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**STRUCTURAL DETERMINATION OF NEW EIGHT-COORDINATE  
NH<sub>4</sub>[Eu<sup>III</sup>(CYDTA)(H<sub>2</sub>O)<sub>2</sub>]·4.5H<sub>2</sub>O AND K<sub>2</sub>[Eu<sub>2</sub><sup>III</sup>(PDTA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O COMPLEXES**© 2011 J. Wang<sup>1,2\*</sup>, P. Hu<sup>1</sup>, B. Liu<sup>2</sup>, R. Xu<sup>3</sup>, X. Wang<sup>2</sup>, D. Wang<sup>2</sup>, L.Q. Zhang<sup>2</sup>, X.D. Zhang<sup>1</sup><sup>1</sup>Department of Chemistry, Liaoning University, Shenyang 110036, P. R. China<sup>2</sup>Department of Pharmacy, Liaoning University, Shenyang 110036, P. R. China<sup>3</sup>Center of Analysis and Test, Liaoning University, Shenyang 110036, P. R. China

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The NH<sub>4</sub>[Eu<sup>III</sup>(Cydta)(H<sub>2</sub>O)<sub>2</sub>]·4.5H<sub>2</sub>O (**I**) (H<sub>4</sub>Cydta = *trans*-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid) and K<sub>2</sub>[Eu<sub>2</sub><sup>III</sup>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O (**II**) (H<sub>4</sub>pdta = propylenediamine-N,N,N',N'-tetraacetic acid) complexes are prepared by heat-refluxing and acidity-adjusting methods respectively, and their composition and structures are determined by elemental analyses and single crystal X-ray diffraction techniques. The complex **I** has a mononuclear structure, crystallizes in the triclinic crystal system with the  $P\bar{1}$  space group; the central Eu<sup>III</sup> ion is eight-coordinated by a hexadentate Cydta ligand and two water molecules. The crystal data are as follows:  $a = 8.653(4)$ ,  $b = 10.041(4)$ ,  $c = 14.405(6)$  Å,  $\alpha = 88.469(6)$ ,  $\beta = 74.892(6)$ ,  $\gamma = 88.256(7)^\circ$ ,  $V = 1207.5(9)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.731$  g/cm<sup>3</sup>,  $\mu = 2.669$  mm<sup>-1</sup>,  $F(000) = 638$ ,  $R = 0.0257$ , and  $wR = 0.0667$  for 3807 observed reflections with  $I \geq 2\sigma(I)$ . The EuN<sub>2</sub>O<sub>6</sub> part in the [Eu<sup>III</sup>(Cydta)(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> complex anion forms a pseudo-square antiprismatic polyhedron. The complex **II** is eight-coordinate as well; it is a binuclear structure that crystallizes in the monoclinic crystal system with the  $C_2/c$  space group; half of the central Eu<sup>III</sup> ion is coordinated by two nitrogen atoms from one hexadentate pdta ligand and six oxygen atoms from the same pdta ligand, one water molecule and carboxylic group from the neighboring pdta ligand respectively. The crystal data are as follows:  $a = 19.866(3)$ ,  $b = 9.1017(12)$ ,  $c = 21.010(3)$  Å,  $\beta = 104.972(2)^\circ$ ,  $V = 3670.1(9)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 2.046$  g/cm<sup>3</sup>,  $\mu = 3.710$  mm<sup>-1</sup>,  $F(000) = 2240$ ,  $R = 0.0213$  and  $wR = 0.0460$  for 4183 observed reflections with  $I \geq 2\sigma(I)$ . Otherwise, the two EuN<sub>2</sub>O<sub>6</sub> parts in the [Eu<sub>2</sub><sup>III</sup>(pdta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> complex anion form a pseudo-square antiprismatic polyhedron.

