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Syntheses, Structures, and Properties of A Series of Novel High-Nuclear 3d-4f Clusters with Mixed Amino Acid as Ligands: $\{Ln_6Cu_{24}\}$(Ln = Gd, Tb, Pr and Sm)

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The first examples of high-nuclear 3d-4f heterometallic clusters with mixed amino acid ligands are reported. Four 30-nuclear clusters $\{Ln_6Cu_{24}\}$(Ln = Gd, Tb, Pr and Sm) were obtained through the self-assembly of Ln^{III}, Cu^{II} and mixed amino acid ligands of glycine (HGly) and β-alaine (HAla). The metal skeleton of clusters **1-4** may be described as a huge $\{Ln_6Cu_{12}\}$ octahedron connected with 12 additional Cu^{II} ions. The temperature dependence of magnetic susceptibilities of compounds **1-4** were also studied.

Introduction

The research on the synthesis and characterization of 3d-4f heterometallic complexes can be dated back to 1985.[1] Currently, the crystal engineering of coordination polymeric solids containing lanthanide ions and transition metal ions has made rapid progress not only because of their attractive structure motifs,[2] but also due to their important physical properties which render them candidates for luminescent sensors,[3] catalysts,[4] adsorption materials,[5-7] and magnetic materials.[2a,8-12]

Amino acids, the most important biological ligands, have proven to be good candidates for constructing high nuclearity clusters due to their various coordination modes. Research on the coordination behavior of metal-amino acid complexes is one of the most essential elements of chemical biology. Employing glycine, L-proline, L-alanine or L-threonine as ligands, our work team synthesized a series of 3d-4f heterometallic clusters including $\{LnM_6\}$, $\{Ln_6Cu_{12}\}$, $\{Ln_6Cu_{24}\}$ clusters, etc.[13,14]

The protein in human beings is made of 20 kinds of amino acids. During a great part of life activities, more than one kind of amino acids are involved. Therefore, the study on 3d-4f heterometallic clusters with mixed amino acids may be significant for understaning the roles of the metal ions and amino acids in the life activities and the mechanism of metabolic in the organism. Previously, to synthesize 3d-4f heterometallic-amino acid clusters, only one kind of amino acid or with other small-size ligands containing either N- or O-donor atoms were employed.[13d,15] To the best of our knowledge, no heteronuclear 3d-4f clusters with mixed amino acids has been reported thus far.

Recently, our research interest has been focused on the syntheses of high-nuclear 3d-4f heterometallic clusters with two kinds of amino acids as coligands. In this paper we report the first examples of high-nuclear 3d-4f heterometallic clusters based on mixed amino acids: $[Gd_6Cu_{24}(\mu_3\text{-OH})_{30}(Gly)_{12}(\beta\text{-Ala})_6(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{25}$ (**1**), $[Tb_6Cu_{24}(\mu_3\text{-OH})_{30}(Gly)_{12}(\beta\text{-Ala})_6(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{20}$ (2), $[Pr_6Cu_{24}(\mu_3\text{-OH})_{30}(Gly)_8\text{-}(\beta\text{-Ala})_{10}(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{27}$(3), and $[Sm_6Cu_{24}(\mu_3\text{-OH})_{30}(Gly)_8(\beta\text{-Ala})_{10}(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{20}$ (**4**). All of these clusters possess a Ln_6Cu_{24} metal skeleton. The crystal structures and the temperature dependence of magnetic susceptibilities of **1-4** were investigated.

Experimental Section

Materials and physical measurements

All reagents and solvents used were received from commercial suppliers without further purification. Aqueous solutions of lanthanum perchlorate were prepared by digesting lanthanide oxides in concentrated perchloric acid. *Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount should be used and handled with great care.* Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS Elemental Analyzer. The infrared spectra of KBr pellet were recorded in the range of 4000-400 cm–1 on a Perkin-Elmer Spectrum One FT-IR Spectrometer. Thermal analyses were performed on a NETZSCH STA 449F3 instrument from room temperature to 900 °C with a heating rate of 10 °C min-1 under nitrogen flow. The magnetic susceptibilities of the crystalline samples were measured with a Quantum Design MPMS-XL SQUID suscepto-meter under an applied magnetic field of 1 kOe in a 2-300 K temperature range. Diamagnetic corrections were made using Pascal's constants.

