclear why **16** packs in a very different way to the other compounds.

The assemblies adopt two distinct geometries. For the compounds with $[M_2(O_2C^tBu)_4]$ as linker (**15–18**), the rings are perfectly staggered with respect to one another and are also completely co-planar (Fig. 12a). The only differences from **15** to **18** are the M–M bond distances, the M–N bond distances, the ring centroid distances and the ring torsion angle (Table 2). For compound **19**, where the link is $[Rh_2(O_2CMe)_4]$, the rings are eclipsed with a torsion angle of 47.55° and a deviation of 50.48° from co-planarity (Fig. 12b). The N–M bond length is 2.223(7) Å, slightly shorter than the average found in the CSD of 2.231(15) Å for similar complexes. The N–M$_2$–N bond angle is 177.26(4)°, measured through the dimer centroid and the M–M bond distance is 2.4038(10) Å, slightly longer than the CSD average of 2.398(4) Å found for related compounds.[18]

Whilst **15**, **18** and **19** exhibit similar M–M distances to other similar complexes found in the CSD, **16** and **17** exhibit a significant shortening of the M–M distances. In the case of **16**, only one similar compound from the CSD has a bond length significantly less than 2.6 Å; one with a {Cr$_7$Ni} bound through a pyridyl group on the thread.[10b] It would appear that the bulky nature of the coordinating ligand forces the Ni⋯Ni and Co⋯Co bonds to shorten. For **15**, favourable 5-coordinate geometry may explain a lack of shortening, while in the case of **18** and **19** the bond order of the metal–metal bond is presumably the controlling factor. For **16**, **17** and **19** the central dimetallic link has all carboxylate ligands around 45° from the plane of the iso-nicotinate ligands, while in **15** and **18** two of the carboxylates are almost co-planar with the iso-nicotinates (Fig. 13).

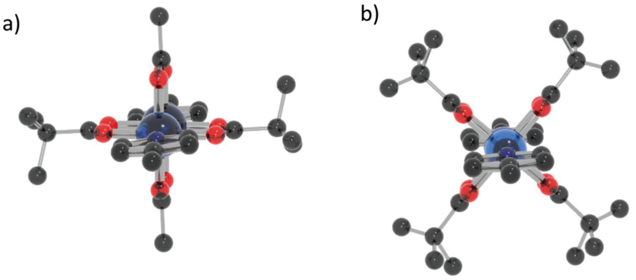

Fig. 13 Orientation of the central metal dimer looking down the co-ordinating iso-nicotinate groups (a) **15** and **18** and (b) **16** and **17**. Colours as Fig. 2, M = light blue.

Compounds **2** and **3** also reacts with $[Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2]$ to give $\{[{}^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2C\text{-}4pyac)]\}_2[Cu_2(O_2C^tBu)_4]$ **20** (Fig. 14) and $\{[{}^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2C\text{-}pyd)]\}_2[Cu_2(O_2C^tBu)_4]$ **21** (Fig. 15). In **20**, the rings bind to the apical positions of the copper sites and the packing is similar to that of **15**, with the rings in a perfectly staggered geometry. However, the central bridging unit in **20** adopts the same as that in **16** and **17**, with the bridging pivalates out of the plane of the pyridyl groups. The Cu–N bond length is 2.146(6) Å, which is similar to that in **15**, but the Cu–Cu distance is 2.5865(14) Å, slightly shorter than **15** and the CSD average.[19]

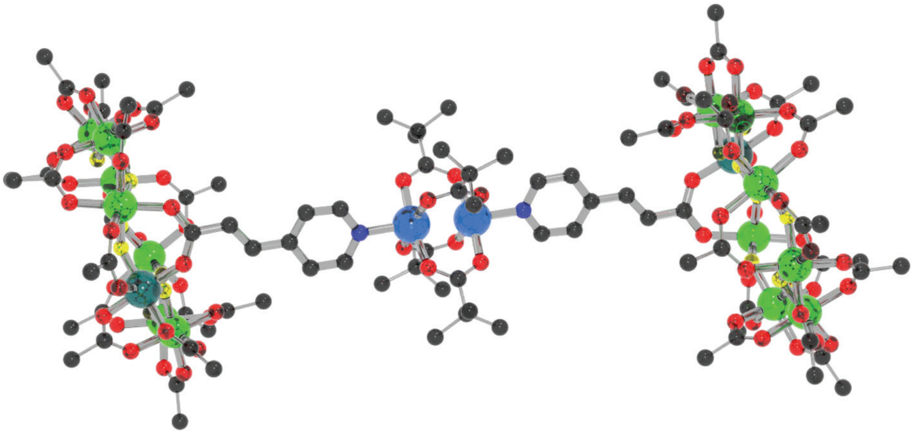

Fig. 14 Structure of **20** in the crystal. Colours and omissions as Fig. 2, Cu = light blue.

