



Short communication

Syntheses, structures and magnetic properties of a series of lanthanide complexes based on p-methoxybenzoic acid



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ABSTRACT

A new series of lanthanide metal complexes $[\text{Ln}(\text{L})_3]_n$ ($\text{L} = \text{p-methoxybenzoic acid}$, $\text{Ln} = \text{Pr } \mathbf{1}$, $\text{Eu } \mathbf{2}$, $\text{Tb } \mathbf{3}$, $\text{Dy } \mathbf{4}$, $\text{Ho } \mathbf{5}$, $\text{Er } \mathbf{6}$, $\text{Yb } \mathbf{7}$) have been synthesized under hydrothermal conditions. Single-crystal X-ray diffraction measurements reveal that these compounds are isostructural, crystallizing in the monoclinic space group $P2_1/c$ and giving 1D chain structures. Magnetic studies reveal antiferromagnetic behavior for complexes **1**, **3**, **5** and **6**, ferromagnetic behavior for complex **4** and spin-canting behavior for **7**.

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In recent years, the coordination complexes are one of the most focused areas of research. And the preparation and structural elucidation of coordination complexes have been attracting significant attention, not only for their intriguing structures [1], but also for the potential applications in a wide variety of areas as functional materials, such as nonlinear optics [2], gas storage [3], separation [4], catalysis [5], luminescence [6] and magnetism [7]. Although great progress in coordination complexes' synthesis has been made, the rational and controllable preparation is still one of the obvious challenges because of many influencing factors, such as the structures of the organic ligands, pH value, metal/ligand ratio and so on. As we all know, one of the general methods to form infinite structure is using O-donor organic ligands, and many efforts have been made in this area. According to this strategy, we try to generate new complexes by using different O-containing ligands.

Benzene with one or more carboxyls and aminos has been proved to be a kind of ideal ligand to form coordination complexes with unique structures and interesting properties, which may have the following advantages: (I) The rigidity of the ligand may reduce the possibility of lattice interpenetration in the product. (II) It has many coordination sites, increasing the possibility of linking with different metal ions. (III) It could adopt various coordination modes, which may cause the generation of novel structures. Lanthanide ions, along with a

large number of unpaired 4f electrons, have high affinity and prefer to bind to hard donor atoms (such as O-donor ligands). The design of lanthanide-based 1D chains is more and more concerned, not only because of their intriguing architectures but also owing to their tremendous potential application prospects in magnetism and luminescent properties [8]. Therefore, it is a very appealing job to synthesize lanthanide complexes. Encouraged by the previous work and our group's long-standing interest in the construction of coordination complexes with interesting topologies and magnetic properties [9], in this paper we report on the syntheses [10] and characterization [11] of a new family of lanthanide complexes $[\text{Ln}(\text{L})_3]_n$ ($\text{Ln} = \text{Pr } \mathbf{1}$, $\text{Eu } \mathbf{2}$, $\text{Tb } \mathbf{3}$, $\text{Dy } \mathbf{4}$, $\text{Ho } \mathbf{5}$, $\text{Er } \mathbf{6}$, $\text{Yb } \mathbf{7}$) based on p-methoxybenzoic acid (HL). Furthermore, magnetic studies reveal the difference of magnetic properties among these complexes.

Single-crystal X-ray diffraction measurements reveal that the structures of **1–7** are isostructural, crystallizing in the monoclinic space group $P2_1/c$, thus only the structure of **4** as a representative is described here in detail. As shown in Fig. 1a, the asymmetric unit contains one crystallographically independent Dy(III) center and three deprotonated L^- ligands. The Dy1 site is coordinated by eight carboxyl oxygen atoms from six L^- ligands, which exhibit a distorted bicapped trigon-prismatic geometry [$\text{Dy1-O} = 2.270(3)–2.610(2) \text{ \AA}$]. The Dy-O bond lengths are in the normal range [12]. In **4**, the completely deprotonated L^- ligands adopt two different coordination modes of $\mu_2: \eta^2, \eta^1$ and $\mu_2: \eta^1, \eta^1$ (Scheme 1. I, II). Along the c-axis direction, Dy(III) ions are in turn bridged by treble carboxylate of L^- ligand to give rise to a 1D chain with the Dy-Dy distance of ca. $3.9257(8) \text{ \AA}$, and Dy-O-Dy angle of ca. $105.003(83)^\circ$ and $107.025(84)^\circ$ (Fig. 1b).

