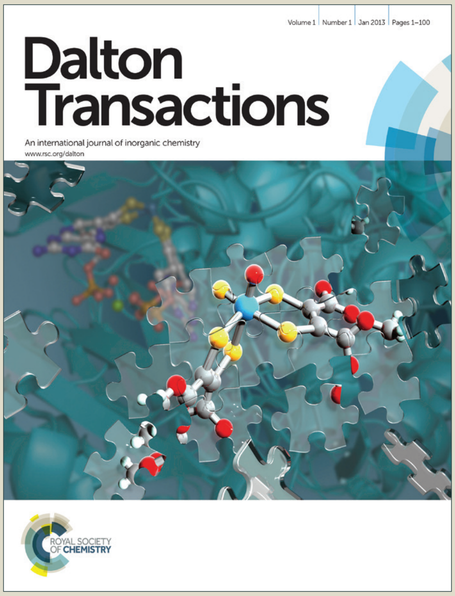
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Ligand field variations: Tuning the toroidal moment of Dy_6 rings

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Two new examples of Dy_6 cyclic coordination clusters have been synthesised in order to discover how the toroidal moment in such a motif can be tuned and optimised.

Cyclic coordination clusters (CCCs) of paramagnetic centres can show fascinating molecular-based magnetic properties arising from the quantum regime. Examples include molecules acting as qubits,[1] molecules exemplifying the molecular realisation of the non-collinear arrangement of Ising spins for a triangle of metal ions,[2] and molecules displaying toroidal moments,[3] the latter being of particular interest in the area of molecular multiferroic materials.[4]

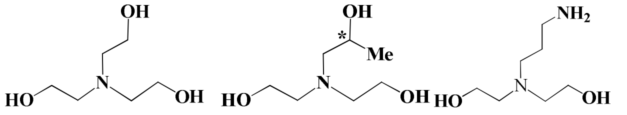
For example, homometallic CCCs containing 3d ions such as Fe^{III} or Cr^{III} have provided a rich playground for chemists and physicists.[5] Wheels composed of repeating units which are connected to each other as cyclic finite chains are particularly fascinating as demonstrated for the recently reported four-dimensional mapping of the spin correlation of an octanuclear Cr^{III} ring.[6] In contrast, only a few CCCs containing 4f ions have been reported; examples include Ln_6, Ho_{12} and Dy_{10}.[7]

Amongst such 4f CCCs, Murray, *et al.*, reported the synthesis of $\{Ln_6\}$ wheels obtained by reacting triethanolamine (H_3tea) with lanthanide nitrates in methanol and in presence of triethylamine as base.[7] It was demonstrated that the Dy congener, $[Dy_6(teaH)_6(NO_3)_6]\cdot 8MeOH$ **(1)** is a SMM.[7a] However, a peculiarity of this $\{Dy_6\}$ compound is that the combination of single-ion uniaxial anisotropy and magnetic interaction between different centres gives rise to a toroidal moment arrangement in the zero-field ground state.[3a] Although there are some examples of molecules with such non-collinear magnetic arrangements in the literature, this molecule is especially interesting since the very high molecular symmetry (S_6) ensures that the ground-state magnetic moment is purely toroidal in that all the dipolar components cancel out exactly. Furthermore, this also means that the hint of slow magnetic relaxation visible in the *ac* susceptibility curves necessarily arises from the excited states, one of which has the single-ion moments arranged ferromagnetically and naturally becomes the ground state when the applied field is large enough. This suggests that varying the strength of the intramolecular magnetic interactions, and therefore the energy gap which separates the toroidal and the ferromagnetic states, should have a strong effect on the magnetic dynamics and on the relaxation properties. The question is, how can we steer this?

In recent work, we demonstrated the impressive effect that changing substituents on benzoate ligands in a series of $\{Fe_2^{III}Dy_2^{III}\}$ coordination clusters can have on their electronic structures. We could demonstrate a correlation between the ±I effect and the observed hyperfine fields in the Mössbauer spectra and then correlate these to Hammett constants.[8] This encouraged us to explore whether changes to the tripodal $teaH_3$ ligand, in terms of modifying one of its three arms by introducing other moieties, could lead to fine-tuning of the ligand field, such that we could enhance the toroidal properties of the Dy_6 system.