Synthesis of 1-4.

$[Gd_6Cu_{24}(\mu_3\text{-OH})_{30}(Gly)_{12}(\beta\text{-Ala})_6(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{25}$ (1) To an aqueous solution (5 mL) of $Gd(ClO_4)_3\cdot 6H_2O$ (2 mmol) were added $Cu(ClO_4)_2\cdot 6H_2O$, HGly and Hβ-Ala. The proportion of the reactants was controlled to be Gd^{3+}:Cu^{2+}:HGly:HAla = 2:8:1:1. Then the pH value of the reaction mixture was carefully adjusted to about 6.6 by the slow addition of 0.1 M NaOH solution. After being stirred for another 2 h, the solution was filtrated and placed in a desiccator filled with phosphorus pentaoxide. Blue crystals were obtained about a month later. Yield: 0.097 g, 17%. Element anal. Calcd for $C_{42}H_{188}Cl_{18}Cu_{24}N_{18}O_{175}Gd_6$: C, 7.36; H, 2.77; N, 3.68; Found: C, 7.32; H, 2.70; N, 3.58. IR (KBr pellet, cm^{-1}): 3213(s, br), 1631(s), 1587(s), 1410(m), 1378(m), 1331(w), 1087(vs), 939(w), 842(w), 735(w), 627(m), 533(w).

$[Tb_6Cu_{24}(\mu_3\text{-}OH)_{30}(Gly)_{12}(\beta\text{-}Ala)_6(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{20}$ (2) **2** was synthesized in the similar way as that described for **1**, except that $Tb(ClO_4)_3\cdot 6H_2O$ (2 mmol) was used to replace $Gd(ClO_4)_3\cdot 6H_2O$. Yield: 0.093 g, 17%. Element anal. Calcd for $C_{42}H_{178}Cl_{18}Cu_{24}N_{18}O_{170}Tb_6$: C, 7.47; H, 2.66; N, 3.74; Found: C, 7.39; H, 2.74; N, 3.73. IR (KBr pellet, cm^{-1}): 3220(s, br), 1630(s), 1587(s), 1409(m), 1378(m), 1330(w), 1087(vs), 987(w), 941(w), 897(w), 842(w), 735(w), 627(m), 530(w).

$[Pr_6Cu_{24}(\mu_3\text{-}OH)_{30}(Gly)_8(\beta\text{-}Ala)_{10}(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{27}$ (3) **3** was synthesized in the similar way as that described for **1**, except that $Pr(ClO_4)_3\cdot 6H_2O$ (2 mmol) was used to replace $Gd(ClO_4)_3\cdot 6H_2O$ and the proportion of the reactants was changed to be Pr^{3+}:Cu^{2+}:HGly:HAla = 2:8:1:2. Yield: 0.165 g, 19%. Element anal. Calcd for $C_{46}H_{200}Cl_{18}Cu_{24}N_{18}O_{177}Pr_6$: C, 8.09; H, 2.95; N, 3.69; Found: C, 7.91; H, 3.06; N, 3.55. IR (KBr pellet, cm^{-1}): 3212(vs, br), 1629(s), 1587(s), 1407(m), 1379(m), 1328(w), 1274(w), 1086(vs), 985(w), 943(w), 894(w), 842(w), 734(w), 627(m), 527(w).

