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A trinuclear copper (II) complex derived from a chiral [3 + 3] phenol-based macrocycle: Synthesis, structure and magnetic properties

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ABSTRACT

An enantiopure trinuclear Cu(II) complex of chiral phenol-based macrocyclic polyamine ligand, which is derived from the [3 + 3] condensation of 3,5-diformyl-4-hydroxyzoic acid ethyl ester with (1*R*,2*R*)-1,2-diaminocyclohexane and followed by borohydride reduction, has been synthesized and characterized. The circular dichroism (CD) spectra confirmed its structural chirality in the bulk sample. Variable temperature magnetic data indicated that there is an antiferromagnetic coupling between the metal centers in the complex.

Recent years have witnessed an explosion of interests in the research of macrocyclic complexes, not only because of their intriguing variety of architectures and multinuclear metals, but also because of their fascinating extraordinary properties in the fields of catalysis, molecular recognition, metalloenzyme and magnetic materials [1]. Currently, there have been extensive studies on the synthesis and construction of the phenol-based metal complexes based on macrocyclic Schiff-bases or reduced Schiff-bases, which are derived from 4-substituted-2,6-diformyl phenols with diamines and also display interesting magnetic, electronic, and/or catalytic properties [2–4]. Until now, a large number of homodinuclear [5] or heterodinuclear [2a,6] discrete complexes with this kind of symmetrical and asymmetrical phenol-based macrocycles have been reported. However, the synthesis of complexes containing more than two metal centers is still in their infancies due to the easy degradation of [3 + 3], [4 + 4] and larger macrocycles in the presence of metal ions [4b,7]. Meanwhile, the diamines mainly focused on achiral diamines, such as ethylenediamine or diethylenetriamine and 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde [5,6,8], and the use of chiral diamines such as 1*R*,2*R*-diaminocyclohexane, 1*R*,2*R*-diphenylethylenediamine, and *R*-1,1-binaphthalenyl-2,2-diamine in the construction of chiral Schiff base Robson-type macrocycles has received limited studies [4b,7,9–12].

On the other hand, considerable efforts have been directed in the last two decades towards the research of polynuclear copper(II) complexes due to their specific properties for a wide range of remarkable applications including catalysts, metal enzyme mimics and molecular-based magnets [13]. Phenol-based chiral macrocyclic polyamine ligands have been widely developed in the construction of chiral polynuclear metal complexes, such as Ln(III) [10] and Zn(II) [7b,11]. Only two trinuclear Cu(II) complexes of chiral macrocycles derived from [3 + 3] condensation products of 1,2-trans-diaminocyclohexane and dicarbonyl compounds have been published, which showed the presence of antiferromagnetic coupling between the triangular metal centers [12]. As part of our ongoing study of phenol-based macrocyclic polyamine ligands and their complexes [4], we report here the synthesis [14], crystal structure [15,16] and magnetic properties of a new chiral trinuclear Cu(II) complex, $[Cu_3(\text{Et-L})(OH)][Cu_3(\text{Me-L})(OH)]\cdot 4ClO_4\cdot 2CH_3OH\cdot C_2H_5OH$ (**1**), by designing a new macrocyclic ligand via the [3 + 3] condensation of (1*R*,2*R*)-1,2-diaminocyclohexane with 3,5-diformyl-4-hydroxyzoic acid ethyl ester and followed by borohydride reduction (Scheme 1), in which Me-H_3L comes from the transesterification of Et-H_3L and methanol during the growth of single crystals of **1** with Et-H_3L and $Cu(ClO_4)_2$ in mixed methanol/water solution at room temperature.

Compared to that of Et-H_3L, IR spectra of complex **1** exhibit distinguishable variations coming from red shift of absorption peaks and a new strong band in the 1115 cm^{-1} region which can be ascribed to the vibration of perchlorates, suggesting that Cu(II) ions have been incorporated into the macrocyclic ligands [17c]. Meanwhile, the peaks of 2935 and 2863 cm^{-1} can be attributable to the C–H (of methylene groups) stretching vibration [17]. The peak of 1701 cm^{-1} can be attributed to the C=O (of ester groups) stretching vibration. Strong absorption bands at 1304 and 1210 cm^{-1} are due to the C–N stretching vibration (see Fig. S3).

