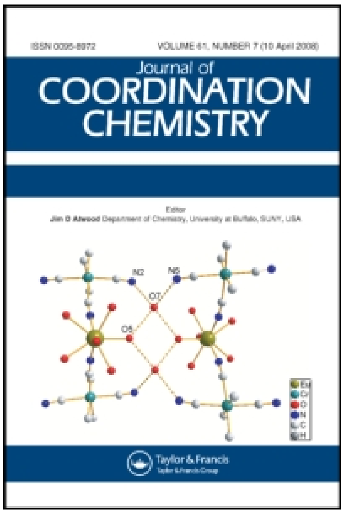

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Synthesis and structure of a polymeric ten-coordinate rare earth metal complex with nta ligand: $\{[\mathrm{Eu^{III}}(\mathrm{C\text{-}nta})(\mathrm{T\text{-}nta})]\cdot 3\mathrm{H_2O}\}_{\text{<b> <i>n</i>}}$ with a novel cage-like 3-D structure

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Synthesis and structure of a polymeric ten-coordinate rare earth metal complex with nta ligand: $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$ with a novel cage-like 3-D structure

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The polymeric ten-coordinate rare earth metal (RE) complex with nta, $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$, has been synthesized in aqueous solution and characterized by FT-IR, elemental analyses, TG-DTA and single-crystal X-ray diffraction technique. The $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$ crystallizes in the cubic system with $P2_13$ space group, $a = b = c = 12.4153(3)$ Å, $V = 1913.69(8)$ Å^3, $Z = 4$, $M = 582.24\,\mathrm{g\,mol^{-1}}$, $D_c = 2.021\,\mathrm{Mg\,m^{-3}}$, $\mu = 3.360\,\mathrm{mm^{-1}}$, $F(000) = 1148$, and its structure is refined to $R_1(F) = 0.0204$ for 1277 observed reflections $[I \geq 2.0\sigma(I)]$. The coordination polyhedron adopts distorted C_{3v} mono-top-capped & tri-lateral-capped trigonal prismatic conformation (MT&TL-TP); the three-dimensional geometry is a cage-like 3-D structure. According to thermal analyses, the collapsing temperature of the crystal structure is 173°C, indicating that its crystal structure is very stable.

Keywords: Eu(III) ion; Nitrilotriacetic acid (H_3nta); Coordination polymer; Cage-like 3-D structure

1. Introduction

Nitrilotriacetic acid (H_3nta), a tetradentate aminopolycarboxylic acid ligand with high specificity for polyvalent metal ions gives water-soluble and stable complexes with potential application in industrial, environmental and biological fields. These include the removal of trace amounts of metal ions from aqueous [1, 2] and metabolic systems [3, 4], and the degradation of disposal materials [5, 6]. In 1972, Martin and Jacobson concluded that rare earth metal (RE) complexes with nta were divided into three crystallographically distinct groups: (i) the La–Ce group; (ii) the Pr–Tb group; (iii) the Dy–Lu group. Complexes within the same group have identical crystal structures [7, 8]. However, reports indicate that this conclusion is no longer appropriate [9]. The 1 : 1 complexes were considered to be typical for RE-nta complexes, such as $[Pr^{III}(nta)(H_2O)_2]\cdot H_2O$ [10] and $[Tm^{III}(nta)(H_2O)_2]\cdot 2H_2O$ [11].

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Recently, there are many reports on the RE-nta complexes with the 1 : 2 ratio, for example, $K_3[Nd^{III}(nta)_2(H_2O)] \cdot 6H_2O$ and $K_3[Er^{III}(nta)_2(H_2O)] \cdot 5H_2O$ [12]. For the title complex, there are three significant points. (1) There are two kinds of nta ligands, tripod-nta (T-nta) and common-nta (C-nta). (2) The ten-member rings composed of five Eu(III) ions and five T-nta ligands are connected by the remaining carboxyl arms of T-nta ligands yielding a cage-like 3-D structure. (3) According to Robertson's definition for ten-coordinate complexes, two idealized modes should be D_{4d} bicapped square antiprism and C_{2v} decatetrahedron, respectively [13]. However, neither is appropriate for the title complex, which is a C_{3v} mono-top-capped & tri-lateral-capped trigonal prism (MT&TL-TP). D_{3h} tricapped trigonal prism (TCTP) could be considered as the origin with another capped atom above the top plane of TCTP, and becoming a MT&TL-TP. To the best of our knowledge, this is the first report of this conformation.

