

# Interactions between metal ions and carbohydrates: the coordination behavior of neutral erythritol to zinc and europium nitrate

Limin Yang<sup>a,b</sup>, Yunlan Su<sup>a</sup>, Yizhuang Xu<sup>a</sup>, Shiwei Zhang<sup>a</sup>, Jinguang Wu<sup>a,\*</sup>,  
Kui Zhao<sup>b</sup>

<sup>a</sup> *The State Key Laboratory of Rare Earth Materials Chemistry and Applications,  
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*  
<sup>b</sup> *Institute of Heavy Ion Physics, School of Physics, Peking University, Beijing 100871, China*

Received 26 March 2004; received in revised form 26 May 2004; accepted 28 May 2004

Available online 2 July 2004

## Abstract

The single crystals of coordinated complexes of neutral erythritol ( $C_4H_{10}O_4$ ) with zinc nitrate and europium nitrate were synthesized and studied using FT-IR and single crystal X-ray diffraction analysis. In the structure of  $Zn(NO_3)_2 \cdot C_4H_{10}O_4$ , ZnEN (E denotes erythritol, N represents nitrate),  $Zn^{2+}$  is coordinated to four hydroxyl groups from two erythritol molecules and two oxygen atoms from two nitrates. Two  $Zn^{2+}$  are connected by one erythritol molecule to form  $Zn(C_4H_{10}O_4)(NO_3)_2$  chain, and layers formed by above chain pile to produce 3D structures. In the structure of  $Eu(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$ , EuEN,  $Eu^{3+}$  is 10-coordinated by six oxygen atoms from three nitrate ions, three hydroxyl groups from one erythritol molecule and one hydroxyl group from ethanol. In the above erythritol complexes, two hydroxyl groups of erythritol coordinate to one metal ion and the other two to another metal ion or erythritol acts as three-hydroxyl groups donor. The OH groups of erythritol act as ligand to coordinate to metal ions on one hand, one the other hand, OH groups form hydrogen bonds network to build three-dimensional structures.

© 2004 Elsevier Inc. All rights reserved.

**Keywords:** Zinc nitrate; Europium nitrate; Carbohydrates; IR spectroscopy; X-ray diffraction

## 1. Introduction

Carbohydrate and carbohydrate derivatives, as the most abundant class of biomolecules, are known to have a large variety of biological functions. Through the interaction between these poly-functional molecules and metal ions in living organisms, the modification of the biological function of both counterparts may be expected [1–7]. The investigation on the interactions between metal ions and simple sugars can improve the understanding of metal ion interactions with sugar residues of biologically important compounds, which needs to assign the binding hydroxyl or other groups, the

change of hydrogen bonds and also to characterize the metal ion coordination of carbohydrates monitoring the ligand conformation and configuration changes forced by the complexation processes.

Erythritol (denoted as E,  $C_4H_{10}O_4$ , meso-1, 2, 3, 4-tetrahydroxybutane), one of the simplest derivatives of carbohydrates, was chosen as a model to study the coordination of hydroxyl groups (OH) to metal ions.

The study of the coordination modes and stability of the complexes in solution indicated that the interaction between metal ions and erythritol in solution is weak [8]. The crystal structures of metal ion-deprotonated erythritol complexes crystallized from strong alkaline solutions have been reported, which is about the coordination of  $O^-$  [9–11]. For natural neutral erythritol, the coordination of OH to metal ions, three calcium chloride complexes, one calcium nitrate and some

\* Corresponding author. Tel.: +86-10-62757951; fax: +86-10-62751708.

E-mail address: [wjg@chem.pku.edu.cn](mailto:wjg@chem.pku.edu.cn) (J. Wu).

lanthanide chloride or nitrate–erythritol complexes were obtained in our previous work [12]. Here, zinc nitrate and europium nitrate were used as reactants to detect the coordination structures of hydroxyl groups of carbohydrates in different environment.

