Synthesis, structure and magnetic properties of a decametallic Ni single-molecule magnet

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Ferromagnetic exchange between the ten Ni^{2+} ions in the complex [Ni$_{10}$(tmp)$_2$(N$_3$)$_8$(acac)$_6$(MeOH)$_6$] leads to a spin ground state of S = 10; single crystal M *vs.* H studies reveal the temperature and sweep rate dependent hysteresis loops expected for a single-molecule magnet.

The majority of single-molecule magnets (SMMs) characterised to date have contained the metal manganese.[1] The reason for this is the rather unusual combination of the large spin ground states often displayed by Mn clusters and the single-ion anisotropy associated with the presence of Jahn–Teller distorted Mn^{3+} ions. SMMs containing Ni^{2+} ions are far less common despite the fact that mononuclear nickel complexes have been shown to possess $|D|$ values greater than 10 cm^{-1}.[2] To date the only Ni^{2+} SMMs are [Ni$_{12}$(chp)$_{12}$(O$_2$CMe)$_{12}$(thf)$_6$(H$_2$O)$_6$],[3] [Ni(hmp)(ROH)Cl]$_4$,[4] [Ni(H$_2$thme)(MeCN)]$_4$(NO$_3$)$_4$,[5] [Ni$_{21}$(cit)$_{12}$(OH)$_{10}$(H$_2$O)$_{10}$]Na$_2$(NMe$_4$)$_{14}$,[6] and [Ni$_8$Na$_2$(N$_3$)$_{12}$(^{t}BuPhCO$_2$)$_2$(mpo)$_4$(Hmpo)$_6$(EtOAc)$_6$].[7]

We have been exploring the reactivity of tripodal alcohols such as 1,1,1-tris(hydroxymethyl)ethane (H$_3$thme), 1,1,1-tris(hydroxymethyl)propane (H$_3$tmp) and their analogues in the synthesis of SMMs and have now extended this work to include the azide ligand. It is now well known that end-on bridging azide ligands often mediate ferromagnetic exchange between paramagnetic centres[8] and magnetostructural correlations between the strength of the interaction and the M–N–M angle in these bridges have now been reported for both Cu^{2+} and Mn^{2+}.[9,10] This property has recently started to be exploited in the preparation of SMMs—elegant examples of which include the synthesis of a [Fe$_9$] cluster[11] in which μ_4-OH$^-$ ions are deliberately replaced by μ_4-N$_3^-$ ions, and in the synthesis of a [Mn$_{25}$] cluster that possesses a spin ground state of $S = 51/2 \pm 1$.[12]

Reaction of Ni(acac)$_2$ with one equivalent of H$_3$tmp and NaN$_3$ in CH$_2$Cl$_2$/MeOH (1 : 1) produces a green solution from which crystals of [Ni$_{10}$(tmp)$_2$(N$_3$)$_8$(acac)$_6$(MeOH)$_6$]·H$_2$O (**1**·H$_2$O) are obtained upon slow evaporation during one week. Complex **1**†‡ (Fig. 1) crystallises in the monoclinic space group $P2_1/n$. The core of the complex contains a planar disc-like [Ni$_{10}$O$_{10}$N$_8$]$^{2+}$ unit held together by a combination of tmp^{3-} and N$_3^-$ ligands and comprises a total of ten edge-sharing [Ni$_3$] triangles. The two tripodal ligands sit in the centre of the cluster above and below the [Ni$_{10}$] plane with each oxygen arm bridging in a μ_3-fashion such that each tmp^{3-} ligand bridges a total of six Ni ions. The azides are all *end-on* and are of two types: those in the centre of the cluster bridge in a μ_3-fashion while those around the periphery of the cluster bridge in a μ_2-fashion. The six acac$^-$ ligands surround the outside of the cluster and are also of two types: two adopt their

