Synthesis and characterisation of a $\{Ni_{21}Ag\}$ cage

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An unusual $\{Ni_{21}Ag\}$ cluster is reported and demonstrates the importance of examining the "counter-ion" present in all reactions involving polymetallic complexes.

It is a clear goal of scientists pursuing the synthesis of polymetallic cage complexes to be able to control and predict the likely product of any reaction. Often this control is achieved by use of rigid polydentate ligands,[1,2] and on other occasions by use of a suitable template.[3,4] Particularly relevant here is work from Saalfrank,[4] where it has been shown that by choice of alkali metal – either sodium or caesium, a metallocrown can be made with either six or eight metal ions in the backbone of the crown. Unfortunately the number of occasions where such an approach is successful is limited, and there is a danger that if we restrict ourselves to the few reactions we understand fully, we will miss much exciting and beautiful chemistry.

We have been studying the reaction of the dinuclear nickel complex, $[Ni_2(H_2O)(piv)_4(Hpiv)_4]$ **1** (Hpiv = pivalic or trimethylacetic acid), with pyrazolinone ligands (Hxpo, see Scheme 1 for Hfpo).[5,6] In a typical reaction, **1** and a suitable Hxpo ligand are mixed in the presence of a metal base, *e.g.* NaOMe. We have shown that the resulting product depends strongly on the s-block metal present, *e.g.* $\{Ni^{II}_5Na^{I}_4\}$ in the presence of Na^I,[5] but $\{Ni^{II}_8M^{II}\}$ with M^{II} = Ba^{II} or Sr^{II}.[6] Here we show that changing the second metal to Ag^I results in a very dramatic change in the nuclearity and structure of the resulting cage.

Mixing of complex **1** (600 mg, 0.63 mmol), Hfpo† (96 mg, 0.63 mmol) and $AgClO_4$ (33 mg, 0.16 mmol) in MeOH (40 mL) gave a green solution that was evaporated to dryness after stirring for 1 h. The resulting green solid was redissolved in MeCN (20 mL), from where green crystals formed after three weeks. The product was found to be, reproducibly, the heterometallic cluster $[Ni_{21}Ag(\mu_4\text{-}OH)_4(\mu_3\text{-}OH)_6(fpo)_{13}(piv)_{20}(Hpiv)_4(MeCN)_{3.5}(H_2O)_{0.5}]$ **2**, as determined crystallographically and by elemental analysis.‡ The pivalate acts as the base in this reaction. The presence of pivalate ligands and trifluoromethyl groups in the structure leads to significant disorder in the X-ray structure (see below).§

Scheme 1 Two tautomeric forms of Hfpo.

The irregular structure of **2** can be envisaged as the letter "m" (Fig. 1), with the Ag^I centre at the tip of the central line of the "m" with the twenty-one Ni^{II} atoms forming the outer curve. The Ag site has a typical coordination geometry, with two N-atoms bound at *ca.* 2.15 Å and with a N–Ag–N angle of 163°; there are two longer contacts to O-atoms (2.54 and 2.64 Å), with the O–Ag bonds almost perpendicular to the N–Ag–N vector.

The outer lines of the "m" each contain ten nickel centres, and are structurally similar (Fig. 2). Each side-arm contains two $\{Ni_4(\mu_4\text{-}OH)\}$ "squares" linked to each other and to additional Ni sites through μ_3-OH groups. Beginning at the tip of each side-arm, the first μ_3-OH bridges between a Ni(II) site and a $\{Ni_4(\mu_4\text{-}OH)\}$ unit, the second μ_3-OH links the two squares in the side-arm, and the third attaches a further nickel to the second square. In terms of Ni centres this generates a 1 : 4 : 4 : 1 array in each arm; the twenty-first Ni centre links these two side-arms. While we have seen μ_3-OH in this chemistry previously,[5,6] the array found here does not resemble the cores found with either alkali or alkaline earth metal bases.

As for the organic ligands, there are three bridging locations displaying positional disorder and occupied by either fpo or piv respectively with fpo/piv ratios of 0.5/0.5, 0.6/0.4 and 0.4/0.6, respectively. The formulation given above for **2** corresponds to the major component.¶ These ligands show a range of coordination modes. Fpo shows four modes: nine fpos bind in the 3.210 mode (Harris notation[10]), one in the 4.310 mode, one in the 2.011 mode and two in the 3.201 mode, with the N-donor bound to the Ag centre. Pivalate also shows four modes: eleven bind as 2.11, six as 3.21, two as 2.20 and one as 2.21. The four Hpiv ligands are all bound to a single Ni centre through a single O-atom. There are also four terminal solvent molecules: three MeCN and one site that is 50 : 50 MeCN : H_2O.

