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The synthesis, structure, and fluorescence properties of two heptanuclear coordination compounds containing trigonal prismatic $[LnCu_6(\mu\text{-}OH)_3(Gly)_6Im_6]^{6+}$ cations (Ln: Eu, Sm)

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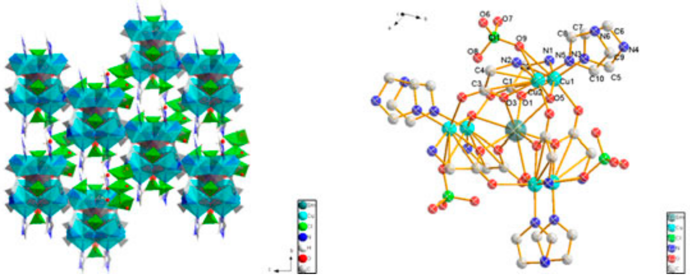

Two heptanuclear trigonal prismatic polyhedra, $[EuCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$ and $[SmCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$ were synthesized through self-assembly of Eu^{3+}(Sm^{3+}), Cu^{2+}, glycine, and imidazole in aqueous solution and characterized by X-ray single crystal diffraction. Both complexes crystallize in the rhombohedral R3 space group ($a = b = 15.8673$ Å, $c = 23.4038$ Å, $V = 5103.0(6)$ $Å^3$, $Z = 3$) and ($a = b = 15.8749$ Å, $c = 23.455$ Å, $V = 5119.1(8)$ $Å^3$, $Z = 3$). In the clusters, Sm^{3+} and Eu^{3+} ions are situated in the center of a prism formed by six copper ions and coordinate to nine oxygens with a tricapped trigonal prismatic coordination polyhedron. Six glycinato ligands and six imidazole terminal ligands (each coordinates to one Cu^{2+}) construct the cluster. The fluorescent excitation and emission spectra showed that the complexes have strong ligand-based fluorescence.

Keywords: Rare earth; Complexes; Cluster; Structure; Fluorescence

1. Introduction

Rare earth elements and transition metal elements as biological trace elements play roles in the human body [1]. Imidazole is involved in important biological processes [2–6] and

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*Corresponding author. Email: xuechuanster@163.com many compounds based on imidazole and different metal ions have been reported [7–13]. Imidazole has two nitrogens for coordination. Amino acids are the basic unit of humans and amino acids have two or more types of coordination sites and can bridge by using a carboxylate [14–20]. The mechanism of action between transition metal complex and DNA [20] and introduction of a transition metal into a lanthanide complex may quench or increase the luminescence intensity of the lanthanide.

Three kinds of heptanuclear 3d–4f clusters with the general formula of LnM_6 (M means transition metal) have been reported [21]. They have the structure motif of an octahedron ($LnNi_6$), trigonal prism ($LnCu_6$ or $LnNi_6$), and wheel ($LnCu_6$). Although many reports about 3d–4f heterometallic compounds have been published, most of them are low-nuclear 3d–4f complexes [22, 23], only a little effort has focused on the design and syntheses of high-nuclear compounds [24–28].

Therefore, it is significant to synthesize oligonuclear 3d–4f clusters using special ligands, which may have special biological properties. Here, europium and samarium ions, copper ions, glycine, and imidazole were chosen to prepare heteropolynuclear complexes. The syntheses and crystal structures of $[LnCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$ (Ln = Eu and Sm) were reported. The fluorescent properties of the complexes were examined.

2. Experimental

2.1. *Synthesis of the title complexes*

$Ln(ClO_4)_3\cdot 6H_2O$ and $Cu(ClO_4)_2\cdot 6H_2O$ (Ln: Sm, Eu) were synthesized by dissolving rare earth oxides or copper oxide in an excess of perchloric acid. Other starting materials were of reagent grade and used without purification. $[LnCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$. To an aqueous solution (10 mL) of $Ln(ClO_4)_3\cdot 6H_2O$ (1 mM, Ln = Sm and Eu),

Table 1. Crystallographic data and structure determination details for the complexes.

