Two 3D Supramolecular Polymers Constructed from an Amino Acid and a High-Nuclear Ln_6Cu_{24} Cluster Node

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Abstract: The first successful attempt to construct 3D supramolecular frameworks with high-nuclear 3d–4f heterometallic clusters as a node is reported. The self-assembly of Ln^{3+}, Cu^{2+} and amino acid in solution leads to the formation of two polymers, 35-nuclear complex $\{Sm_6Cu_{29}\}$ **1** with a primitive cubic net-like structure and 36-nuclear complex $\{Nd_6Cu_{30}\}$ **2** with a face-centred cubic network type structure. Glycine and L-proline, respectively, were used as ligands. It should be noted that **2** has a chiral framework. X-ray structure analyses show that **1** crystallizes in the triclinic $P\bar{1}$ space group (a = 19.6451(8), b = 20.4682(8), c = 20.7046(8) Å, α = 89.453(1), β = 66.290(1), γ = 68.572(1)°, V = 7003.0(5) Å^3 and Z = 1) and **2** belongs to the cubic $P2(1)3$ space group (a = b = c = 32.4341(3) Å, V = 34119.7(5) Å^3 and Z = 4). Both complexes utilize Ln_6Cu_{24} octahedral clusters as nodes and *trans*-Cu(amino acid)$_2$ groups as bridges. Electrical conductivity measurements reveal that both polymers behave as semiconductors.

Keywords: amino acids · cluster compounds · coordination polymers · supramolecular chemistry

Introduction

In the past decade the design and synthesis of inorganic–organic hybrid supramolecular frameworks based upon the principle of crystal engineering have made rapid progress because of their potential applications as microporous, magnetic, nonlinear optical and fluorescent materials.[1] Many interesting coordination polymers with cavity or porosity structures have been obtained by using metal ions and bridging ligands containing O-donor or N-donor, such as bipyridine, polycarboxylates and their related species.[2] The structure motif of earlier research in this area started with single metal coordination centers as nodes; further on, polymetal units were utilized to construct supramolecular arrays. For example, dimetal units,[3] polynuclear zinc unit,[1a] Ln_4 unit,[4] Cd_8 unit[5] have been used as geometry-setting metallic components in the assembly of metal-organic frameworks. The merits of this trend are obvious: 1) The functional supramolecular frameworks can inherit interesting magnetic, optical, electrical and thermostable properties from the newly introduced clusters; 2) the size of cave or pore of coordination solids could increase considerably after the utilization of clusters as nodes; this is of great significance for the design and synthesis of supramolecular architecture analogous to important minerals such as quartz, clays and zeolites.

The synthesis and characterization of 3d–4f heterometallic complexes are an active research area since the pioneering work of Gatteschi.[6] Up to now metal-organic open frameworks with both single 3d and 4f ions as nodes have been extensively explored.[7] However, the similar research on heteronuclear 3d–4f nodes is still very rare[8] (only two 1D complexes and one 2D complex have been reported thus far).

Recently our research interest has been focused on the coordination chemistry of 3d–4f amino acid systems and many interesting results have been obtained.[8a,9] In this paper we will show that with the *trans*-Cu(AA)$_2$ (AA: amino acid) group as the linker, a 3D complex $\{Sm_6Cu_{29}\}$ **1** with a primitive cubic net-like structure and a 3D complex $\{Nd_6Cu_{30}\}$ **2** with a face-centred cubic network type structure were constructed with glycine and L-proline, respectively, as

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the ligand. It should be noted that **2** gives a chiral framework. The common feature of the two complexes is that they both use Ln_6Cu_{24} octahedral-like clusters as a node. To the best of our knowledge, the complexes represent the first example of using high-nuclear 3d–4f heterometallic clusters as nodes for the construction of 3D supramolecular networks, thus revealing new possibilities in the construction of supramolecular frameworks. Herein, we report the crystal structures, electrical conductivity and magnetic measurements of both frameworks.

Results and Discussion

Description the structure of Ln_6Cu_{24} node: Both complexes use Ln_6Cu_{24} octahedral-like clusters as the node. Figure 1 shows the metal skeleton of the Ln_6Cu_{24} node. This node is composed of two parts: the Ln_6Cu_{12} octahedral inner core and twelve outer Cu^{II} ions.