Bulk magnetization data from complex **2** were collected under constant magnetic fields (300 or 5000 G) in the 2–300 K temperature range.|| The data are represented in Fig. 3 as $\chi_M T$ *vs.* T plots (where χ_M is the paramagnetic susceptibility), which are superimposable for both fields, and have been corrected for a temperature independent paramagnetism (TIP) parameter of 21×10^{-4} cm^3 mol^{-1}. At room temperature, the value of $\chi_M T$ equals 26.0 cm^3 K mol^{-1}, very close to that expected for 21 magnetically uncoupled Ni^{II} centers in the $^3A_2$ ground state ($S = 1$) with $g = 2.2$ (25.4 cm^3 K mol^{-1}). This value diminishes with decreasing temperature until a small plateau near 7 cm^3 K mol^{-1} in the approximate range of 10–20 K, followed by a sharp drop down to a value 4.4 cm^3 K mol^{-1} at 2 K. This behaviour indicates the presence of predominantly antiferromagnetic interactions within the cluster, to reach a non-diamagnetic ground state with a relatively low spin number. The position of the plateau at low

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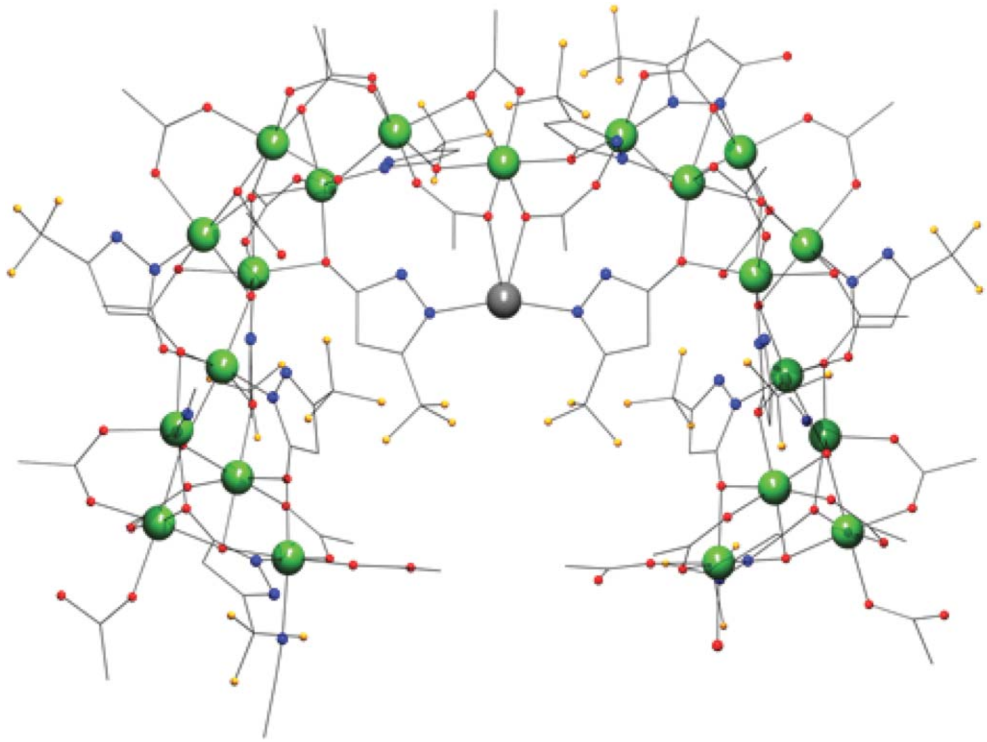

Fig. 1 Povray representation of the major component of **2**. H atoms and Me groups from pivalate have been removed for clarity. Code for atoms: green, Ni; gray, Ag; red, O; blue, N; orange, F; rest, C.

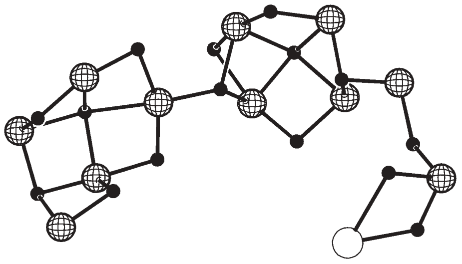

Fig. 2 [$Ni_{10}O_{12}$] core of each side-arm of **2** attached through an oxygen atom to the central [$NiAgO_2$] moiety that links both arms of the cluster.

