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A Half-sandwich Organometallic Single-Ion Magnet with Hexamethylbenzene Coordinating to the Dy(III) Ion

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A half-sandwich organolanthanide complex, [(C_6Me_6)Dy($AlCl_4$)$_3$], where Dy(III) is coordinated with a π-bonded arene was synthesized and magnetically characterized. This complex displays slow magnetic relaxation and a hysteresis loop associated with single-ion magnet behavior. The orientation of the magnetic anisotropy axis is analyzed using *ab initio* calculations.

Recently, organolanthanide complexes have attracted considerable attention thanks to their significant contributions at the frontier of single-molecule magnets (SMMs).[1] Complexes containing the most popular ligands[2] in organometallic chemistry, Cp^- (cyclopentadiene anion) and/or COT^{2-} (cyclooctatetraene dianion) as well as their derivatives, account for the largest number in organolanthanide SMMs, and some of them have impressive magnetic behavior.[1] For example, [(Cp*)Er(COT)] ($[Cp^*]^-$ = pentamethylcyclopentadiene anion) shows obvious slow relaxation of magnetization as the first organometallic single-ion magnet (SIM).[3] A large coercivity of 7 kOe was observed in $[Er(COT)_2]^-$.[4] It is noteworthy that these two types of negative charged building blocks have one thing in common: carbon-cyclic π ligands. From this point of view, neutral carbon-cyclic π ligand containing complexes probably have similar magnetic behavior as those with negative charged carbon-cyclic π ligands due to the similarity of their ligands in aromaticity. Herein we report, for the first time, the synthesis, magnetic characterization, and theoretical analysis of the half-sandwich mononuclear organolanthanide complex [(C_6Me_6)Dy($AlCl_4$)$_3$], where the Dy(III) ion is coordinated with a neutral π-bonded arene ligand. Our investigations show that this complex exhibits SIM behavior and the coordinating arene plays an important role in determining the orientation of the magnetic anisotropy axis of Dy(III) ion.

All manipulations and syntheses were conducted under an argon or dinitrogen atmosphere without coordinating solvents. The synthesis was performed according to the reported method[5] with certain modifications. Single crystals suitable for X-ray diffraction were grown from hot toluene solution by decreasing the temperature from 70 to 60 to 50 °C sequentially over three days. The single-crystal structural analysis revealed that [(C_6Me_6)Dy($AlCl_4$)$_3$] crystallizes in the space group $P\bar{1}$ and the molecular structure consists of one Dy(III) ion, three aluminium tetrachloride ligands, and one hexamethylbenzene (HMB) (Fig. 1). This complex is different from the more common classes of organolanthanide complexes that have anionic carbocyclic cyclopentadienyl or cyclooctatetraenyl ligands in that there is a neutral π-bonded arene ligand present.[6] Since previous research of the lanthanide π-bonded arene complexes primarily focused on the bonding and reactivity in lieu of magnetic behavior,[6,7] this study is the first to investigate the magnetic behavior of this type of complex and to explore the effects of the coordinating π-bonded arene on the magnetic anisotropy of Ln(III).

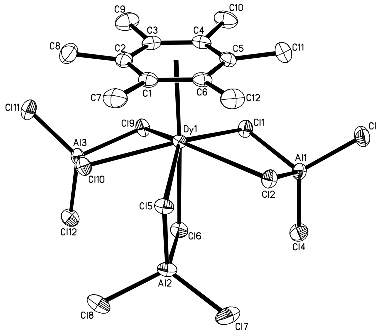

Fig. 1 Thermal ellipsoid plot of [(C_6Me_6)Dy($AlCl_4$)$_3$] drawn at the 50% probability level. Selected bond lengths [Å]: Dy-C, 2.7993(18)-2.8885(19), Dy-Centroid (HMB), 2.471, Dy-C(average), 2.846, Dy-Cl, 2.7860(5)-2.8256(5), Dy-Cl(average), 2.801. Hydrogen atoms are omitted for clarity.

In this structure, the Dy(III) ion is coordinated with a neutral π-bonded arene ligand and six chloride atoms. The average bond lengths of Dy-C and Dy-Cl are 2.846 Å and 2.801 Å, respectively, with the distance of Dy-centroid (HMB) and Dy-Cl6 being 2.471 Å and 2.7911(5) Å. Compared to the length of Ln-C (cyclopentadienyl derivatives) contacts (2.60-2.82 Å for the total series of lanthanides),[6] the slightly larger bond length of Dy-C(HMB) indicates weaker bonding between

Dy(III) and the π-bonded arene. The angle between the HMB plane and the equatorial plane formed by five Cl atoms (Cl1, Cl2, Cl5, Cl9, Cl10) is 3.480º. The local symmetry of Dy(III) ion is described as quasi-C_s, or more strictly speaking, no symmetry at all. If assuming that the arene is a ring or a point, the local geometry of the Dy(III) ion can be described as a distorted pentagonal bipyramid (quasi-D_{5h}) with the centroid (HMB) and the Cl6 atom at the apical positions.[5] The continuous-shape-measure (CShM) method[8] was used to analyze the distortion from the pentagonal-bipyramidal geometry, and the CShM value is 1.041, indicating a small distortion from the ideal D_{5h} symmetry. The shortest distance of adjacent Dy(III) ions in the lattice is 8.964 Å, which is sufficiently large to avoid obvious intermolecular interactions. More detailed crystallographic information is summarized in Table S1 and S2 (ESI†).