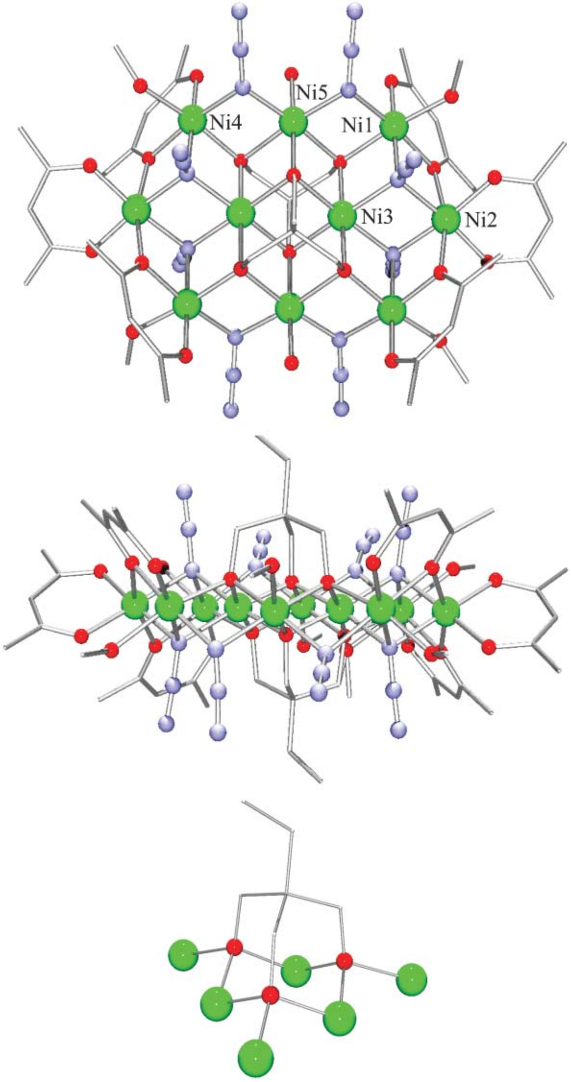

Fig. 1 The structure of complex **1** viewed perpendicular (top) and parallel (middle) to the [Ni$^{II}_{10}$] plane. The bridging mode of the tmp^{3-} ligand (bottom).

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Table 1 The M–X–M bridging angles present in complex **1**

	μ_3-N	μ_2-N	μ_3-O	μ_2-O
Angle range/°	94.5–98.7	96.7–98.2	92.3–96.4	98.4–98.1

more usual mode in simply chelating one Ni^{2+} ion, while the remaining four bridge two metal ions in the more unsual η^1,η^2,μ_2-mode. All of these bridging angles are summarized in Table 1. The coordination geometries of Ni1, Ni4 and Ni5 are completed by terminal MeOH molecules.

The core of complex **1** is reminiscent of the hexagonal close-packed structure present in CdI_2 and of the cores found in (amongst others) [Mn_7],[13] [Mn_{13}],[14] [Fe_{19}],[15] [Mn_{21}],[16] [Co_{24}][17] and [Ni_{21}].[6]

Variable temperature dc magnetic susceptibility data were collected on **1** (Fig. 2) in the temperature range 300–2.0 K in an applied field of 0.3 T. The room temperature $\chi_M T$ value of approximately 16 cm^3 K mol^{-1} slowly increases upon cooling to approximately 100 K where it then increases rapidly to a maximum value of approximately 58 cm^3 K mol^{-1} at 10 K before dropping back to approximately 30 cm^3 K mol^{-1} at 2.0 K. The room temperature value (g = 2.2) expected for a [Ni^{II}_{10}] unit is approximately 12 cm^3 K mol^{-1}. This behaviour is indicative of ferromagnetic exchange between the metal centres resulting in a S = 10 ground state-which would give a $\chi_M T$ value of approximately 66 cm^3 K mol^{-1}. The low temperature decrease is assigned to zero-field splitting (zfs), Zeeman effects and/or intermolecular antiferromagnetic interactions.

