Synthesis, Structure and Magnetic Property of a Tricapped Trigonal Prismatic Tb\textsuperscript{III}-Based 3d-4f Complex

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Abstract. A novel 3d-4f Co\textsuperscript{II}/Tb\textsuperscript{III} cluster [Co\textsubscript{6}Tb(Pic)\textsubscript{6}O\textsubscript{3}Cl\textsubscript{3}](H\textsubscript{2}O)\textsubscript{6}(1) (Pic = 2-Picolinic acid) has been synthesized and characterized via X-ray crystallographic and magnetic measurements. X-ray crystallographic and continued shape measurements analysis revealed that the central Terbium (III) is coordinated in TbO\textsubscript{9} geometry with D\textsubscript{3h} symmetry. Magnetic studies indicated the complex presents a magnetic anisotropy with ferrimagnetic interactions.

1. Introduction
Single molecule magnets (SMMs) [1-6] have been intensively studied due to their bistable behaviour and their potential applications in quantum information at the molecular scales [7-10]. Normally, these researches could be classified in to three parts: one is focus on the 3d transition metal-based SMMs [11-19], one is centred on 4f/5f lanthanide/actinide-based SMMs [20-26], and the other is the heterometallic (3d-4f/5f) SMMs [27-32]. In addition, a number of the heterometallic (3d-4f/5f) SMMs not only provide a large possibility for super-exchange interactions between the 3d and 4f/5f metal ions, but also many of them could exhibit a large magnetocaloric effect which can be used as cryogenic magnetic coolants [27, 31, 33]. Herein, we opt the Terbium(III) and cobalt(II) as the ions of the 3d/4f heterometallic clusters, by in-situ one-pot solvothermal reaction obtained a green crystal. The X-ray analysis revealed an 3d-4f complex [Co\textsubscript{6}Tb(Pic)\textsubscript{6}O\textsubscript{3}Cl\textsubscript{3}](H\textsubscript{2}O)\textsubscript{6}(1) packed as a ring second structure, and related magnetic behaviour was studied.

2. Experimental Results and Discussion

2.1. Materials and Methods
All the materials for synthesis were obtained commercially and used without further purification. The Infrared (IR) spectra were recorded with a range of 400–4000 cm\textsuperscript{-1} on a Nicolet 5DX spectrometer (KBr pellets). Magnetic data were collected using a Quantum Design MPMS XL7 SQUID magnetometer. The diamagnetic correction was performed by a rough estimation (\(\chi_d = M_r \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}\)), \(M_r\) is the molecular weight.

2.2. Synthesis
A microwave-assisted reaction of Tb(NO\textsubscript{3})\textsubscript{3}, CoCl\textsubscript{2} with the ligand dppo (1,3-di(2-pyridyl)-1,3-propanedione) in a MeOH/MeCN (V/V, 1:5) mixture solution at 130\textdegree C for about 10 min, and the green
block crystals obtained weekly. In the process, in-situ reaction converted dppo’ to new pic’ ligand and formed complex 1. IR/cm\(^{-1}\): 3368, 2993, 1720, 1634, 1598, 1565, 1062, 970, 761.

2.3. Description of the Crystal Structure

First, the single crystal X-ray analysis showed that 1 crystallized in the hexagonal \(P6_3\) space group (table 1 left). In complex 1, six Co\(^{III}\) ions form a large trigonal prism and a Tb\(^{III}\) ion is situated at the center. The six Co\(^{III}\) ions belong to three bases, in each base, the two Co\(^{III}\) ions are connected to form an \(\mu_3\)-oxygen atom, a \(\mu_2\)-chloride ion and terminal oxygen atom from water. The three bases and central Tb\(^{III}\) ion are connected by picolinic acid ligands and \(\mu_3\)-oxygen atoms formed a heptanuclear trigonal prismatic Co\(_6\)Tb clusters. The central Tb\(^{III}\) ion is bridged six oxygen atoms from six pic ligands respectively and also bridged by three oxygen atoms (figure 1), which performs the distorted trigonal prism coordination geometry, and in further, the analysis from continued shape measurements (CShM) [34, 35] (figure 1 right, table 1 right) confirmed it. The value from analysis indicates the closing degree of the coordination geometry to the ideal model (value: zero), thus, the non-zero values indicate that the Tb\(^{III}\) coordination sites can be described as distorted.