Formula	$C_{30}H_{57}Cl_6Cu_6SmN_{18}O_{42}$	$C_{30}H_{57}Cl_6Cu_6EuN_{18}O_{42}$
Mr	2086.23	2087.84
Crystal system	Trigonal	Trigonal
Space group	R3	R3
a (Å)	15.8749(14)	15.8673(12)
b (Å)	15.8749(14)	15.8673(12)
c (Å)	23.455(2)	23.4038(16)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
Volume (Å^3)	5119.1(8)	5103.0(6)
Z	3	3
d_{Calcd} (g/cm^3)	1.944	2.038
F (0 0 0)	3111	3972
Measured reflections	8598	8539
Independent reflections	3219	3704
R(int)	0.0400	0.0344
Goodness of fit on F^2	1.053	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0307$, $\omega R_2 = 0.0732$	$R_1 = 0.0364$, $\omega R_2 = 0.0904$
R indices (all data)	$R_1 = 0.0337$, $\omega R_2 = 0.0753$	$R_1 = 0.0400$, $\omega R_2 = 0.0929$
Largest diff. peak and hole (e nm^{-3})	0.977 and −0.596	1.051 and −0.755

Table 2. Selected bond lengths (Å) and angles (°) for the complexes.

Sm(1)–O(1)	2.48(4)	Eu(1)–O(1)	2.47(5)
Sm(1)–O(3)	2.49(4)	Eu(1)–O(3)	2.47(4)
Sm(1)–O(5)	2.46(4)	Eu(1)–O(5)	2.45(4)
Cu(1)–O(1)	1.98(4)	Cu(1)–O(1)	2.00(5)
Cu(1)–O(2)	2.22(4)	Cu(1)–O(2)	2.26(5)
Cu(1)–O(5)	1.99(4)	Cu(1)–O(5)	1.97(4)
Cu(1)–N(1)	1.99(7)	Cu(1)–N(1)	1.98(7)
Cu(1)–N(3)	1.94(5)	Cu(1)–N(3)	1.99(7)
Cu(2)–O(3)	2.00(4)	Cu(2)–O(3)	1.99(5)
Cu(2)–O(4)	2.28(5)	Cu(2)–O(4)	2.22(5)
Cu(2)–O(5)	1.97(4)	Cu(2)–O(5)	1.99(4)
Cu(2)–N(2)	1.98(6)	Cu(2)–N(2)	1.97(7)
O(5)#1–Sm(1)–O(5)	120.000(1)	O(5)#1–Eu(1)–O(5)	120.000(1)
O(3)–Sm(1)–O(5)	74.07(2)	O(3)–Eu(1)–O(5)	65.51(15)
O(3)#1–Sm(1)–O(3)	74.85(3)	O(3)#1–Eu(1)–O(3)	75.58(17)
O(1)–Sm(1)–O(5)	65.26(13)	O(1)–Eu(1)–O(5)	65.19(14)
O(1)–Sm(1)–O(3)	139.19(12)	O(1)–Eu(1)–O(3)	90.46(16)
O(1)#1–Sm(1)–O(1)	75.56(15)	O(1)#1–Eu(1)–O(1)	74.75(18)
N(3)–Cu(1)–O(1)	173.2(3)	N(3)–Cu(1)–O(1)	176.7(3)
O(5)–Cu(1)–N(1)	166.0(2)	O(5)–Cu(1)–N(1)	165.2(3)
N(3)–Cu(1)–O(2)	93.5(2)	N(3)–Cu(1)–O(2)	90.6(3)
O(1)–Cu(1)–O(2)	93.04(17)	O(1)–Cu(1)–O(2)	90.97(19)
O(5)–Cu(1)–O(2)	91.39(17)	O(5)–Cu(1)–O(2)	92.16(19)
N(1)–Cu(1)–O(2)	94.8(3)	N(1)–Cu(1)–O(2)	95.0(3)
N(2)–Cu(2)–O(5)	165.4(2)	N(2)–Cu(2)–O(5)	166.1(3)
N(5)–Cu(2)–O(3)	175.1(2)	N(5)–Cu(2)–O(3)	174.0(3)
N(5)–Cu(2)–O(4)	91.3(2)	N(5)–Cu(2)–O(4)	92.7(3)
N(2)–Cu(2)–O(4)	94.7(3)	N(2)–Cu(2)–O(4)	95.1(3)
O(5)–Cu(2)–O(4)	92.15(17)	O(5)–Cu(2)–O(4)	91.18(18)
O(3)–Cu(2)–O(4)	91.02(17)	O(3)–Cu(2)–O(4)	93.06(19)
Cu(1)–O(1)–Sm(1)	103.81(16)	Cu(1)–O(1)–Eu(1)	103.53(18)
Cu(1)–O(5)–Sm(1)	103.78(15)	Cu(1)–O(5)–Eu(1)	105.14(18)
Cu(2)–O(3)–Sm(1)	103.11(16)	Cu(2)–O(3)–Eu(1)	103.65(18)
Cu(2)–O(5)–Cu(1)	119.8(2)	Cu(2)–O(5)–Cu(1)	119.2(2)

Note: Symmetry transformations used to generate equivalent atoms: #1, $-x+y+1$, $2x+1$, z.