$[Sm_6Cu_{24}(\mu_3\text{-}OH)_{30}(Gly)_8(\beta\text{-}Ala)_{10}(ClO_4)(H_2O)_{12}]\cdot(ClO_4)_{17}\cdot(H_2O)_{20}$ (4) **4** was synthesized in the similar way as that described for **3**, except that $Sm(ClO_4)_3\cdot 6H_2O$ (2 mmol) was used to replace $Pr(ClO_4)_3\cdot 6H_2O$. Yield: 0.113 g, 13%. Element anal. Calcd for $C_{46}H_{186}Cl_{18}Cu_{24}N_{18}O_{170}Sm_6$: C, 8.16; H, 2.77; N, 3.73; Found: C, 8.06; H, 2.92; N, 3.59. IR (KBr pellet, cm^{-1}): 3400(vs, br), 1631(s), 1591(s), 1409(m), 1379(m), 1328(w), 1276(w), 1088(vs), 961(w), 941(w), 894(w), 830(w), 739(w), 707(w), 627(m), 559(w), 533(w).

X-ray crystallography

Data collection was performed on Rigaku Saturn 70 diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. Empirical absorption corrections were applied with SADABS program.[16] The structures were solved by direct methods and refined by the full-matrix leasts quares on F^2 using the SHELXTL-97 program.[17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon atoms were generated geometrically (C-H bond fixed at 0.97 Å). Crystallographic data and structure determination summaries are listed in Table 1. And the selected bond lengths and angles of the complexes are listed in Table S1-S2 in the Supporting Information.

Results and discussion

Crystal structure of 1 and 2

The crystal structures of compounds **1** and **2** are similar except for the numbers of solvent water molecules. Therefore, only the structure of **1** is discussed in detail. As shown in Figure 1, the $[Gd_6Cu_{24}]$ cluster of **1** is composed of the $[Gd_6Cu_{12}]$ octahedral inner core and six outer $[Cu_2]$ units. The inner $[Gd_6Cu_{12}]$ core can be well-described as a huge octahedron with pseudocubic O_h symmetry. Six Gd^{III} ions are located at the vertices of a nonbonding octahedron, and twelve inner Cu^{II} ions are located at the midpoints of the octahedral edges (Figue 2a). The average distances of Gd···Gd, Gd···Cu (inner), and Cu (inner)···Cu (inner) are 7.0, 3.5, and 3.4 Å, respectively, in agreement with those reported for the compounds bearing the $[Ln_6Cu_{12}]$ motif.[14,15a] 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 Gd^{III} ions and three Cu^{II} ions linked by three μ_3-OH^- groups (Figure 2b). 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 Gd-O-Cu fall in the range of 111-121 and 102-106°, respectively. Therefore, the octahedron could be imagined as being composed of Gd-O-Cu-O quadrilateral (about 2.4×2 Å) and Cu_3-O_3 (about 2 Å) distorted hexagonal windows.

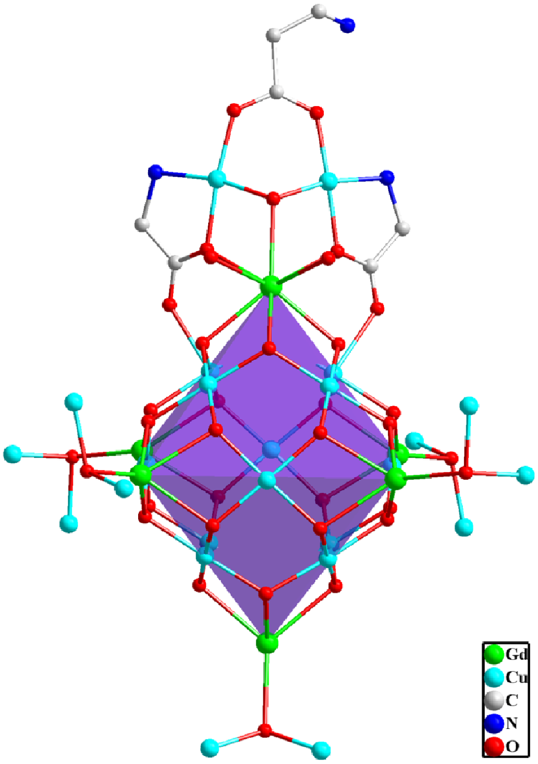
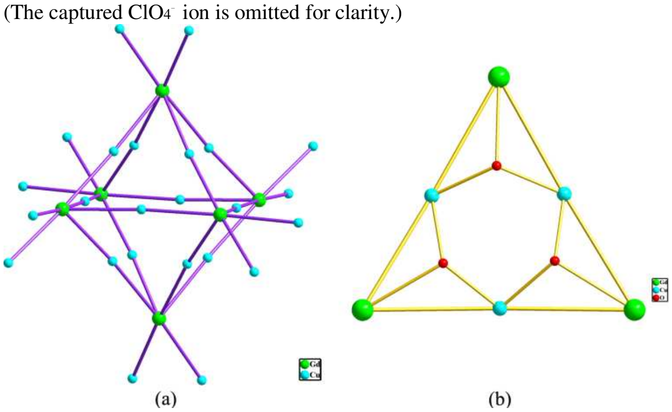
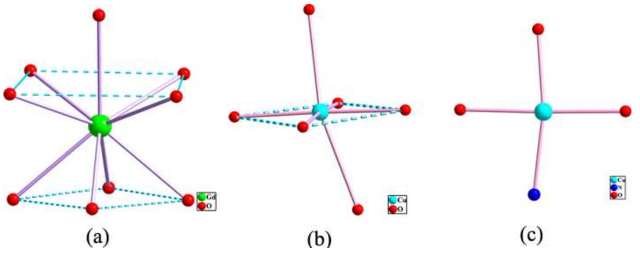