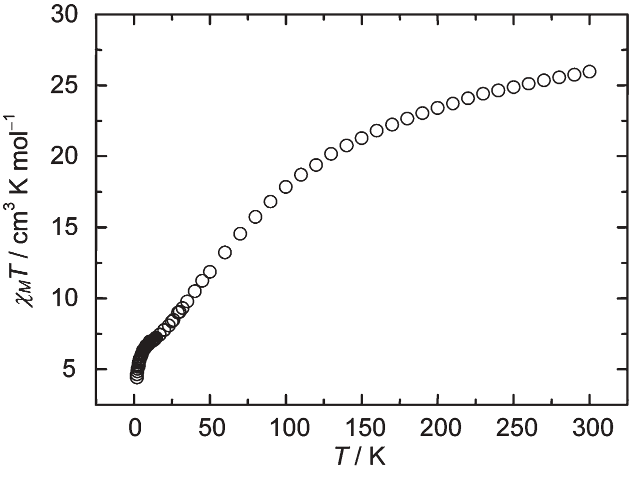

Fig. 3 Plot of $\chi_M T$ *vs.* T per molecule of **2**.

temperature suggests a spin ground state of $S = 3$ (expected value: 7.3 cm^3 K mol^{-1} for $g = 2.2$). There is a very large number of ways in which the different Ni^{II} centers can interact to lead to such a ground state spin number. The drop at the lowest temperatures is most likely due to the effect of zero field splitting or the presence of intermolecular antiferromagnetic ordering. Magnetization measurements with **2** were performed at 2 K and variable field up to 5 T. The plot of reduced magnetization ($M/N\mu_B$) *vs.* H does not help to confirm the $S = 3$ ground state. With a value of 9.0, $M/N\mu_B$ has not reached saturation at the strongest field, being higher than expected for the asymptotic value of this ground state (6.6 for $g = 2.2$). This is probably caused by gradual population of closely lying higher multiplicity states, since they might become more stable as the field increases.

Compound **2** is only the second synthesized Ni^{II} cluster with a nuclearity of 21.[11] The first such complex is an aggregate where the Ni ions are assembled by a combination of citrate and OH$^-$ ligands. To our knowledge, the only coordination cage containing more Ni^{II} ions is a [Ni$^{II}_{24}$] wheel.[12] The difference between **2** and the nonanuclear cages that result if s-block metals are present is dramatic, and impossible to rationalise. One possible explanation is that the "soft" Ag^I ion requires N-donor atoms, and this causes the Ni–fpo array to wrap around the silver. This suggests a general method for "templating structures" using ambidentate ligands and a mixture of hard/soft metal ions. It is also noticeable that much larger cages – {Ni_{24}}[12] and {Ni_{21}} – result in the absence of s-block metals: again something that needs to be considered when larger 3d-block metal clusters are targeted.

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Notes and references

† Hfpo = 3-trifluoromethyl-3-pyrazolin-5-one.

‡ Anal. Calcd (Found) for **2** (−2 MeCN)[a]: C, 35.2 (35.2); H, 4.5 (4.5); N, 6.4 (6.2). [a] Loss of solvate MeCN molecules upon exposure to air is expected among these complexes (see ref. 6).

§ The disorder also affected the occupation of some positions on Ni by either piv^- or fpo^-. The formula of **2** represents the major component, whereas the true composition is reflected by the crystallographic formula above.

¶ Crystal data for $[\text{Ni}_{21}\text{Ag(OH)}_{10}(\text{fpo})_{12.5}(\text{piv})_{20.5}(\text{Hpiv})_4(\text{MeCN})_{3.5}(\text{H}_2\text{O})_{0.5}]\cdot0.75\ \text{MeCN}\cdot0.25\ \text{MeOH}$ ($\text{C}_{181.25}\text{H}_{274.25}\text{AgF}_{37.50}\text{N}_{29.25}\text{Ni}_{21}\text{O}_{72.25}$): monoclinic, $P2_1/c$, a = 48.308(3), b = 15.6944(10), c = 38.405(2) Å, β = 106.099(2)°, V = 27975(3) Å^3, M = 6072.3, Z = 4, T = 150(2) K, $R1$ = 0.1401. Data collection, structure solution and refinement used programs SMART,[7] SAINT[7] and SHELXL.[8] Figures were produced using SCHAKAL.[9] Full details have been deposited and will be published later. CCDC 266644. See http://www.rsc.org/suppdata/cc/b5/b503712c/ for crystallographic data in CIF or other electronic format.

‖ Variable temperature magnetic measurements on **2** (8.6 mg) in the region 2–300 K were made using an MPMS-XL SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 300 or 5000 G field. The data have been adjusted for the diamagnetism of the sample using Pascal's constants.

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