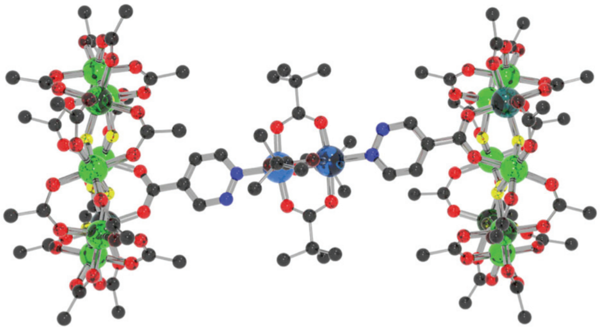

Fig. 15 Structure of **21** in the crystal. Colours and omissions as Fig. 2, Cu = light blue.

The structure of **21** is similar to that of **15**, with the carboxylates of the central copper in plane with the pyridyl moieties and similar Cu–N bond lengths (2.15(2) and 2.160(12) Å). The Cu–N bond distances are shorter than that for pyridazine bound to copper(II) acetate (2.211(3) Å), implying that **3** is a better donor than plain pyridazine. This could either be due to the presence of the ring or the carboxylate group in the *para*-position. Unfortunately, no structure is known for 4-pyridazinecarboxylic acid bound to a dimetalic copper pivalate complex, so a direct comparison with the free carboxylic acid is not possible.

It adopts the same perfectly staggered geometry as **15** with the central dimer also adopting the same geometry with respect to the iso-nicotinate groups with a similar ring centroid – dimer centroid angle of 77.13(3)° and a slightly longer Cu–Cu distance of 2.612(4) Å.

The focus of this paper is the structural chemistry of these materials. Magnetic studies of the substituted rings and linked arrays show variable temperature susceptibility behaviour that matches that of the sum of components. As we have reported previously[9c,10] interactions between such components tend to too weak to measure using conventional magnetometers and very low temperatures are required to measure the exchange interactions directly. Such measurements are only useful if new physics is to be uncovered. We have recently reported the use of double electron–electron resonance spectroscopy[20,21] to study such interactions in other supramolecular species; such studies will be undertaken for some of the compounds reported here in the future.

Conclusions and future perspectives

In summary, we have shown that N-heterocycle functionalised $\{Cr_7Ni\}$ rings can act as Lewis bases towards simple metal salts and metal carboxylate dimers to form linked ring systems. The simplicity of the method, using some of the most basic principles of simple coordination chemistry, coupled with a diverse range of metal salts and carboxylate dimers, means we can produce a range of coordination complexes where functionalised $\{Cr_7Ni\}$ act as bulky ligands. We have established that $\{Cr_7Ni\}$ rings functionalised with different N-heterocycles can all act as bulky Lewis bases, with some subtle variations based on the heterocycle present. This allows a degree of control over the synthesis of linked $\{Cr_7Ni\}$ systems and allows us to work towards the design and realisation of a quantum gate.

This approach to linking $\{Cr_7Ni\}$ furthers its potential for use as a *qubit* in quantum information processing and quantum simulation applications by addressing one DiVincenzo criteria that $\{Cr_7Ni\}$ does not fulfil.[22] Future work will look to the introduction of fully switchable linkers with a look to entanglement of linked $\{Cr_7Ni\}$ in order to implement quantum gate operations. We will also look at introducing hetero-functionality to the $\{Cr_7Ni\}$ in order to fulfil the schematic for a quantum simulator put forward by Santini *et al.*[23]

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References

1 C. B. Simmons, J. R. Prance, B. J. Van Bael, T. S. Koh, Z. Shi, D. E. Savage, M. G. Lagally, R. Joynt, M. Friesen, S. N. Coppersmith and M. A. Eriksson, *Phys. Rev. Lett.*, 2011, **106**, 156804.

2 V. Mourik, K. Zuo, S. M. Frolov, S. R. Plissard, E. P. A. M. Bakkers and L. P. Kouwenhoven, *Science*, 2012, **336**, 1003.

3 R. McConnell, H. Zhang, J. Hu, S. Ćuk and V. Vuletić, *Nature*, 2015, **519**, 439.

4 D. J. Wineland, M. Barrett, J. Britton, J. Chiaverini, B. DeMarco, W. M. Itano, B. Jelenković, C. Langer, D. Leibfried, V. Meyer, T. Rosenband and T. Schätz, *Phil. Trans. R. Soc. Lond. A*, 2003, **361**, 1349–1361.

