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Slight Synthetic Changes Eliciting Different Topologies: Synthesis, Structure and Magnetic Properties of Novel Dinuclear and Nonanuclear Dysprosium Complexes

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Using the Schiff-base ligand, 1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H₂hmc), generates dinuclear and nonanuclear compounds, [Dy₂(Hhmc)₂(NO₃)₆]·MeCN (1) and [Dy₂(µ₂-OH)₂(Hhmc)₂(NO₃)₆(DMF)₄]OH·H₂O·THF·DMF (2), respectively, through the addition of different bases. Single-crystal X-ray diffraction analysis revealed a unique Dy₉ core structure of complex 2 and the magnetic properties of both compounds are fully studied.

Lanthanide-based metal clusters have been of increasing interest due to their fascinating structural diversity as well as their electronic, optical, and catalytic properties. In particular, cluster chemistry based on paramagnetic ions has received considerable research interest regarding magnetic properties, especially as Single-Molecule Magnets (SMMs). Understanding the correlation between structural models and physical properties will offer more information for designing new SMMs. For example, the effect of electron-withdrawing ligands on the energy barriers of SMMs has been investigated through a series of dinuclear complexes with a similar core structure, but different counter ions. Moreover, self-assembly of nanoscale high-nuclearity metal clusters via methods of coordination chemistry has been a challenging task which led to the supermolecular assemblies exhibiting novel structural characteristics. The synthesis of high-nuclearity pure lanthanide clusters with novel topologies continues to be a challenge due to the variable and high coordination numbers, as well as poor directionality inherent to lanthanide ions. To the best of our knowledge, all nonanuclear lanthanide compounds published thus far have been diabolol shape (or sandglass shape) where the clusters assemble in two square pyramidal pentanuclear units via the apical metal center lanthanide ion. Besides their magnetic properties, nonanuclear lanthanide compounds have also shown photosensitized luminescence and optical Faraday effects. Thus, lanthanide clusters have many interesting properties yet to be fully explored.

Ligands play an important role in lanthanide cluster syntheses. Polydentate Schiff-base ligands derived from o-vanillin have been widely applied for the syntheses of multinuclear lanthanide clusters. Polynuclear lanthanide clusters ranging from dinuclear to dodecanuclear have been synthesized using this ligand system, which provides O- and N-based multi-chelating sites for lanthanide ion complex formation. Increasing the denticities of the ligands may be one of the most successful strategies toward forming high-nuclearity lanthanide complexes. For example, dinuclear complexes were obtained by using (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine (H₂hmi) (Scheme 1a). Designing pyrazine groups in place of pyridine groups offered an additional N atom for metal chelation (Scheme 1b) and penta- and hexa- and octa-

Scheme 1. Coordination modes of (a) (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine (H₂hmi), (b) (2-hydroxy-3-methoxybenzylidene)pyrazine-2-carboxy-hydrazide and (c) 1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H₂hmc).
Herein, we report the syntheses, structures, and magnetic properties of a novel dinuclear and nonanuclear DyIII clusters which were synthesized by simply altering the basicity of the reaction conditions.

To a solution of Dy(NO3)3·6H2O (0.50 mmol) in MeCN (15mL) was added a solution of H2hmc (0.25 mmol) and pyridine (0.080 mL, 1.0 mmol) in THF (15 mL). The resulting pale yellow solution gave well-formed pale green crystals in 62% (0.1082 g) yield. The structure of the dinuclear complex, [Dy2(Hhmc)3(NO3)3]·THF·MeCN (1), crystallized in the triclinic P-1 space group (Fig. 1).

Fig. 1. Molecular structure of complex 1. Colour code: Dy (yellow), O (red), N (blue) and C (gray). H atoms were omitted for clarity.