Further context for this is that theoretical models suggest that extremely small changes in the ligand environment can significantly modify the resulting magnetic anisotropy and easy-axis orientation of the Dy^{III} ion.[9] In this respect, the core of **1** is an excellent system to allow us to examine the sensitivity of Dy^{III} ions to small changes in the ligand field induced by variations on one arm of the ligand. Since ab-initio calculations suggest that the intramolecular coupling between different magnetic centres giving rise to the toroidal ground state essentially arises from dipole-dipole interactions, changing the direction of the single-ion anisotropy axis on each Dy site whilst maintaining the same molecular symmetry should have a significant effect on the energy gap because of the strong angular dependence of dipolar magnetic interactions.[3a] In other words, we expect to observe a correlation between the stability of the purely toroidal ground state in an applied magnetic field and the dynamic (slow) relaxation properties.

Here we report the use of two different amino alcohol ligands Me-$teaH_3$ and $apadH_4$ which are related to $teaH_3$ (scheme 1) in order to examine their influence on the magnetic behaviour of the hexanuclear core motif seen for **1**. Thus, two hexanuclear $\{Dy_6\}$ CCCs $[Dy_6(Me\text{-}teaH)_6(NO_3)_6]\cdot 6MeCN$ **(2)** and $[Dy_6(apadH_2)_6(NO_3)_6)]\cdot 2THF$ **(3)** with cores isostructural to that of **1** could be obtained.



Scheme 1. Left: Triethanolamine ($teaH_3$); Middle : *rac.*1-[*N*,*N*-*bis*-(2-hydroxyethyl)amino]-2-propanol (Me-$teaH_3$); Right: 2,2`-(3-aminopropylazanediyl)diethanol ($apadH_4$).