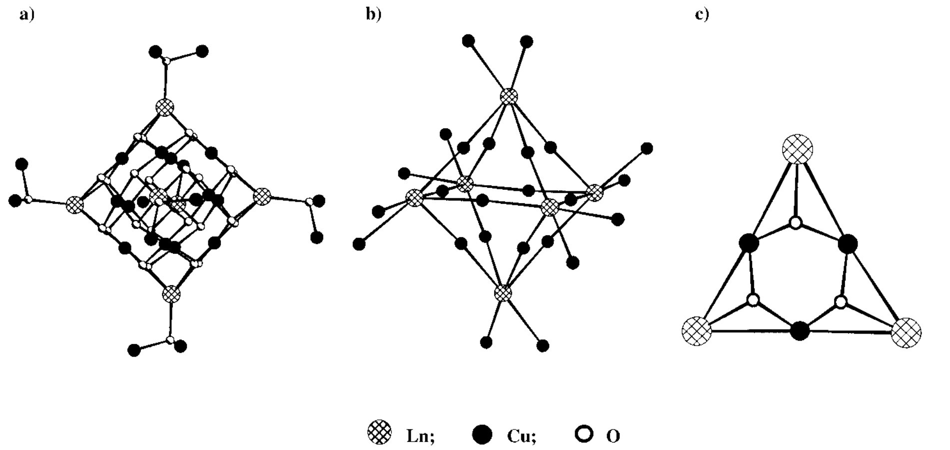


Figure 1. a) Metal-hydroxide framework of the $\{Ln_6Cu_{24}OH_{30}\}$ node; b) metal framework of the Ln_6Cu_{24} node; c) structure of one of the faces of the Ln_6Cu_{24} octahedron.

The inner core may be described as a huge Ln_6Cu_{12} octahedron with pseudocubic O_h symmetry. Six Ln^{III} ions with an average distance of about 7 Å located at the vertices of a non-bonding octahedron and twelve inner Cu^{II} ions located at the midpoints of the octahedral edges. The average Ln···Cu(inner) and Cu(inner)···Cu(inner) distances are about 3.5 and 3.4 Å, respectively. Twenty-four inner μ_3-OH^- groups, each one linking one Ln^{III} and two Cu^{II} ions, were used to construct the framework. Each surface of the octahedron is composed of three lanthanide ions and three Cu^{II} ions linked by three μ_3-OH^- groups. The μ_3-OH^- groups deviate about 0.6–0.75 Å outwards from the plane defined by the metal ions. The angles of Cu-O-Cu and Ln-O-Cu are in the range of 111–121 and 102–106°, respectively. In another word the octahedron could be regarded as being composed of Ln-O-Cu-O quadrilateral (about 2.4×2 Å) and Cu_3–O_3 (about 2 Å) distorted hexagonal windows.

Twelve outer Cu^{II} ions, every two are connected to one Ln^{III} ion with the help of one outer μ_3-OH^-; two η_4-coordinated glycine ligands were used to construct the Ln_6Cu_{24} node. The average Ln···Cu(outer) distance is about 3.5 Å, while that of two neighboring outer Cu^{2+} is about 3.0 Å; this is shorter than that of the Cu(inner)···Cu(inner) distance. It should be noted that a distorted ClO_4^- anion, which may play the role of a template, is captured in the cage.[10a] The anion uses oxygen atoms to coordinate to the inner copper ions.

The coordination polyhedron of the nine-coordinated Ln^{III} with an O_9 donor set may be best described as a monocapped square antiprism (Figure 2). The lower plane is determined by four inner μ_3-OH^- groups. Two carboxylate oxygen atoms and two water molecules form the upper plane. The whole coordination polyhedron is completed by the additional binding of one outer μ_3-OH^- "cap". The Ln–O bond lengths are in the range of 2.5–2.6 Å.

The inner Cu^{II} ion has a slightly distorted six-coordinated octahedral configuration with an O_6 donor set. Four μ_3-OH^- groups coordinate from the equatorial position with bond lengths of about 2 Å while the other two oxygen atoms from one ClO_4^- and one carboxylate group coordinate from the axial position with the bond lengths of about 2.3–2.4 Å. Some of outer Cu^{II} ions are four-coordinated by three oxygen and one nitrogen atoms in square planar geometry, while others adopt five-coordinated NO_4 square-pyramidal geometry (the fifth-coordinated sites of them could be occupied by carboxylate oxygen atoms or water molecules).