## 2. Experimental

### 2.1. Materials and methods

Erythritol ( $C_4H_{10}O_4$ , Sigma) and the other reagents (Analytical Reagent) were obtained from commercial sources and used as supplied. The procedure of preparation of metal ion–erythritol complexes was as follows: 3 mmol erythritol and 3 mmol zinc nitrate or europium nitrate were dissolved in a 1:1  $H_2O/EtOH$  (10 ml) mixture. The solution was put on a water bath and the temperature was about 80 °C. This was heated until a concentrated solution was obtained. Small amount of  $EtOH$  (~0.5 ml for each time) was kept being added into the solution during the heating process when the solution was about 4 ml to prolong the reaction time to about 48 h, leading to the formation of complexes. The resultant concentrated solution was filtered and cooled down for crystallization at room temperature. Elemental analysis calcd for  $Zn(NO_3)_2 \cdot C_4H_{10}O_4$  ZnEN: C, 15.42; H, 3.24; N, 8.99. Found: C, 15.63; H, 3.42; N, 9.23%. Elemental analysis calcd for  $Eu(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$  EuEN: C, 14.24; H, 3.19; N, 8.30. Found: C, 13.46; H, 3.13; N, 7.94%.

### 2.2. Physical measurements

Elemental analyses of the sample were carried out on an Elementar Vario EL elemental analyzer. Infrared spectra of the resultant crystals were measured on a Nico-plan infrared microscope attached on a Nicolet Magna-IR 750 FT-IR spectrometer. All the spectra were recorded at a resolution of  $4\text{ cm}^{-1}$  and 64 scans were co-added. The Raman spectra of erythritol, ZnEN and EuEN ( $3700\text{--}100\text{ cm}^{-1}$ ) were collected on a Nicolet FT-Raman 950 spectrometer and 1000 scans at  $8\text{ cm}^{-1}$  resolution.

### 2.3. X-ray crystallographic analysis

Data for the transition metal nitrate–erythritol complex ZnEN and lanthanide nitrate–erythritol complex EuEN were collected on a Rigaku RAXIS RAPID IP spectrometer with graphite monochromatized  $Mo\ K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) at room temperature (293 K), respectively. The structures of the two compounds were resolved by direct methods with SHELX 98 and refined using the full-matrix least-squares on  $F^2$  method. Empirical absorption corrections were applied and aniso-

tropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms are generated by HFIX instructions or difmap and refined using a riding model.

## 3. Results and discussion

In this work, two single crystals of the metal nitrate–erythritol complexes ( $Zn(NO_3)_2 \cdot C_4H_{10}O_4$ , ZnEN and  $Eu(NO_3)_3 \cdot C_4H_{10}O_4 \cdot C_2H_5OH$ , EuEN) (E denotes erythritol, N represents nitrate) were obtained and their structures were determined using single crystal X-ray diffraction analysis. Crystal parameters and details of the data collection and refinement of the two complexes are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Tables 2 and 3. Selected bond length and angles are listed in Tables 4 and 5. The geometric parameters for hydrogen bonding systems for the two complexes are shown in Table 6.

### 3.1. X-ray single crystal structures of ZnEN and EuEN

The single crystal X-ray diffraction analysis on ZnEN is shown in Fig. 1. The crystal is monoclinic system with space group of Cc.  $Zn^{2+}$  is coordinated to four hydroxyl groups from two erythritol molecules and two oxygen atoms from two nitrates. Two  $Zn^{2+}$  are connected by one erythritol molecule to form  $Zn(C_4H_{10}O_4)(NO_3)_2$  chain, and layers formed by above chain pile to produce 3D structures. The distances between  $Zn^{2+}$  and O atoms from the four hydroxyl groups of erythritol are different from one another. The molar ratio between metal ion and erythritol is 1:1 in ZnEN. Erythritol provides two hydroxyl groups to coordinate to one metal ion and other two to another metal ion. Nitrate is monodentate ligand to coordinate with  $Zn^{2+}$  via one of its oxygen atom and the coordination number of  $Zn^{2+}$  is six. Six Zn–O bond lengths are different from one another in ZnEN, reflecting that the environment of metal ion is a distorted octahedron and the  $O_h$  symmetry around  $Zn^{2+}$  shell is broken. In this complex there are three shorter (one nitrate group and two OH from two different erythritols) and three larger (one nitrate group and two OH from two different erythritols) distances. Zn–O bond length ranges from 2.048 to 2.135 Å. The average Zn–O distances for ZnEN is 2.10 Å. Zn–O distances are 2.039–2.169 Å for  $Zn(NO_3)_3 \cdot 2H_2O$  and 2.06–2.17 Å for  $Zn(NO_3)_3 \cdot 4H_2O$  [13–16]. Other reported complexes with a  $ZnO_6$  coordination belong to the types  $Zn(\text{pyridine oxide})_6^{2+}$ ,  $Zn(\text{urea})_6^{2+}$ , and  $Zn(\text{DMSO})_6$  with average Zn–O bond lengths of 2.10, 2.10 and 2.11 Å, respectively [17–19]. The Zn–O bond lengths for Zn-aldehyde complexes are from 2.06 to 2.18 Å [20]. Therefore, all bond distances to metal group in ZnEN are not