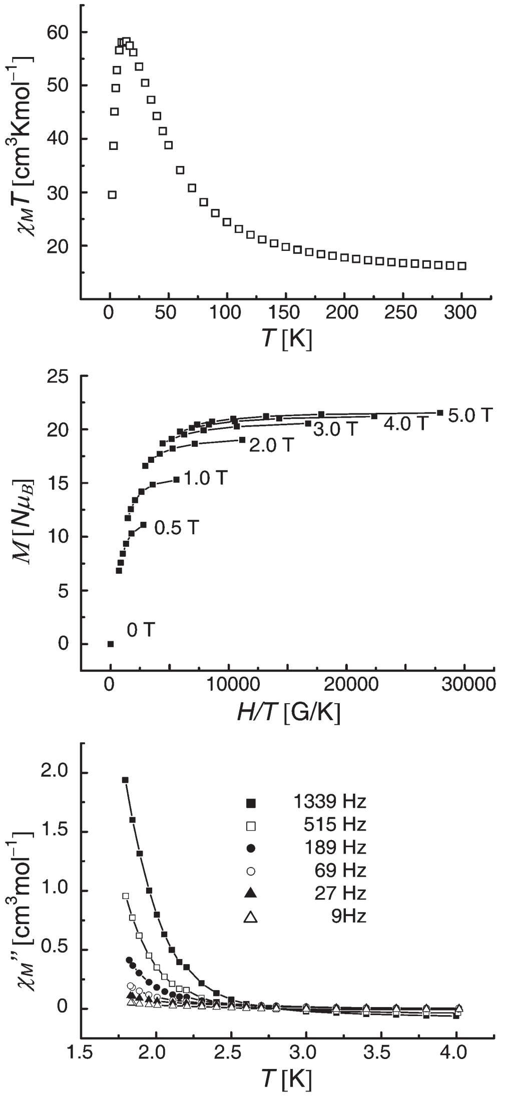

Fig. 2 Plot of $\chi_M T$ *vs.* T for complex **1**·0.5H_2O measured in the temperature range 2.0–300 K in a field of 0.3 T (top); plot of reduced magnetisation ($M/N\mu_B$) *vs.* H/T in the ranges 1.8–6.8 K and 0–5 T (middle); plot of out-of-phase ac susceptibility in the 4.0–1.8 K temperature range (bottom). The solid lines are a guide to the eye only.

In order to determine the spin ground state for complex **1**, magnetisation data were collected in the ranges 0–50 kG and 1.8–6.8 K and these are plotted as reduced magnetisation ($M/N\mu_B$) *vs.* H/T in Fig. 2. For a complex entirely populating the ground state and experiencing no zero-field splitting, the observed isofield lines should superimpose and saturate at a value ($M/N\mu_B$) equal to gS.

The data show that saturation occurs for a value slightly above 20 and that the various isofield lines do not superimpose, clearly indicating the presence of a S = 10 ground state with appreciable zfs. Given the magnitude of S, ac susceptibility studies were carried out in the 1.8–4.0 K range in a 4.0 G field oscillating at frequencies