Fig. 1. Metal-hydroxide framework of $\{Gd_6Cu_{24}OH_{30}\}$ of the cation of **1**. (The captured ClO_4^- ion is omitted for clarity.)



(a) (b)

Fig. 2. (a) Metal framework of the cation of **1**; (b) Structure of one face of the octahedron of **1**.



(a) (b) (c)

Fig. 3. Coordination polyhedron of the Ln^{3+} and Cu^{2+} ions in **1.**

There are also twelve outer Cu$^{\mathrm{II}}$ ions in the cluster. Each Gd$^{\mathrm{III}}$ ion interconnects two outer Cu$^{\mathrm{II}}$ ions with the help of one outer μ_3-OH$^-$ group and two μ_3-η_2:η_1:η_1 coordinated Gly ligands, which use a NO donor set to chelate one outer Cu$^{\mathrm{II}}$ ion and also employ its two oxygen atoms to coordinate to one inner Cu$^{\mathrm{II}}$ ion and the Gd$^{\mathrm{III}}$ ion, respectively. The two outer Cu$^{\mathrm{II}}$ ions are further bound by one *syn-syn* Ala. The average Gd···Cu (outer) distance is about 3.5 Å, while the neighboring Cu (outer)···Cu (outer) distance is 3.0 Å, shorter than that of the Cu (inner)···Cu (inner). Short distances may cause strong magnetic exchanges between Cu$^{\mathrm{II}}$ copper ions.

The coordination polyhedron of the nine-coordinated Gd$^{\mathrm{III}}$ ion with an O_9 donor set may be best described as a monocapped square antiprism (Figure 3a). The Gd$^{\mathrm{III}}$ ion coordinates to four inner μ_3-OH$^-$ groups (lower plane), two oxygen atoms from two Gly ligands, two terminal H_2O molecules (upper plane), and one outer μ_3-OH$^-$ "cap". The Gd-O bond distances are in the range of 2.43-2.58 Å.

The coordination geometry of inner Cu$^{\mathrm{II}}$ ion can be described as a slightly distorted six-coordinated octahedral configuration with an O6 donor set (Figure 3b). 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.

Figure 4 shows the structure of one of the vertices of the octahedron of **1**. The outer Cu$^{\mathrm{II}}$ ions all have four-coordinated square-planar geometry and NO_3 donor set (Figure 3c). Every outer Cu$^{\mathrm{II}}$ ion is chelated by one amino nitrogen atom and and one carboxylate oxygen atom from Gly ligand and further coordinated by one carboxylate oxygen atom from β-Ala and one outer μ_3-OH$^-$ group. Selected bond lengths and angles of **1** are listed in Table S2 of the Supporting Information.