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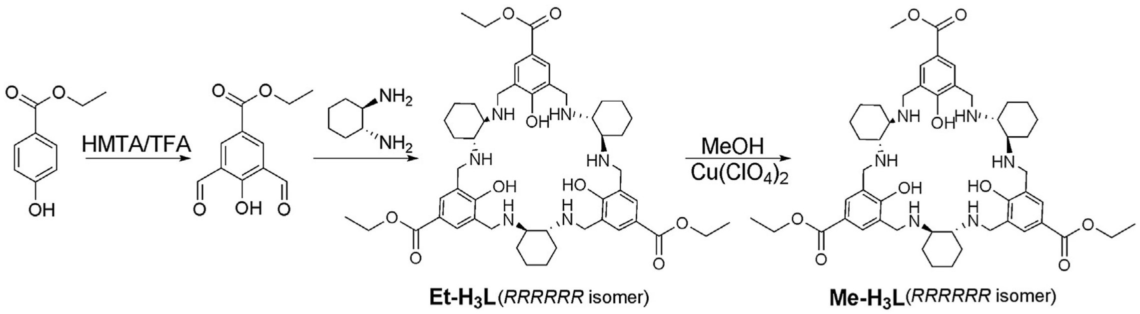

Scheme 1. Synthesis of Et-H_3L and Me-H_3L.

Single-crystal X-ray diffraction reveals that **1** crystallizes in monoclinic $P2_1$ space group, with the asymmetric unit of four perchlorates, two methanol and one ethanol molecules, as well as two similar trinuclear Cu(II) units: [Cu_3(Et-L)(OH)] and [Cu_3(Me-L)(OH)]. The macrocyclic ligands in [Cu_3(Et-L)(OH)] and [Cu_3(Me-L)(OH)] are a little different, but the two trinuclear Cu(II) units have the same coordination environments and modes of the corresponding Cu(II) ions and the macrocyclic ligands, as well as the similar bond length and bond angles (Fig. 1 and Table S1). Thus, only the structure of [Cu_3(Et-L)(OH)] is depicted in detail. The deprotonated macrocyclic ligand in [Cu_3(Et-L)(OH)] shows a highly distorted, irregular saddle-shaped conformation, which reflects the helical twist and the considerable folding of the macrocycle [12]. Meanwhile, the macrocyclic ligand provides two amine nitrogen atoms from the same diaminocyclohexane for each Cu(II) and offers one bridging, two bridging, one bridging and one terminal deprotonated phenol oxygen atom for Cu_1, Cu_2 and Cu_3, respectively, being different from the reported chiral trinuclear Cu(II) complexes of macrocyclic amines, in which each deprotonated phenol oxygen atom bridges two adjacent Cu(II) atoms [12]. In [Cu_3(Et-L)(OH)], each Cu(II) ion exhibits different geometry (Fig. 1a). Both Cu_1 and Cu_3 display an approximate square-planar geometry, being surrounded by two adjacent amine nitrogen atoms and two oxygen atoms. For Cu_1, the two oxygen atoms come from a bridging phenoxo oxygen atom O_4 and a bridging hydroxyl group; while for Cu_3, the two oxygen atoms originate from a bridging phenoxo oxygen atom O_1 and a terminal phenoxo oxygen atom O_7. Cu_2 is square pyramidal with the base of the pyramid defined by two adjacent amine nitrogen atoms, a bridging phenoxo oxygen atom O_4 and a bridging hydroxyl group. The apical is occupied by another bridging phenoxo oxygen atom O_1 with the $Cu_2 \cdots O_1$ distance of 2.413(7) Å, which is substantially longer than the $Cu_2 \cdots O_4$ and $Cu_2 \cdots O_{20}$ distances of 1.979(6) and 1.905(7) Å, respectively, and is typical for square pyramidal Cu(II) complexes (Fig. 1 and Table S1) [12]. Additionally, in the axial positions, Cu_2 and Cu_3 have a very weak interaction with a perchlorate and an oxygen atom from an ester group of an adjacent macrocyclic ligand, respectively, with the $Cu \cdots O$ distances of 2.707(8)–2.862(11) Å. Cu_1 and Cu_2, as well as Cu_2 and Cu_3, are bridged by a deprotonated phenol oxygen atom, with the $Cu_1 \cdots Cu_2$ and $Cu_2 \cdots Cu_3$ distances of 2.876(3) and 3.900(1) Å, as well as the Cu_1–O_4–Cu_2 and Cu_2–O_1–Cu_3 angles of 95.0(3) and 132.9(3)°, respectively. Cu_1 and Cu_3 are not bridged by a phenoxo oxygen atom and the $Cu_1 \cdots Cu_3$ distance is 4.062(4) Å. It's noting that after coordination to the Cu(II) ions, the achiral nitrogen atoms N_1 and N_{11} of the amines in the free ligands adopt *R* configuration and all the other nitrogen atoms adopt *S* configuration, being different from those that we reported, in which all the nitrogen atoms adopt *S* configuration after they are ligated to metal ions [17c–h]. This may be ascribed to the folding of the macrocycles, which makes the configurations of the corresponding nitrogen atoms changed in order to meet the needs of coordination to Cu(II) ions.