$Cu(ClO_4)_2{\cdot}6H_2O$ (2.184 g, 6 mM) was added and the mixture was magnetically stirred at 60 °C for 5 h to get a clear solution. Then glycine (0.45 g, 6 mM) was put in the solution for further reaction (2 h). After the pH of the reaction mixture was carefully adjusted to 6.0 by slow addition of 1.0 M NaOH solution, 6 mM imidazole was added. The solution was filtered to remove the precipitate after a further 4 h of stirring and placed in a desiccator filled with Silica gel. Blue crystals were obtained about a month later.

2.2. *X-ray structure determinations*

Suitable single crystals were used in the X-ray single diffraction study. Data collections were performed on a CCD area detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å at 298(2) K) in the ω-scan mode. Unit cell parameters were obtained by least-squares methods in the θ ranges of 2.556–28.183° for the complex. The structures were solved by direct methods with SHELXS-97 [29] and refined by full-matrix least-squares methods on F^2 with SHELXL-97 [30]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogens were generated geometrically, assigned appropriated isotropic thermal parameters, and included in structure factor calculations.

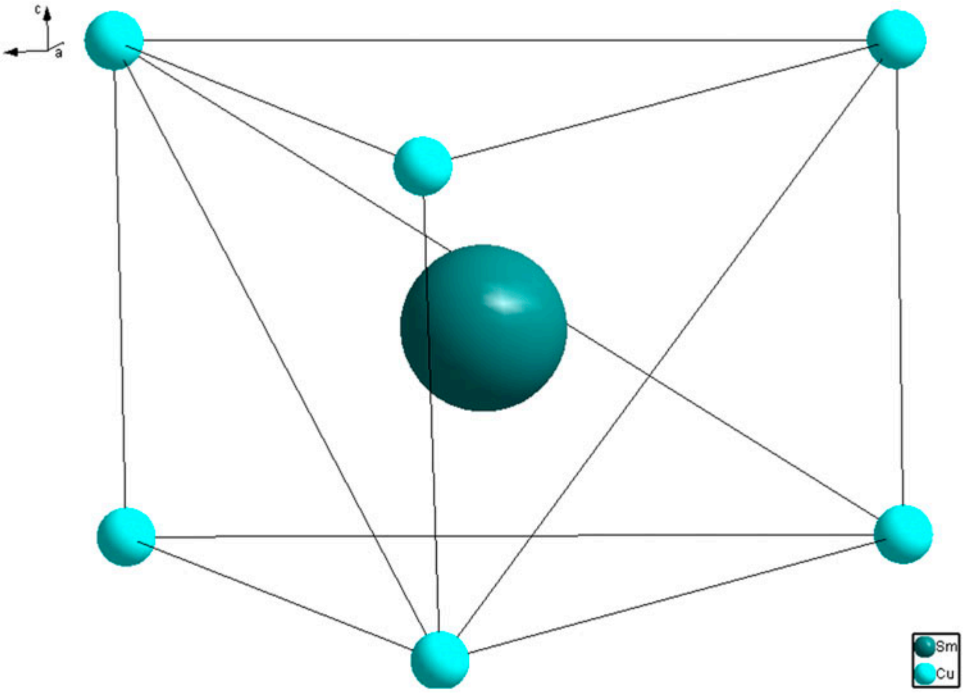


Figure 1. The 3-D structure of Cu(II) and Sm(III).