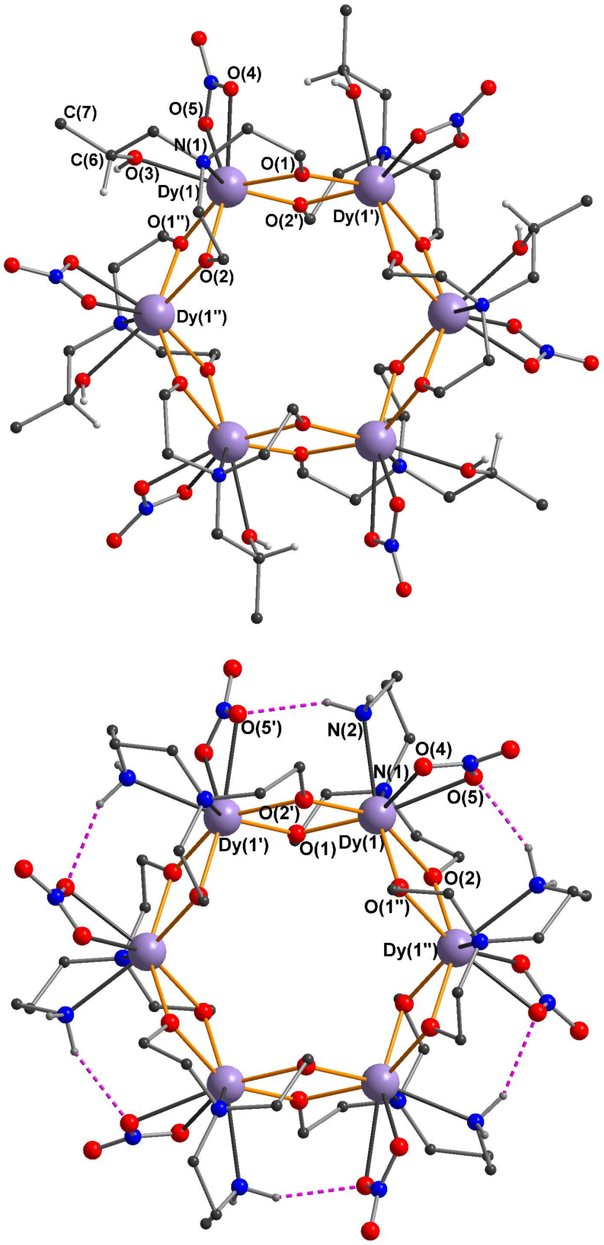


Figure 1. The molecular structures of the Dy$_6$ clusters in **2** (above) and **3** (below). Dy violet, O red, C dark grey, N blue, H pale grey; H-bonds shown as dashed purple lines; "organic" H atoms (except those on the chiral carbons in **2**) and lattice solvent omitted for clarity. Primed atoms at y, -x+y, -z; double-primed atoms at x-y, x, -z

Compounds **2** amd **3** were, as for **1**,[7c] synthesised from the direct reaction of Dy(NO$_3$)$_3$·6H$_2$O and the ligand in the presence of NEt$_3$ as base, but with a Dy:ligand ratio of 1:2 (see ESI). Since apadH$_4$ is more basic than the other two ligands (with the third arm bearing an amine instead of alcohol) the amount of the added base NEt$_3$ was reduced in this case

Structurally, compounds **2** and **3** (Fig. 1) crystallise[‡] in the rhombohedral space group $R\bar{3}$ with Z = 3, as was also the case for **1**.[7c] Indeed, **1** and **2** are almost isomorphous; apart from the extra methyl substituent on each non-bridging ligand arm in **2**, the –OH groups in **2** now form hydrogen-bonds to lattice MeCN, as opposed to MeOH in **1**. Even the unit cell for **3** is not too dissimilar and the packing here is still related to that in **1** and **2**. In both **2** and **3**, Dy(1) is chelated by the O and N atoms of an organic ligand with the oxygens of the two deprotonated ethanol arms each bridging to an adjacent Dy in the ring. The 2-propanol (**2**) or 3-aminopropyl (**3**) ligand arms are not deprotonated and simply ligate Dy(1). The principal structural differences between **2** and **3** involve this arm: the longer arm in **3** has twisted the ligand geometry compared to **2** (and **1**) and the amino substituent in **3** forms an intramolecular hydrogen bond to the nitrate ligand on the adjacent Dy, pulling the nitrate away from its position in **2**. In **2**, the $\bar{3}$ site symmetry requires that the chiral but racemic (Me-teaH)$^-$ ligands are arranged such that the three ligands to one side of the Dy$_6$ plane are all *R* and the three on the other side are all of the *S* enantiomer.

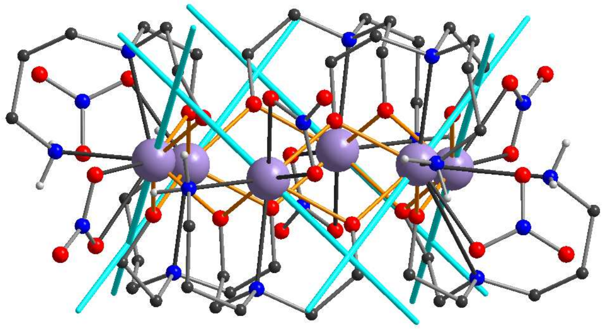


Figure 2. Structure of **3**, showing the orientation of the six Dy^{III} magnetic moments (cyan lines), calculated using *Magellan*.[10] Atom colours as for Figure 1

Using CASSCF *ab initio* calculations, Chibotaru *et al*. could determine the orientation of the magnetic moments of the six Dy^{III} cations in **1**, and showed how these combine to give an overall toroidal magnetic moment.[3a] The much simpler electrostatic ligand field approach used by Chilton *et al*. in their *Magellan* software[10] in fact gives very similar orientations for the Dy moments in **2** and **3** and the results for **3** are shown in Fig. 2.