**Key words:** Eu<sup>III</sup>, Cydta, pdta, complex, synthesis, structure.**INTRODUCTION**

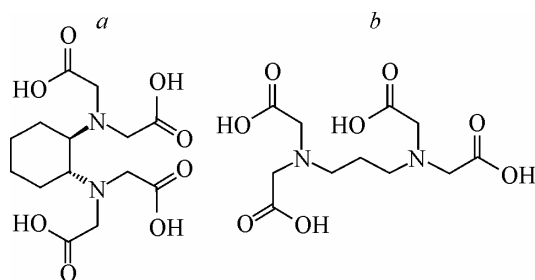
As well known, many rare-earth metal ions in aqueous solutions or the solid state possess fascinating luminescent properties [ 1, 2 ]. Especially, the Eu<sup>III</sup> complexes with various ligands, due to their high and sharply spiked fluorescence emission efficiency, long lifetime, and large Stokes shift [ 3 ], exhibit very intense luminescence among the other rare-earth metal materials, as reported in the previous studies [ 4 ]. Their long lifetime (hundreds of microseconds) and large Stokes shifts are useful for fluorescent immunoassays [ 5 ]. So, the Eu<sup>III</sup> complexes are successfully applied in materials science as luminescent probes [ 6 ] and sensory materials [ 7 ]. Aminopolycarboxylic acids as chelating agents can form extraordinarily stable and water-soluble complexes with almost all metal ions [ 8 ] including all rare-earth metal ions. Their complexes are widely used for industrial, environmental, and biological applications [ 9—11 ]. Because the luminescent characteristics and chemical properties of metal com-

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plexes depend on their geometric configuration and coordinate structure, the research on the crystal and molecular structures of the  $\text{Eu}^{\text{III}}$  complexes with aminopolycarboxylic acid ligands would be beneficial for other fields of application.

In general, the rare-earth metal complexes with various aminocarboxylic acid ligands adopt eight-, nine- and ten-coordinate structures depending on the ionic radius and electronic configuration. The  $\text{Eu}^{\text{III}}$  ion, one of the rare-earth metal ions, is known to have a relatively large radius and a few electronic configurations of high-spin  $f^6$ , so it has a chance to form nine- or ten-coordinate complexes [12–14]. However, it is not absolute. If a ligand has a special chemical composition or a three-dimensional structure, the  $\text{Eu}^{\text{III}}$  ion would tend to form eight-coordinate complexes, but not nine- or ten-coordinate ones. So, we chose two special ligands, namely Cydta with a rigid ring and pdta with one more methylene than in ordinary aminopolycarboxylic acids, to validate this supposition.

It is fortunate that two new  $\text{NH}_4[\text{Eu}^{\text{III}}(\text{Cydta})(\text{H}_2\text{O})_2]\cdot 4.5\text{H}_2\text{O}$  (**I**) and  $\text{K}_2[\text{Eu}_2^{\text{III}}(\text{pdta})_2(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  (**II**) complexes were synthesized and their crystal and molecular structures were determined. As we predicted, both the two complexes adopt an eight-coordinate structure with a pseudo-square antiprismatic configuration, but for different reasons: the former is a mononuclear structure so the rigid ring may play an important role in its eight-coordinate structure, while the latter is a binuclear structure, which would be the reason of its eight-coordinate structure. The molecular structures of Cydta (*a*) and pdta (*b*) ligands are given in Scheme 1.



Scheme 1. Molecular structure of *trans*-1,2-cyclohexanediamine- $\text{N},\text{N},\text{N}',\text{N}'$ -tetraacetic acid ( $\text{H}_4\text{Cydta}$ ) (*a*) and propylenediamine- $\text{N},\text{N},\text{N}',\text{N}'$ -tetraacetic acid ( $\text{H}_4\text{pdta}$ ) (*b*)

## EXPERIMENTAL

**Synthesis of I.**  $\text{H}_4\text{Cydta}\cdot\text{H}_2\text{O}$  (= *trans*-1,2-cyclohexanediamine- $\text{N},\text{N},\text{N}',\text{N}'$ -tetraacetic acid hydrate) (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.7317 g, 5.0 mmol) was added to 100 ml of warm water and  $\text{Eu}_2\text{O}_3$  (99.999 %, Beijing HENGYE ZHONGYUAN Chemical Co., Ltd., China) (0.8978 g, 2.5 mmol) powder was added slowly to the above solution. The solution became transparent after the mixture had been stirred and refluxed for 15.0 h, and then the pH value was adjusted to 6.0 by dilute aqueous  $\text{NH}_3$ . Finally, the solution was concentrated to 25 ml. A colorless crystal appeared after three weeks at room temperature.