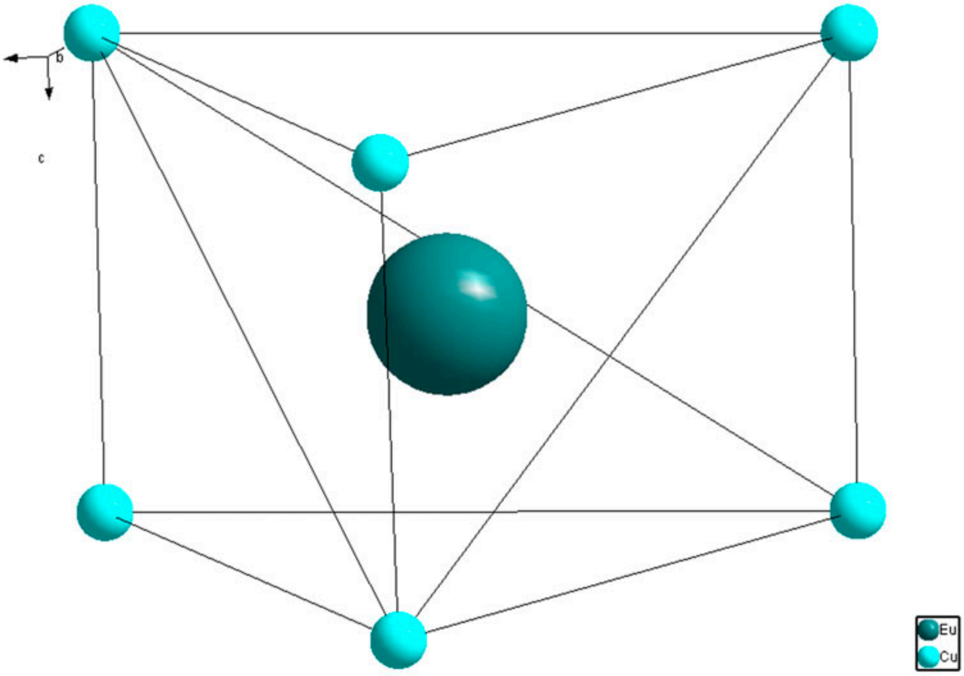


Figure 2. The 3-D structure of Cu(II) and Eu(III).

A summary of crystal data and structure refinement for the compounds is provided in table 1. Selected bond lengths and angles are listed in table 2. The atomic coordinates and equivalent isotropic displacement parameters are given in Supplementary Material. Further information concerning the crystal structure determinations in CIF format is available in the Supplementary Material.

2.3. *Excitation and fluorescence analysis*

Fluorescence excitation and emission spectra were determined on a Hitachi RF-3010 fluorescence photometer with slit width of 3 nm. The phosphorescence spectra were monitored by F-4500 FL spectrophotometer at room temperature. The scan speed was 240 nm min^{-1}.

3. Results and discussion

3.1. *Description of structure*

The structures of the cations are shown in figures 1–4. It can be seen from figures 1 and 2 that six Cu^{2+} ions exist around a Ln^{3+} ion. There are two kinds of Cu^{2+} in the cation with Cu(1)···Sm distance of ca. 3.53 Å and the Cu(2)···Sm distance ca. 3.54 Å, the Cu(1)···Eu distance is ca. 3.53 Å and the Cu(2)···Eu distance is ca. 3.52 Å.

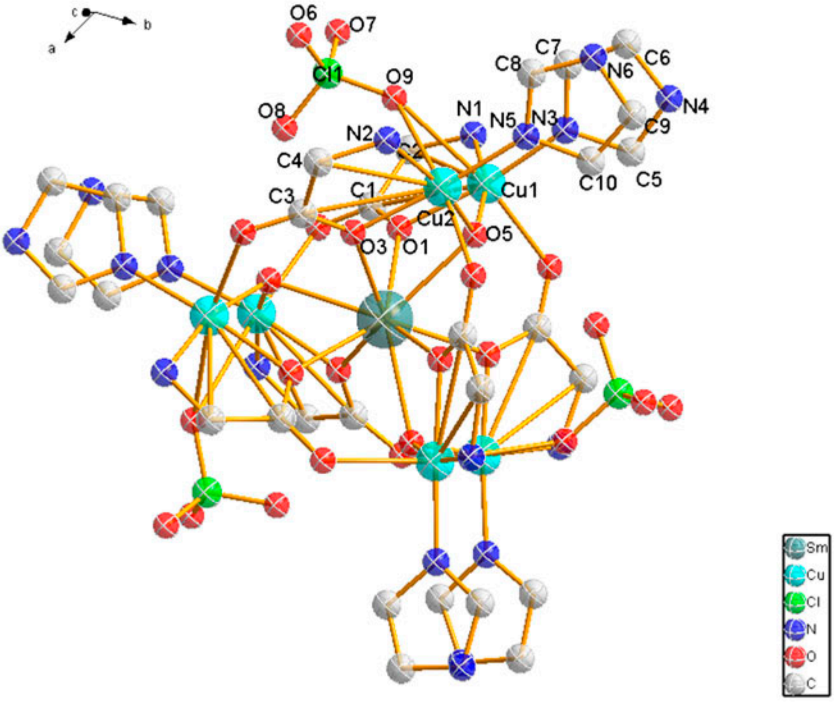


Figure 3. The 3-D structure of the counter cation Sm(III).

