

Enantiopure sandwich-type nonanuclear  $\text{Ln}^{\text{III}}_3\text{Mn}^{\text{III}}_6$  clusters†

Yong Zheng, Xiang-Jian Kong, La-Sheng Long,\* Rong-Bin Huang and Lan-Sun Zheng

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Three enantiopure isostructural sandwich-type clusters,  $\text{Ln}^{\text{III}}_3\text{Mn}^{\text{III}}_6$  ( $\text{Ln} = \text{Dy}$  (1),  $\text{Tb}$  (2) and  $\text{Gd}$  (3)) have been synthesized through reactions of a chiral Schiff-base ligand ((*S,E*)-4-(2-hydroxybenzylideneamino)-2-hydroxybutanoic acid,  $\text{H}_3\text{L}$ ) with manganese and lanthanide ions, showing intramolecular antiferromagnetic interaction.

3*d*-4*f* heterometallic complexes have attracted considerable attention due to their structural diversity,<sup>1</sup> and potential applications in magnetic,<sup>2</sup> luminescent,<sup>3</sup> and electrical materials.<sup>4</sup> Recently, the magneto-chiral dichroism (MChD) effect in chiral paramagnetic complexes has encouraged material scientists to prepare multifunctional molecular materials containing chirality and magnetism simultaneously.<sup>5</sup> Although it is expected to obtain such a kind of complexes through achiral multidentate ligands to bridge paramagnetic carriers by spontaneous resolution,<sup>6</sup> unambiguously, utilizing chiral multidentate ligands to bridge paramagnetic carriers, such as transition metal ions and lanthanide ions,<sup>7,8</sup> is the most effective strategy to synthesize this kind of complexes. Following this strategy, many chiral transition metal clusters,<sup>7,9</sup> lanthanide clusters<sup>8,10</sup> and few chiral 3*d*-4*f* heteroclusters have been synthesized.<sup>11</sup> However, no enantiopure 3*d*-4*f* heterometallic clusters have been reported so far.

$\text{H}_3\text{L}$  is a chiral pentadentate Schiff-base ligand containing N-/O-donor atoms. Although an enantiopure  $\text{Fe}_3$  cluster has been obtained on the basis of this ligand,<sup>7c</sup> it remains a challenge to synthesize enantiopure 3*d*-4*f* heterometallic complexes based on the ligand, despite that such a kind of ligand is a promising candidate for preparing polynuclear 3*d*-4*f* heterometallic complexes.<sup>12</sup> Herein, we report three enantiopure sandwich-type heteronuclear 3*d*-4*f* metallic clusters,  $[\text{Ln}^{\text{III}}_3\text{Mn}^{\text{III}}_6(\text{L})_6(\mu_2\text{-OMe})_6(\text{OAc})(\text{H}_2\text{O})_2(\text{HOMe})_3](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Dy}$  (1),  $\text{Tb}$  (2) and  $\text{Gd}$  (3)).

Compound 1 to 3 were synthesized through the reaction of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{L}^-$  formed *in situ* and triethylamine (TEA) in MeOH in the molar ratio of 2 : 1 : 2 : 4.† Single-crystal structural and elemental analyses reveal

that 1 to 3 crystallized in the same chiral space group  $P2_12_12$  (no. 18) and are isomorphous.‡ Thus, only the structure of 1 is discussed in detail. The asymmetric unit of 1 consists of a cation,  $[\text{Dy}^{\text{III}}_3\text{Mn}^{\text{III}}_6(\text{L})_6(\mu_2\text{-OMe})_6(\text{OAc})(\text{H}_2\text{O})_2(\text{HOMe})_3]^{2+}$ , two nitrate counter anions and several disordered guest molecules. As shown in Fig. 1a, the cation in 1 contains three  $\text{Dy}^{\text{III}}$  ions, six  $\text{Mn}^{\text{III}}$  ions, six  $\text{L}^3$  ligands, six  $\mu_2\text{-OMe}$  ligands and six terminal ligands (one acetate, two aqua ligands and three methanol molecules). The deprotonation of O atoms and the oxidation states of the Mn in the cation cluster were established by combination of charge balance considerations, bond valence sum (BVS) calculations (Supporting information, Table S1†),<sup>13</sup> and inspection of  $\text{Mn}^{\text{III}}$  Jahn–Teller axes.