The glycinato ligand adopts a η_4-coordinated mode, chelating to two Cu$^{\mathrm{II}}$ ions and one Gd$^{\mathrm{III}}$ ion through the carboxylate and amino groups (Scheme 1). The Ala ligand is bidentate and each coordinates to two neighboring outer Cu$^{\mathrm{II}}$ ions.

A particularly interesting structural feature of this {Gd_6Cu_{24}} cluster is that a distorted ClO_4^- anion, which may play the role of a template, is captured in the cage.[18, 19] The anion uses oxygen atoms to coordinate to the inner copper ions.

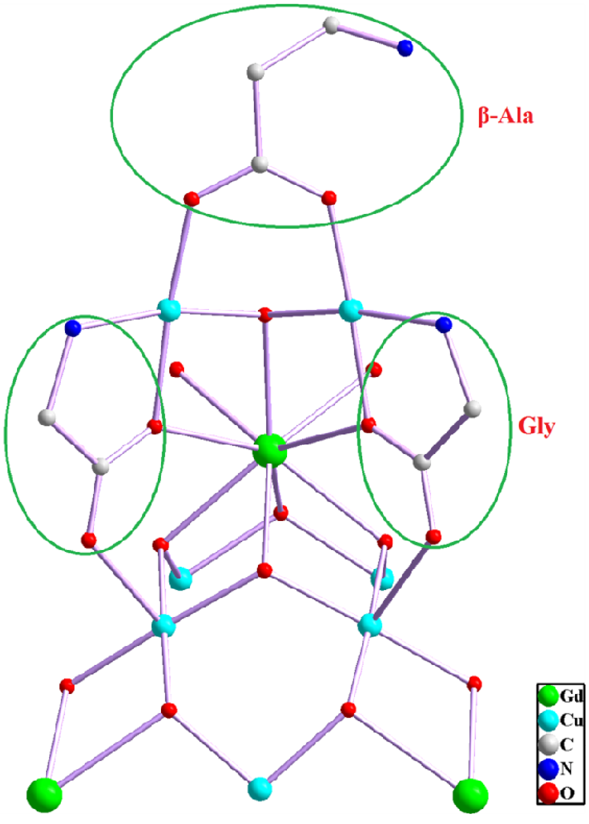
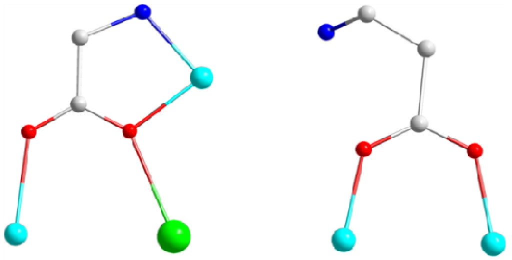


Fig. 4. Stereoview of the structure of one of the vertices of the octahedron of **1**.



Scheme 1. Coordinate modes of Gly and β-Ala Ligands of **1**.

Crystal structure of 3 and 4

When the proportion of the reactants (Ln^{3+}:Cu^{2+}:HGly:HAla) was changed from 2:8:1:1 to 2:8:1:2, compounds **3** and **4** can be obtained. Compounds **3** and **4** have the similar crystal structures for the numbers of solvent water molecules. Therefore, only the structure of **3** is discussed in detail.

The structure of **3** is almost the same as that of **1** except that four of the six μ_3-η_2:η_1:η_1 coordinated Gly ligands are replaced by four β-Ala ligands, which also use a NO donor set to chelate one outer Cu$^{\mathrm{II}}$ ion and also employ its two oxygen atoms to coordinate to one inner Cu$^{\mathrm{II}}$ ion and the Pr$^{\mathrm{III}}$ ion, respectively. Selected bond distances and angles are shown in Tables S4. Figure 5 shows the structure of one of the vertices of the octahedron of **3**. The coordination environments of Ln$^{\mathrm{III}}$, inner and outer Cu$^{\mathrm{II}}$ ions of **3** are also almost the same as that of **1**.