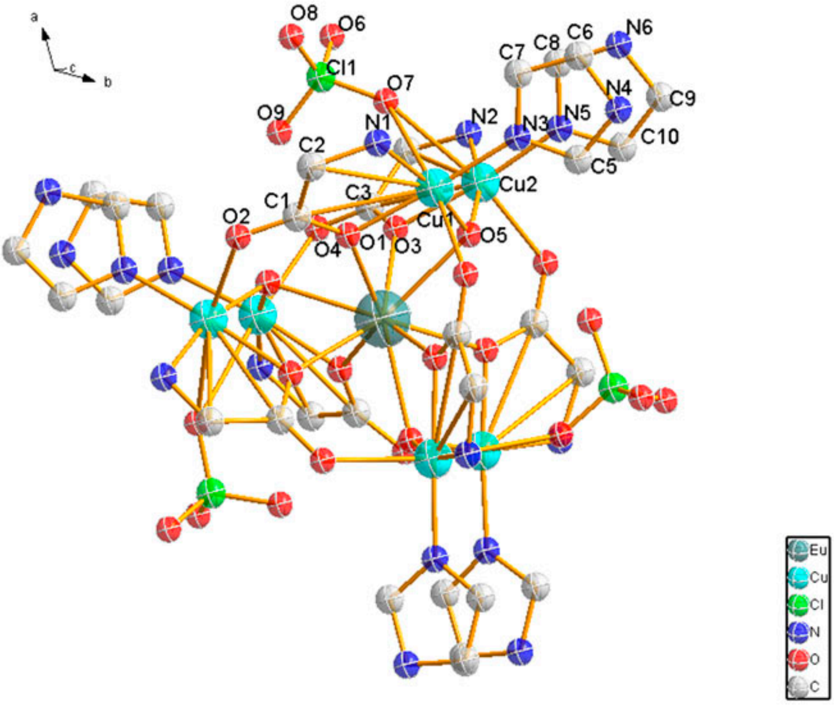


Figure 4. The 3-D structure of the counter cation Eu(III).

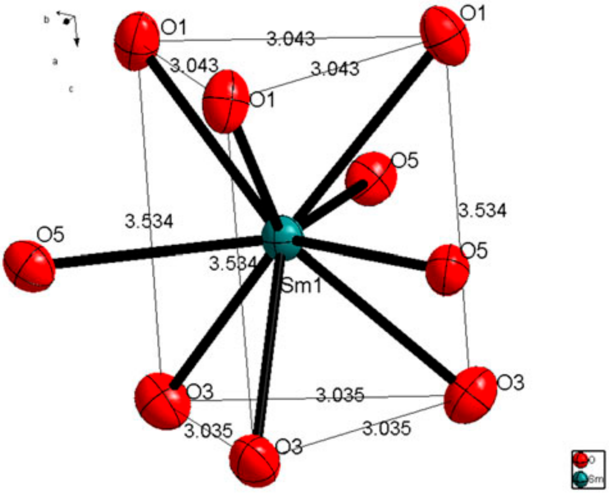


Figure 5. The 3-D structure of Sm(III) and O.

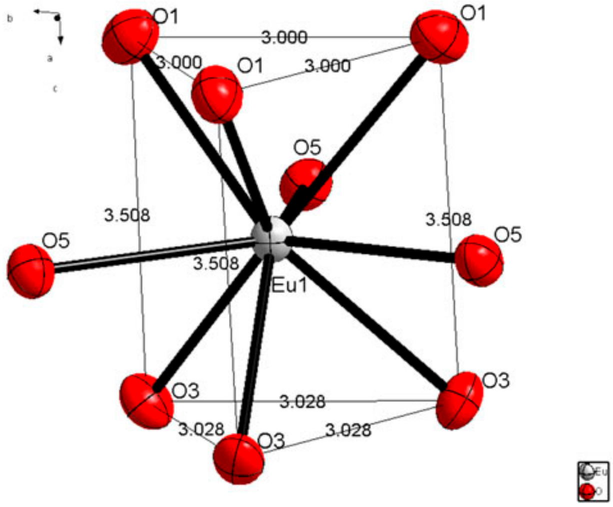
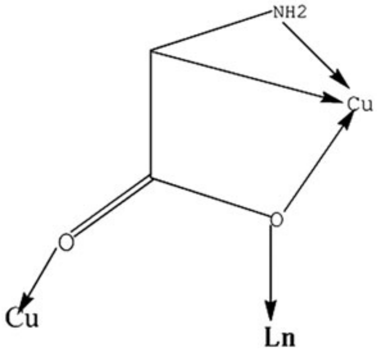


Figure 6. The 3-D structure of Eu(III) and O.



Scheme 1. The chelating structure of Cu(II).