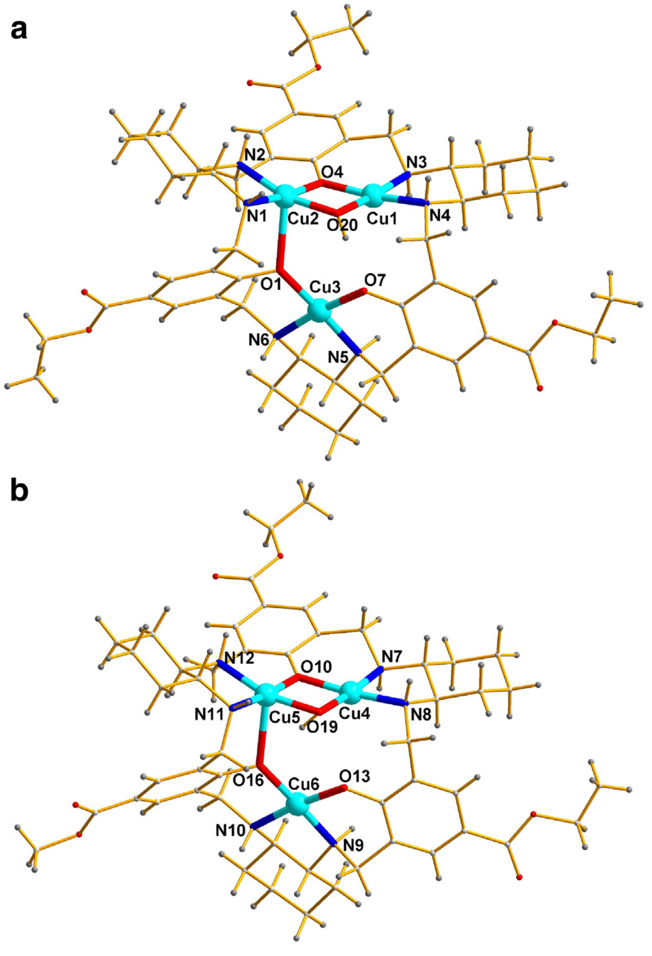

Fig. 1. The trinuclear Cu(II) units of [Cu_3(Et-L)(OH)] (a) and [Cu_3(Me-L)(OH)] (b) in **1**.

Phase purity of the bulky crystalline sample of **1** was confirmed by a good match between the experimental and simulated powder X-ray diffraction (PXRD) patterns, as shown in Fig. S4.

The thermogravimetric analysis of powder sample **1** was carried out from 31 to 898 °C under nitrogen atmosphere at the heating rate of 10 $°C\ min^{-1}$, as shown in Fig. S5. There is a distinct weight loss between 31 and 242 °C (expt. 2.5%, calcd. 4.0%), which shows the release of the free methanol and ethanol molecules. Then, the weight loss of 71.4% in a range of 242–898 °C indicates the removal of the macrocyclic ligands and the decomposition of the whole structure.

Circular dichroism (CD) spectroscopy is a very powerful technique to check the chirality of bulk materials [17,18]. The chiral nature of the ligand Et-H_3L and complex **1** was confirmed by solid state CD spectroscopy using powdered bulk crystals in a KBr matrix (Fig. 2). The ligand and **1** were found to display similar dichroic signals in their CD spectra with four positive Cotton effects at frequencies of 206, 246, 273, 322 and

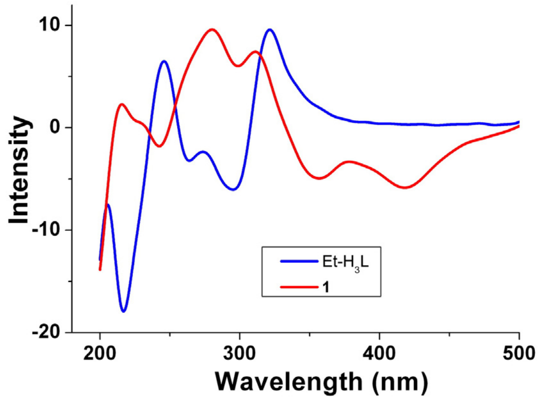

Fig. 2. CD spectra of Et-H$_3$L and **1** in the solid state at room temperature.