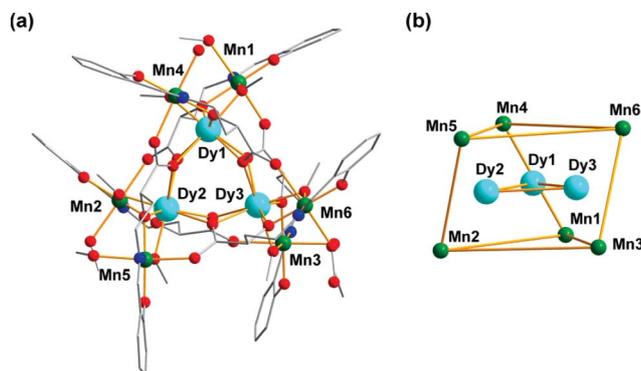


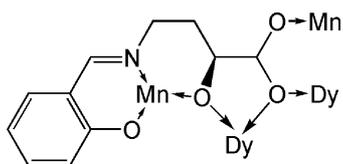
Fig. 1 View of the cationic structure (a) and backbone of 1 (b). Color scheme: cyan spheres,  $\text{Dy}^{\text{III}}$ ; green spheres,  $\text{Mn}^{\text{III}}$ ; gray lines, C; red spheres, O; blue spheres, N. Hydrogen atoms are omitted for clarity.

Each  $\text{L}^3$  ligand chelates one  $\text{Mn}^{\text{III}}$  ion through its one N, one  $\text{O}_{\text{phenolic}}$  and  $\text{O}_{\text{alkoxide}}$  atom to form a  $[\text{MnL}]$  unit. Three  $[\text{MnL}]$  units connected through the carboxylate from one  $[\text{MnL}]$  unit monodentately coordinated to the  $\text{Mn}^{\text{III}}$  ion from adjacent  $[\text{MnL}]$  units generates a ring-like structure. Linking two ring-like structures through three  $\text{Dy}^{\text{III}}$  ions with each  $\text{O}_{\text{carboxylate}}$  and  $\text{O}_{\text{alkoxide}}$  from one  $[\text{MnL}]$  unit respectively coordinated to two  $\text{Dy}^{\text{III}}$  ions and one  $\text{Dy}^{\text{III}}$  ion leads to the nonanuclear  $\text{Ln}^{\text{III}}_3\text{Mn}^{\text{III}}_6$  cluster arranged in  $D_3$ -symmetry, in which, the equilateral triangle of  $\text{Dy}_3$  is sandwiched in a twisted trigonal prism formed with six  $\text{Mn}^{\text{III}}$  ions (Fig. 1b). Meanwhile, all the six  $\text{L}^3$  ligands display the same  $\eta^1:\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$  chelating/bridging mode as shown in Scheme 1.

Solidifying the backbone of the cluster through adjacent  $\text{Mn}^{\text{III}}$  and  $\text{Dy}^{\text{III}}$  ions in the cluster bridged by a  $\mu_2\text{-OMe}$  and finishing the coordination sphere of the six  $\text{Mn}^{\text{III}}$  ions in the cluster

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: [lslong@xmu.edu.cn](mailto:lslong@xmu.edu.cn); Fax: +86 592 218 3047

† Electronic supplementary information (ESI) available: Bond valence sum (BVS) calculations, CD spectra of  $\text{H}_2\text{L}^-$  and X-Ray Powder Diffraction patterns of 1 and 3. CCDC reference numbers 808237 and 808238. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10044k

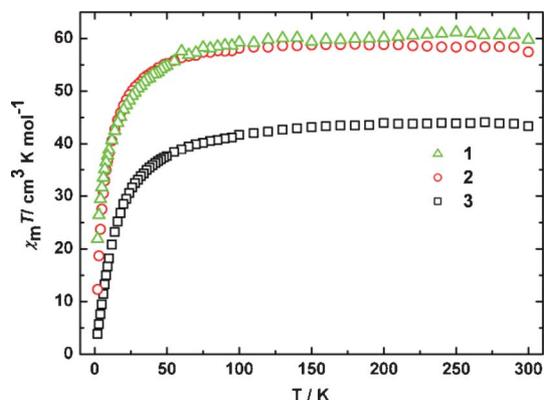


**Scheme 1** The  $\eta^1:\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$  chelating/bridging mode of  $L^{3-}$  ligand in **1**.