For  $\text{EuC}_{14}\text{H}_{35}\text{N}_3\text{O}_{14.5}$ : Found (%): Eu 25.95, C 26.10, H 5.45, N 6.51; Calcd. (%): Eu 25.94, C 26.08, H 5.47, N 6.52.

This formula is approximately consistent with the result of the diffraction analysis.

**Synthesis of II.** ( $\text{H}_4\text{pdta}$  = propylenediamine- $\text{N},\text{N},\text{N}',\text{N}'$ -tetraacetic acid) (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.5313 g, 5.0 mmol) was added to 100 ml of warm water and  $\text{Eu}_2\text{O}_3$  (0.8798 g, 2.5 mmol) powder was added slowly to the above solution. The solution became transparent after the mixture had been stirred and refluxed for 12.0 h, and then the pH value was adjusted to 6.2 by dilute  $\text{KHCO}_3$  aqueous. Finally, the solution was concentrated to 25 ml. A colorless crystal appeared after two weeks at room temperature.

For  $\text{K}_2\text{C}_{22}\text{H}_{44}\text{N}_4\text{O}_{24}\text{Eu}_2$ : Found (%): Eu 26.87, C 23.35, H 3.94, N 4.97; Calcd. (%): Eu 26.88, C 23.37, H 3.92, N 4.95.

This formula is approximately consistent with the result of the diffraction analysis.