The temperature dependence of $\chi_M T$ (χ_M is the molar dc magnetic susceptibility) was measured in the temperature range 2-300 K with a 1 kOe magnetic field applied (Fig. 2). The $\chi_M T$ value at room temperature is 13.94 emu K mol^{-1}, which is consistent with the theoretical value of 14.17 emu K mol^{-1} expected for a free Dy(III) ion ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, $g = 4/3$). On lowering the temperature, $\chi_M T$ starts to decrease gradually from 100 K and reaches 11.02 emu K mol^{-1} at 2 K, which can be ascribed to the depopulation of excited Stark sublevels. The maximum value of $M(H)$ at 2 K and 50 kOe is 5.58 Nβ, which deviates considerably from the theoretical saturation value of 10 Nβ (Fig. S1, ESI†). Moreover, the curves of $M(HT^{-1})$ at different temperatures cannot be superimposed (Fig. S2, ESI†), suggesting significant magnetic anisotropy.[9]

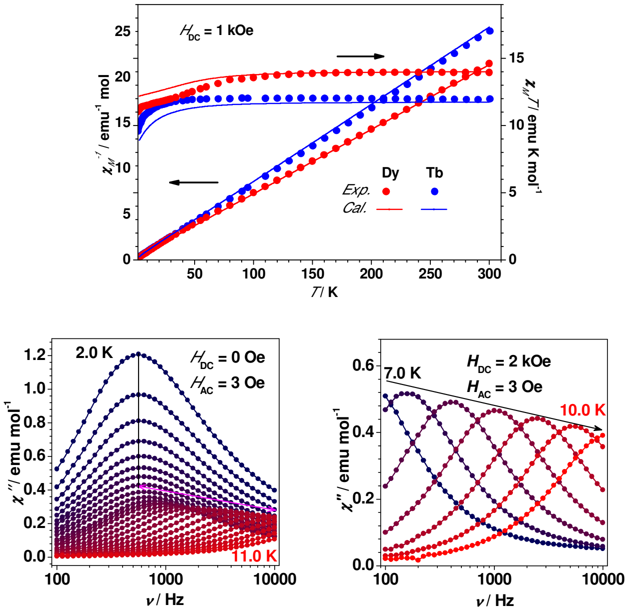

Fig. 2 Top: The temperature dependence of $\chi_M T$ of the **Dy** and **Tb** complexes with a 1 kOe dc field applied by experimental measurements and *ab initio* calculations. Bottom: Frequency dependence of out of phase ac susceptibility signal of [(C_6Me_6)Dy($AlCl_4$)$_3$] without static field (left) or under a 2 kOe field (right).

The dynamic magnetic properties were investigated by studying the temperature (T) and frequency (ν) dependence of alternating current magnetic susceptibilities. The measurements show that [(C_6Me_6)Dy($AlCl_4$)$_3$] exhibits SIM behavior. In the absence of an applied magnetic field, a slow relaxation process (Fig. 2 and S3, ESI†) can be observed below 10 K under the condition of an oscillating field H_{ac} = 3 Oe and the frequency range 100 - 10000 Hz. In $\chi''(\nu)$ plots, the peak of out of phase magnetic susceptibilities (χ'') shifts to lower frequency from 10 K to 7 K. Both the tail in $\chi''(T)$ plots and the T-independent behaviors in $\chi''(\nu)$ plots in the low temperature region reveal strong quantum tunneling of the magnetization. Applying an appropriate dc field can restrain the quantum tunneling effect. As shown in Fig. 2 and Fig. S4-S5 (ESI†), a dc field of 2 kOe was applied, and the maxima of χ'' can be observed for all measured frequencies, suggesting that the quantum tunneling effect is suppressed effectively.

The energy barriers of [(C_6Me_6)Dy($AlCl_4$)$_3$] are determined by fitting the Arrhenius law [$\tau = \tau_0 \exp(U_{eff}/k_B T)$] (Fig. 3) using $\chi''(\nu)$ data. Under zero dc field, the relaxation time (lnτ) is dependent on temperature above 7 K, which is a thermal activated relaxation process, while the gradual crossover below 7 K indicates the arising of the quantum tunneling process. The relaxation time of quantum tunneling of the magnetization is 0.28 ms. The energy barriers are 101 K with $\tau_0 = 5.1 \times 10^{-10}$ s in zero dc field, and 128 K with $\tau_0 = 4.2 \times 10^{-11}$ s under a 2 kOe dc field, respectively.