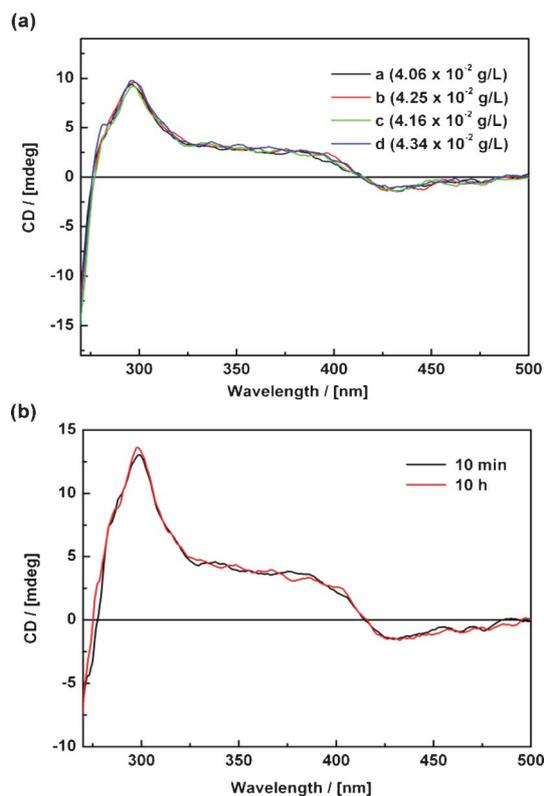
respectively with six terminal ligands (one acetate, two aqua ligands and three methanol molecules) generates a cation cluster of  $[\text{Dy}^{\text{III}}_3\text{Mn}^{\text{III}}_6(\text{L})_6(\mu_2\text{-OMe})_6(\text{OAc})(\text{H}_2\text{O})_2(\text{HOME})_3]^{2+}$  (Fig. 1a). In the cation cluster, each  $\text{Dy}^{\text{III}}$  ion is eight coordinated by four  $\text{O}_{\text{carboxylate}}$  and two  $\text{O}_{\text{alkoxide}}$  respectively from four  $L^{3-}$  ligands and two  $\mu_2\text{-OMe}$ , displaying trigondodecahedron geometry. Each  $\text{Mn}^{\text{III}}$  ion is in an elongated octahedron geometry coordinated by  $\text{NO}_2$  donors from one  $L^{3-}$ , one  $\text{O}_{\text{carboxylate}}$  from another  $L^{3-}$  ligand, a  $\mu_2\text{-O}$  from one methanol. The sixth terminal ligand is methanol, water molecule or acetate.

The Mn–O, Mn–N and Dy–O bond distances are 1.847(5)–2.288(6) Å, 1.980(7)–2.042(7) Å and 2.280(4)–2.497(5) Å, respectively, well agreement with those in  $\text{Dy}^{\text{III}}\text{–Mn}^{\text{III}}$  clusters reported previously.<sup>14</sup> The shortest distances of Mn...Mn, Dy...Mn and Dy...Dy are 5.6524(20), 3.3396(12) and 3.9614(9) Å respectively. The Mn–O–Dy and Dy–O–Dy angles range from 104.0(2) to 105.8(2)° and 107.89(16) to 109.0(2)°.