2. Experimental section

2.1. *Synthesis of the title complex*

The complex was prepared by mixing Eu_2O_3 (0.3520 g, 1.0 mmol) powder and H_3nta (0.7644 g, 4.0 mmol) powder in 100 mL water. The mixture was heated under stirring and refluxing for 1.0 h. The solution became transparent, and then the pH value was adjusted to 6.0 by dilute aqueous ammonia. Finally the resulting solution was concentrated to 20 mL and colorless crystals of Eu(III) complex were obtained after two weeks at room temperature. The elemental analyses for C, H and N were carried out on a Perkin–Elmer 240 elemental analysis instrument. The Eu(III) content was measured by edta titration after microwave digestion. Anal. Found (%): Eu 26.13, C 24.71, H 3.14, N 4.80; Calcd (%): Eu 26.10, C 24.75, H 3.12, N 4.81. The formula ($C_{12}H_{18}EuN_2O_{15}$) is approximately consistent with the result of X-ray diffraction analysis.

2.2. *Determination of FT-IR spectra*

The FT-IR spectra of the complex and H_3nta were determined on a Perkin–Elmer Spectrum One FT-IR spectrometer. Results are given in figure 1.

2.3. *Determination of TG-DTA*

TG-DTA curves of the complex were determined by Mettler-Toledo 851^e thermogravimetric analyzer in the presence of Ar (20 mL min^{-1}) from room temperature to 800°C at a heating rate of 10°C min^{-1}. Results are shown in figure 2.

2.4. *Single-crystal X-ray diffraction*

The data were collected on a Bruker SMART CCD type X-ray diffractometer system with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures

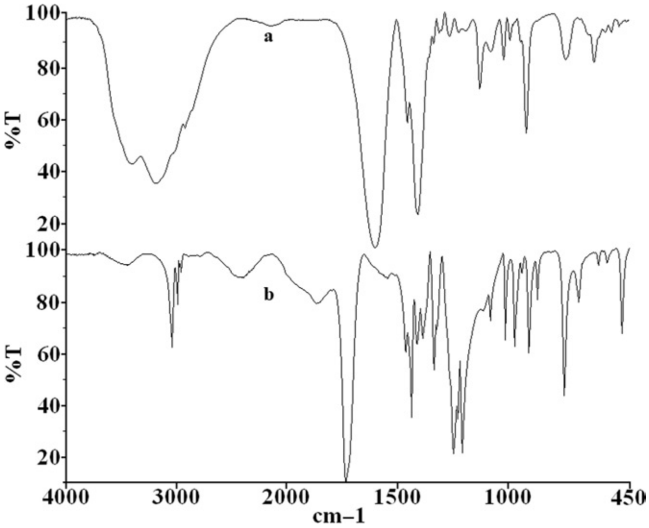

Figure 1. The FT-IR spectra of $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$ and H_3nta. (a) $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$; (b) H_3nta.