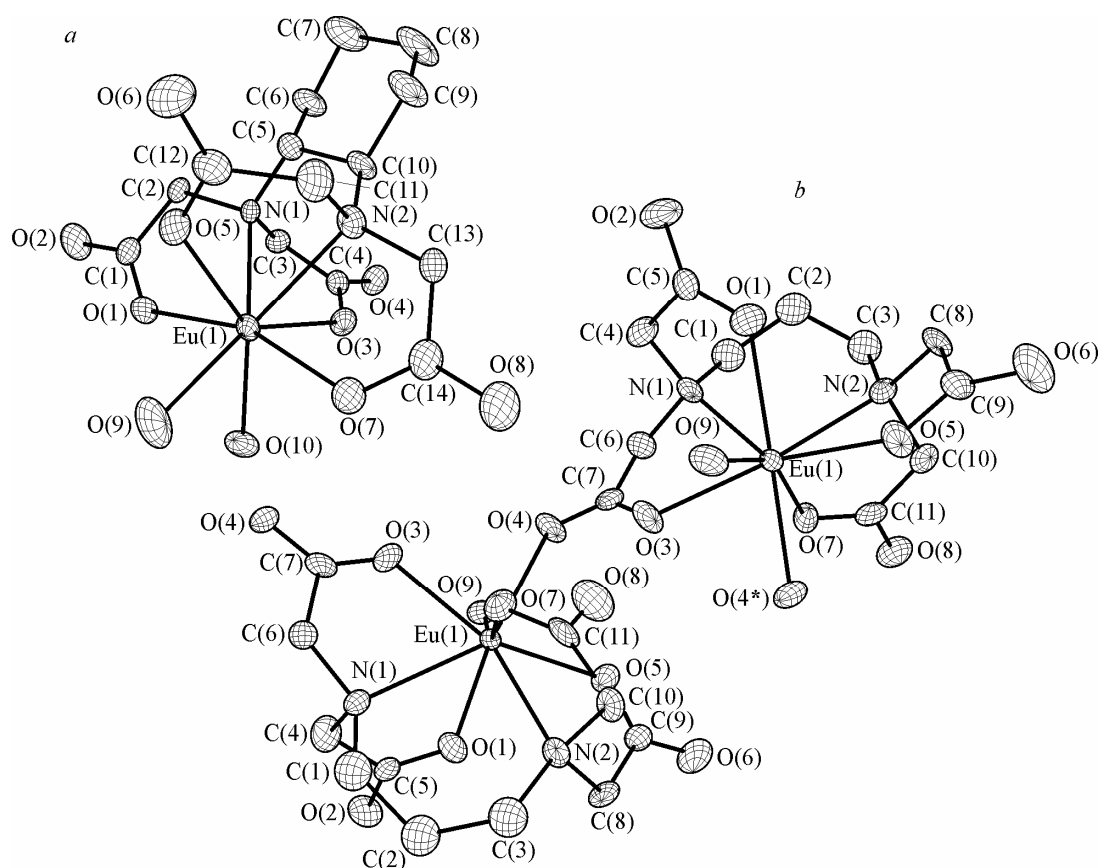


Fig. 1. Molecular structure of the complexes I (a) and II (b)

**X-ray structure determination.** X-ray intensity data were collected on a Bruker SMART CCD X-ray diffractometer system with graphite-monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All the calculations were performed using the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. Fig. 1 illustrates the perspective views of two complexes; Fig. 2 shows their coordination polyhedra; Fig. 3 and 4 show their molecular packings in a unit cell. The crystal data and structure refinement for two complexes are listed in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters for all the non-hydrogen fractions are presented in Table 2 for two complexes, and the selected bond distances and bond angles of two complexes are listed in Table 2.

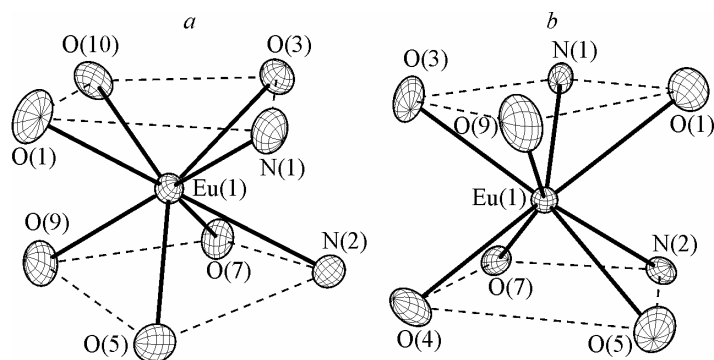


Fig. 2. Coordination polyhedron of the complexes I (a) and II (b)