The tetradeutate ligand coordinates to the Dy centers in the dinuclear unit via three O atoms (O1, O2 and O3) and one N1 atom. The metal centers are bridged by the phenoxo groups of two ligands with a Dy-O-Dy angle of 104.14(7)°. The Dy-Dy distance is 3.7076(4) Å. Both DyIII ions are nine coordinate and the remaining four coordination sites of each lanthanide ion are filled by two nitrate anions. The Dy centers are in a distorted pentagonal, interpenetrating tetrahedral arrangement where four oxygen atoms of two nitrate form a distorted tetrahedral position which is interpenetrated by the pentagonal plane of N1, O2, O3, O1a and O2a from Hhmc. Charge balance considerations for the molecule indicate that the ligand must have one negative charge resulting from the ligand being in the keto-form, and one deprotonated O2 atom which is different from the similar dinuclear complexes synthesized with the H2hmi ligand33 (Fig. S1).

Since not all potential coordination sites of H2hmc were occupied in complex 1, we added NEt3 instead of pyridine in the reaction which promotes full deprotonation of H2hmc (H on O4). A suspension of Dy(NO3)3·6H2O (0.282 g, 0.616 mmol) and H2hmc (0.098 g, 0.274 mmol) in THF/DMF (5:1 ratio) was treated with 3.65 mmol of Et3N. The resulting yellow solution yielded rectangular, light yellow crystals of the nonanuclear complex [Dy3(μ3-O)(μ-OH)3(hmc)3(NO3)3(DMF)5](OH)·H2O·THF·DMF (2) in 17.9% yield after one week. No crystals were obtained without an excess of base since the deprotonation of H2O into μ3-O and μ-OH was linked to DyIII ions. Complex 2 crystallizes in the monoclinic C2/C space group and the structure is composed of nine DyIII ions which are all eight coordinate. (Fig. 2) The ligands coordinated with DyIII in two different coordination modes where four DyIII ions (Dy3a, Dy2, Dy4 and Dy5) were held together by η2:η1:η1:η1-hmc and three DyIII atoms (Dy1, Dy3 and Dy5) were linked by η1:η:η:η:η:η:hmc (Fig. 3).

Fig. 3. Representation of the core structure highlighting the coordination modes of the ligands.

Fig. 2. Molecular structure of complex 2. Color code: Dy (yellow), O (red), N (blue) and C (gray). H atoms were omitted for clarity.
The metal skeleton can be regarded as four Dy triangles fused in a vertex-sharing fashion and all the triangles are capped by four $\mu_2$-O atoms (O1, O1a, O4 and O4a) (Fig. 4, top). The nonnuclear complex can be viewed as two pentanuclear fragments which are assembled via the apical metal (Dy1) through two $\mu_2$-O (O1 and O1a), two $\mu_2$-OH (O5 and O5a) and two phenoxy oxygen atoms (O12 and O12a). The remaining coordination sites of Dy1 are filled by two methoxy groups of the ligands (O14 and O14a), thus causing Dy1 to adopt a distorted square antiprism geometry (Fig. 4, bottom). The asymmetric unit, [Dy$_5$(μ$_2$-O)$_3$], can be regarded as vertex-sharing triangle units assembled via a metal ion, Dy3. In addition, two oxygen atoms (O2 is hydroxide and O6 is the carbonyl group of the ligand) were bridged between Dy2 and Dy4. All Dy atoms are eight coordinate and the rest of the coordination sites are filled by four DMF and four nitrite molecules. It should be mentioned that the coordination environment of Dy2, Dy3 and Dy4 centres are distorted dodecahedra, while Dy5 centres are distorted square antiprisms. (Fig. S2) For charge balance considerations, one hydroxide counter ion has been assigned which is common for nonnuclear lanthanide complexes.

The temperature dependence of the dc magnetic susceptibility (1.8 - 300 K) was measured under an applied dc field of 1000 Oe. The $\chi'$ vs. $T$ plot (Fig. 5). The room temperature values of the $\chi'$ products for complexes 1 and 2 were 27.80 and 124.58 cm$^3$Kmol$^{-1}$, respectively. The theoretical spin only value for a single Dy$^{III}$ ion is 14.17 cm$^3$Kmol$^{-1}$ ($^{6}H_{15/2}$, $S$ = 5/2, $L$ = 5, $g$ = 4/3), and thus are 28.39 and 127.53 cm$^3$Kmol$^{-1}$ for two and nine Dy$^{III}$ ions, respectively, which are both near the experimental values observed. The decrease at low temperature can be attributed to antiferromagnetic interactions between Dy$^{III}$ ions, the thermal depopulation of crystal field states, and/or magnetic anisotropy arising from the Dy$^{III}$ ions, where the $\chi'$ values of complexes 1 and 2 drop to 9.49 and 81.36 cm$^3$Kmol$^{-1}$ at 1.8 K, respectively.