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Table 1
Crystal data and structure refinement for **1–7**.

Compound	1	2	3	4	5	6	7
Formula	C ₂₄ H ₂₁ O ₉ Pr	C ₂₄ H ₂₁ O ₉ Eu	C ₂₄ H ₂₁ O ₉ Tb	C ₂₄ H ₂₁ O ₉ Dy	C ₂₄ H ₂₁ O ₉ Ho	C ₂₄ H ₂₁ O ₉ Er	C ₂₄ H ₂₁ O ₉ Yb
<i>M_r</i>	594.32	605.37	612.34	615.91	618.34	620.67	626.45
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	13.487 (3)	13.460 (3)	13.430 (3)	13.430 (3)	13.402 (3)	13.378 (3)	13.300 (3)
<i>b</i> /Å	22.451 (5)	22.526 (5)	22.608 (5)	22.646 (5)	22.698 (5)	22.736 (5)	22.908 (5)
<i>c</i> /Å	7.8385 (16)	7.7191 (15)	7.6674 (15)	7.6514 (15)	7.6323 (15)	7.6225 (15)	7.6250 (15)
α /°	90	90	90	90	90	90	90
β /°	104.43 (3)	104.59 (3)	104.50 (3)	104.55 (3)	104.51 (3)	104.46 (3)	104.21 (3)
γ /°	90	90	90	90	90	90	90
<i>V</i> /Å ³	2298.6 (9)	2265.0 (8)	2253.9 (8)	2252.4 (8)	2247.7 (8)	2245.0 (8)	2252.1 (8)
<i>Z</i>	4	4	4	4	4	4	4
<i>D_c</i> /g·cm ⁻³	1.717	1.775	1.805	1.816	1.827	1.836	1.848
<i>F</i> (000)	1184	1200	1208	1212	1216	1220	1228
<i>S</i>	1.043	1.063	1.037	1.046	1.076	1.042	1.023
<i>R</i> ₁	0.0281	0.0299	0.0315	0.0270	0.0358	0.0289	0.0303
ωR_2	0.0632	0.0631	0.0633	0.0569	0.0974	0.0541	0.0592

$$^a R_1 = \sum (|F_0 - F_c|) / \sum |F_0|; \omega R_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)]^{1/2}.$$

Further analysis of the crystal packing reveals that extensive weak hydrogen-bonds are also existent in this structure (C(8)–H(8)⋯C(5) 2.891(3) Å, 142.64°; C(19)–H(19)⋯O1, 3.255 Å, 139.15°; C(15)–H(15)⋯O9, 3.290 Å, 142.07°), which may play a key role in constructing the 2D layer. Moreover, in this case, these hydrogen-bonds may play a complementary role for stabilizing the network structure.

Variable-temperature magnetization measurements of **1**, **3**, **4**, **5**, **6** and **7** were performed in the 1.8–300 K range at 1000 Oe applied field. Magnetic studies suggest that this series of lanthanide complexes show different magnetic properties. The $\chi_M T$ vs *T* curves are shown in Fig. 2. The $\chi_M T$ values at room temperature for **1**, **3**, **5** and **6** are 1.53, 11.40, 13.37 and 11.35 cm³ mol⁻¹ K, respectively. These values are consistent with the calculated values of 1.60 cm³ mol⁻¹ K (*g*_{Pr} = 4/5), 11.82 cm³ mol⁻¹ K (*g*_{Tb} = 3/2), 14.07 cm³ mol⁻¹ K (*g*_{Ho} = 5/4) and 11.48 cm³ mol⁻¹ K (*g*_{Er} = 6/5) in the free-ion approximation. The $\chi_M T$ values of **1**, **3**, **5** and **6** decrease monotonously with reducing temperature down to 0.06, 4.83, 2.68 and 4.44 cm³ mol⁻¹ K at 1.8 K, respectively. The temperature dependence of the reciprocal susceptibility (χ_M^{-1}) can be fitted by the Curie–Weiss law ($\chi_M = C/(T - \theta)$) for **1**, **3**, **5** and **6** above 1.8 K, giving a Curie constant *C* = 1.82, 11.80, 13.76 and 11.21 cm³ mol⁻¹ K, a Weiss constant θ = –51.35, –14.76, –8.60 and –10.09 K for **1**, **3**, **5** and **6**, respectively (Fig. S1). These negative values suggest antiferromagnetic interactions between the adjacent metal ions [9].