Table 1

Crystal data and structure refinement for **I** and **II**

Complex	NH <sub>4</sub> [Eu <sup>III</sup> (Cydta)(H <sub>2</sub> O) <sub>2</sub> ] $\cdot$ 4.5H <sub>2</sub> O	K <sub>2</sub> [Eu <sub>2</sub> <sup>III</sup> (pdta) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] $\cdot$ 6H <sub>2</sub> O
Formula weight	629.40	1130.72
Temperature, K	294(2)	293(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C_2/c$
Unit cell dimensions:		
<i>a</i> , <i>b</i> , <i>c</i> , Å	8.653(4), 10.041(4), 14.405(6)	19.866(3), 9.1017(12), 21.010(3)
$\alpha$ , $\beta$ , $\gamma$ , deg.	88.469(6), 74.892(6), 88.256(7)	90, 104.972(2), 90
Volume, Å <sup>3</sup>	1207.5(9)	3670.1(9)
<i>Z</i>	1	8
$\rho_{\text{calcd}}$ , mg/cm <sup>3</sup>	1.731	2.046
Absorption coefficient, mm <sup>-1</sup>	2.669	3.710
<i>F</i> (000)	638	2240
Crystal size, mm	0.30 $\times$ 0.24 $\times$ 0.20	0.40 $\times$ 0.33 $\times$ 0.22
$\theta$ range for data collection, deg.	1.46 to 25.01	3.01 to 27.45
Limiting indices	$-8 \leq h \leq 10$ , $-11 \leq k \leq 9$ , $-13 \leq l \leq 17$	$-22 \leq h \leq 25$ , $-11 \leq k \leq 11$ , $-27 \leq l \leq 27$
Reflections collected	5906	14539
Independent reflections	3807 [ <i>R</i> (int) = 0.0285]	4183 [ <i>R</i> (int) = 0.0284]
Completeness to $\theta_{\text{max}}$ , %	99.35	99.7
Max. and min. transmission	1.000000 and 0.602844	0.4958 and 0.3184
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.056	1.001
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0416, <i>wR</i> <sub>2</sub> = 0.1134	<i>R</i> <sub>1</sub> = 0.0213, <i>wR</i> <sub>2</sub> = 0.0460
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0475, <i>wR</i> <sub>2</sub> = 0.1179	<i>R</i> <sub>1</sub> = 0.0236, <i>wR</i> <sub>2</sub> = 0.0472
Largest difference peak and hole, eÅ <sup>-3</sup>	2.083 and -1.373	1.056 and -0.649
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	

## RESULTS AND DISCUSSION

**Molecular and crystal structure of I.** It can be seen from Fig. 1, *a* that in the complex **I**, the central Eu<sup>III</sup> ion is eight-coordinated by two nitrogen atoms and four oxygen atoms from one Cydta ligand and by two oxygen atoms from two water molecules. **I** the Eu<sup>III</sup>—O bond distances range from 2.354(4) to 2.400(5) Å, and the Eu<sup>III</sup>—O average bond distance is 2.3688(4) Å. The two Eu<sup>III</sup>—N bond

Table 2

Selected bond distances *d* (Å) of **I** and **II**

Bond	<i>d</i>	Bond	<i>d</i>	Bond	<i>d</i>	Bond	<i>d</i>
<b>I</b>				<b>II</b>			
Eu—O(1)	2.365(4)	Eu—O(9)	2.374(5)	Eu(1)—O(1)	2.38(3)	Eu(1)—O(4*)	2.38(3)
Eu—O(3)	2.363(4)	Eu—O(10)	2.400(5)	Eu(1)—O(3)	2.37(3)	Eu(1)—O(9)	2.44(3)
Eu—O(5)	2.357(5)	Eu—N(1)	2.578(5)	Eu(1)—O(5)	2.35(3)	Eu(1)—N(1)	2.61(3)
Eu—O(7)	2.354(4)	Eu—N(2)	2.600(5)	Eu(1)—O(7)	2.38(3)	Eu(1)—N(2)	2.61(3)

distances are 2.578(5) Å ( $\text{Eu}^{\text{III}}-\text{N}(1)$ ) and 2.600(5) Å ( $\text{Eu}^{\text{III}}-\text{N}(2)$ ) respectively, and the  $\text{Eu}^{\text{III}}-\text{N}$  average bond distance is 2.589(3) Å, which are both longer than the  $\text{Eu}^{\text{III}}-\text{O}$  bond distances. It indicates that the  $\text{Eu}^{\text{III}}-\text{O}$  bonds are more stable than the  $\text{Eu}^{\text{III}}-\text{N}$  bonds. It is worth noting that  $\text{Eu}^{\text{III}}-\text{O}(9)$  (2.374(5)) and  $\text{Eu}^{\text{III}}-\text{O}(10)$  (2.400(5) Å) with the O atoms from water molecules are both longer than the other  $\text{Eu}^{\text{III}}-\text{O}$  bonds. This means that the Cydta ligand coordination to the  $\text{Eu}^{\text{III}}$  ion is more stable than that of water molecules.