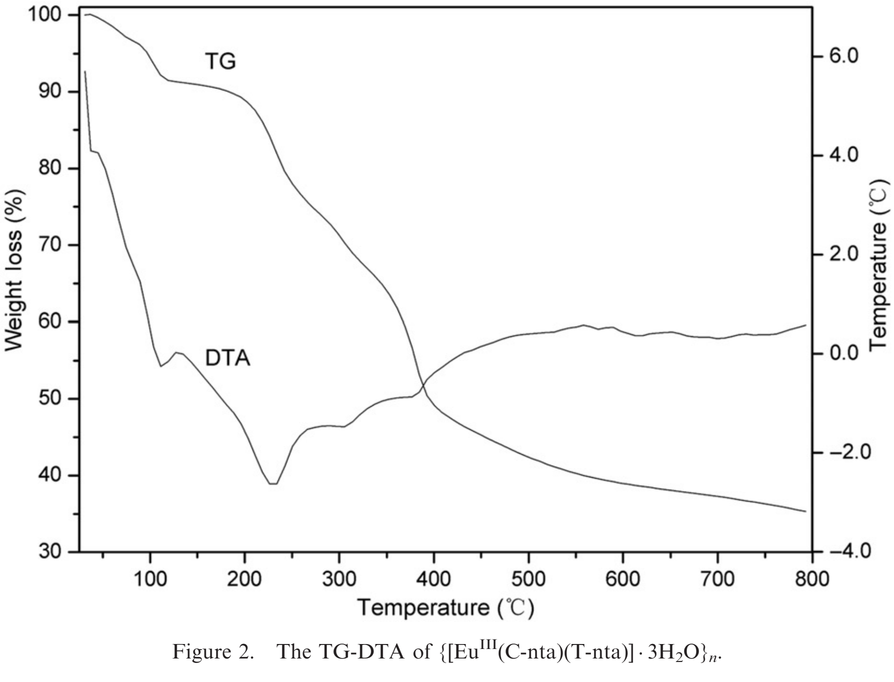

Figure 2. The TG-DTA of $\{[Eu^{III}(C\text{-}nta)(T\text{-}nta)]\cdot 3H_2O\}_n$.

were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All the calculations were performed by the SHELXL-97 program on PDP11/44 and Pentium MMX/166 computers. The details of crystal data collection and refinement parameters are listed in table 1.

Table 1. Crystal data and structure refinement for title complex.

Chemical formula	$C_{12}H_{18}EuN_2O_{15}$
Formula weight	582.24
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	$P2_13$
a (Å)	12.4153(3)
b (Å)	12.4153(3)
c (Å)	12.4153(3)
β (°)	90
Volume (Å^3)	1913.69(8)
Z	4
Calculated density (Mg m^{-3})	2.021
Absorption coefficient (mm^{-1})	3.360
$F(000)$	1148
Crystal size (mm^3)	0.28 × 0.18 × 0.10
Theta range for data collection (°)	2.32–26.03
Limiting indices	$-15 \le h \le 13$, $-14 \le k \le 15$, $-15 \le l \le 11$
Reflections collected/unique	11082/1277
Independent reflections	1277 [$R(\text{int}) = 0.0732$]
Completeness to $\theta = 26.03$ (%)	100.0
Max. and min. transmission	0.7386 and 0.4487
Data/restraints/parameters	1277/0/91
Goodness-of-fit on F^2	1.169
Final R indices [$I > 2\sigma(I)$]*	$R_1 = 0.0204$, $wR_2 = 0.0607$
R indices (all data)	$R_1 = 0.0207$, $wR_2 = 0.0608$
Largest diff. peak and hole (e Å^{-3})	0.463 and −0.287
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2

*$R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *FT-IR spectra*

Comparison of the FT-IR spectra between nta ligand and the complex reveal considerable changes.

As shown in figures 1(a) and (b), the ν(C–N) of the complex is at 1126 cm^{-1} and red-shifts 80 cm^{-1} compared with that (1206 cm^{-1}) of H_3nta, indicating that nitrogen of H_3nta coordinate to Eu(III). The ν_{as}(COO) of the complex is at 1599 cm^{-1}, red-shifted 134 cm^{-1} compared with that (1733 cm^{-1}) of H_3nta; the ν_s(COO) of the complex is at 1408 cm^{-1}, blue-shifted 23 cm^{-1} compared with that (1385 cm^{-1}) of H_3nta. These changes confirm that the oxygen atoms from the carboxyl groups coordinate to Eu(III), too [14, 15]. There is a broad ν(OH) band of H_2O near 3406 cm^{-1} revealing the presence of H_2O in the complex.

3.2. *Thermal analyses*

As shown in figure 2, the TG curve of the complex exhibits a typical three stage decomposition. Corresponding to the weight loss of each stage, there are obvious endothermic peaks in the DTA curve.