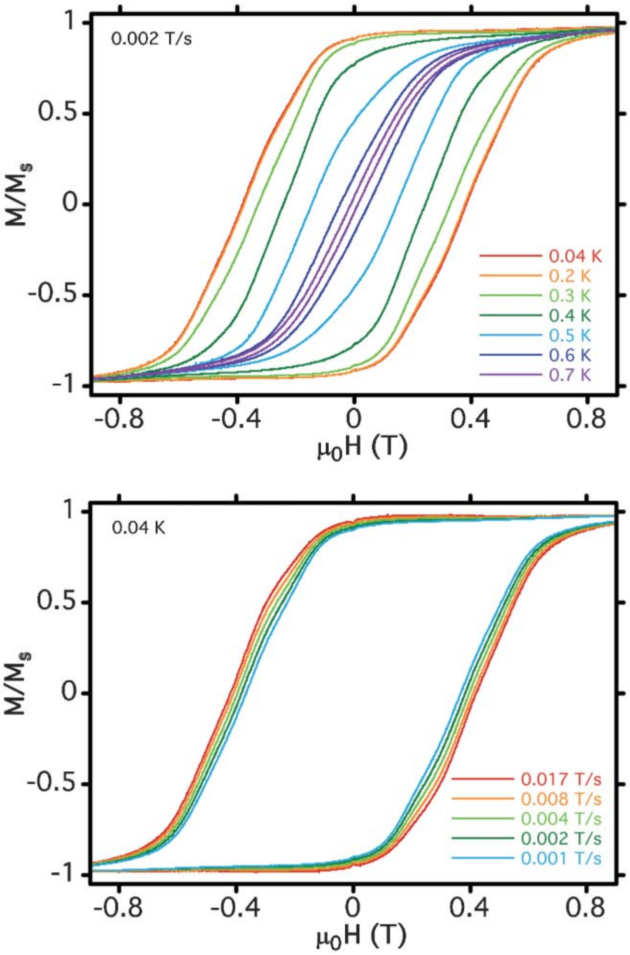

Fig. 3 Single crystal magnetisation (M) *versus* field (H) hysteresis loops for complex **1** at the indicated field sweep rates and temperatures; the magnetisation is normalised to its saturation value.

up to 1339 Hz. Frequency-dependent out-of-phase ac susceptibility signals were seen below approximately 2.5 K (but no peaks were observed) along with a concomitant decrease in the in-phase signal. The magnitude of the in-phase $\chi'_M T$ *vs.* T signals at >3 K supports the aforementioned spin ground state.

In order to probe the possible SMM behaviour further, single crystal hysteresis loop and relaxation measurements were performed using a micro-SQUID setup.[18] Fig. 3 presents typical magnetization (M) *vs.* applied dc field (H) measurements at various field sweep rates and temperatures. Hysteresis loops were observed whose coercivity was strongly temperature and sweep rate dependent, increasing with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic-like behaviour of a SMM.

Relaxation data were determined from dc relaxation decay measurements. First a large dc field of 1.4 T was applied to the sample at 5 K to saturate the magnetisation in one direction and the temperature lowered to a specific value between 1.8 and 0.95 K. When the temperature was stable the field was swept from 1.4 T to zero at a rate of 0.14 T s^{-1} and the magnetisation in zero field measured as a function of time. This allows the construction of an Arrhenius plot that yields a value for the effective energy barrier for the reorientation of the magnetisation of $U_{\mathrm{eff}} \approx 14$ K—among the largest known for any Ni SMM.

In conclusion, complex **1** possesses one of the largest known spin ground states for any Ni cluster and is a rare example of a ferromagnetic Ni SMM. The combination of tripodal alcohols and azide ligands with paramagnetic metal ions thus promises to deliver many new and exciting clusters.

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Notes and references

† Complex **1** analysed (C, H, N) as **1**·0.5H_2O. Crystals were kept in contact with mother liquor to avoid solvent loss and were crystallographically identified as **1**·H_2O.

‡ Diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. The structure[19] is disordered about an inversion centre. The tmp based on C11 is half-occupied; the symmetry-related position was modelled as being occupied by 2 azides and a methoxide. Crystal data: $C_{43}H_{84}N_{30}Ni_{10}O_{24}$, M = 1992.50, green blocks, monoclinic, *P*21/*n*, a = 10.8253(6), b = 14.5088(8), c = 24.9691(13) Å, β = 91.851(4)°, V = 3919.7(4) Å^{-3}, Z = 2, μ = 2.430 mm^{-1}, 72251 reflections collected of which 6897 were independent (R_{int} = 0.0668), 476 parameters and 24 restraints, R_1 = 0.0758 [based on $F > 4\sigma(F)$], wR_2 = 0.2012 (based on F^2 and all data). CCDC 278999. See http://dx.doi.org/10.1039/b510097f for crystallographic data in CIF or other electronic format.

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