**The effect of additional magnetic ligand on the magnetic relaxation and toroidal moment of Dy$_6$ complex**

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Two new $\mu_4$-O bridged hexanuclear lanthanide complexes, [Dy$_6$L$'_4$(μ$_4$-O)$(\text{NO}_3)_4$]-4CH$_3$OH (1) and [Sm$_6$L$'_4$(μ$_4$-O)(CH$_3$COO)$_4$]-2CH$_3$OH (2), have been assembled by using methyl modified Schiff-base ligand H$_3$L$'$ (2,6-bis((2-hydroxypropylimino)methyl)-4-methylphenol). The complex 1 shares a similar $\mu_4$-O bridged Dy$_6$ core as the parent Dy$_6$-2, while coordination geometries and magnetic interactions are slightly changed upon the modulation of the ligand, which results in distinct single-molecule magnetic (SMM) and single-molecule toroic (SMT) properties.

**Introduction**

The design and construction of single-molecule magnets (SMMs) has attracted increasing attention since the discovery of SMM behaviour, because they have potential applications in processing and storing magnetic information at a molecular level. Thus a large number of SMMs, including 3d complexes, 3d/4f complexes and 4f complexes, have been reported. Thereinto, 4f-based complexes are particularly appealing due to the strong magnetic anisotropy of 4f ions, and a flurry of ground-breaking results have been produced. It is noteworthy that some cyclic Dy$_3$ complexes have exhibited SMM behaviours and toroidal moments that arise from a vortex arrangement of local magnetic moments of the individual Dy(III) centers. These systems are defined as single-molecule toroics (SMTs), which are promising candidates for future applications in quantum computing and information storage. Toroidal moment is generally influenced by the molecular symmetry, local magnetic moment as well as magnetic interactions. However, the study on magneto-structural relationships of SMTs is rare. In this regard, we have been interested in investigating the magneto-structural relationships of SMTs with one typic ligand. Recently, we have successfully assembled a Dy$_6$ SMTs with enhanced toroidal moment that was formed by linkage of two Dy$_3$ units (the complex is defined as Dy$_6$-2). To go a step further, we modified slightly the Schiff-base ligand by adding a methyl, and assembled two $\mu_4$-O bridged hexanuclear lanthanide clusters, [Dy$_6$L$'$$_4$(μ$_4$-O)$(\text{NO}_3)_4$]-4CH$_3$OH (1) and [Sm$_6$L$'$$_4$(μ$_4$-O)(CH$_3$COO)$_4$]-2CH$_3$OH (2). Though Dy$_6$-2 and complex 1 have similar structures, the coordination geometries and magnetic interactions are changed upon the slight modulation of the ligand. The coordination environment of Dy$_6$(m) ions will influence the local tensor of anisotropy and crystal-field splitting. Thus they exhibit dissimilar magnetic behaviour. Complex 1 shows SMM behaviour with obvious quantum tunnelling of the magnetization (QTM) and SMT property with large conventional magnetization.

**Experimental section**

**General**

All starting materials were of A.R. Grade and were used as commercially obtained without further purification. 2,6-Diformyl-4-methylphenol (DFMP) were prepared according to a previously published method. The Schiff-base ligand H$_3$L$'$ (2,6-bis((2-hydroxypropylimino)methyl)-4-methylphenol) (shown in Scheme 1) was prepared by the in situ condensation of DFMP and (DL)-1-amino-2-propanol in a 1:2 ratio in methanol.

Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. Fourier transform IR spectra (4000–300 cm$^{-1}$) were measured using KBr pellets by a Fourier transform infrared spectrometer Nicolet 6700. All magnetization data were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The complexes possessing a certain nuclearity and topology, in this regard, we have been interested to investigate the magneto-structural relationships of SMTs with one typic ligand. Recently, we have successfully assembled a Dy$_6$ SMTs with enhanced toroidal moment that was formed by linkage of two Dy$_3$ units (the complex is defined as Dy$_6$-2). To go a step further, we modified slightly the Schiff-base ligand by adding a methyl, and assembled two $\mu_4$-O bridged hexanuclear lanthanide clusters, [Dy$_6$L$'$$_4$(μ$_4$-O)$(\text{NO}_3)_4$]-4CH$_3$OH (1) and [Sm$_6$L$'$$_4$(μ$_4$-O)(CH$_3$COO)$_4$]-2CH$_3$OH (2). Though Dy$_6$-2 and complex 1 have similar structures, the coordination geometries and magnetic interactions are changed upon the slight modulation of the ligand. The coordination environment of Dy$_6$(m) ions will influence the local tensor of anisotropy and crystal-field splitting. Thus they exhibit dissimilar magnetic behaviour. Complex 1 shows SMM behaviour with obvious quantum tunnelling of the magnetization (QTM) and SMT property with large conventional magnetization.
variable-temperature magnetization was measured with an external magnetic field of 1000 Oe in the temperature range of 1.9–300 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal’s tables and sample holder calibration.

