SMM behaviour and magnetocaloric effect in heterometallic 3d-4f coordination clusters with high azide : metal ratios

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We present the synthesis and characterization of heterometallic compounds with a very large azide to metal ratio. Their interesting structure gives rise to fascinating magnetic properties.

Azide is a fascinating ligand attracting interest due to its many applications including molecular magnetism. When azide couples two paramagnetic metals in an end-to-end (µ1,1-N3) fashion antiferromagnetic interactions are favoured. When it couples in an end-on way (µ1,1-N3) ferromagnetic interactions dominate over a broad angle range. The discovery that the magnetic interactions in azide bridged compounds are easily controlled has led to the synthesis of a wide variety of homometallic compounds ranging from discrete clusters to 3d frameworks exhibiting interesting magnetic and multiferroic properties. Since a high spin ground state is a crucial component for Single Molecule Magnets (SMMs) formed from ions without strong spin orbit coupling, azide ligands have been extensively used in this field. Especially in heterometallic 3d 4f compounds the use of the azido ligand’s end-on bridging mode is attractive because it is a controlled way to induce ferromagnetic interactions between the transition metals. These kind of ferromagnetic interactions in 3d 4f compounds are not only attractive in Single Molecule Magnets but also in magnetic coolers, where a high spin ground state drives higher entropy changes in adiabatic cooling processes. However, the synthesis of heterometallic coordination compounds containing bridging azide is tricky because the chelating bridging ligands used in these compounds are in competition with non-chelating azide anions, often resulting in compounds with terminal azido ligands. In order to achieve compounds with a high azide content and, if possible, including bridging azides, we used stable homoleptic azidotribates of iron and manganese in combination with lanthanide salts and aminoalcohols. We were able to obtain two structurally different coordination compounds with a very high metal to azide ratio: TBA[Fe2Gd12(N3)15(OH)3(tipaH3)2] 1 (5:15) (TBA = Tetrabutylammonium and tipaH3 = triisopropanolamin) and TBA2[Mn4Dy2(2eAH3)(N3)12] (teAH3 = triethanolamin) (6:12). Indeed compound 1 has the highest azide content in a discrete cluster seen so far. Compound 1 crystallises in the triclinic space group P1 with Z = 2. The crystal structure consists of the anionic coordination cluster [Fe2Gd12(µ3-OH)3(µ-N3)14(N3)11(tipaH3)2]3+ surrounded by three tetrabutyl ammonium cations. The cluster core can be considered as three Gd2Fe(µ3-OH)3 triangles sharing their Gd-Gd edges to give a Fe2Gd2 trigonal-bipyramidal core with the two GdIII ions at the apices and the three FeII ions describing the central triangular plane. Within the Gd2Fe(µ3-OH)3 triangles, the Fe-O and Gd-O bond lengths lie in the range 2.0659(17)-2.0857(17) Å and 2.3984(18)-2.4882(17) Å, while the Gd-O-Gd and Gd-O-Fe angles are 96.71(6)-97.75(6)° and 108.80(7)-124.71(8)°, respectively. Each Gd is chelated by a neutral (tipaH3) ligand. The tipaH3 ligand was racemic, but every molecule demonstrates a chiral separation with an S,S,S and a R,R,R configuration at each of the GdIII centres. This [Fe2Gd12(µ3-OH)3(tipaH3)2]3+ core approximates to C3v symmetry, but broken by the azide ligands. Each Fe centre is ligated by five azides resulting in slightly distorted octahedral NSO coordination environments and each bridge to one of the Gd centres. Six such bridges would maintain the C3v symmetry, but would require each Gd to be ten-coordinate. Three of the azide bridges (involving N(11), N(21) and N(41) have similar geometries, with Fe-N 2.048(2)-2.145(2) Å, Gd-N 2.525(2)-2.597(2) Å and Fe-N-Gd 102.93(9)-106.79(9)°. Gd(1)-N(31) is
longer at 2.853(3) Å and this bond is shown dashed in Figure 1; other Gd-N distances are all over 3 Å. The hydroxyl groups of the organic ligands each form a hydrogen bond to a non-bridging azide ligand, adding stability to the structure.

Solid state direct current (dc) magnetic susceptibility data on dried analytically pure samples of 1 and 2 were collected between 1.8 – 300 K in an applied field of 0.1 T (Figure 3, Table 1, Figure S3 – S6).

For both complexes the experimental values at 300 K are close to the theoretical values for non-interacting metal ions of 29.3 cm³ K mol⁻¹ for 1 and 42.42 cm³ mol⁻¹ for 2. In the case of 1 the χT product is almost constant down to 50 K, below which it rises to a value of 97.6 cm³ mol⁻¹ K at 2 K, which can be compared to the theoretical value for a fully ferromagnetic S = 29/2 ground state of 112.3 cm³ mol⁻¹ K, indicating that most or all of the interactions between the spin centres are ferromagnetic. In order to quantify this behaviour a Heisenberg type spin Hamiltonian was employed for the fit of the data with PHIL. To avoid overparametrisation the six J_{Gd} are constrained to be equal:

\[ \hat{H} = -2 \left( \hat{S}_{Gd} \hat{J}_1 \hat{S}_{Gd} \right) - 2 \left( \hat{S}_{Fe} \hat{J}_1 \hat{S}_{Fe} \right) + g_{Gd} \mu_B \hat{S}_{Gd} + g_{Fe} \mu_B \hat{S}_{Fe} \]

In the case of 2 the χT value drops slightly to a value of 38.28 cm³ mol⁻¹ K at 48 K after which it drops more rapidly to a value of 13.56 cm³ mol⁻¹ K at 1.8 K. This behaviour is likely to result from a combination of the depopulation of excited states and weak antiferromagnetic interactions. This is typical for the Mn^{II}–2Azide butterfly motif at the centre of the structure. Studies of the magnetisation (M) of 1 at different fields and temperatures gives a saturation value of 28.2 µB at 2 K and 7 T consistent with the maximum spin ground state of S = 29/2.