For **4** and **7**, the $\chi_M T$ values at room temperature (Fig. 3) are 14.07 and 2.23 cm³ mol⁻¹ K, respectively, which are all a little bit lower than the expected values of 14.17 cm³ mol⁻¹ K (*g*_{Dy} = 4/3) and 2.57 cm³ mol⁻¹ K (*g*_{Yb} = 8/7). As temperature decreases, the $\chi_M T$ value of **4** increases gradually to the maximum of 14.31 cm³ mol⁻¹ K at 74.9 K, then decreases to 9.18 cm³ mol⁻¹ K at 1.8 K. The data for **4** can be fitted by the Curie–Weiss law ($\chi_M = C/(T - \theta)$), giving a Curie constant *C* = 13.94 cm³ mol⁻¹ K and a Weiss constant θ = +2.25 K. With lowering of the temperature, the $\chi_M T$ value of **7** reduces gradually to the minimum of 1.19 cm³ mol⁻¹ K and then increases slightly to 1.33 cm³ mol⁻¹ K at 1.8 K. The data (96.0–300 K) for **7** is in accordance with the Curie–Weiss law, showing *C* = 2.68 cm³ mol⁻¹ K and θ = –61.70 K. Magnetic studies reveal ferromagnetic behavior for complex **4** and spin-canting behavior for **7** [9,13].

For further proof of the results above, field-dependent magnetization measurements *M*–*H* of **4** and **7** were carried out at 2 K under a magnetic field up to 80 kOe. Upon increasing the applied external magnetic field, complexes **4** and **7** show a drastic increase of the

magnetization at low fields, and then slowly reach the maximum values of 6.28 and 1.55 *N*β, respectively, which are all lower than the expected saturation values of 10 and 4 *N*β for **4** and **7**. Sigmoidal-shaped hysteresis loops were provided in Fig. 4, indicating the soft ferromagnetic behavior because of undetectable coercivity in **4** and **7**.

The structures of **1–7** are isostructural, thus complexes **3**, **4** and **6** were chosen as representatives for thermal gravimetric analysis (TGA) under N₂ atmosphere. From the curves, complexes demonstrate a good thermal stability and only one-step process of weight loss happened, for no lattice water molecules are included in the structures of **3**, **4** and **6**. For complex **3**, a main weight loss happened in the temperature range of 308–605 °C, which indicates the decomposition of coordination framework (observed, 30.49%; calculated, 29.87%). The TG curve for **4** displays the main weight loss in the temperature range of 315–617 °C, which can be attributed to the decomposition of the organic ligands (observed, 29.72%; calculated, 30.28%). In the case of complex **6**, a weight loss between 298 °C and 631 °C is ascribed to the decomposition of the organic ligands (observed, 30.75%; calculated, 30.81%). As shown in Fig. 5, the trends of the three TG curves are roughly similar and the change in each TG curve is in conformity with the molecular formula of each complex, showing that complex **3**, **4** and **6** are isostructural.

In summary, a new series of lanthanide metal complexes based on *p*-methoxybenzoic acid have been successfully synthesized. They are all isostructural, exhibiting 1D chain, which is in turn bridged by treble carboxylate of L⁻ ligands and further forms a 2D layer by weak hydrogen-bonds. Magnetic studies of these complexes show different magnetic properties depending on the difference of metal ions.

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Appendix A. Supplementary data

Additional figures and crystal data for **1–7** are available as electronic supplementary information in the online version, at <http://dx.doi.org/10.1016/j.inoche.2016.01.020>.

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