### X-ray crystallography

Suitable single crystals of 1 and 2 were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 185(2) K on a Bruker ApexII CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F² with full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 programs.59,60 The locations of Dy(III) ion were easily determined, and O, N, and C atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The H atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms. CCDC 1566095 and 1566096 contain the supplementary crystallographic data for this paper.†

#### Synthesis of [DyL’4(μ₄-O)(NO₃)₄]·4CH₃OH (1)

A solution of Dy(NO₃)₃·6H₂O (137.8 mg, 0.30 mmol) in 5 ml methanol was added in a solution of DFMP (0.15 mmol) and (DL)-1-amino-2-propanol (0.3 mmol) in 5 ml methanol in presence of triethylamine. The mixture was continual stirred at room temperature for 20 min. The resulting reaction mixture was sealed in an autoclave and maintained at 90 °C for 3 days, and then cooled slowly to room temperature to yield yellow single crystals suitable for X-ray diffraction. Yield: 33 mg, (27%, based on the metal). Elemental analysis (%) calcd for Dy₆C₆₄H₉₂N₁₄O₂₉: C, 36.27; H, 3.14; N, 4.09; Found: C, 36.16; H, 3.97; N, 4.53. IR (KBr, cm⁻¹): 2856 (w), 1646 (vs), 1549 (m), 1497 (m), 1452 (s), 1396 (m), 1368 (w), 1323 (s), 1281 (m), 1231 (m), 1082 (m), 1042 (s), 902 (w), 873 (w), 813 (m), 775 (m), 739 (w).

#### Synthesis of [SmL’₄(μ₄-O)(CH₃COO)₄]·2CH₃OH (2)

A procedure similar to that for 1 was followed except that Dy(NO₃)₃·6H₂O was replaced by Sm(CH₃COO)₃·H₂O (0.3 mmol, 105.2 mg). Yield: 27 mg (23%, based on the metal salt). Elemental analysis (%) calcd for Sm₆C₇₀H₹₄N₈O₂₃·4CH₃OH: C, 36.16; H, 3.97; N, 4.53. IR (KBr, cm⁻¹): 2910 (w), 1644 (s), 1548 (vs), 1444 (s), 1395 (m), 1323 (m), 1231 (w), 1138 (m), 1033 (s), 928 (w), 854 (w), 816 (w), 678 (w).

### Results and discussion

To explore the effect of additional methyl groups on the lanthanide compound, the symmetrical Schiff-base H₄L’ (Scheme 1) was formed by the in situ condensation of DFMP and (DL)-1-amino-2-propanol (1 : 2) in methanol. Similar to the procedure for Dy₆-2, the reactions of in situ formed H₄L’ with Dy(NO₃)₃·6H₂O/Sm(CH₃COO)₃·H₂O in the presence of triethylamine under solvothermal condition produce block-shaped crystals of [DyL’₄(μ₄-O)(NO₃)₄]·4CH₃OH (1) and [SmL’₄(μ₄-O)(CH₃COO)₄]·2CH₃OH (2). The structures of 1 and 2 were established by single crystal X-ray diffraction. The crystal data and structure refinement are summarised in Table 1.

As shown in Fig. 1, complex 1 crystallizes in the triclinic space group P1 and consists of six Dy(III) ions, four (L’)₄⁻ ligands, one μ₄-O anion and four NO₃⁻ anions. The core of 1, similar to the Dy₆-2, consists of two [Dy₃(μ₃-O)₂(μ₄-O)]₄ triangular units linked by one μ₄-O²⁻ ion in an edge-to-edge arrangement. The triangular Dy₃ units in 1 are more equilateral than that in Dy₆-2 with Dy···Dy distances in range 3.4933(8)–3.4017(6) Å. The dihedral angle between the two Dy₃ planes in 1 is 30.101(12)° that is slightly larger than that in Dy₆-2 with 29.6568°.