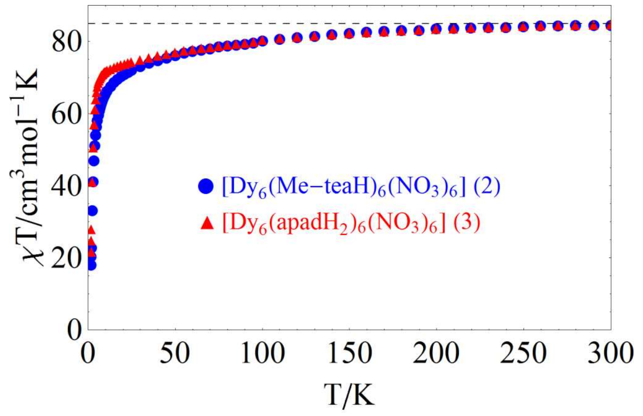


Figure 3. dc magnetic susceptibility measured as a function of temperature for **2** and **3**.

The shape of the *dc* magnetic susceptibility measured for compounds **2** and **3** (Fig. 3) is qualitatively similar to that published for **1**.[3a,7c] We found no evidence of any effective magnetic moment reduction at room temperature with respect to the value expected for six non-interacting Dy^{III} ions.[11] The latter observation is consistent with the fact that superexchange interactions are relatively weak, as was already previously suggested for **1**. We also note that the *dc* susceptibility curves measured for **2** and **3** are practically superimposed for temperatures higher than 50 K. This indicates that the total zero-field splitting of the lowest-energy $^6H_{15/2}$ manifold of Dy, and therefore the overall ligand-field strength, is essentially the same in all the investigated complexes. On the other hand, the different values of χT between 10 and 30 K can be attributed to the different energy separations between the ground state and the lowest excited states arising from the different strength of the effective intra-site interactions, whereas the abrupt drop below 10 K probably reflects the zero net dipolar moment of the ground state.

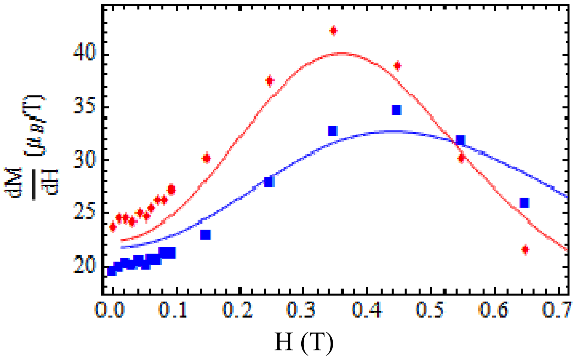


Figure 4. First derivative of the magnetization with respect to field for **2** (blue) and **3** (red) as a function of the applied field; the maximum of this quantity corresponds to the position of an inflection point in the magnetization curves. Points are experimental data measured at 2 K, lines are calculated curves.

In this respect, however, the magnetisation curves measured at low temperature are much more informative. An inflection point, which indicates the presence of a level crossing between the toroidal and the ferromagnetic state,[3a] is in fact present at a certain field value which can be best highlighted by plotting the first derivative of the curves (Fig. 4). The position of this inflection point is clearly different for **2** and **3**. The former complex requires a higher magnetic field than the latter to stabilise the ferromagnetic intramolecular ordering. We have fitted the magnetisation curves assuming that the single-ion ground state composition along the series remains that outlined in Ref. 3a, along with all other parameters, and have only changed the value of the angle θ between the Dy anisotropy axis and the S_6 molecular symmetry axis. Good results are obtained putting θ = 34° for **2** and 51° for **3** (to be compared with the 43° previously reported for **1**). This is consistent with our physical expectations. The S_6 axis is of course perpendicular to the plane which contains the six magnetic centres, and because of this symmetry a smaller value of θ implies that the moments on two neighbouring Dy ions are closer to an antiparallel (i.e. 180°) arrangement, which maximizes the (effective) antiferromagnetic dipole-dipole interaction and therefore also leads to a larger energy gap. We should note, however, that this does not mean that the absolute value of the toroidal moment is also larger: on the contrary, in a perfectly antiferromagnetic state this would be exactly zero, and only grows larger when the moments are closer to the S_6 plane.