The glycine ligand adopts a η_4-coordinated mode, chelating two Cu^{II} and one Ln^{III} ions through the carboxylate and amino groups (Scheme 1c).

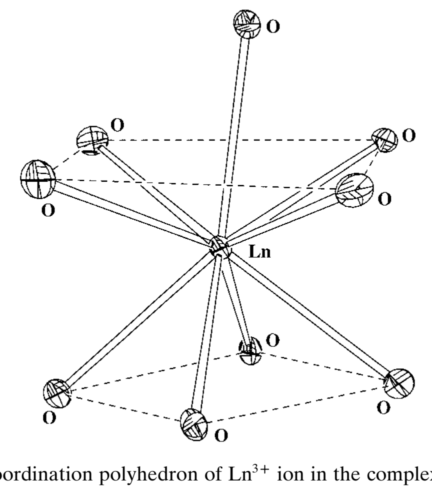
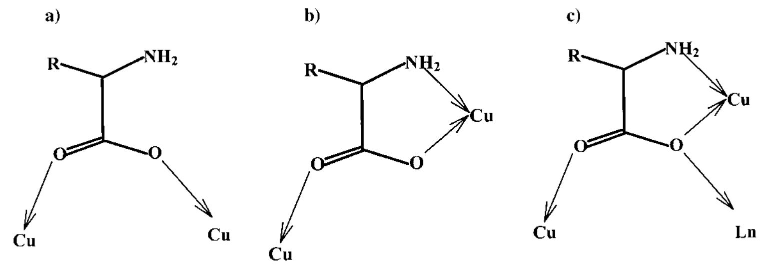


Figure 2. Coordination polyhedron of Ln^{3+} ion in the complexes.



Scheme 1. Three coordination modes of amino acid. a) η_2-coordination mode; b) η_3-coordination mode; c) η_4-coordination mode.

Figure 5 shows the "brick-wall"-like structure of **1** with channels running parallel to the *b* directions and Figure 6 shows one of the "brick" units. From Figure 6b we can see that each Sm_6Cu_{24} unit is connected through ten *trans*-Cu(Gly)$_2$ bridges to six neighboring Sm_6Cu_{24} units and the network topology might be described as a distorted primitive cubic network. The quasi-rectangular channel thus formed has a crystallographic dimensions of about 7×31 Å^2.

Complex 1: The structure of the cation is shown in Figure 3. Selected bond lengths and angles are given in the Supporting Information, Tables S1 and S2, respectively. In **1**, glycine was used as the ligand. Complex **1** is a three-dimensional network based on the Sm_6Cu_{24} node and *trans*-Cu(Gly)$_2$ bridge. Figure 4 and Figure S1 and S2 in the Supporting Information show the structures of the vertices of the octahedron. Cu10, Cu10A are four-coordinated in square-planar geometry and have an NO_3 donor set which consists of one amino nitrogen and one carboxylate atoms from glycine, one outer μ_3-OH^- and one water molecule. Cu7, Cu7A, Cu9, Cu9A are also four-coordinated just as that of Cu10, although the water molecule is replaced by a carboxylate oxygen from the *trans*-Cu(Gly)$_2$ bridge. The other Cu^{2+} ions (Cu8, Cu8A, Cu11, Cu11A, Cu12, Cu12A) adopt five-coordinated NO_4 square-pyramidal geometry. The fifth-coordinated sites of them are occupied by carboxylate oxygen atoms from the *trans*-Cu(Gly)$_2$ bridge. In **1**, only Cu11 and Cu12 are bridged by a η_2-coordinated glycine.

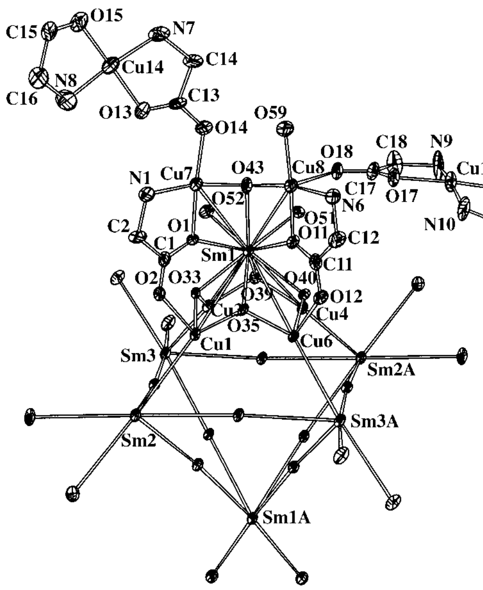


Figure 4. Structure of one of vertices (Sm1) of the octahedron of **1** (ellipsoids at 25 % probability).