The dc magnetic susceptibility for **1** to **3** were measured in the temperature range of 2.0 to 300 K under an applied magnetic field of 1000 Oe. The  $\chi_M T$  vs.  $T$  plots are given in Fig. 2. The  $\chi_M T$  products of **1**, **2** and **3** at room temperature are 59.73, 57.45 and 43.32  $\text{cm}^3 \text{mol}^{-1} \text{K}$  (300 K), respectively, close to the expected value of 60.51, 53.46 and 41.64  $\text{cm}^3 \text{mol}^{-1} \text{K}$  for six independent  $\text{Mn}^{\text{III}}$  ions ( $S = 2$ ,  $g = 2.0$ ) and three independent  $\text{Ln}^{\text{III}}$  ions ( $\text{Dy}^{\text{III}}$ ,  ${}^6\text{H}_{15/2}$ ,  $g = 4/3$ ,  $\text{Tb}^{\text{III}}$ ,  ${}^7\text{F}_6$ ,  $g = 3/2$  and  $\text{Gd}^{\text{III}}$ ,  ${}^8\text{S}_{7/2}$ ,  $g = 2.0$ ).<sup>15</sup> With the decrease of the temperature, the  $\chi_M T$  values for **1** to **3** decrease slowly before *ca.* 50 K, and after 50 K, the  $\chi_M T$  values begin to drop abruptly and reach to the minimum of 21.90 for **1**, 12.31 for **2** and 3.84  $\text{cm}^3 \text{mol}^{-1} \text{K}$  for **3** at 2 K. For **1** and **2**, the decreasing of  $\chi_M T$  values is possibly due to the thermal depopulation of excited Stark sublevels and/or weak antiferromagnetic interactions between adjacent spin carriers.<sup>16</sup> However, the decreasing of  $\chi_M T$  value for **3** can be attribute to weak intramolecular antiferromagnetic interaction as the  $\text{Gd}^{\text{III}}$



**Fig. 2** Temperature dependence of the  $\chi_M T$  at 1000 Oe for the clusters **1** to **3**.



**Fig. 3** The CD spectra of **1** (a, for one crystal; b, c, d: for bulk samples) in methanol (a); and CD spectra of **1** in MeOH after 10 min and 10 h (b).

has a pure spin ground-state  ${}^8\text{S}_{7/2}$ .<sup>17</sup> Consistently, the data over the temperature range of 50–300 K fit well with the Curie–Weiss law with  $C = 45.45 \text{ cm}^3 \text{mol}^{-1} \text{K}$ ,  $\theta = -9.23 \text{ K}$  for **3**.

Cluster **1** was selected as an example to confirm the enantiopurity of these compounds. As shown in Fig. 3, not only the CD spectra from different batch of bulk samples are almost same, but also almost same as that for one crystal when their concentrations very close (Fig. 3a). Owing to the CD spectra of the  $\text{H}_2\text{L}^{2-}$  itself in MeOH being silent (Supporting information, Fig. S1†), while the CD spectra for single-crystal **1** in MeOH at different times almost keep unchanged (Fig. 3b), these facts indicate that the cationic cluster in **1** in MeOH is undissociated. Thus, the CD spectra for the bulk sample in MeOH very similar to that for one crystal in MeOH at similar concentration means that bulk sample of **1** is crystallized in enantiopure form. Although the CD spectra of one crystal for **2** and **3** were not investigated, based on the CD spectra of bulk samples of **1**, **2** and **3** (Supporting information, Fig. S2†), it is reasonable to deduce that bulk samples of **2** and **3** also crystallize in enantiopure form.

In conclusion, we, based on the chiral Schiff-base ligand  $\text{H}_3\text{L}$ , have successfully obtained three enantiopure sandwich-type heterometallic  $\text{Mn}^{\text{III}}\text{–Ln}^{\text{III}}$  clusters. Investigation on their magnetic property shows weak antiferromagnetic interactions between adjacent spin carriers in the  $\text{Mn}^{\text{III}}\text{–Gd}^{\text{III}}$  cluster.

