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# A novel 2D net-like supramolecular polymer constructed from $Ln_6Cu_{24}$ node and *trans*-$Cu(Gly)_2$ bridge†

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**A 2D net-like lanthanide-copper heterometallic supramolecular network {$Ln_6Cu_{27}$} 1 was synthesized with $Ln_6Cu_{24}$ octahedral cluster as the node and *trans*-Cu(glycinato)$_2$ group as the linker. The compound represents the first example of 2D polymer with high-nuclear 3d–4f heterometallic cluster as the node.**

The synthesis and characterization of 3d–4f heterometallic complexes is an active research area since 1985.[1] And currently the crystal engineering of coordination polymeric solids containing lanthanide ions and transition metal ions has made rapid progress due to their potential applications as functional materials[2] and diverse structure motifs.[3] But despite extensive research on metal–organic open framework with both single 3d and 4f ions as nodes, little is known about 3d–4f heteronuclear cluster nodes.[4] The use of polymetal units to construct supramolecular arrays can not only make the functional supramolecular frameworks inherit interesting magnetic, optical, electrical and thermostable properties from the introduced clusters but also make the size of cave or pore of coordination solids increase observably, which is of great significance for the design and synthesis of supramolecular architectures analogous to important minerals such as quartz, clays and zeolites, just as that observed in the famous metal–organic frameworks with dimetal unit,[5] polynuclear zinc unit[6] and $Ln_4$ unit[7] as nodes.

We have proven that amino acids are excellent ligands for the construction of 3d–4f heteronuclear clusters.[4(a),8] In this paper we will show that with the help of *trans*-$Cu(Gly)_2$ as linker, a novel 33-nuclear net-like complex $Na_2[Ln_6Cu_{27}(Gly)_{20}(\mu_3\text{-}OH)_{30}(H_2O)_{22}(ClO_4)](ClO_4)_{23}(H_2O)_{28}$ **1** (Ln = Er, Eu, Gd) was obtained through the self-assembly. The most striking structural feature of this compound is the presence of a high-nuclear 3d–4f heterometallic $Ln_6Cu_{24}$ octahedral-like node in the 2D network. Here we only discuss the structure of **1**·Er as example.[9]

**1**·Er was prepared by the reaction of $Er(ClO_4)_3$, $Cu(ClO_4)_2$ and glycine in aqueous solution at high pH (about 6.6). Blue crystals were obtained several weeks later. As shown in Fig. 1, the $Er_6Cu_{24}$ octahedral-like node may be described as a huge $Er_6Cu_{12}$ octahedron (inner core) with pseudocubic $O_h$ symmetry and twelve outer $Cu^{II}$ ions. Six $Er^{III}$ ions are located at the vertices and twelve inner $Cu^{II}$ ions are located at the midpoints of each edge of the octahedron with edge distance of about 7 Å. The average Er···Cu(inner) and Cu(inner)···Cu(inner) distances are about 3.5 and 3.4 Å respectively. Each $Er^{III}$ ion also interconnects two outer $Cu^{II}$ ions with the help of one outer $\mu_3$-$OH^-$ and two $[3.1_1 2_{23} 1_3]$-coordinated glycine ligands (Scheme 1). The average Er···Cu(outer) distance is about 3.5 Å while that of two neighboring outer $Cu^{2+}$ is about 3.0 Å, shorter than that of Cu(inner)···Cu(inner). Thirty $\mu_3$-$OH^-$ groups, each one linking one $Er^{III}$ and two $Cu^{II}$ ions, were used to construct the metal framework. $Er^{III}$ has an $O_9$ donor set and the coordination polyhedron may be best described as a monocapped square antiprism. Inner $Cu^{II}$ ion has a slightly distorted six-coordinated octahedral configuration with an $O_6$ donor set. To the twelve outer $Cu^{II}$ ions, four are four-coordinated with $NO_3$ square planar geometry, the other eight adopt five-coordinated $NO_4$ square-pyramidal geometry.

A particularly novel structural feature of the node is the encapsulated $\mu_{12}$-$ClO_4^-$ anion at the centre of the $Er_6Cu_{12}$ octahedral inner metal cage (each oxygen atom of the $ClO_4^-$ anion coordinates to three inner $Cu^{2+}$ ions). The template role of this anion is confirmed by the unsuccessful attempt to synthesise analogous structures with $Cl^-$ as the anion. Previously, it had been reported that a template $ClO_4^-$ is essential in the synthesis of $Ln_6Cu_{12}$ clusters.[10] Now we provide another elegant demonstration of the rather under appreciated potential role of the anions in the self-assembly process.

Fig. 2 shows the 2D net-like structure of **1**·Er. In the crystal, each $Er_6Cu_{24}$ unit was firstly polymerized through two *trans*-$Cu(Gly)_2$ bridges to yield a 1D chain running parallel to the *b* direction. Then these chains are further connected by one *trans*-$Cu(Gly)_2$ group. That is, each $Er_6Cu_{24}$ unit is connected through six *trans*-$Cu(Gly)_2$