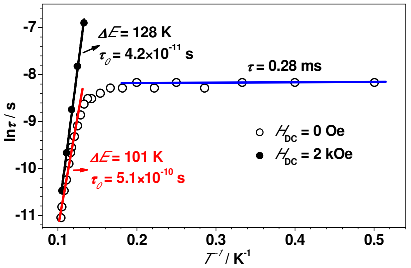

Fig. 3 Plot of ln(τ) *vs.* T^{-1} for [(C_6Me_6)Dy($AlCl_4$)$_3$] under the zero-dc field and a 2 kOe dc field.

The blocking temperature is another important factor in evaluating magnetic bistability of SMMs, and it is probably more rigorous than the energy barrier in consideration of device applications.[10] In our system, the hysteresis loop emerges at 3 K with a 200 Oe/s sweep rate of the magnetic field and becomes larger as the temperature decreases (Fig. S6, ESI†). Unfortunately, the coercive field and remanent magnetization are absent under our measurement condition.

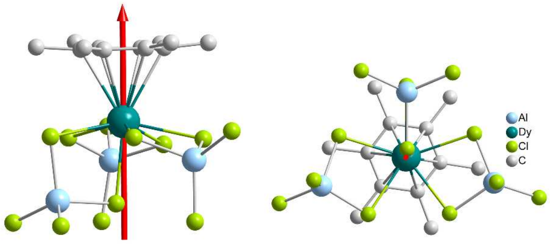

Fig. 4 The calculated easy axis orientation from *ab initio* method (red arrow) viewed perpendicular (left) and parallel (right) to the Dy-centroid (HMB) direction. Hydrogen atoms are omitted for clarity.

Recently, *ab initio* calculations have proved to be reliable in determining the orientation of the magnetic anisotropy axis of Ln(III)-SMMs.[11] We performed *ab initio* calculations on the electronic structure of [(C_6Me_6)Dy($AlCl_4$)$_3$] using MOLCAS

7.8.[12] The calculated effective g_z value is 19.6985 with g_x = 0.01455 and g_y = 0.0258, which approaches the Ising-limit value of 20. Unexpectedly, the calculated easy axis orientation is coincident with the Dy(III)-centroid (HMB) direction (2.5º) (Fig. 4). Based on electrostatic analyses[13] and reported CASSCF calculation results,[11] the HMB and the apical Cl are located above and below the oblate-shaped electron density of the Dy(III) ion, respectively. Since the HMB lies on the easy axis which is along the negative charge dense direction, it probably has a significant impact on the easy axis orientation.

To quantify the detailed negative charge distribution, a Mulliken population analysis of relevant atom charges (Table S3, ESI†) was conducted. Along the molecular *pseudo*-axis, that is, the Dy-centroid (HMB) direction, the total charge on the coordinating carbon atoms is -1.52, and the charge of the apical Cl is -0.38. The coordinating chloride atoms in the equatorial plane have a charge of -2.21 which is larger than those along the *pseudo*-axis. However, three aluminium atoms in $[AlCl_4]^-$ with the total of 2.84 positive charges largely offset the charge of Cl-plane. Due to the strong repulsion by the "pure" negative charged atoms along the *pseudo*-axis, the oblate-shaped electron density of the Dy(III) ion is more stable on the equatorial plane than along the *pseudo*-axis. Therefore, although the π-bonded arene is a neutral ligand, it is important in determining the orientation of the magnetic anisotropy axis in the present system.

As shown by *ab initio* calculations, the energy gap between the ground and first excited Kramers doublet states (Table S4, ESI†) is 80.4 cm^{-1} (115 K), which is in excellent agreement with the experimental value, suggesting that the relaxation mechanism probably is an Orbach process *via* the first excited Kramers doublet state.

Attracted by the interesting structure and magnetic behavior of $[(C_6Me_6)Dy(AlCl_4)_3]$, we synthesized its Tb analogue illustrated in Fig. S7 (Table S1 and S2, ESI†). In spite of the same ligand geometry as the Dy complex, no slow magnetic relaxation process was observed in the absence of a static field (Fig. S8, ESI†). As far as magnetic anisotropy is concerned, the calculated effective g_z value is 16.4483, indicating a severe deviation from the value of Ising-limit state ($M_J = 6$, $g_z = 18$). The calculated easy axis orientation deviates significantly from the Tb(III)-centroid (HMB) direction (37.5º) (Fig. S9, ESI†). The different easy axis orientations of the two complexes are mainly ascribed to the different shapes of the electron density distribution within the lowest M_J states, similar to the [Na{Ln(DOTA)}] system reported by Sessoli.[11(c)]

Conclusions

In summary, we report the synthesis and magnetic behavior of half-sandwich organolanthanides coordinated with a π-bonded arene for the first time. The Dy complex is a SIM with an energy barrier of 101 K and a hysteresis loop observed at 3 K. As *ab initio* calculations show, the π-bonded arene is of vital importance to impact the easy axis orientation which is along the *pseudo* C_5 molecular axis. In contrast to the Dy complex, no SIM behavior was observed in the Tb analogue. These results will encourage further exploration of this new type of SIM since the influence of different arene ligands on the orientation of the magnetic anisotropy axis and magnetic behavior should be very interesting structurally and magnetically.

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Notes and references

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