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## Notes and references

‡ A mixture of LiOH·H<sub>2</sub>O (0.5 mmol) and (S)-4-amino-2-hydroxybutanoic acid (0.5 mmol) in methanol (10 mL) was stirred for 20 min, then 2-hydroxybenzaldehyde (0.5 mmol) was added to the solution and stirred for about 1 h at room temperature. The resulting Schiff-base (H<sub>2</sub>L<sup>-</sup>) formed *in situ* was added 0.5 mmol of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, 0.25 mmol Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 1.0 mmol TEA, and stirred again for another 4 h at ambient condition, the resulting dark brown solution was layered with *n*-hexane. Block dark crystals were collected in few days. **1** (Yield: 40.0% based on Mn). Anal. Calcd (%) for C<sub>77</sub>H<sub>109</sub>N<sub>8</sub>O<sub>49</sub>Mn<sub>6</sub>Dy<sub>3</sub>: C, 33.66; H, 4.00; N, 4.08; Found (%): C, 33.55; H, 4.07; N, 3.98. IR (KBr, cm<sup>-1</sup>): 3415(b, s), 2929(w), 1600(vs), 1547(m), 1472(w), 1449(m), 1384(vs), 1305(m), 1202(w), 1136(m), 1080(w), 977(w), 909(w), 793(w), 761(w), 633(m), 591(w), 544(m), 518(w), 462(w). **2** (Yield: 40.0% based on Mn). Anal. Calcd (%) for C<sub>77</sub>H<sub>109</sub>N<sub>8</sub>O<sub>49</sub>Mn<sub>6</sub>Tb<sub>3</sub>: C, 33.79; H, 4.01; N, 4.09. Found: C, 33.43; H, 3.96; N, 4.09. IR (KBr, cm<sup>-1</sup>): 3422(b, s), 2924(w), 1599(vs), 1547(m), 1471(w), 1449(m), 1384(vs), 1309(m), 1202(w), 1136(m), 1080(w), 977(w), 909(w), 793(w), 758(w), 631(m), 591(w), 542(m), 518(w), 462(w). **3** (Yield: 50% based on Mn). Anal. Calcd (%) for C<sub>77</sub>H<sub>109</sub>N<sub>8</sub>O<sub>49</sub>Mn<sub>6</sub>Gd<sub>3</sub>: C, 33.85; H, 4.02; N, 4.10. Found (%): C, 33.68; H, 3.98; N, 4.13. IR (KBr, cm<sup>-1</sup>): 3423(b, s), 2922(w), 1621(vs), 1620(vs), 1548(m), 1472(w), 1448(m), 1384(vs), 1305(m), 1203(w), 1134(m), 1081(w), 977(w), 909(w), 801(w), 762(w), 629(m), 543(m), 516(w), 462(w).

§ Crystal data for **1**: C<sub>77</sub>H<sub>109</sub>N<sub>8</sub>O<sub>49</sub>Mn<sub>6</sub>Dy<sub>3</sub>, *M* = 2747.86, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2 (no. 18), *a* = 28.061(6), *b* = 28.125(6), *c* = 14.303(3) Å, *V* = 11288(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.617 g cm<sup>-3</sup>, Mo-Kα, λ = 0.71073 Å, completeness = 99.7% (to θ<sub>max</sub> = 27.48°), *T* = 173(2) K, total data 108571, unique data 25844, μ = 2.694 mm<sup>-1</sup>, Flack parameter = 0.044(9), 1270 parameters, *R*<sub>1</sub> = 0.0496 (*I* > 2σ), *wR*<sub>2</sub> = 0.1293 (all data), and *S* = 1.053. Crystal data for **2**: C<sub>77</sub>H<sub>109</sub>N<sub>8</sub>O<sub>49</sub>Mn<sub>6</sub>Tb<sub>3</sub>, *M* = 2737.12, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2 (no. 18), *a* = 27.991(6), *b* = 28.123(6), *c* = 14.285(3) Å, *V* = 11245(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.617 g cm<sup>-3</sup>, Mo-Kα, λ = 0.71073 Å, completeness = 99.8% (to θ<sub>max</sub> = 27.48°), *T* = 173(2) K, total data 103412, unique data 25761, μ = 2.597 mm<sup>-1</sup>, Flack parameter = 0.054(13), 1289 parameters, *R*<sub>1</sub> = 0.0651 (*I* > 2σ), *wR*<sub>2</sub> = 0.1819 (all data), and *S* = 1.036. Because it is difficult for us to obtain high quality single crystals suitable for single-crystal study, the conclusion of **3** being an isomorphous to **1** is thus demonstrated from X-ray powder diffraction of **3** (Supporting information, Fig. S3†). The structures were solved by direct methods and all non-H atoms were subjected to anisotropic refinement on *F*<sup>2</sup> using SHELXTL-97. There are six guest water molecules per formula unit of both complexes, as indicated in the difference density map. They are however severely disordered and were therefore removed by SQUEEZE in structural refinement. CCDC 808237, 808238 contain the crystallographic data for this paper.† These data can be obtained via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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