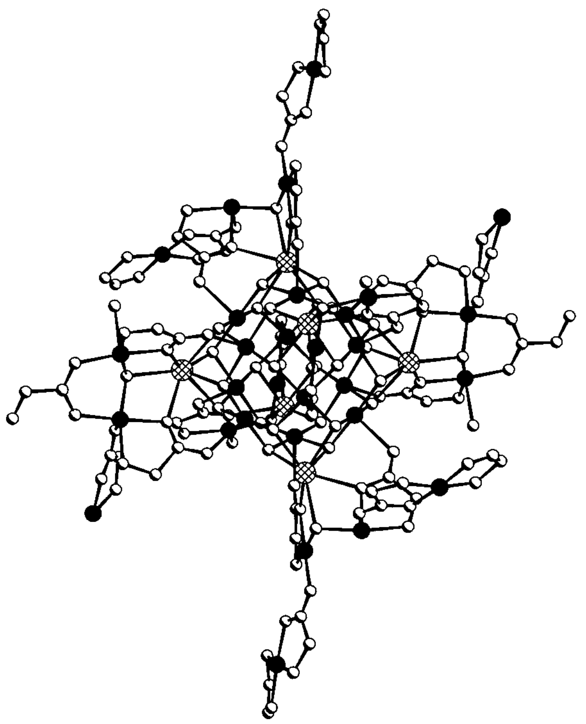


Figure 3. Structure of the cation of **1** (the captured ClO_4^- ion is omitted for clarity).

Complex 2: When the chiral amino acid proline was used as the ligand—instead of glycine—a 3D complex **2**, which crystallized in the chiral *P*2(1)3 space group, could be obtained under the same reaction conditions. The structure of the cation is shown in Figure 7. Selected bond lengths and angles are shown in Tables S3 and S4, Supporting Information. Complex **2** is also a three-dimensional network based on the Nd_6Cu_{24} node and *trans*-Cu(Pro)$_2$ bridge and represents a rare example of construction of chiral framework from simple reagents and reaction. Figures S3 and S4 in the Supporting Information show the structures of the vertices of the octahedron. Of the twelve outer copper ions, three (Cu7, Cu7A and Cu7B) are four-coordinated in square-planar geometry and have an NO_3 donor set which consists of one amino nitrogen atom and one carboxylate atom from glycine, one outer μ_3-OH^- and one carboxylate oxygen from the *trans*-Cu(Pro)$_2$ bridge. Three (Cu5, Cu5A and Cu5B) are five-coordinated in a square-pyramidal geometry. The square-coordinated plane is just like that of Cu7 and a water

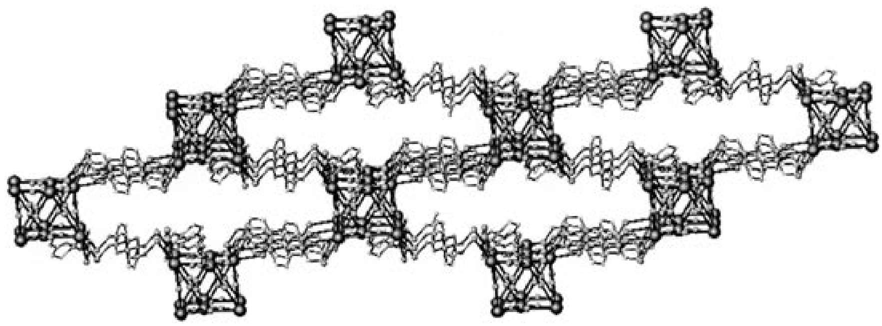


Figure 5. 3D "Brick-wall"-like structure of **1** viewed along the *b* direction. All η_4-coordinated glycine ligands have been omitted for clarity.