In figures 1 and 2, the distance of the two parallel layers, each of which is composed of three Cu^{2+} ions, is ca. 3.42 Å. The ionic radii of the central lanthanide ions seem to have an effect on this distance. In each layer, the three Cu^{2+} ions form an equilateral triangle, so the copper framework may be described as a “flat” equilateral trigonal prism. Every two identical Cu^{2+} (1 or 2) ions are connected by a chelating glycine (the Cu(1)···Cu(1) distance is ca. 5.32 Å and the Cu(2)···Cu(2) distance is ca. 5.37 Å (Sm), the Cu(1)···Cu(1) distance is ca. 5.37 Å and the Cu(2)···Cu(2) distance is ca. 5.32 Å) (Eu)). Cu(1) and Cu(2) are connected by a HO_2 set that one O from perchlorate and the other O and H are donated by hydroxyl.

Sm^{3+} or Eu^{3+} ions have a nine-coordinate O_9 donor set and coordination polyhedra may be best described as tricapped trigonal prism (figures 5 and 6). The six carboxylate oxygens from six glycines form six apices and the three oxygens from three μ_3-OH^- groups form three caps. The Sm–O bond length between Sm^{3+} and glycine is ca. 2.50 Å and Eu–O bond

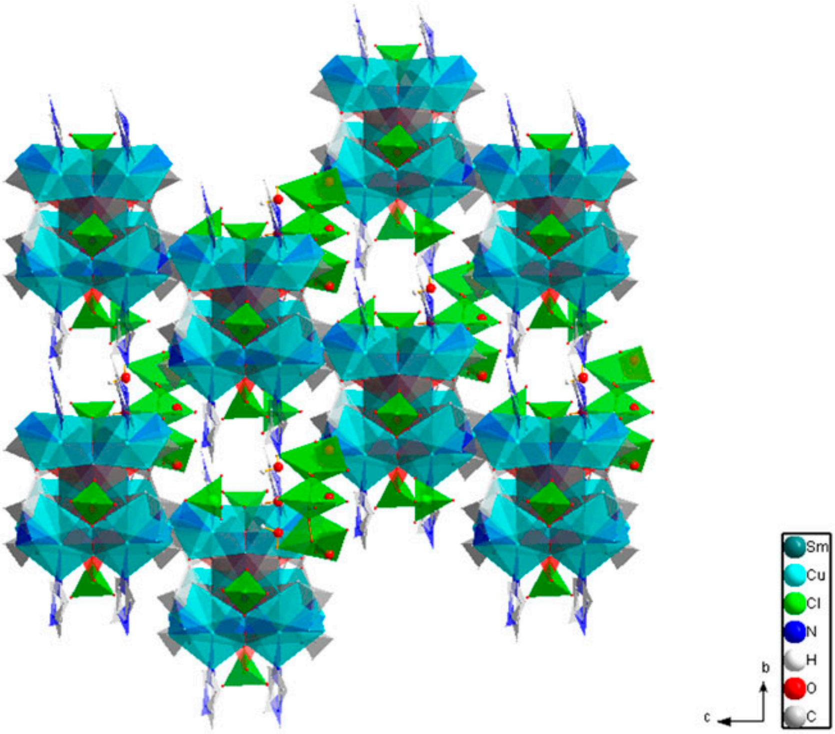


Figure 7. The structure of hydrogen bonds of the Sm(III) complex.

length between Eu^{3+} and glycine is ca. 2.47 Å, while the length between Sm^{3+} and O from μ_3-OH^- is ca. 2.47 Å. Each Cu^{2+} has an N_2O_3 donor set, which consists of one nitrogen of a glycine, one nitrogen of an imidazole, two carboxyl oxygens from two glycinates, and a μ_3-OH^-. The distances of Cu–O and Cu–N (equatorial position) are ca. 2.0 Å, shorter than that of Cu–O(2) (axial position, ca. 2.25 Å). Longer bonding distance may imply a weaker bond. To Cu, small deviations of bond angles from the idealized pyramidal geometry are found for N(2)–Cu(2)–O(5) (165.4(2)°), N(5)–Cu(2)–O(3) (175.1(2)°), N(1)–Cu(1)–O(2A) (94.8(3)°), O(5)–Cu(1)–O(2A) (91.39(17)°), O(1)–Cu(1)–O(2A) (93.04(17)°) and N(3)–Cu(1)–O(2A) (93.5(2)°), N(2)–Cu(2)–O(5) (165.4(2)°), N(5)–Cu(2)–O(3) (175.1(2)°), N(1)–Cu(1)–O(2A) (95.0(3)°), O(5)–Cu(1)–O(2A) (92.16(19)°), O(1)–Cu(1)–O(2A) (90.97(19)°) and N(3)–Cu(1)–O(2A) (90.6(3)°). Cu^{2+} has a distorted square pyramidal configuration.