The coordination mode of glycinato ligand is as same as that of **1**. The β-Ala ligands adopt two coordination modes, one is η_4-coordinated mode, chelating to two Cu$^{\mathrm{II}}$ ions and one Pr$^{\mathrm{III}}$ ion through the carboxylate and amino groups, the other is bidentate mode, coordinating to two neighboring outer Cu^{II} ions (Scheme 2).

Syntheses

The strategy for the syntheses of high-nuclear 3d-4f clusters using HGly and HAla as mixed ligands led to the formation of {Ln$_6$Cu$_{24}$} (Ln = Gd, Tb, Pr and Sm) compounds. We found that pH value and the reactant proportion play important roles in the syntheses of these coumpounds. 6.6 is a suitable pH value while higher pH values will lead to a large amount of precipitate and are not preferred. Another key role is the reactant proportion. We found that it is necessary to maintain a high metal to ligand ratio because a low ratio will lead to the final product being contaminated by a small number of light-blue helix crystals (X-ray structure analysis shows it is $Cu_3(Gly)_4(ClO_4)_2$). Furthermore, the ratio of HGly to HAla must be lower than 1:1. If the proportion of HGly is more than HAla, only HGly will participate in the coordination to the metal ions. That might be attributing to the more suitable steric configuration of Gly to chelating metal ions than β-Ala.

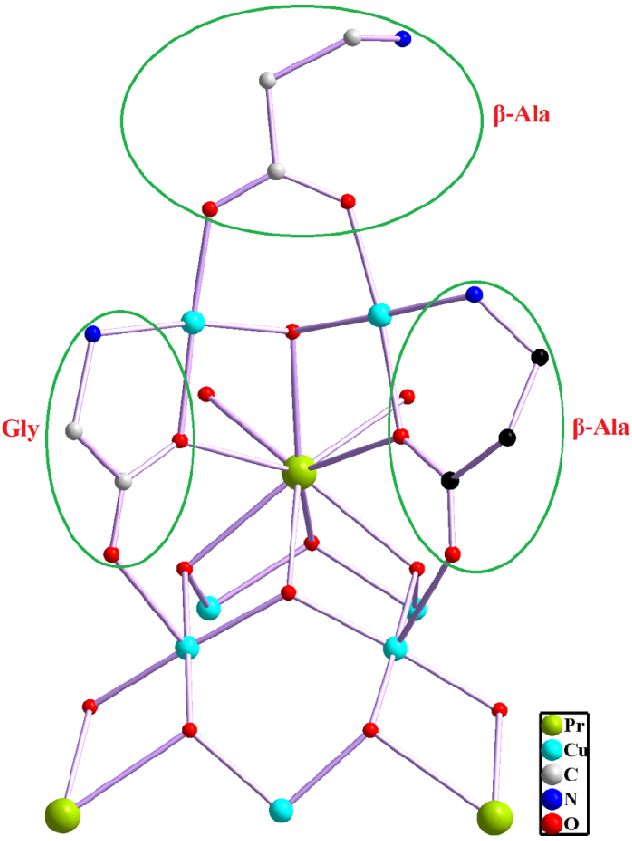
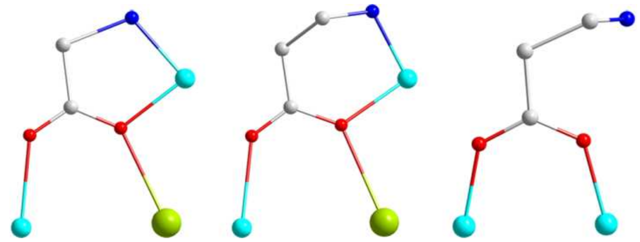


Fig. 5. Stereoview of the structure of one of the vertices of the octahedron of **3**.



Scheme 2. Coordinate modes of Gly and β-Ala Ligands of **3**.