5 W. F. Koehl, B. B. Buckley, F. J. Heremans, G. Calusine and D. D. Awschalom, *Nature*, 2011, **479**, 84.

6 W. L. Yang, Z. Y. Xu, H. Wei, M. Feng and D. Suter, *Phys. Rev. A*, 2010, **81**, 032303.

7 J. J. L. Morton, A. M. Tyryshkin, R. M. Brown, S. Shankar, B. W. Lovett, A. Ardavan, T. Schenkel, E. E. Haller, J. W. Ager and S. A. Lyon, *Nature*, 2008, **455**, 1085.

8 (*a*) M. Leuenberger and D. Loss, *Nature*, 2001, **410**, 789; (*b*) F. Meier, J. Levy and D. Loss, *Phys. Rev. Lett.*, 2003, **90**, 47901; (*c*) J. Lehmann, A. Gaita-Ariño, E. Coronado and D. Loss, *Nat. Nanotechnol*, 2007, **2**, 312; (*d*) F. Troiani and M. Affronte, *Chem. Soc. Rev.*, 2011, **40**, 3119; (*e*) S. Nakazawa, S. Nishida, T. Ise, T. Yoshino, N. R. Mori, D. Rahimi, K. Sato, Y. Morita, K. Toyota, D. Shiomi, M. Kitagawa, H. Hara, P. Carl, P. Höfer and T. Takui, *Angew. Chem., Int. Ed.*, 2012, **51**, 9860; (*f*) D. Aguilà, L. A. Barrios, V. Velasco, O. Roubeau, A. Repollés, P. J. Alonso, J. Sesé, S. J. Teat, F. Luis and G. Aromí, *J. Am. Chem. Soc.*, 2014, **136**, 14215.

9 (*a*) F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.*, 2005, **94**, 207208(1); (*b*) C. J. Wedge, G. A. Timco, E. T. Spielberg, R. E. George, F. Tuna, S. Rigby, E. J. L. McInnes, R. E. P. Winpenny, S. J. Blundell and A. Ardavan, *Phys. Rev. Lett.*, 2012, **108**, 107204(1); (*c*) G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. A. Muryn, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte and R. E. P. Winpenny, *Nat. Nanotechnol.*, 2008, **4**, 173.

10 (*a*) G. F. S. Whitehead, F. Moro, G. A. Timco, W. Wernsdorfer, S. J. Teat and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2013, **52**, 9932; (*b*) G. F. S. Whitehead, B. Cross, L. Carthy, V. A. Milway, H. Rath, A. Fernandez, S. L. Heath, C. A. Muryn, R. G. Pritchard, S. J. Teat, G. A. Timco and R. E. P. Winpenny, *Chem. Commun.*, 2013, **49**, 7195; (*c*) G. F. S. Whitehead, J. Ferrando-Soria, L. G. Christie, N. F. Chilton, G. A. Timco, F. Moro and R. E. P. Winpenny, *Chem. Sci.*, 2014, **5**, 235; (*d*) A. Chiesa, G. F. S. Whitehead, S. Carretta, L. Carthy, G. A. Timco, S. J. Teat, G. Amoretti, E. Pavarini, R. E. P. Winpenny and P. Santini, *Sci. Rep.*, 2014, **4**, 7423; (*e*) J. Ferrando-Soria, A. Fernandez, E. Moreno Pineda, S. A. Varey, R. W. Adams, I. J. Vitorica-Yrezabal, F. Tuna, G. A. Timco, C. A. Muryn and R. E. P. Winpenny, *J. Am. Chem. Soc.*, 2015, **137**, 7644.

11 (*a*) F. K. Larsen, E. J. L. McInnes, M. H. El, 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; (*b*) E. J. L. McInnes, G. A. Timco, G. F. S. Whitehead and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2015, **54**, 14244.

12 G. Chaboussant, R. Basler, H.-U. Güdel, S. Ochsenbein, A. Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Dalton Trans.*, 2004, 2758.

13 K. O. Abdulwahab, M. A. Malik, P. O'Brien, G. A. Timco, F. Tuna, C. A. Muryn, R. E. P. Winpenny, R. A. D. Pattrick, V. S. Coker and E. Arenholz, *Chem. Mater.*, 2014, **26**, 999.

14 (*a*) Q.-X. Liu, Z.-X. Zhao, X.-J. Zhao, Y. Bi, J. Yu and X.-G. Wang, *CrystEngComm*, 2014, **16**, 7023; (*b*) W.-J. Hu, L.-Q. Liu, M.-L. Ma, X.-L. Zhao, Y. A. Liu, X.-Q. Mi, B. Jiang and K. Wen, *Inorg. Chem.*, 2013, **52**, 9309; (*c*) X. Fang, X. Yuan, Y.-B. Song, J.-D. Wang and M.-J. Lin, *CrystEngComm*, 2014, **16**, 9090; (*d*) J. E. Beves, E. C. Constable, C. E. Housecroft, M. Neuburger and S. Schaffner, *CrystEngComm*, 2008, **10**, 344; (*e*) Q. Zhao, X.-M. Liu, W.-C. Song and X.-H. Bu, *Dalton Trans.*, 2012, **41**, 6683.