Each cation has three μ_3-OH^- groups. Each coordinates to Sm^{3+} and Eu^{3+} and the two corresponding Cu^{2+} ions (Cu(1) and Cu(2)). They are located in the same plane with Sm^{3+} or Eu^{3+}, forming two equilateral triangles with sides of ca. 4.28 and 4.26 Å. The Cu(2)–O(5)–Cu(1)) is 119.8(2)° and 119.2(2)°. These data also decrease with the decrease of the ion radii of samarium and europium. The glycinato ligand adopts a π-coordination mode, chelating to two Cu^{2+} and one Sm^{3+} or Eu^{3+} ions (scheme 1).

The six-membered chelate rings (N–Cu–O) formed in the π-coordination mode is 82.9(2) (Sm: N(1)–Cu(1)–O(1)), 83.3(3) (Eu: N(1)–Cu(1)–O(1)) and 82.7(2) (Sm: N(2)–Cu(2)–O(3)), 83.2(2) (Eu: N(2)–Cu(2)–O(3)).

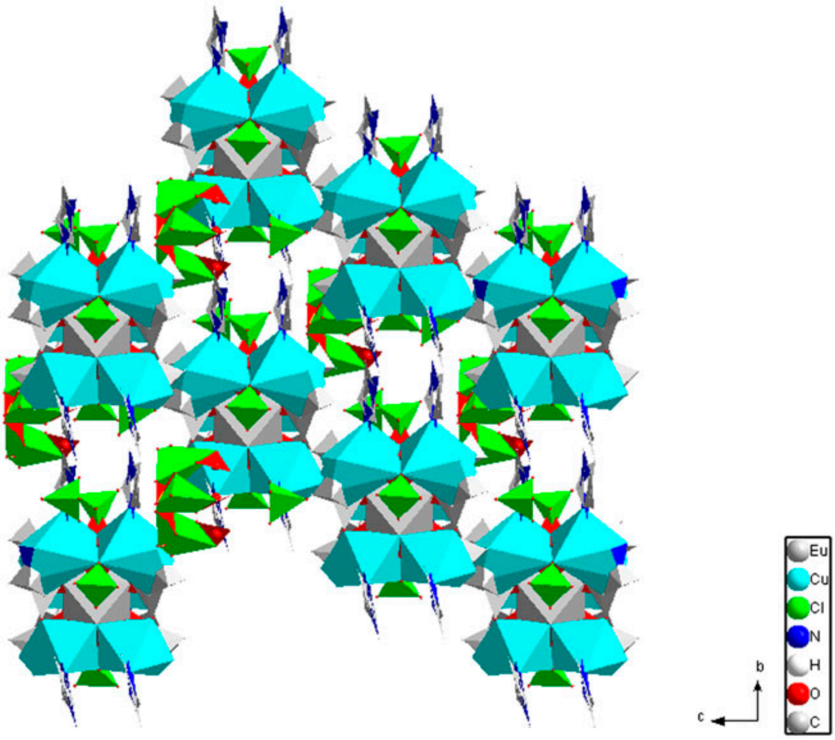


Figure 8. The structure of hydrogen bonds of the Eu(III) complex.

Table 3. The bond lengths (Å) and angles (°) of hydrogen bonds for the Sm complex.

D	H	A	D–H	H···A	D···A	D–H···A	Symmetry for A
N1	H1A	O4	0.900	2.581	3.223	128.88	$-x + y + 4/3, -x + 5/3, z - 1/3$
N1	H1B		0.900				
N2	H2A		0.900				
N2	H2B	O18	0.900	2.201	3.038	154.49	$-x + y + 1/3, -x + 2/3, z - 1/3$
N4	H4	O17	0.860	2.053	2.669	127.97	$-x + y + 2/3, -x + 1/3, z - 2/3$
N4	H4	O19	0.860	2.262	3.110	168.87	$-x + y + 2/3, -x + 1/3, z - 2/3$
N6	H6	O18	0.860	2.560	3.373	158.03	$x + 1/3, y + 2/3, z - 1/3$
N6	H6	O15	0.860	2.583	3.243	134.35	$x + 1/3, y + 2/3, z - 1/3$
O5	H5A	O8	0.850	2.170	3.010	169.61	$-x + y, -x + 1, z$

Table 4. The bond lengths (Å) and angles (°) of hydrogen bonds for the Eu complex.