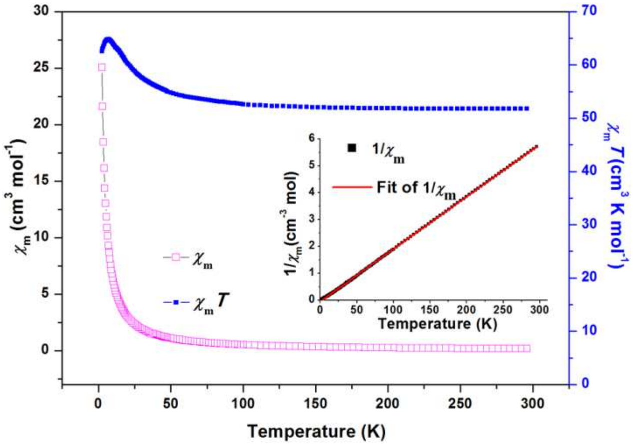
Magnetic properties

Temperature-dependent magnetic susceptibilities of **1-4** were measured in the temperature range of 2-300 K with an applied direct current (dc) magnetic field of 1000 Oe (Figure 6).

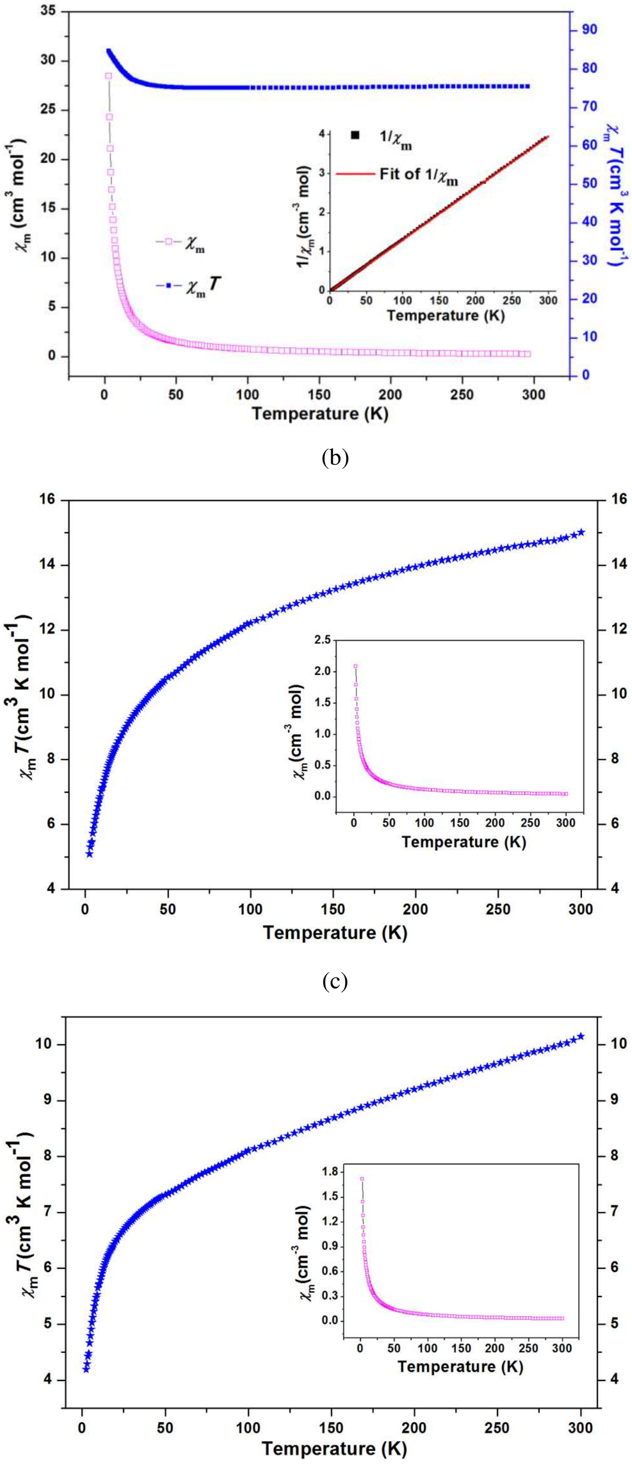
At room temperature, the $\chi_m T$ values per Ln$_6$Cu$_{24}$ unit are 51.77, 75.54, 15.01, and 10.15 cm^3 mol^{-1} K for **1-4**, respectively, being comparable with the expected values (56.25, 79.88, 17.22 and 9.54 cm^3 mol^{-1} K, respectively) for 6 Ln^{III} in the free-ion state and 24 spin-only Cu^{II} ions (S=1/2, g=2).