It is interesting to correlate the above observations with the magnetisation dynamics. For both **2** and **3** a sizeable imaginary component is observed in the *ac* susceptibility curves (Fig. S2), as previously reported for **1**. However, whereas **1** and **2** do not show any peak in their χ'' vs T curves (and a relaxation process so fast that no maximum can be observed within the apparatus window even under an external *dc* field) compound **3** has a significantly higher blocking temperature, showing a well-defined maximum in χ'' above 2 K for frequencies of 100 Hz and above. Once again, this is perfectly in line with our expectations, because complex **3** displays the smallest energy gap (and inflection field) between the toroidal and the ferromagnetic states. For the reasons stated above, it is also the complex with the largest absolute value of the toroidal moment; however, for obvious reasons its purely non-magnetic zero-field ground state cannot support slow relaxation, and therefore the SMM properties become better when the ferromagnetic arrangement is easier to achieve.

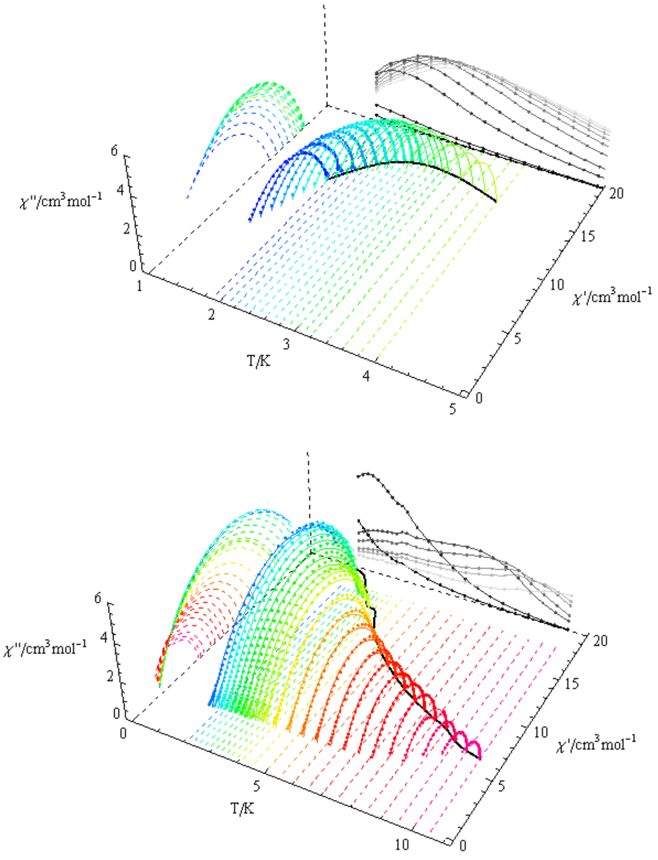


Figure 5. Cole-Cole plots measured for **3** as a function of temperature, with a dc applied field of 0 (upper graph) and 2 kOe (lower graph) respectively; points are experimental data, the full coloured lines are fits as described in the Supporting Information. The dashed straight lines on the T vs χ' plane indicate the χ"=0 reference axis for each measured temperature with its corresponding colour. The χ' vs χ" plane shows the same data with the colours distinguishing different temperatures. The T vs χ" plane shows the temperature dependence of χ" with different measuring frequencies between 1 and 1500 Hz, with larger frequencies indicated by paler shades of grey. The thick black curve on the T vs χ' plane represents the projected intersection of the Cole-Cole plots where χ" = 0.