D	H	A	D–H	H···A	D···A	D–H···A	Symmetry for A
N1	H1A	N6	0.900	2.588	3.386	148.13	$-x + y+4/3, -x + 2/3, z - 1/3$
N1	H1B	O15	0.900	2.265	3.143	164.93	
N2	H2A	O2	0.900	2.602	3.221	126.61	
N2	H2B		0.900				
N4	H4		0.860				
N6	H6	O6	0.860	2.443	3.133	137.69	$-y + 1, x - y, z$
O5	H5A	O9	0.850	2.156	2.996	170.14	$x, y - 1, z$

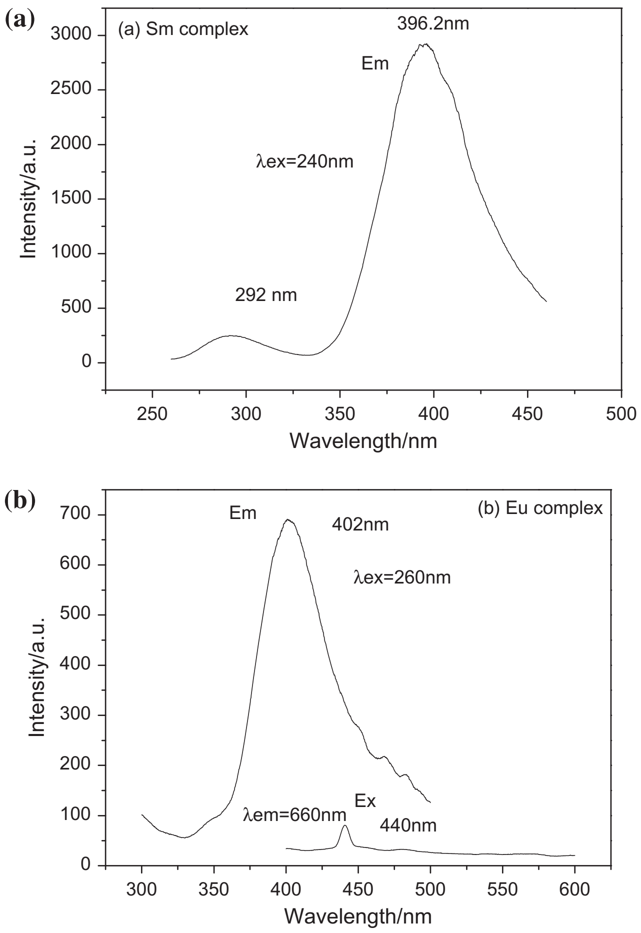


Figure 9. The fluorescent excitation and emission spectra of Sm(III) (a) and Eu(III) (b) complexes.

Each imidazole is a terminal ligand, coordinating to Cu^{2+}. The two corresponding imidazole ligands in the two layers are almost parallel, with a distance of 3.3 Å, which falls within the limit of a π–π stacking interaction. The large network of intra- or intermolecular hydrogen bonds helps to stabilize the crystal (figures 7 and 8). The bond distances and angles are listed in tables 3 and 4. Three of the perchlorates are disordered due to rotation of the perchlorate.

3.2. *Excitation and emission spectra of the complexes*

The fluorescent excitation and emission spectra of Sm(III) (a) and Eu(III) (b) complexes are shown in figure 9(a) and (b). The excitation spectra were obtained by monitoring the emission of the Eu(III) complex at 660 nm. Eu(III) complex had excitation spectra, which were dominated by a broad band from 400 to 600 nm with the maximum peak at 440 nm. The Sm(III) complex has no excitation spectra. In spectra of the Sm(III) and Eu(III) complexes, there was a wide excitation band from 200 to 400 nm. The strong emission intensities between 250 and 350 nm indicated that both ligands were beneficial to absorb energy and transfer it to Sm(III) or Eu(III) ions, and emitted the characteristic fluorescence of Sm(III) and Eu(III) ions. There were stronger emissions between 350 and 500 nm with the maximum peaks at 396 and 402 nm for Sm(III) and Eu(III) ions, respectively. The peak on emission spectra of imidazole is 400 nm, implying that the luminescent behavior is ligand-based emission.

4. Conclusion

Two heptanuclear trigonal prismatic polyhedra, $[EuCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$ and $[SmCu_6(\mu\text{-}OH)_3(Gly)_6Im_6](ClO_4)_6\cdot 3H_2O$ were in rhombohedral R3 space groups. According to unit cell parameters, both compounds belong to hexagonal crystal group. In the clusters, Sm^{3+} and Eu^{3+} are situated in the center of a prism formed by six coppers and coordinate to nine oxygens with a tricapped trigonal prismatic coordination polyhedron. Six glycinato ligands and six imidazole terminal ligands (each coordinates to one Cu^{2+}) were used in the construction of the cluster. The fluorescent excitation and emission spectra showed that the complexes have strong fluorescent properties, not only for the rare earth ions, but also for the six imidazole terminal ligands.

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.1000884].

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