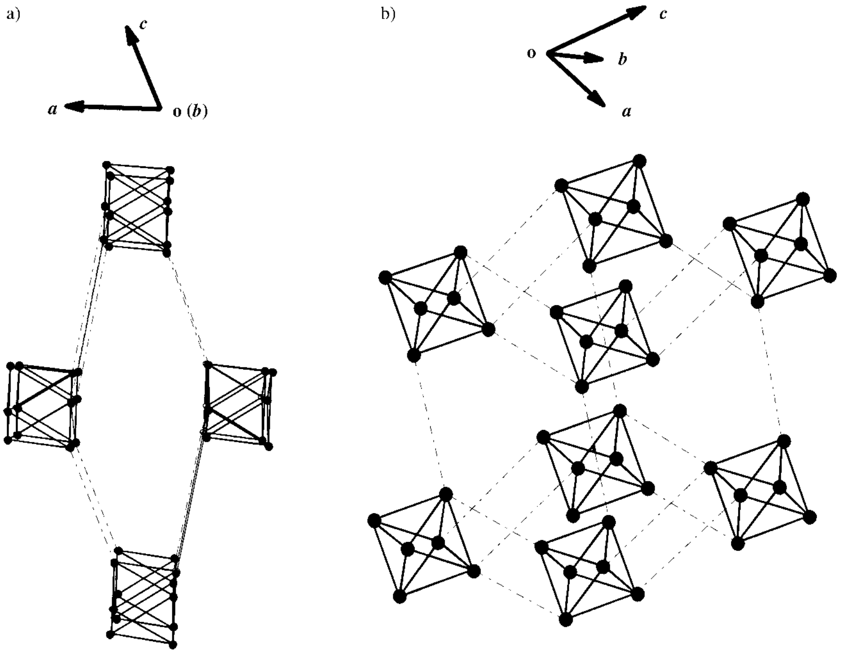


Figure 6. Schematic diagram of one of the "brick"-like channels of **1**, dot line denotes the *trans*-Cu(Gly)$_2$ bridge. a) Down view of the channel along the *b* direction; b) side view of the channel.

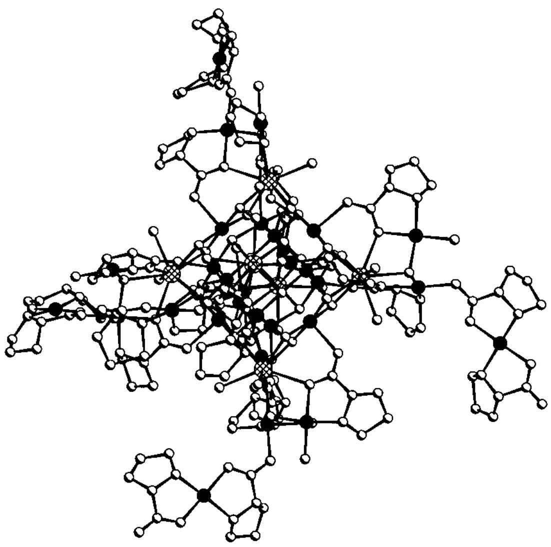


Figure 7. Structure of the cation of **2** (the captured ClO_4^- ion is omitted for clarity).

molecule occupies the fifth apical place. The other six (Cu6, Cu6A, Cu6B, Cu8, Cu8A and Cu8B) are also five-coordinated. The square plane is determined by one amino nitrogen atom and one carboxylate atom from glycine, one outer μ_3-OH^- and one water molecule, while the carboxylate oxygen from the *trans*-Cu(Pro)$_2$ bridge coordinates from apical place.

The steric effect of the L-proline side chain, compared with glycine, is responsible for the great structural difference of **2**. In **2**, each Nd_6Cu_{24} unit is connected to twelve neighboring Nd_6Cu_{24} units with the help of twelve *trans*-Cu(Pro)$_2$ bridges; the structure might be described as a cubic close packed network (also known as face-centred cubic), a type of packing of prime importance in crystallography (as shown in Figure 8a).