Upon cooling, the $\chi_m T$ value of **1** increases gradually to 52.2 cm^3 mol^{-1} K at 150 K and then increases rapidly to a maximum 64.9 cm^3 mol^{-1} K at 6 K, which indicates a dominant ferromagnetic interaction between the metal centers. With further cooling, the $\chi_m T$ value decreases sharply to 62.5 cm^3 mol^{-1} K at 2 K, which may be associated with the intercluster antiferromagnetic interactions and the crystal-field effects.[21] The Weiss constant determined in the range of 2-300 K is 2.61 K, which also indicates that the magnetic interaction of Gd-Cu is ferromagnetic. With the decrease in temperature, the $\chi_m T$ value of **2** remains almost constant down to ca. 60 K, where it begins to increase smoothly until reaching a maximum of 84.8 cm^3 mol^{-1} K around 2 K. This phenomenon corresponds to an overall ferromagnetic interaction, and the Weiss constant determined in the range of 2-300 K is 0.20 K, suggesting that the magnetic interaction of Tb-Cu is ferromagnetic.

The magnetic behavior of **3** and **4** are different from those of **1** and **2**. With the decrease in temperature, **3** and **4** exhibit a continuous decrease in $\chi_m T$ and the Weiss constants are negative (-33.0 and -33.5 K for **3** and **4**, respectively). According to the literature, the Cu(inner)···Cu(inner) exchange interaction is antiferromagnetic.[19a] For the two neighbouring outer Cu ions connected by a μ_3-OH$^-$ group and a carboxylate group, because the ∠Cu(outer)-OH-Cu(outer) and the Cu(outer)···Cu(outer) distance are all about 100° and 3 Å, respectively, an antiferromagnetic interaction is also suggested.[21] The deviations from the the Curie-Weiss law and the decline of the $\chi_m T$ versus T curves may be due to the orbital contribution from the Ln ions or the antiferromagnetic coupling of Ln-Cu.[12c,13]



(a)



(b)

(c)

(d)

Fig. 6 The temperature dependence of χ_m and $\chi_m T$ for **1-4**. The insets of (a) and (b) show the plot of $1/\chi_m$ versus T. The solid line corresponds to the best theoretical fit.

Conclusions

In summary, four 30-nuclear 3d-4f Ln_6Cu_{24} compounds can be obtained with glycine and β-alanine as mixed ligands through controlling the reactant to a reasonable proportion at a pH value of about 6.6. The ratio of glycine and β-alanine in the compounds could be changed by changing the reactant ratio of them. The use of mixed amino acids instead of only one kind of amino acid or one kind of amino acid cooperating with other small-size ligands for the synthesis of 3d-4f heteronuclear compounds makes them possible in biochemical applications. The Gd and Tb containing compounds are ferromagnetic. Further investigation of the construction of 3d-4f clusters based on other amino acids as mixed ligands is in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The selected bond lengths and angles, IR and TGA curves of compounds **1-4**. CCDC reference numbers are 1037330, 1037333, 1037331 and 1037332 for compounds **1-4**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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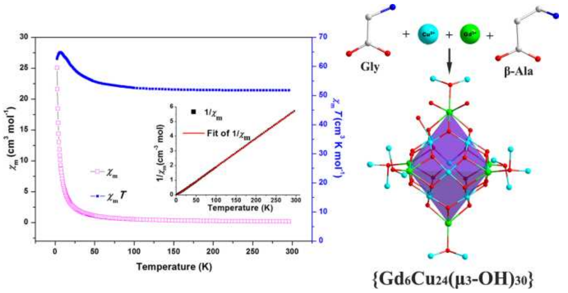
Graphical Abstract



The first examples of high-nuclear 3d-4f heterometallic clusters $\{Ln_6Cu_{24}\}$(Ln = Gd, Tb, Pr and Sm) with mixed amino acid ligands are reported.