Table 1 Summary of the magnetic data of 1

| χT(295 K) | 29.3 cm³ K mol⁻¹ |
| 28.3 µB |
| 1.94 |
| 0.011 cm⁻¹ (0.016 K) |
| 0.267 cm⁻¹ (0.38 K) |

Table 1: Summary of the magnetic data of 1.
(Figure S3). This large value makes 1 a possible candidate for use in magnetic cooling devices. The magnetocaloric effect (MCE) can be evaluated from the magnetisation data (Figure 4) using the Maxwell equation to relate the entropy change with changes in magnetisation:

\[ \Delta S(T, \Delta H) = \int \frac{\delta M(T, H)}{\delta T} dH \]

The maximum entropy change is 21.1 J Kg\(^{-1}\) K\(^{-1}\) at a field change of 7 T and a temperature of 6 K.

The potential maximum entropy change is 34.4 J Kg\(^{-1}\) K\(^{-1}\). The difference between the calculated and observed value might be the result of a small but significant anisotropy of the Fe\(^{III}\) ions.\(^{14}\) Since the core-structure contains a ferromagnetically coupled Gd\(_2\) unit it is instructive to compare the MCE of 1 with that of other compounds carrying such a unit.\(^{8}\) Compared to the maximum entropy change seen in Gd dinuclear compounds the value is in the low range and clearly surpassed by e.g. Gd\(_2\)(OAc)\(_6\)(H\(_2\)O)\(_4\) which has an entropy change value of 66.5 J Kg\(^{-1}\) K\(^{-1}\).\(^{11c}\) However, an advantage of compound 1 is the fact that it reaches its maximum entropy change already at 6 K, compared to a \(T_{\text{max}}\) of about 1 K for the pure Gd compounds. This is related to the strength of the Gd-Fe coupling which is essentially twenty times larger than the Gd-Gd interactions. Thus 3d-4f coupling offers the means for tuning \(T_{\text{max}}\) and therefore the attainable liquefaction temperature for cryogens. In order to probe the anisotropic nature of 2 we performed alternating current (ac) susceptibility measurements. These show temperature and frequency dependent signal between 1 to 1500 Hz and 1.8 to 3.8 K. (Figure 5) A striking feature of these plots is the onset of a second signal at low temperatures, but with no clear maxima in the accessible frequency range. To determine the height of the energy barrier against the reversal of magnetization the positions of the frequency dependent maxima were fitted to an Arrhenius law (Figure S6). Given an energy barrier of 43.8 K with a pre-exponential relaxation factor of \(1.47 \times 10^{10}\) s\(^{-1}\). There is clearly more than one relaxation process, as seen from the Cole-Cole plot resulting from the in-phase vs. out-of-phase susceptibility, where two relaxation processes are obvious, but the second relaxation process does not achieve a full semicircle. Between 2.2 and 2.4 K both relaxation processes can be accessed.

Since they show a frequency dependent behaviour, QTM is an unlikely source for the second relaxation process, reminiscent of the situation for Co\(^{II}\)Dy\(^{III}\) butterflies.\(^{9}\) Due to the strong spin orbit coupling of the Dy\(^{III}\) ions a fit of the magnetic properties is impossible. However, the weak magnetic interactions between the 3d and 4f metal ions allow for an analysis of different parts of the structure. The strongest interactions are expected to be found in the central (Mn\(^{II}\)\(_2\)) unit. Their Jahn-Teller axis are perpendicular to the bridging plane so that mostly dx\(^2\)-y\(^2\) orbitals take part in the coupling of the two ions. Jones et al. defined this kind of bridging as a type 1 bridge for which antiferromagnetic interactions between J = -8.2 cm\(^{-1}\) and J = -15.5 cm\(^{-1}\) are to be expected.\(^{10}\) This (Mn\(_2\)) unit is part of the (Mn\(_2\)Dy\(_2\)) butterfly core. In the literature several Mn\(^{II}\)Dy\(_2\) structures with a similar motif are known,\(^{11}\) however the interactions between the spin centres differ greatly from strong antiferromagnetic interactions\(^{11d,e}\) to ferromagnetic interactions\(^{11c}\) with only one compound showing slow relaxation of the magnetisation with an energy barrier of 29 K.\(^{11f}\) Thus it is more likely that the high temperature regime relaxation results from the whole molecule whereas at low temperature individual ion processes may dominate.
Conclusions
In conclusion we present two new heterometallic coordination compounds containing a very high azide to metal ratio. These compounds were synthesised from the reaction of homoleptic azidometallate precursors with tripodal ligands and lanthanide salts. In both compounds the interactions through the bridging azides cause interesting magnetic effects. In compound 1, with a Fe₄Gd₂ core with 15 coordinating azides, the interactions between the metal centers are ferromagnetic. This leads to a high spin ground state of S = 29/2. This high spin ground state can be used in devices for magnetic cooling. There is a high maximum entropy change of 21.1 J K⁻¹ K⁻¹ at a field change of 7 T and a temperature of 6 K. On the other hand the Mn₈Dy₃ compound proves to be the first example of a Mn₈-Dy SMM showing more than one relaxation processes.

Conflict of Interest
There are no Conflicts to declare.

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Notes and references