From another point of view, **2** could also be viewed as building from $\{Nd_6Cu_{24}\}_4$ tetrahedral building block with an edge of about 23 Å (the distance between the ClO_4^- atoms captured in the metal cage), as shown in Figure 8b. This block not only has a large pore itself, but also can form superlattices with large pore size and high pore volume compared with the close-packed lattices of the colloidal nanoparticles. Complex **2** represents a very rare example of transition metal coordination polymer constructed from high-nuclear tetrahedral building block except the chalcogenide supertetrahedral frameworks.[11]

Discussion of the Structures

The effective free volumes of **1** and **2** are about 3976 and 16283 Å^3, comprising 56.8 and 47.7% of the crystal volume, respectively, as calculated by the program PLATON.[12] (Hydrogen atoms on coordinated OH^- and water molecules are not included in calculations.) This value is large among the known microporous networks, close to that observed in the 3D supramolecule with Cd_8 as nodes.[5] Free water molecules and ClO_4^- ions are encapsulated in the large pores.

The spontaneous aggregation of small building blocks in solution that recognize each other through multiple molecular recognition sites has been proven as an effective way of

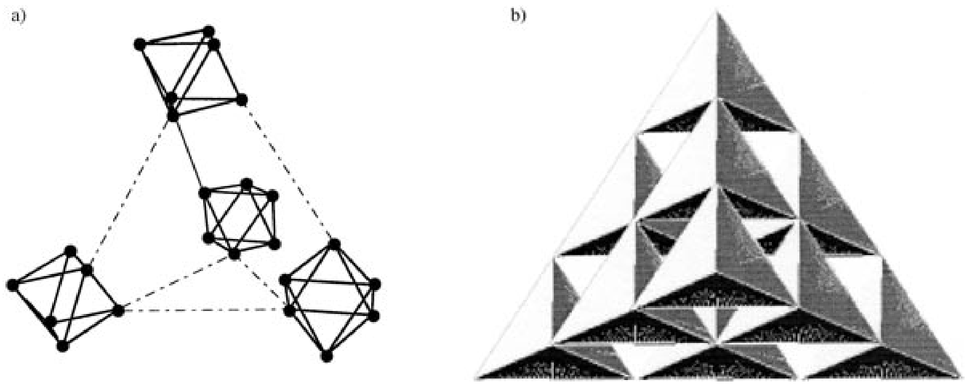


Figure 8. a) Schematic diagram of the tetrahedral building block of **2** showing the face-centred cubic network, dot line denotes the *trans*-Cu(Pro)$_2$ bridge; b) schematic packing diagram of the tetrahedral building block.

constructing fascinating frameworks. The complexes reported here can be regarded as two units: one is the *trans*-Cu(AA)$_2$ (AA: amino acid) used as a linker, the other is the Ln_6Cu_{24} node. The length of this bridge (the distance of two spare carboxylate oxygen atoms) is about 7.83 Å, compared with the extensively studied rigid ligands: 7.34 Å of terephthalic acid and 7.08 Å of 4,4′-bipyridine. In most cases, this *trans*-Cu(AA)$_2$ group uses two spare carboxylate oxygen atoms to coordinate to the outer Cu^{II} (with a square-pyramidal geometry) of the Ln_6Cu_{24} unit from apical position and thus the giant 3D supramolecular complexes with Ln_6Cu_{24} cluster as nodes could be obtained by self-assembly. So the fifth coordinated site of the outer Cu^{II} of the Ln_6Cu_{24} unit could be imagined as the "recognition site".

In fact, the structure of the Ln_6Cu_{12} inner core is similar to the {Ln_6Cu_{12}} cluster with η_2-coordinated betaine as ligand.[10b] But as amino acids have more coordination modes (Scheme 1) than betaine, our complexes become more beautiful and intriguing than the 0D 18-nuclear complexes: 1) the η_4-coordinated mode of the amino acid ligands brings twelve more Cu^{2+} ions into the system, thus a higher-nuclear cluster is obtained; and 2) the η_3-coordinated mode of the amino acid ligands introduces *trans*-Cu(AA)$_2$ linker into the system and thus these 3D polymers with the high-nuclear clusters as nodes were obtained.

Electrical conductivity and magnetic properties: The electrical conductivities of **1** and **2** were determined with powder sample from grounded crystals (Figure 9). The electrical conductivity of **1** at 263.15 K is 1.72×10^{-4} S cm^{-1} and increases to 2.57×10^{-3} S cm^{-1} at 318.15 K, which indicates that **1** is a semiconductor. But in cases of **2**, the value is only 4.27×10^{-7} S cm^{-1} at 273.15 K and increases to about 6.84×10^{-6} S cm^{-1} at 310 K, respectively. The difference in the electrical conductivity between **1** and **2** indicates that the packing mode of the Ln_6Cu_{24} building block might have a great influence.