It is shown in Fig. 2, *a* that the coordination polyhedron of the  $\text{Eu}^{\text{III}}\text{N}_2\text{O}_6$  moiety in **I** adopts a pseudo-square antiprismatic structure, in which the set of O(1), O(3), O(10), and N(1) and the set of O(5), O(7), O(9), and N(2) compose two approximately parallel square planes. The torsion angle of the two square planes is about 45°. In addition, there is no capped atom in the eight-coordinate configuration of this complex. This means that no repulsion to the top or bottom square plane is observed. So, it is distorted only slightly in the coordination geometry of the  $[\text{Eu}^{\text{III}}(\text{Cydta})(\text{H}_2\text{O})_2]^-$  complex anion, close to a standard square antiprismatic conformation.

The Cydta ligand has the same coordination number as the edta ( $\text{H}_4\text{edta}$  = ethylenediamine-*N,N,N',N'*-tetraacetic acid) ligand, but possesses a rigid cyclohexane ring. The coordination structure and geometric configuration of **I** is affected due to the diversification of the ligand structure. Maybe because this rigid cyclohexane ring takes more space than the catenulate ligand such as edta, the ligand with a rigid cyclohexane ring holds it back as well as a water molecule near the central metal ion. Thereby, it leads to a decrease in the coordination number of the central metal ion. As to the central  $\text{Eu}^{\text{III}}$  ion with a relatively large radius of 1.087 Å and a few electronic configurations of low-spin  $f^6$ , it is most likely to be nine-coordinate if coordinated to the catenulate chelate ligand. For instance,  $\text{Na}[\text{Eu}(\text{edta})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$  [15],  $(\text{NH}_4)[\text{Eu}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  [16], and  $\text{K}[\text{Eu}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$  [14] are all nine-coordinate with a monocapped square antiprismatic conformation, whereas **I** is eight-coordinate and has a square antiprismatic conformation. By this token, the rigid cyclohexane ring is a factor that affects the coordination structure and geometric configuration of the complexes.

In one unit cell, as shown in Fig. 3, there is only one molecule of **I** (two half of **I**, in fact). The molecules are linked with each other through a hydrogen bond and electrostatic bonding with  $\text{NH}_4^+$  ions and crystallize in the triclinic system and the  $P\bar{1}$  space group. Each  $\text{NH}_4^+$  ion is bonded to one  $[\text{Eu}^{\text{III}}(\text{Cydta})(\text{H}_2\text{O})_2]^-$  complex anion by the electrostatic interaction and links another adjacent  $[\text{Eu}^{\text{III}}(\text{Cydta})(\text{H}_2\text{O})_2]^-$  complex anion by a hydrogen bond with a coordinate carboxylic O atom (O(1)). The hydrogen bonds in one unit cell link the crystal water molecules, the  $\text{NH}_4^+$  ion, and coordinate and non-coordinate carboxylic O atoms of the Cydta ligands. So, as a whole crystal, a network structure is formed through the hydrogen bonds and electrostatic bonding.