2.4. Magnetic Properties

The direct-current magnetic susceptibilities has been collected in a temperature range of 300-2 K on polycrystalline samples (figure 2). The room temperature \(\chi_mT\) (\(\chi_m\): the molar susceptibility) value (26.96 cm\(^3\) K mol\(^{-1}\)) of 1 was obtained from magnetic measurements with an applied dc magnetic field of 1000 Oe (figure 2 left). Upon cooling, the \(\chi_mT\) values of 1 keep constant in the temperature range of 300-100 K, and then decrease to the minimum gradually at 20 K due to the temperature depopulation of split crystal field sublevels from Tb\(^{III}\)/Co\(^{III}\) ions, from 20 K to 2 K, the \(\chi_mT\) values of 1 increased, which exhibits a ferrimagnetic coupling behaviour for complex 1.

The variation (2.0, 2.5, 3.0, 3.5 and 4.0 K) of the magnetization \(M\) under the applied dc field \(B\) of 1 was also investigated, the \(M\) vs. \(BT^{-1}\) data (figure 2 right) demonstrates that the isotherm curves which is not overlaying, which confirmed the presence of low-lying excited states and/or non-negligible magnetic anisotropy for complex 1, and in further, 1 would display SMMs behaviour [20].

The alternating-current susceptibility datas of 1 (figure 3) has been carried out with ac frequencies ranging from 0.1 to 1500 Hz under an oscillating-drive field of 3 Oe. Unfortunately, we cannot observe the slow magnetic relaxation from the data of the out-of-phase susceptibilities (imaginary part), probably owing to its large quantum tunnelling of the magnetization (QTM), which makes the relaxation too fast to signal in the ac susceptibility characterization, but in nature, probably due to the distorted around the central Tb\(^{III}\) ion of 1, which exhibit tricapped trigonal prism coordination geometry.

**Figure 1.** The molecular structure of 1. Tb (green), O (red), N (blue), Co (Pink), C (black), the H atoms and water molecules were omitted for clarity. Left and middle: the molecular structure with different view; right: the distorted coordination geometry around the central Tb\(^{III}\) ion.
Table 1. Crystallographic data structure refinement (left) and results of the continued shape measurements (right) for complex 1.

| Complex  | 1 | Label | Symmetry | CShM |
|----------|---|-------|----------|------|
| formula  | 0.17(C36Cl3Co6N6O21Tb):2(O) | EP-9 | $D_{3h}$ | 37.968 |
| $M_r$    | 558.48 | Enneagon |   |   |
| cryst size / mm$^3$ | 0.3 x 0.15 x 0.15 | OPY-9 | $C_8v$ | 22.212 |
| cryst syst | Hexagonal | HPBY-9 | $D_{3h}$ | 20.999 |
| space group | $P6_3$ | Octagonal pyramid | | |
| $a$, Å  | 20.6782 (13) | JTC-9 | Johnson triangular cupola J3 |
| $b$, Å  | 20.6782 (13) | | |
| $c$, Å  | 14.453 (3) | JTC-9 | | |
| $\alpha$, deg | 90 | JICU-9 | Capped cube J8 |
| $\beta$, deg | 90 | | |
| $\gamma$, deg | 120 | CCU-9 | Spherical-relaxed capped cube |
| cell volume, Å$^3$ | 5352.0 (13) | JCSAPR-9 | | |
| $Z$ | 12 | CSAPR-9 | Spherical capped square antiprism |
| T, K  | 293 | | |
| $F_{000}$ | 3168 | JCSAPR-9 | | |
| $\mu$ / mm$^{-1}$ | 5.92 | | | |
| $\theta$ range / deg | 3.0 – 20.8 | JTCTPR-9 | Tricapped trigonal prism J51 |
| reflns collected | 20868 | | |
| reflns unique | 3626 | TCTPR-9 | Spherical tricapped trigonal prism |
| $R_{int}$ | 0.060 | | |
| $R_1$ | 0.080 | | |
| $wR_2$ (all data) | 0.251 | | |
| GOF | 1.05 | | |
| largest diff. peak and hole (e·Å$^{-3}$) | -0.64, 1.81 | MFF-9 | Muffin |
| | | | | |
Figure 2. Temperature dependent magnetic susceptibility (left) and $M$ vs. $BT^{-1}$ curve (right) at different temperatures for complex 1.

Figure 3. Frequency dependent ac magnetic susceptibilities of complex 1.

3. Conclusions
In summary, a TbIII-based 3d-4f complex with an anisotropy has been synthesized successfully. The TbIII achieved a TbO9 9-coordinate configuration presenting the distort $D_3$ symmetry from the CSHM analysis. The magnetic studies of 1 demonstrates that the SMMs behaviour is largely affected by symmetry of the central TbIII ion and the molecule, if we want to obtain the large effective energy barrier and slow relaxation of SMMs, a better control of the molecule symmetry to decrease QTM would be an effective way.

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