Temperature dependent magnetic susceptibilities of complexes **1** and **2** were measured in the range 2–300 K at 2000and 5000 G, respectively (Figure 10). Antiferromagnetic interactions were observed for **1** and **2**, respectively, as confirmed by the Weiss constants (−43.7 K for **1** and −38.2 K for **2**, respectively). According to the literature,[10] the Cu(inner)···Cu(inner) exchange interaction is antiferromagnetic. The two neighboring outer Cu ions are connected by a μ_3-OH$^-$ and a carboxylate groups, and as the ∡Cu(outer)-OH-Cu(outer) angle and the Cu(outer)···Cu(outer) distance are both about 100° and 3 Å, an antiferromagnetic interaction is also suggested.[13] The Cu (bridge)···Cu (outer) distance is about 5.3 Å and a glycine ligand is used to connect them in η_3-co-

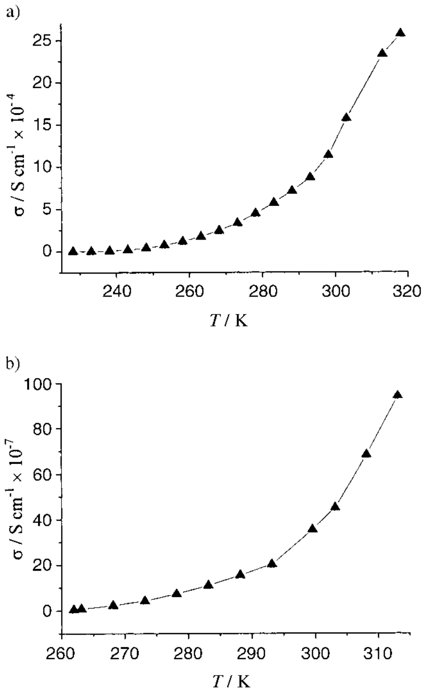


Figure 9. Temperature dependence of the electrical conductivity a) **1**; b) **2**.

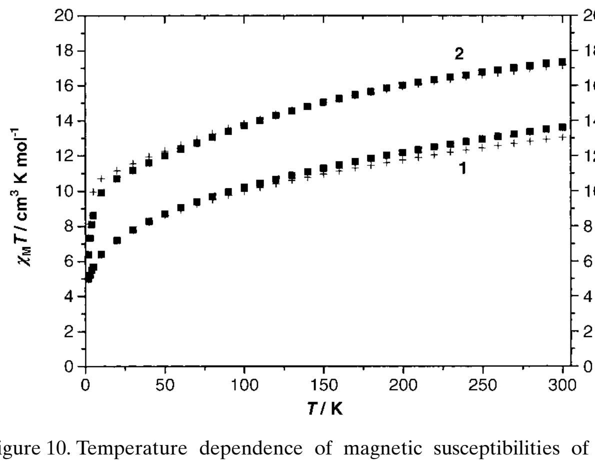


Figure 10. Temperature dependence of magnetic susceptibilities of the two complexes. +: 2–300 K at 5000 G; ■: 2–300 K at 2000

ordination mode (*syn–anti*). According to the literature,[14] a weak ferromagnetic coupling was observed, when two Cu^{II} ions were connected by a carboxylate group in *syn–anti* coordination mode. Thus, a similar weak ferromagnetic interaction is also suggested between the bridge and outer copper ions in **1** and **2**.

Conclusion

In summary, two 3D polymers with high-nuclear Ln_6Cu_{24} octahedral clusters as nodes have been synthesized. The side chain of the amino acid proline plays an important role in the connecting mode of the nodes, which might lead to the clear structural motif difference between **1** with glycine, and **2** with L-proline as the ligand, respectively. Future work will be aimed at the syntheses of other multi-dimensional complexes of different structure motifs with Ln_6Cu_{24} as the node using other chiral amino acids.