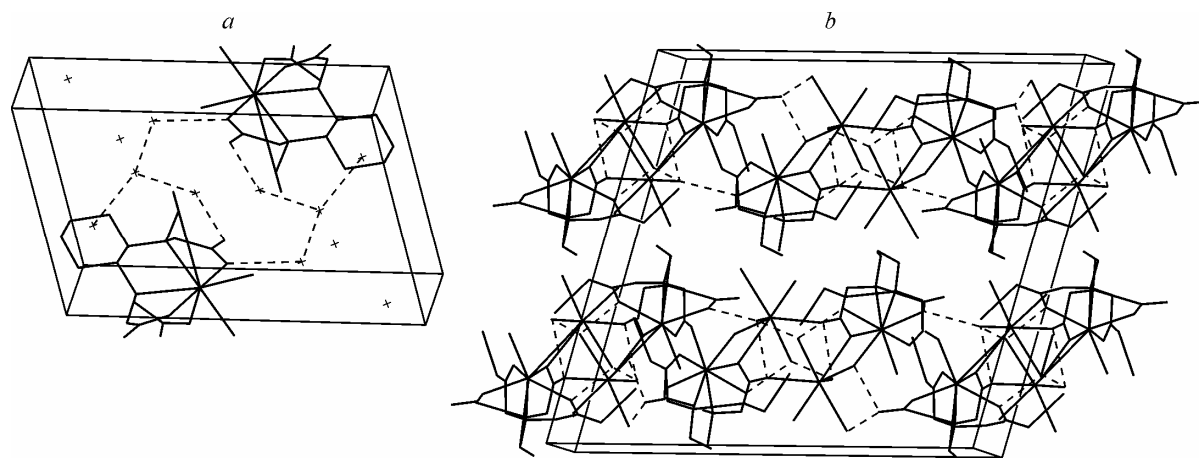


Fig. 3. Arrangement of complex **I** (*a*) and **II** (*b*) in unit cell (dashed lines represent intermolecular hydrogen bonds)

**Molecular and crystal structure of II.** Fig. 1, *b* shows that in each part of the binuclear molecule, the central  $\text{Eu}^{\text{III}}$  ion in the  $\text{K}_2[\text{Eu}_2^{\text{III}}(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  complex is eight-coordinated by two nitrogen atoms and four oxygen atoms both from one pdta ligand, one oxygen atom (O(4)) from another adjacent pdta as well as one oxygen atom from one water molecule. The  $\text{Eu}^{\text{III}}\text{—O}$  bond distances range from 2.35(3) to 2.44(3) Å and the  $\text{Eu}^{\text{III}}\text{—O}$  average bond distance is 2.383(3) Å. Two  $\text{Eu}^{\text{III}}\text{—N}$  bond distances are 2.61(3) Å, which are both longer than the  $\text{Eu}^{\text{III}}\text{—O}$  bonds distances. This indicates that the  $\text{Eu}^{\text{III}}\text{—O}$  bonds are more stable than the  $\text{Eu}^{\text{III}}\text{—N}$  bonds. The  $\text{Eu}^{\text{III}}\text{—O(9)}$  bond distance (O(9) from the water molecule) is longer than other  $\text{Eu}^{\text{III}}\text{—O}$  bond distances, which indicates that the coordination of the pdta ligand to the  $\text{Eu}^{\text{III}}$  ion is more stable than that of water molecules.

It is shown in Fig. 2, *b* that the coordination polyhedron of the  $\text{Eu}^{\text{III}}\text{N}_2\text{O}_6$  moiety in the complex II adopts a pseudo-square antiprismatic configuration, in which the set of O(1), O(3), O(9), and N(1) and the set of O(5), O(7), O(4\*), and N(2) compose two approximately parallel square planes. The torsion angle of the two square planes is about  $45^\circ$ . Similarly, there is no capped atom in the geometry configuration of this complex, therefore no repulsion to the top or bottom square plane is observed. On the other hand, to the top approximate square plane, the dihedral angle between the O(1), O(3), N(1) and O(1), O(3), O(8) planes is  $0.075^\circ$ , and to the bottom approximate square plane, the dihedral angle between the O(5), O(7), N(2) and O(5), O(7), O(9) planes is  $5.526^\circ$ . So, it is distorted slightly in the coordination geometry of the  $[\text{Eu}_2^{\text{III}}(\text{pdta})_2(\text{H}_2\text{O})_2]^{2-}$  complex anion, close to a standard square antiprismatic conformation.

Although the central  $\text{Eu}^{\text{III}}$  ion possesses a relatively large radius and a few electronic configurations of high-spin  $f^6$ , the complex II has an eight-coordinate structure. It may be attributed to the shape of the pdta ligand and the binuclear structure. The pdta ligand is a sexadentate ligand as the same as edta ligand. However, there is one more methylene in the pdta ligand as compared to the edta ligand. So, the complex II possesses a six-membered ring unlike the five-membered ring in the complex of a rare-earth metal ion with the edta ligand. Small space is left for the ninth coordinate atom due to the six-membered ring. On the other hand, the binuclear structure also takes some space, which would hold back water molecule or other coordinate atom as the ninth coordinate atom. So, the complex II forms an eight-coordinate structure, whereas the  $\text{K}[\text{Eu}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$  complex forms a nine-coordinate structure [14].