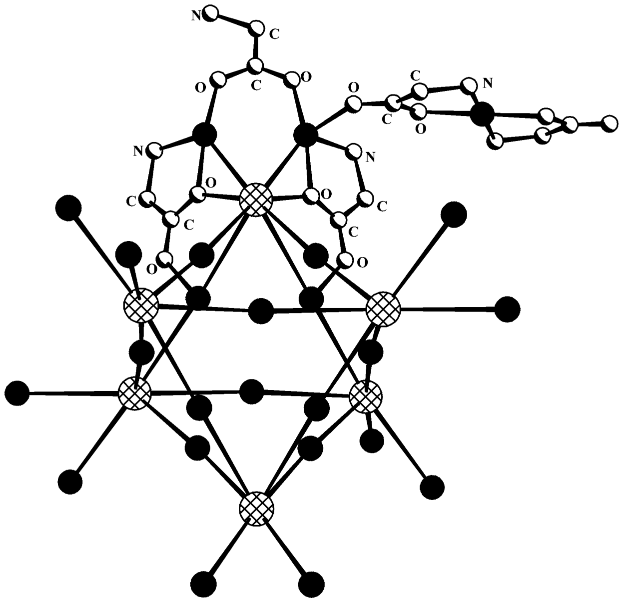
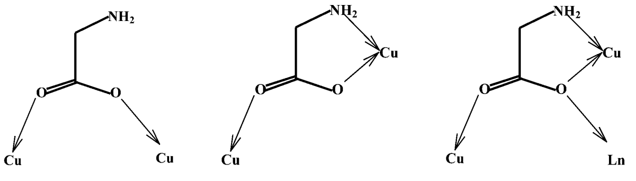


**Fig. 1** The metal framework of the $Er_6Cu_{24}$ node, ● Cu ▨ Er.



[2.110] $[2.1_1 1_2 1_2]$ $[3.1_1 2_{23} 1_3]$

**Scheme 1** Three coordination modes of glycinato ligands indicated by the Harris notation.[11]

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† Electronic supplementary information (ESI) available: synthesis, detailed structure figures, electrical conductivity–temperature and $\chi_M T$ *vs T* graphs for the complex. See http://www.rsc.org/suppdata/cc/b4/b400447g/

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bridges to four neighboring $Er_6Cu_{24}$ units, resulting in a 2D net-like structure.

In fact, the structure of the $Ln_6Cu_{12}$ inner core is similar to the $\{Ln_6Cu_{12}\}$ cluster with $\eta_2$-coordinated betaine as ligand.[10] But as the amino acid has more coordination modes than betaine, this makes the structure of our complex much more beautiful and intriguing than the 0D 18-nuclear complex: (1) [2.110]-coordinated glycines, each coordinates to neighbouring outer $Cu^{2+}$ ions; (2) $[3.1_12_{23}1_3]$-coordinated glycines, each chelates to one inner $Cu^{II}$, one outer $Cu^{II}$ and one $Er^{III}$ ions. Twelve more $Cu^{2+}$ ions were introduced into the system, thus a higher-nuclear cluster is obtained; (3) $[2.1_11_21_2]$-coordinated glycines, two of which coordinate to one bridge $Cu^{2+}$ ion. The *trans*-$Cu(Gly)_2$ linker thus formed is used to bridge high-nuclear nodes and the 2D polymer was obtained.

The length of the *trans*-$Cu(Gly)_2$ linker (the distance of the two spare carboxylate oxygen atoms) is about 7.83 Å, compared with 7.34 Å of terephthalic acid and 7.08 Å of 4,4′-bipyridine. This linker uses two spare carboxylate oxygen atoms to coordinate to the outer $Cu^{II}$ of the $Er_6Cu_{24}$ unit and the two nodes are thus bridged.

The electrical conductivity of **1**·Er was determined as powder sample from ground crystals. The electrical conductivity of **1**·Er is about $1.25\times10^{-7}$ S $cm^{-1}$ at 238.15K and increases as the temperature rises, which indicates that it is a semiconductor. Temperature dependent magnetic susceptibility of complex **1**·Er was also measured. At room temperature, the $\chi_M T$ value for it is 80.97 $cm^3$ $mol^{-1}$ K, compared with the expected value (78.98) for **1**·Er $\{Er_6Cu_{27}\}$. Upon cooling, the complex shows a continuous decreasing of $\chi_M T$, suggesting an overall antiferromagnetic coupling, as confirmed by the negative Weiss constant (−6.9K). According to the literature,[10,12] the Cu(inner)···Cu(inner) and Cu(outer)···Cu(outer) exchange interactions are all antiferromagnetic, but the Cu (bridge)···Cu (outer) exchange interaction may be weakly ferromagnetic. The overall antiferromagnetic interaction of the complex also indicates that the magnetic interaction of Er–Cu may be antiferromagnetic.

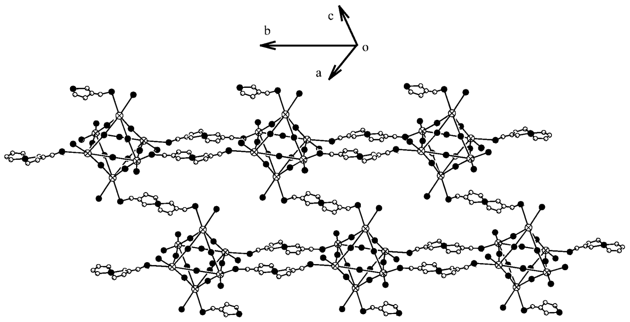

**Fig. 2** The schematic diagram of the 2D net-like structure of **1**·Er.

In summary, with the help of three coordination modes of the amino acid, the first example of 2D net-like supramolecular network with high-nuclear Ln–Cu cluster as node could be obtained. We may anticipate other novel compounds could be obtained through the different linking of this unusual $Ln_6Cu_{24}$ node and *trans*-Cu(amino acidate)$_2$ linker. More work on this subject is in progress.

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