267 nm, as well as 216, 280, 311 and 378 nm, respectively, and three negative Cotton effects at frequencies of 217, 263 and 295 nm, as well as 242, 299 and 357 nm, respectively, which exhibits the chirality of the compounds and is in agreement with the chiral space group of **1**.

The magnetic properties of **1** were determined over the temperature range 2–300 K at an applied field of 1000 Oe. Plots of magnetic susceptibility χ_M and its product of $\chi_M T$ vs T are shown in Fig. 3. The value $\chi_M T$ at 300 K for six Cu(II) ions equals 1.98 cm^3 K mol^{-1}, which is slightly lower than the value expected for six magnetically isolated copper(II) ions (2.25 cm^3 K mol^{-1} for $S_{Cu} = 1/2, g = 2$). On cooling, $\chi_M T$ continuously decreases and reaches 0.83 cm^3 K mol^{-1} at 2 K. The temperature dependence of magnetic susceptibilities above 100 K obeys the Curie–Weiss law $\chi_M = C / (T - \theta)$ with a Weiss constant $\theta = -108(2)$ K and a Curie constant $C = 2.77(2)$ cm^3 K mol^{-1}, indicating a dominant antiferromagnetic interaction between the metal centers.

In conclusion, a chiral trinuclear Cu(II) complex has been synthesized with Cu(ClO$_4$)$_2$ and a chiral phenol-based macrocycle, which comes from the [3 + 3] condensation of 3,5-diformyl-4-hydroxyzoic acid ethyl ester with (1*R*,2*R*)-1,2-diaminocyclohexane and followed by borohydride reduction. The good agreement of the patterns of experimental and simulated powder X-ray diffraction (XRD) confirmed the phase purity of as-synthesized bulk products. The circular dichroism (CD) spectra proved that the complex is structural chirality in the bulk sample. Analysis of variable-temperature magnetic susceptibility data indicated that there are antiferromagnetic interactions between the metal centers.

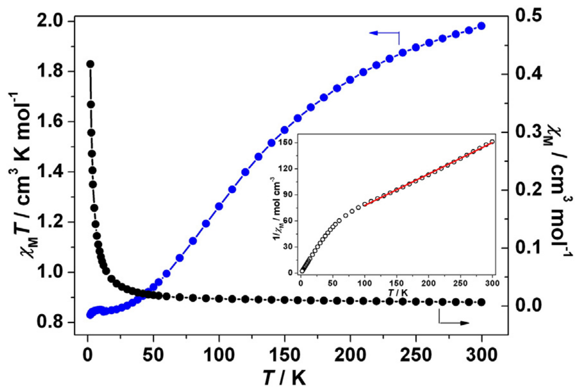

Fig. 3. Temperature dependence of χ_M and $\chi_M T$ for **1**. Inset: temperature dependence of χ_M^{-1} for **1**; the red solid line represents the best fit of the Curie–Weiss law $\chi_M = C / (T - \theta)$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

IR, XRD and X-ray crystallographic files in CIF format of **1**. CCDC reference number: 1004400. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.07.032. This data include MOL file and InChiKey of the most important compounds described in this article.

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[14] The synthesis of Et-H_3L was in the Supplementary materials. **1** was prepared by adding a methanol solution (6 mL) of Et-H_3L (182 mg, 0.2 mmol) to a solution (H_2O, 4 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (68 mg, 0.2 mmol). The resulting blue solution was stirred for half an hour at room temperature, then filtered. The filtrate was left evaporated in air for 3 weeks. Blue block crystals of **1** were obtained. Yield: 62% (56 mg) based on Cu(II).

[15] Crystal data for **1**: $C_{105}H_{152}Cl_4Cu_6N_{12}O_{39}$, $Mr = 2729.49$, monoclinic, space group $P2_1$, $a = 13.146(2)$ Å, $b = 15.897(3)$ Å, $c = 29.052(5)$ Å, $\beta = 96.195(2)°$, $V = 6035.9(18)$ Å^3, $Z = 2$, $D_{calcd.} = 1.502$ g/cm^3, $\mu = 1.213$ mm^{-1}, Flack $x = 0.02(2)$, $R_{1[I > 2\sigma(I)]} = 0.0915$, $wR_{2(\text{for all data})} = 0.1909$. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97 [16]. Anal. calcd (%): C 46.20, H 5.61, and N 6.16; found: C 46. 16, H 5.64, and N 6.19.

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