One unit cell, as shown in Fig. 3, *b*, contains four molecules. The molecules are connected with each other through hydrogen bonds and electrostatic bonding with  $\text{K}^+$  ions and crystallize in the monoclinic system and the  $C_2/c$  space group. Each  $\text{K}^+$  ion is seven-coordinated by one coordinate carboxylic O atom (O(5)) from one pdta ligand, and two non-coordinate carboxylic O atoms (O(2) and O(6)) from the other two adjacent pdta. One coordinate water molecule (O(9)) and three crystal water molecules (O(10), O(11) and O(12)) provide other four coordinate atoms. So, the  $\text{K}^+$  ion links three adjacent  $[\text{Eu}_2^{\text{III}}(\text{pdta})_2(\text{H}_2\text{O})_2]^{2-}$  complex anions. The hydrogen bonds in one unit cell link the coordinate water molecule, crystal water molecules, and coordinate and non-coordinate carboxylic O atoms of the pdta ligands. Otherwise, O(4) as a bridge links the two parts of one binuclear molecule. With this mode, each pdta ligand coordinates to two neighboring  $\text{Eu}^{\text{III}}$  ions. So, as seen from Fig. 4, it forms

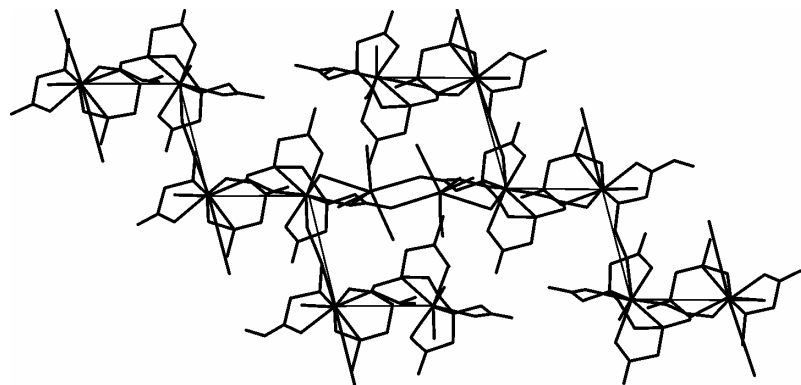


Fig. 4. Infinite long zigzag-type chains and their relationship

a one-dimensional infinite long zigzag-type chain. It also can be seen that each two zigzag chains are connected through  $\text{K}^+$  ions, which link the head of one chain with the inflection point of another chain. Thus, the zigzag chains connected closely by  $\text{K}^+$  ions expand infinitely in another dimension, and form a net-like plane. The planes do not contact with each, which is indicated by Fig. 3.

### CONCLUSIONS

In conclusion, two novel rare-earth metal complexes with aminopolycarboxylic acid (Cydta, pdta) have been successfully synthesized. With a certain ionic radii and electronic configurations of the central  $\text{Eu}^{\text{III}}$  ion, although different ligands, they are both eight-coordinate and have a pseudo-square antiprismatic conformation, but different crystal and molecule structures. The complex **I** is mononuclear; it crystallizes in the triclinic crystal system with the  $P\bar{1}$  space group, while the complex **II** is binuclear and crystallizes in the monoclinic crystal system with the  $C_2/c$  space group.

**Supplementary materials.** CCDC 725098  $\text{NH}_4[\text{Eu}^{\text{III}}(\text{Cydta})(\text{H}_2\text{O})_2] \cdot 4.5\text{H}_2\text{O}$ , CCDC 725099  $\text{K}_2[\text{Eu}_2^{\text{III}}(\text{pdta})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ , contain the supplementary crystallographic data for this article. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033.

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