The isotherm magnetisation (M) measurements (Fig. S3 and S4 for complexes 1 and 2, respectively) below 7 K reveal a rapid increase in magnetization at low magnetic fields. Above 1.5 T a more gradual increase is observed for both complexes, reaching near saturation at low temperatures (M = 10.33 and 41.88 μB at 1.8 K under 5 and 7 T, respectively). This behavior displays the presence of magnetic anisotropy within the system which is expected for Dy$^{III}$. This is further confirmed in Fig. S2 and S3, where the nonsaturation and non-superposition of isotherm temperature lines was apparent in the reduced magnetisation plots at indicated temperatures for both complexes.

The magnetic relaxation dynamics of both complexes were probed by alternating current (ac) magnetic susceptibility measurements. In the literature, similar dinuclear Dy complexes observed SMM properties with remarkably large energy barriers, however, complex 1 instead displayed a tail in the out-of-phase ($\chi''$) signal at low temperature under an 1000 Oe applied dc field, with no signal obtained under zero applied dc field. This observation can be explained by two possible reasons: (i) the ferromagnetic interaction between Dy$^{III}$ ions of the aforementioned literature complexes was not observed in the dc magnetic measurements of complex 1, resulting in a lower spin ground state (S), or (ii) the different core geometries of Dy$^{III}$ ions in complex 1 result in weaker or non-collinear anisotropy axes. Overall, the magnetostructural correlation of bridged dinuclear lanthanide complexes needs to be understood by comparing more lanthanide dinuclear complexes or through further theoretical calculation.

![Figure 6](https://example.com/figure6.png)

**Fig. 6.** Frequency dependence of the out-of-phase ($\chi''$) susceptibility of complex 2 under a 2500 Oe applied dc field.

For complex 2, a tail in the out-of-phase ($\chi''$) signal was observed at low temperature under zero applied dc field. Thus, find-field experiments were performed in order to elucidate the optimal field for observation of a visible peak. Under a 2500 Oe applied dc field a signal was observed for a low-frequency (slow) relaxation process. (Fig. 6 and S5) Since an applied dc field was necessitated in order to observe a peak, and that peak is not frequency-dependent, quantum
tunnelling of the magnetization was most likely leading to fast relaxation dynamics at zero-field and under applied fields. Since Dy$^{3+}$ has a half-integer spin, as well as significant inherent anisotropy, the absence of slow relaxation dynamics most likely is due to mixing between ground and thermally accessible excited electronic states.

Similarly within the literature there are Dy$_5$ complexes,$^{71}$ which also possess a core with two Dy triangles fused in a vertex-sharing fashion, which is similar to the subunit of complex 2. These complexes have been shown to exhibit slow relaxation of magnetization. However, there is no out-of-phase ac signal noticed for complex 2. This correlation was also observed between Dy$_5$ complexes with a square pyramidal unit$^{8}$ and Dy$_9$ complexes with diabolo-shaped core.$^{69, 66}$ Indeed, the structural differences clearly affect the anisotropy of each Dy site and their respective orientations. Here we presented another example of a head-to-head arrangement of two SMM units in Dy$_9$ which presumably cancelled the net anisotropy of the units and lead to the absence of slow relaxation.

Conclusions

Treating the ligand, H$_2$hmc, with an appropriate base can cause deprotonation to one or two phenoxides leading to dinuclear and nonanuclear dysprosium complexes. The dinuclear core is similar to complexes found within the literature, however, complex 1 is not a SMM. The novel nonanuclear Dy$^{3+}$ core of complex 2 was assembled by two unique pentanuclear units via the apical metal center. This metal cluster will offer a new model for further mechanistic studies related to SMM properties or other physical properties of multi-nuclear lanthanide chemistry.

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Notes and references