The first stage weight loss, starting from room temperature to 135°C, corresponds to expulsion of crystal water. In the corresponding temperature range of DTG curve, there are two weight loss peaks (67°C, 103°C), which means that the expulsion of crystal water molecules is in two steps: (1) from room temperature to 82°C, the weight loss ratio is about 3.35% with two of nine water molecules expulsed; (2) from 82 to 135°C, the weight loss ratio is about 5.44%. The gross weight loss ratio of the first stage is about 8.79%, close to the calculated value (9.28%). In the DTA curve, there is an obvious endothermic peak at 111°C corresponding to the second water expulsion process, which proves that it needs more energy than the first. The second stage weight loss attributed to decomposition of the coordination polymer from 173 to 464°C. In the DTG curve, there are three weight loss peaks at 234°C, 305°C and 377°C, respectively, indicating that the decomposition proceeded in three steps: (1) from 173 to 274°C, the weight loss ratio is about 15.70%. The crystal structure of coordination polymer collapsed, and the polymer changed into the aminocarboxylate. In the DTA curve, there is a very obvious endothermic peak at 226°C corresponding to this transformation. (2) From 274 to 321°C, the weight loss ratio is about 6.73%. The sample was destroyed continuously, attributable to decomposition of aminocarboxylate. In the corresponding temperature range of DTA curve, there is a small endothermic peak at 305°C. (3) From 321 to 464°C, the weight loss ratio is about 23.56%. The sample was destroyed completely by decompositions of carboxylate. There is also a small endothermic peak at 377°C. The third stage weight loss attributed to decompositions of carbonate starts from 464 to 793°C. The weight loss ratio is about 9.09%. The total weight loss ratio is about 64.68% according to the mass loss calculation. It is estimated that, in the remainder, the main species is Eu_2O_3, and there is still a little $Eu_2(CO_3)_3$ left.

3.3. *Molecular and crystal structures*

As shown in figure 3, the molar ratio of Eu(III) ions to nta ligands is 1 : 2, but there are two kinds of nta ligands in the complex. One is T-nta, which provides six carboxylic oxygen atoms participating in the coordination. Each T-nta is spread out such that each of its carboxyl arms coordinates to a different Eu(III). As a result, three adjacent Eu(III) ions are connected together. The other refers to C-nta, which provides four coordination atoms, namely, one amine nitrogen atom and three carboxylic oxygen atoms, coordinated to the same Eu(III). The C-nta is similar to a satellite of Eu(III). For Eu-nta complexes with 1 : 2 molar ratio, the coordination number is usually nine, and their chelate rings are five-member rings, e.g. $Na_3[Eu^{III}(nta)_2(H_2O)] \cdot 5H_2O$ [16] reported by Kang *et al.* However, in the complex, the Eu(III) is ten-coordinate. Three chelate rings of the C-nta ligand are still five-member rings, and three angles of ∠O–Eu–N are the same (63.19(7) Å); three chelate rings of the T-nta ligand are four-member rings and three ∠O–Eu–O angles are the same (50.95(10) Å) too. Four-member rings need less coordination space than five-member rings, so the coordination space left by C-nta ligand could admit three four-member rings allowing the coordination number to be ten. Eu(1), for example, possesses C_{3v} symmetry, and N(2) and Eu(1) are on the threefold rotation axis. The average Eu–O bond length (2.522(3) Å) is a little shorter than that of Eu–N (2.650(6) Å), indicating that Eu–O bonds are more stable than the Eu–N bond.