15 (*a*) C. Richardson and P. J. Steel, *Inorg. Chem. Commun.*, 1998, **1**, 260; (*b*) C. M. Fitchett and P. J. Steel, *Inorg. Chim. Acta*, 2000, **310**, 127; (*c*) W.-L. Jia, R.-Y. Wang, D. Song, S. J. Ball, A. B. McLean and S. Wang, *Chem. – Eur. J.*, 2005, **11**, 832; (*d*) B. Antonioli, D. J. Bray, J. K. Clegg, K. Gloe, K. Gloe, O. Kataeva, L. F. Lindoy, J. C. McMurtrie, P. J. Steel, C. J. Sumby and M. Wenzei, *Dalton Trans.*, 2006, 4783; (*e*) X. Ma, L.-H. Huo, Z.-P. Deng, T.-P. Liu, H. Zhao and S. Gao, *Inorg. Chem. Commun.*, 2014, **43**, 94.

16 (*a*) L. Chen, L. K. Thompson and J. N. Bridson, *Can. J. Chem.*, 1993, **71**, 1086; (*b*) L. Carlucci, G. Ciani, M. Moret and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1994, 2397.

17 (*a*) S. Belanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson and T. G. Carrell, *J. Am. Chem. Soc.*, 1999, **121**, 557; (*b*) N. M. Shavaleev, A. Barbieri, Z. R. Bell, M. D. Ward and F. Barigelletti, *New. J. Chem.*, 2004, **28**, 398; (*c*) P. de Wolf, P. Waywell, M. Hanson, S. L. Heath, A. J. H. M. Meijer, S. J. Teat and J. A. Thomas, *Chem. – Eur. J.*, 2006, **12**, 2188.

18 (*a*) F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 600; (*b*) K. Aoki, M. Inaba, S. Teratani, H. Yamazaki and

Y. Miyashita, *Inorg. Chem.*, 1994, **33**, 3018; (*c*) M. Handa, T. Nakao, M. Mikuriya, T. Kotera, R. Nukada and K. Kasuga, *Inorg. Chem.*, 1998, **37**, 149; (*d*) J. F. Berry, F. A. Cotton, C. Lin and C. A. Murillo, *J. Cluster Sci.*, 2004, **15**, 531; (*e*) D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Dalton Trans.*, 2011, **40**, 7403.

19 (*a*) G. Speier and V. Fulop, *J. Chem. Soc., Dalton Trans.*, 1989, 2331; (*b*) C. B. Aakeröy, A. M. Beatty, J. Desper, M. O'Shea and J. Valdes-Martinez, *Dalton Trans.*, 2003, 3956; (*c*) A. Karmakar, K. Bania, A. M. Baruah and J. B. Baruah, *Inorg. Chem. Commun.*, 2007, **10**, 959; (*d*) A. V. Yakovenko, S. V. Kolotilov, O. Cador, S. Golhen, L. Ouahab and V. V. Pavlishchuk, *Eur. J. Inorg. Chem.*, 2009, 2354; (*e*) M. Fontanet, A.-R. Popescu, X. Fontrodona, M. Rodriguez, I. Romero, F. Teixidor, C. Viñas, N. Aliaga-Alcalde and E. Ruiz, *Chem. – Eur. J.*, 2011, **17**, 13217.

20 A. Ardavan, A. Bowen, A. Fernandez, A. Fielding, D. Kaminski, F. Moro, C. A. Muryn, M. Wise, A. Ruggi, E. J. L. McInnes, K. Severin, G. A. Timco, C. Timmel, F. Tuna, G. F. S. Whitehead and R. E. P. Winpenny, *NPJ Quantum Information*, 2015, **1**, 15012.

21 A. Fernandez, J. Ferrando-Soria, E. M. Pineda, F. Tuna, I. J. Vitorica-Yrezabal, C. Knappke, J. Ujma, C. A. Muryn, G. A. Timco, P. E. Barran, A. Ardavan and R. E. P. Winpenny, *Nat. Commun.*, 2015, DOI: 10.1038/ncomms10240.

22 D. Loss and D. P. DiVincenzo, *Phys. Rev. A*, 1998, **57**, 120.

23 P. Santini, S. Carretta, F. Troiani and G. Amoretti, *Phys. Rev. Lett.*, 2011, **107**, 230502.