It is notable that all donors in ligand H₄L’ are coordinated, and each of the four (L’)₄⁻ binds five Dy(III) ions utilizing their tridentate pocket (O₃N) along with bridging alkoxide oxygen (Scheme 1). This is different from some Schiff-base ligands that only coordinated partially.38 Two arms of alkoxide oxygens in ligands bridge distinctly: while one arm bridges two Dy(III) ions of one triangular edge, the other arm links three Dy(III) ions upon the other triangular unit. Additionally, the phenoxido oxygen bridges two Dy(III) ions from two triangular units. Therefore, alkoxide oxygens from four ligands fasten Dy₃ triangles, one μ₄-O anion and four phenoxido oxygens of ligands further strengthen the “Dy₃ + Dy₃” construction from center and periphery, respectively. This is the same with the reported Dy₆-2.

| Compound | Crystal data and structure refinement for complexes 1 and 2 |
|----------|----------------------------------------------------------|
|          | 1                                                         | 2 |
|          | Dy₆C₆₄H₉₂N₁₄O₂₉                                           | Sm₆C₇₀H₹₄N₈O₃₂ |
|          | 2468.50                                                   | 2317.63 |
|          | Triclinic                                                | Monoclinic |
| Space group | P1                                      | C2/c |
| a (Å)    | 12.4459(5)                                               | 18.6094(11) |
| b (Å)    | 13.8185(5)                                               | 17.218(1) |
| c (Å)    | 25.2852(10)                                              | 25.3390(14) |
| α (°)    | 90                                                       | 90 |
| β (°)    | 90                                                       | 90 |
| γ (°)    | 90                                                       | 90 |
| V (Å³)   | 4142.13(3)                                               | 8110.5(8) |
| Z        | 2                                                        | 8 |
| F(000)   | 1,979                                                    | 4,1899 |
| Mw       | 2376.0,030                                               | 4504,0744 |
| R₁, wR₁ [I > 2σ(I)] | 0.0455,0.1085 | 0.0495,0.1146 |
| R₁, wR₂ [all data] | 0.0750,0.1271 | 0.0887,0.1394 |
| GOF      | 1.006                                                    | 1.008 |

† Crystallographic data for complexes 1 and 2 are available in CCDC 1566095 and 1566096.
Such a robust edge-to-edge arrangement will enhance the toroidal magnetic moment of the molecule.

The coordination spheres of Dy$_5$ and Dy$_6$ ions are completed respectively by two nitrate ions, and all Dy$^{III}$ ions are eight-coordinate (Fig. 2). This is different from Dy$_6$$^{-}$$^2$, where five Dy$^{III}$ centers are eight-coordinate and one Dy$^{III}$ ion is nine-coordinate. The exact geometries of all Dy$^{III}$ centers were determined by using the SHAPE 2.1 and the results are listed in Table S1.†

For complex 1, Dy1/Dy3/Dy5/Dy6 centers are situated in distorted square antiprismatic geometries, and Dy2/Dy4 centers are situated in distorted triangular dodecahedron. For Dy$_6$$^{-}$$^2$, Dy1/Dy3/Dy5 centers are situated in distorted square antiprismatic geometries, Dy2/Dy4 centers are situated in distorted triangular dodecahedron, and Dy6 ion is in monocapped square antiprism. The changes probably have a great impact on the magnetic anisotropy and further the magnetic properties.34–37

In addition, the Dy–O bond lengths fall in the range of 2.457(8)–2.490(8) Å with the average bond of 2.47 Å. Those average bonds in complex 1 are similar to that of Dy$_6$$^{-}$$^2$ (average bonds are 2.48 and 2.38 Å for Dy–O and Dy–N, respectively). This indicates the metal–ligand interactions of complex 1 and Dy$_6$$^{-}$$^2$ are similar.

In [Dy$_6$L$_4$(μ$_4$-O)(NO$_3$)$_4$] core, the four ligands are twisted along the C–N bonds, and each ligand straddles two triangles to coordinate five Dy$^{III}$ ions, resulting in formation of quadruple-stranded helicates (Fig. 3).38–40 Significantly, two stereoisomers of right- (Δ) and left-hand (Λ) configurations are in crystal, forming a racemic mixture. The packing arrangement of 1 reveals that Δ- and Λ-configuration helicates are alternate along the crystallographic a axis (Fig. 4).