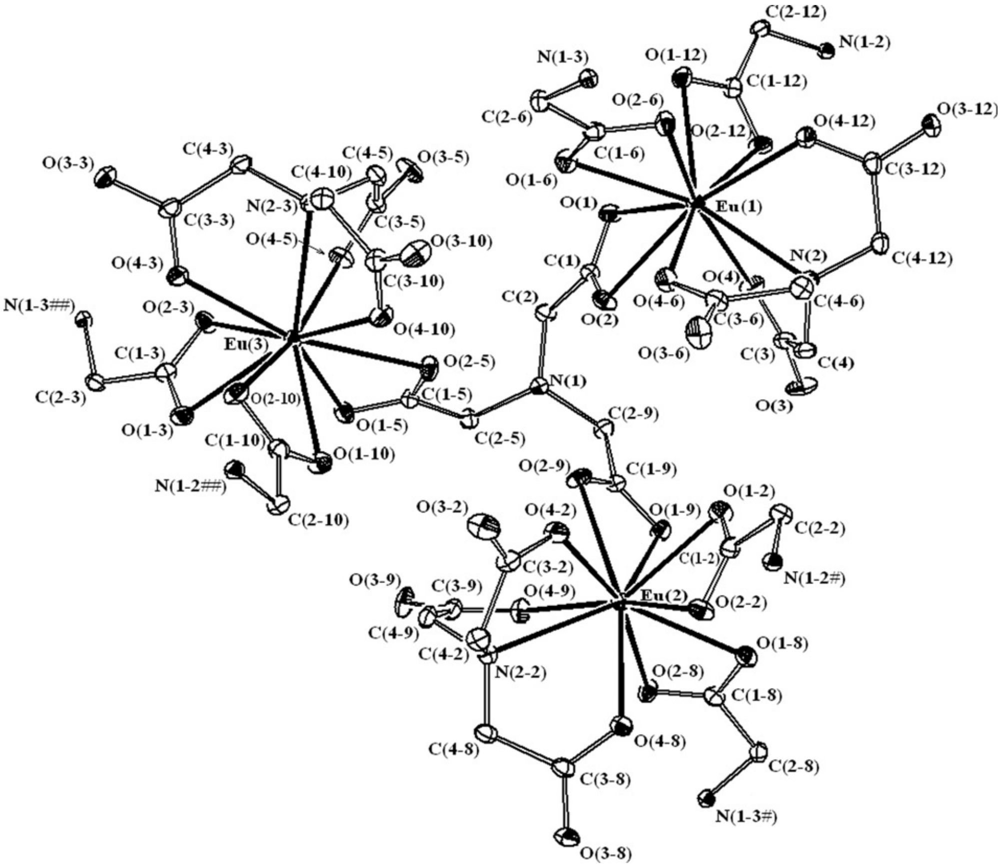

Figure 3. The structure of $\{[\mathrm{Eu^{III}(C\text{-}nta)(T\text{-}nta)}] \cdot 3\mathrm{H_2O}\}_n$.

As shown in figure 4, the coordination polyhedron around Eu(III) adopts C_{3v} mono-top-capped and tri-lateral-capped trigonal prism (MT&TL-TP) conformation. The top plane is composed of O(4), O(4–6) and O(4–12), and the bottom plane is composed of O(1), O(1–6) and O(1–12). Three lateral-capped atoms, O(2), O(2–6) and O(2–12), constitute the mid plane. The three planes are all equilateral triangles (top: side length = 3.775(6) Å; mid: side length = 4.360(4) Å; bottom: side length = 3.150(3) Å), and are parallel to one other. The top-capping atom N(2) locates on the top plane. The threefold rotation axis comes through N(2), Eu(1), and the centers of three planes, vertically. Three planes overlap one another, and the rotation angles are about 61° between the top and mid planes and 19° between the top and bottom planes, respectively.

The title complex crystallizes in the cubic system with $P2_13$ space group. In a cubic unit cell, eight vertexes and the centers of six faces are located through the nitrogen atoms from T-nta ligands, and the midpoints of twelve edges and the center of the cube are occupied by the nitrogen atoms from C-nta ligands. It seems the framework is