The relaxation time as a function of temperature for **3** in the absence of external *dc* field was extracted by fitting the ac susceptibility curves (Fig. S3). The Arrhenius fit of the data resulted in a very small effective barrier (about 3 K) and a relatively long time constant (2.7×10^{-5} s). This, together with the non-negligible exponent α obtained in the analysis of the Cole-Cole plots (Fig. 5) indicates that there is more likely a distribution rather than a single relaxation process and suggests that significant quantum tunnelling (QT) effects are present. In order to test this hypothesis, we performed *ac* susceptibility measurements under an applied *dc* field of 2 kOe. The results are compared with the zero-field ones in Fig. 5. The low-temperature points are still dominated by a QT-like behaviour, but at higher temperatures a change in the slope of the curve indicate the onset of a thermally-activated relaxation process. Fitting this part of the curve results in an effective barrier U_{eff} = 36 K and a characteristic time constant $\tau_0 = 5.2\times10^{-8}$ s, which is in line with values expected for Orbach relaxation processes. The fact that U_{eff} is comparable to the temperature range in which the measured *dc* susceptibility curves for **2** and **3** separate indicates that the change in the ligand-field potential which arises from the presence of the amine function coordinating on the Dy^{III} ions is indeed responsible for the improved barrier to magnetic relaxation. This in turn implies, that ligand modification can lead to a dramatic improvement of the SMM properties while the $\{\text{Dy}_6\}$ core arrangement remains essentially the same. The different nature of electron-density has been recently shown to affect the exchange coupling in two different Dy_6 wheels.[12]

Conclusions

The important features we report here are that the first compound we describe has properties similar to those of the original compound but the ligand used is now a chiral racemate and we get perfect separation into R and S enantiomers above and below the plane containing the Dy_6 cycle.

The second compound has an amino-arm in place of one alcohol arm of the triethanolamine ligand. This change in the local ligand field results in a larger toroidal moment and at the same time to a higher energy barrier of 36 K within the observed relaxation regime. This offers an exquisite means to fine-tune SMM and toroidal moment properties.

Notes and references

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We thank Dr. Yanhua Lan for collecting the magnetic data and Danny Wagner. We thank the DFG (3MET/TR88) and STN-Program of the Helmholtz Gesellschaft for financial support.

† Electronic Supplementary Information (ESI) available: Synthetic details, crystallographic details, *ac* magnetic susceptibility data and fitting procedure and parameters for the Cole-Cole plot analysis. See DOI: 10.1039/b000000x/

‡ **Crystal data:**

2: $\text{C}_{54}\text{H}_{108}\text{Dy}_6\text{N}_{18}\text{O}_{36}$, 2560.58 g mol^{-1}, trigonal, $R\bar{3}$, a = 17.5124(14), c = 24.2551(19) Å, V = 6442.1(9) Å^3, Z = 3, T = 100(2) K, ρ_{calc} = 1.980 g cm^{-3}, F(000) = 3726, μ(Mo-$K\alpha$) = 5.244 mm^{-1}; 33133 data, of which 3048 unique (R_{int} = 0.0296), 176 parameters, final wR_2 = 0.0451, S = 1.164 (all data), R_1 (3003 data with I > 2σ(I)) = 0.0182. CCDC 920636.

3: $\text{C}_{50}\text{H}_{112}\text{Dy}_6\text{N}_{18}\text{O}_{32}$, 2452.58 g mol^{-1}, trigonal, $R\bar{3}$, a = 15.7780(10), c = 26.4045(19) Å, V = 5692.6(7) Å^3, Z = 3, T = 200(2) K, ρ_{calc} = 2.146 g cm^{-3}, F(000) = 3570, μ(Mo-$K\alpha$) = 5.925 mm^{-1}; 15286 data, of which 2499 unique (R_{int} = 0.0343), 152 parameters, final wR_2 = 0.0576, S = 1.011 (all data), R_1 (2174 data with I > 2σ(I)) = 0.0238. CCDC 920637.

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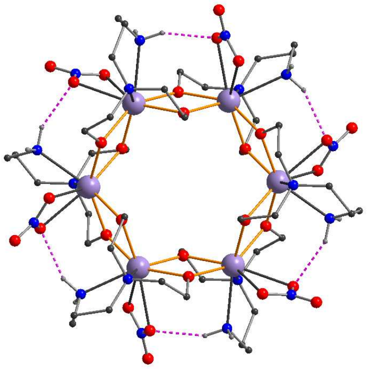

We show how the toroidal moment in Dy_6 cyclic coordination clusters can be tuned and optimised.