Complex 2 crystallizes in the monoclinic space group C2/c, the asymmetric unit contains four Sm$^{III}$ ions, two (L)$^3$ ligands and two CH$_3$COO$^-$ ions. The structure of 2 is essentially isomorphous to 1 (Fig. S1†), consists of a μ$_4$O$^{2-}$ ion linked two triangular units in an edge-to-edge arrangement, where Sm⋯Sm distances are in range of 3.4439(10)–3.6234(96) Å, the dihedral angle between the two Sm$_3$ planes in 2 is 28.176° that is smaller than that in 1. In the asymmetric unit, Sm2 and Sm3 ions are eight-coordinate with 6O$_2$N, and both display distorted triangular dodecahedral geometries based on SHAPE 2.1.
The coordination spheres of Sm1 and Sm4 ions are filled respectively by two CH3COO/CO3 ions, forming eight-coordinate Sm1 and Sm4 ions with 8O. The exact geometries of Sm1 and Sm4 ions are both distorted square antiprisms based on SHAPE 2.1. In addition, the Sm–O bond lengths fall in the range of 2.331(6)–2.506(8) Å, the Sm–N bond lengths fall in the range of 2.507(9)–2.552(9) Å.

In [Sm6L04(m4-O)(CH3COO)4] core, each of four ligands coordinates five Sm(III) ions and straddles two triangular units, producing formation of quadruple-stranded helicates (Fig. S3†). As shown in Fig. S4,† the two stereoisomers of D and L configurations form a racemic mixture, which can be seen in molecular structures and crystal packing.

**Magnetic studies**

The direct current (dc) susceptibility studies of complexes 1 and 2 were investigated under a 1000 Oe field in the temperature range 2–300 K (Fig. 5). At room temperature, the $\chi_M T$ value of complex 1 is 86.37 cm$^3$ K mol$^{-1}$. The value is in agreement with the expected theoretical value (85.02 cm$^3$ K mol$^{-1}$) for six free Dy(m) ions ($J_{H}^{15/2}, S = 5/2, L = 5, g = 4/3, C = 14.17$ cm$^3$ K mol$^{-1}$). On cooling, $\chi_M T$ decreases throughout the whole temperature range: firstly, $\chi_M T$ decreases monotonously down to 50 K, then decreases abruptly to 21.03 cm$^3$ K mol$^{-1}$ at 2.0 K. The thermal variation of the $\chi_M T$ indicates the progressive depopulation of the excited Stark sublevels of Dy(m) ions and/or weak molecular magnetic interactions.41,42 Actually, this profile of $\chi_M T$ is similar but higher to that of Dy6-2, and the minimum is larger than that of Dy6-2 (6.59 cm$^3$ K mol$^{-1}$ at 2.0 K), which indicates the weaker magnetic interaction in complex 1. The large minimum (21.03 cm$^3$ K mol$^{-1}$) also indicates the magnetic ground state of complex 1 is different from the net toroidal moment.16,20,43

(Fig. S2 and Table S2†). The coordination spheres of Sm1 and Sm4 ions are filled respectively by two CH3COO- ions, forming eight-coordinate Sm1 and Sm4 ions with 8O. The exact geometries of Sm1 and Sm4 ions are both distorted square antiprisms based on SHAPE 2.1. In addition, the Sm–O bond lengths fall in the range of 2.331(6)–2.506(8) Å, the Sm–N bond lengths fall in the range of 2.507(9)–2.552(9) Å.

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(Fig. 5) (Top) Plots of $\chi_M T$ vs. T for 1 (black square) and Dy6-2 (red circle) in a dc field of 1000 Oe (2–300 K); (bottom) plots of $\chi_M T$ vs. T for 2 in a dc field of 1000 Oe.

**Fig. 5** (Top) Plots of $\chi_M T$ vs. T for 1 (black square) and Dy6-2 (red circle) in a dc field of 1000 Oe (2–300 K); (bottom) plots of $\chi_M T$ vs. T for 2 in a dc field of 1000 Oe.
For complex 2, the $\chi_M T$ value (Fig. 5) observed at room temperature is 1.58 cm$^3$ K mol$^{-1}$, which is significantly larger than the theoretical one. This is attributed to the first or even the higher excited states ($\epsilon_1 H^{2/2}, \epsilon_6 H^{3/2}, \ldots, \epsilon_4 H^{15/2}$) of the Sm$^{III}$ ion that can be populated obviously at room temperature. On cooling, the $\chi_M T$ value decreases continuously to a minimum of 0.10 cm$^3$ K mol$^{-1}$ at 2.0 K.