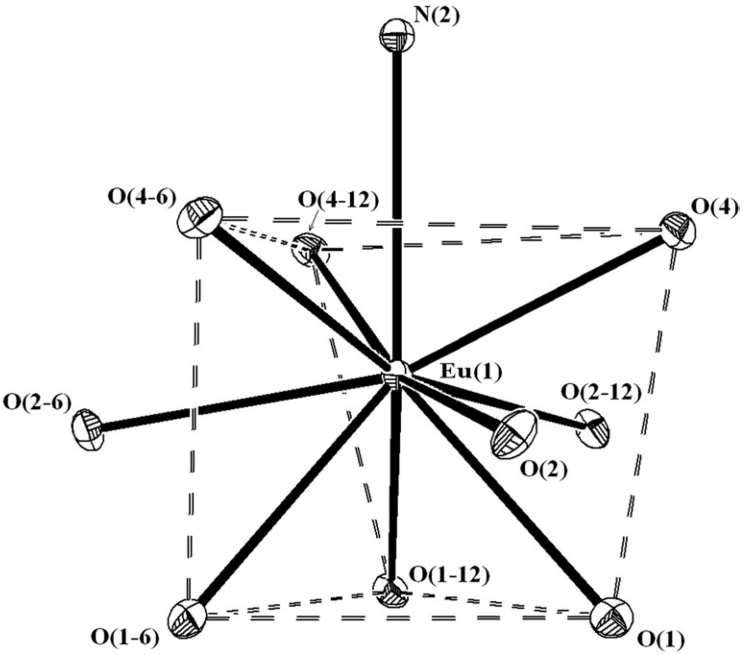

Figure 4. The coordinating polyhedron around Eu(III) in $\{[\mathrm{Eu^{III}(C\text{-}nta)(T\text{-}nta)}]\cdot 3\mathrm{H_2O}\}_n$.

structured by two kinds of nitrogen atoms. Five Eu(III) ions are connected by five T-nta ligands yielding a ten-member ring. In a ten-member ring, the length of ten edges is the same (5.056 Å). There are two values, 97.59° and 116.29°, for the angles between two adjacent edges, which appear alternatively.

Figure 5 shows how the ten-member rings arrange in four unit cells. There are two kinds of arrangement modes, and they appear alternatively. Between the ten-member rings with the same arrangement mode, but without a common edge, there are many carboxyl arms connecting them. Ultimately, a 3-D cage-like structure appears.

N1 represents the T-nta ligand; N2 represents the C-nta ligand. Thin solid lines represent the carboxyl arms of T-nta ligands, which make five Eu(III) ions and five T-nta ligands connected together yielding many ten-member rings. The carboxyl arms, which connect two different ten-member rings yielding the cage-like structure, are represented by thick solid lines.

4. Conclusion

$\{[\mathrm{Eu^{III}(C\text{-}nta)(T\text{-}nta)}]\cdot 3\mathrm{H_2O}\}_n$ with cage-like 3-D structure, a polymeric rare earth metal complex with nta ligand, was successfully synthesized. Differing from other Eu(III)-nta complexes, its coordination number is ten, and the coordination polyhedron adopts a special conformation, distorted C_{3v} MT&TL-TP, the first time this