Experimental Section

Materials and instrumentation: $[Ln(ClO_4)_3]\cdot 6H_2O$ were synthesized by dissolving lanthanide oxide in excess perchloric acid. Other starting materials were reagent grade and used without further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. Magnetic measurements were carried out with a Quantum Design PPMS model 6000 magnetometer.

Conductivity measurements: The cylindrical pellets of the samples (0.2 cm in thickness and 0.3 cm in diameter) were coated with silver paint on either side. The conductivity measurements were carried out using a standard setup coupled with Agilent 4284A LCR Meter in the frequency range from 20 Hz to 1 MHz. The temperature was measured using Pt-Rh thermocouple positioned closed to the samples.

Synthesis of the complexes

$\{[Sm_6Cu_{29}(\mu_3\text{-}OH)_{30}(Gly)_{24}(ClO_4)(H_2O)_{22}](ClO_4)_{14}\cdot(OH)_7\cdot(H_2O)_{24}\}_n$ (1): Glycine (0.3 g, 4 mmol) was added to an aqueous solution (10 mL) of $Sm(ClO_4)_3\cdot 6H_2O$ (0.557 g, 1 mmol). The pH value of the reaction mixture was carefully adjusted to about 6.6 by slow addition of 0.1 M NaOH solution and the solution was stirred at 50°C for about two hours. Then $Cu(ClO_4)_2\cdot 6H_2O$ (2 g, 6 mmol) was added and pH value of the reaction mixture was again adjusted to about 6.6. After another two hours of stirring, the solution was filtrated and placed in a desiccator filled with phosphorus pentaoxide. Blue crystals were obtained about a month later (0.27 g, 21.7%). Elemental analysis (%) calcd for $C_{48}H_{225}Cl_{15}Cu_{29}N_{24}O_{191}Sm_6$: C 7.72, H 3.04, N 4.50, Cl 7.91; found: C 7.67, H 2.64, N 4.82, Cl 8.34.

$\{[Nd_6Cu_{30}(\mu_3\text{-}OH)_{30}(Pro)_{24}(ClO_4)(H_2O)_{21}]\cdot(ClO_4)_{12}\cdot(OH)_{11}\cdot(H_2O)_6\}_n$ (2): The synthesis procedure was almost the same as that of **1** except that $Nd(ClO_4)_3\cdot 6H_2O$ and L-proline were used (0.23 g, 17.3%). Elemental analysis (%) calcd for $C_{120}H_{287}Cl_{13}Cu_{30}N_{24}Nd_6O_{168}$: C 18.04, H 3.62, N 4.21,Cl 5.77; found: C 17.86, H 3.23, N 3.82, Cl 6.36.

X-ray crystallography: Intensity data for the three complexes were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data reductions and cell refinements were performed with Smart-CCD software.[15] An absorption correction by using SADABS software was applied.[16] The structures were solved by direct methods using SHELXS-97[17] and were refined by full-matrix least squares methods using SHELXL-97. The crystallographic data are summarized in Table 1.

CCDC-214694 (**1**) and -214695 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic and data collection parameters for **1** and **2**.

	1	**2**
formula	$C_{48}H_{225}Cl_{15}Cu_{29}N_{24}O_{191}Sm_6$	$C_{120}H_{287}Cl_{13}Cu_{30}N_{24}Nd_6O_{168}$
M_r	7472.03	7987.23
crystal system	triclinic	cubic
space group	$P\bar{1}$	$P2(1)3$
a [Å]	19.6451(8)	32.4341(3)
b [Å]	20.4682(8)	32.4341(3)
c [Å]	20.7046(8)	32.4341(3)
α [°]	89.453(1)	90
β [°]	66.290(1)	90
γ [°]	68.572(1)	90
V [Å^3]	7003.0(5)	34119.7(5)
Z	1	4
ρ_{calcd} [g cm^{-3}]	1.772	1.555
$F(000)$	3677	15880
measd reflns	36598	84319
indep reflns	24553	20067
R(int)	0.0705	0.1048
GOF F^2	1.062	1.269
R[a]	0.1119	0.0857
R_w[b]	0.2866	0.2185

[a] $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b] $R_w=\{\Sigma w[(F_o^2-F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{1/2}$, $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P=(F_o^2+2F_c^2)/3]$. **1**, $a=0.1478$, $b=269.7649$; **2**, $a=0.0915$, $b=569.8305$.

Acknowledgments

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