The field dependence of magnetization ($M$) was measured between 1.9 and 5 K. As shown in Fig. 6, it is obviously that $M$ under variable field at 1.9 K shows a “S” shape, which is consistent with SMTs. The peak (d($M$/$M_S$)/d$H$) vs. field suggests inflection around 12 kOe. The inflection is less evident than that in Dy$_6$-2. $M$ reaches a maximum value 33.83 $\mu_B$ at about 45 kOe, which is far lower than the expected saturation value of 60 $\mu_B$ for six noninteracting Dy$^{III}$ ions. This can be mostly attributed to crystal-field effects and the possible weak antiferromagnetic interactions that make the low-lying excited states accessible. Meanwhile, the non-superposition of the $M$ vs. $H/T$ data implies the presence of significant magnetic anisotropy. The static magnetic behaviours, including the dc susceptibility and the field dependence of $M$, reveal that the ground state of 1 could be a toroidal magnetic moment and the conventional magnetic moment should be larger than that of Dy$_6$-2.

Furthermore, the anisotropy axes of complex 1 were calculated using the Magellan program based on an electrostatic model (Fig. 7 and Table S3†). The results indicate that complex 1 shows toroidal moment in both Dy$_6$ units. This agrees with the magnetic properties. The ab initio calculations are planned to provide quantitative evaluation of the anisotropy axes and Dy–Dy coupling interactions.

To compare the magnetic relaxation between Dy$_6$-2 and 1, the dynamics of the magnetization of 1 were investigated using alternating current (ac) susceptibility measurements (Fig. 8). Under zero dc field, the variable-temperature ac susceptibility of 1 shows the temperature dependence maximum, which signals the freezing of the spins by the anisotropy barrier and is typical for SMM behaviour. Both 1 and Dy$_6$-2 show broad peak in the out-of-phase susceptibility, but the former appears at 7 K that is lower than that of Dy$_6$-2 (at about 9 K). This indicates lower effective energy barrier for complex 1. Obviously, unlike the Dy$_6$-2, the rise in the out-of-phase and in-phase susceptibility on cooling at low temperatures indicates the presence of QTM for 1, which may be due to the weak magnetic interaction that is too weak to suppress the QTM. This agrees well with the dc magnetic susceptibility that indicates weaker magnetic interaction in complex 1.

The reported isomorphous Dy$_6$-2 displayed impressive dynamic magnetic properties with effective suppression of QTM and remarkable toroidal moment. However, obvious QTM is present and toroidal moment is less distinct in 1. Comparing the structure data of complex 1 and Dy$_6$-2, they have the identical metal–ligand interaction, but distinctive coordination geometries mainly on Dy6 ion. For Dy$_6$-2, Dy6 ion is nine-coordinate with a mono-capped square antiprism. While Dy6
center in complex 1 is eight-coordinate situated in distorted square antiprismatic geometries, which is due to the steric hindrance from additional methyl groups of ligands (Fig. 1). The changes in coordination geometries have a great impact on the orientation of the easy axes. Consequently, the toroidal moment retains in complex 1 but with a large conventional magnetization, SMM behaviour also is observed but with a non-ignorable QTM. It should be note that the weaker magnetic interaction in complex 1 could not suppress the QTM.

**Conclusions**

In conclusion, methyl modified Schiff-base ligand has been successfully used to synthesize two new hexanuclear lanthanide complexes, [Dy6L4(μ3-O)(NO3)4]-4CH3OH (1) and [Sm6L4(μ2-O)(CH3COO)4]-2CH3OH (2), under solvothermal condition. Single crystal X-ray diffraction studies revealed that complex 1 has a μ3-O bridged Dy6 core, μ2-O bridged two [Dy6(μ2-O)6(μ3-O)4] triangular units in an edge-to-edge arrangement, that is the same as the parent Dy6-2. While the coordination geometries especially on Dy6 site and magnetic interactions change, which result in distinct magnetic properties. Complex 1 shows SMM behaviour with a non-ignorable QTM and SMT behaviour with a large conventional magnetization. The work provides an efficient strategy to probe the magneto-structural relationships of SMTs, further to design the special SMTs and SMMs.

**Conflicts of interest**

There are no conflicts to declare.

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