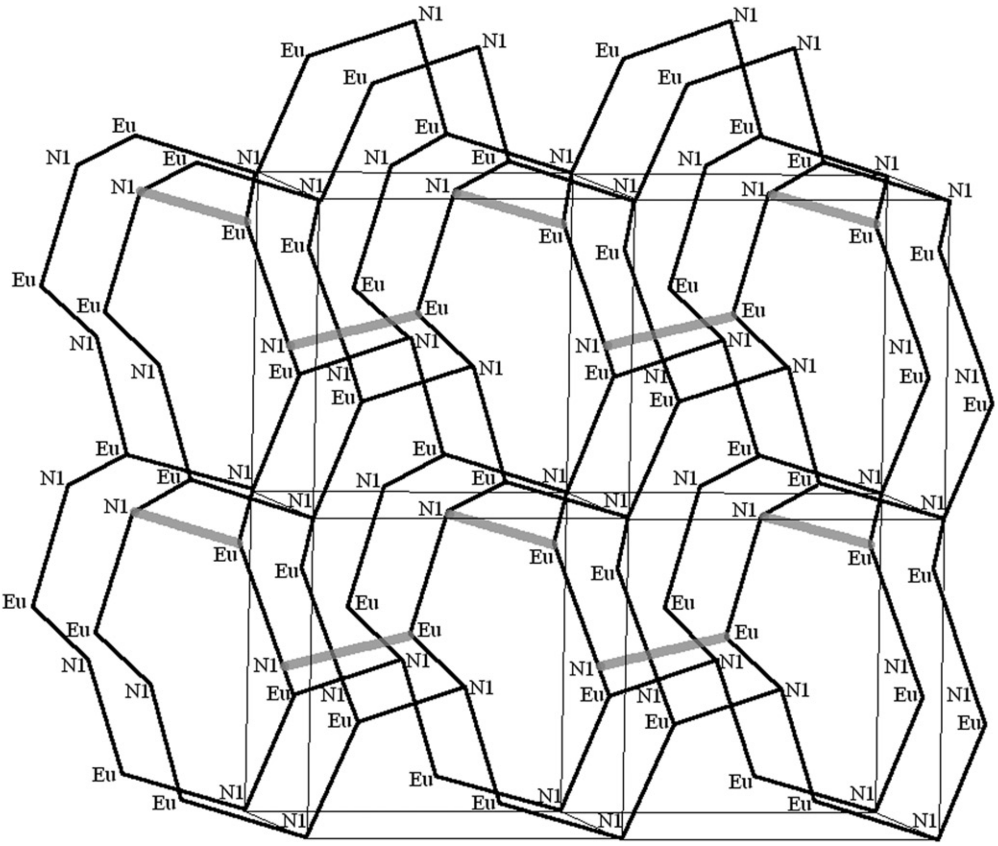

Figure 5. The 3-D cage-like structure of $\{[\mathrm{Eu^{III}}(\text{C-nta})(\text{T-nta})]\cdot 3\mathrm{H_2O}\}_n$.

conformation has been reported. According to thermal analyses, the collapsing temperature of crystal structure is 173°C, which indicates that it is very stable.

Acknowledgments

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References

[1] T. Yokoyama, T. Asami, M. Kanesato, T.M. Suzuki. *Chem. Lett.*, **2**, 383 (1993).
[2] Y. Inoue, H. Kumagai, Y. Shimomura, T. Yokoyama, T.M. Suzuki. *Anal. Chem.*, **69**, 1517 (1996).
[3] A.H. Robbins, D.E. Meree, M. Williamson, S.A. Collet, N.H. Xuong, W.F. Furey, B.C. Wang, C.D. Stout. *J. Mol. Biol.*, **221**, 1269 (1991).

[4] H. Li, J.D. Otvos. *J. Inorg. Biochem.*, **70**, 187 (1998).
[5] H. Bolton Jr, D.C. Girvin, A.E. Plymale, S.D. Harvey, D.J. Workman. *Environ. Sci. Technol.*, **30**, 931 (1996).
[6] L. Xun, R.B. Reeder, A.E. Plymale, D.C. Girvin, H. Bolton Jr. *Environ. Sci. Technol.*, **30**, 1752 (1996).
[7] L.L. Martin, R.A. Jacobson. *Inorg. Chem.*, **11**, 2785 (1972).
[8] L.L. Martin, R.A. Jacobson. *Inorg. Chem.*, **11**, 2789 (1972).
[9] K.F. Belyaeva, M.A. Porai-Koshits, N.D. Mitrofanova, L.I. Martynenko. *Zh. Struct. Khim.*, **9**, 541 (1968).
[10] J. Wang, X.D. Zhang, Y. Zhang, Z.R. Liu. *Russ. J. Struct. Chem.*, **45**, 114 (2004).
[11] Y. Chen, B.Q. Ma, Q.D. Liu, J.R. Li, S. Gao. *Inorg. Chem. Comm.*, **3**, 319 (2000).
[12] J. Wang, X.D. Zhang, X. Ling, W.G. Jia, H.F. Li. *J. Mol. Struct.*, **611**, 39 (2002).
[13] B.E. Robertson. *Inorg. Chem.*, **16**, 2735 (1977).
[14] R.E. Sievers, J.C. Bailar Jr. *Inorg. Chem.*, **1**, 174 (1962).
[15] K. Nakamoto. *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons Inc., New York (1986).
[16] J.G. Kang, J.P. Hong, S.K. Yoon, J.H. Bae, Y.D. Kim. *J. Alloys Comp.*, **339**, 248 (2002).