Table 1  
Crystal and structure refinement for ZnEN and EuEN

	ZnEN	EuEN
Crystal size (mm <sup>3</sup> )	0.40 × 0.35 × 0.10	0.30 × 0.20 × 0.15 mm <sup>3</sup>
Crystal shape/crystal colour	Block/colourless	Block/colourless
Chemical formula	Zn(NO <sub>3</sub> ) <sub>2</sub> · C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	Eu(NO <sub>3</sub> ) <sub>3</sub> · C <sub>4</sub> H <sub>10</sub> O <sub>4</sub> · C <sub>2</sub> H <sub>5</sub> OH
Formula weight	311.51	506.18
Crystal system	Monoclinic	Monoclinic
Space group	Cc	P2 <sub>1</sub> /c
<i>a</i> (Å)	13.678(3)	7.8754(16)
<i>b</i> (Å)	7.1156(14)	12.976(3)
<i>c</i> (Å)	9.883(2)	15.275(3)
$\alpha$ (°)	90	90
$\beta$ (°)	91.07(3)	101.40(3)
$\gamma$ (°)	90	90
<i>Z</i>	4	4
<i>V</i> (Å <sup>3</sup> )	961.7(3)	1530.2(5)
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	2.151	2.197
$\mu$ (mm <sup>-1</sup> )	2.610	4.181
F(000)	632	992
Reflections collected/unique	2564/1024 [ <i>R</i> <sub>int</sub> = 0.0691]	9142/3347 [ <i>R</i> <sub>int</sub> = 0.0416]
Reflections with <i>I</i> > 2σ( <i>I</i> )	874	2569
Data/restraints/parameters	1024/4/161	3347/0/222
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.023	0.915
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0468	0.0228
<i>WR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1206	0.0470

Table 2  
Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for ZnEN<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Zn	9757(2)	1855(1)	8450(3)	26(1)
O(1)	10852(7)	3843(15)	9042(10)	29(2)
O(2)	9372(8)	2700(18)	10381(11)	28(2)
O(3)	10121(9)	7369(19)	11435(11)	30(3)
O(4)	8696(9)	6244(17)	12911(9)	33(3)
O(5)	10613(7)	-257(17)	9416(11)	36(3)
O(6)	11381(9)	-170(20)	7522(12)	57(4)
O(7)	11943(13)	-1710(20)	9318(16)	56(4)
O(8)	8990(7)	-354(15)	7522(11)	37(3)
O(9)	8205(7)	-200(20)	9314(10)	43(3)
O(10)	7604(14)	-1848(19)	7774(16)	56(4)
N(1)	11315(12)	-810(20)	8740(15)	44(4)
N(2)	8224(7)	-734(16)	8231(10)	19(2)
C(1)	10989(12)	3950(20)	10453(12)	29(3)
C(2)	9997(11)	4110(20)	11070(14)	29(3)
C(3)	9531(10)	6010(20)	10863(13)	24(3)
C(4)	8515(9)	6160(20)	11444(16)	28(3)

<sup>a</sup> *U*<sub>eq</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

ancillary bonds. The bond angles of Zn(NO<sub>3</sub>)<sub>3</sub> · 4H<sub>2</sub>O are 78.2–98.6°, here the bond angles of Zn(NO<sub>3</sub>)<sub>3</sub> · C<sub>4</sub>H<sub>10</sub>O<sub>4</sub> are 75.1–119.1°, which indicate that the environment of zinc cation is a highly distorted octahedron.

The structure data of erythritol itself are as follows: O–C bond lengths are 1.425(1) and 1.433(1) Å, C–C bond lengths are 1.523(1) and 1.539(1) Å, O–C–C bond angles are 107.7(1), 109.7(1) and 112.2(1)°, C–C–C bond angles are 112.9(1)°, torsion angles, O–C–C–O, 62.9(1);

Table 3  
Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for EuEN<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Eu	1230(1)	6043(1)	2463(1)	21(1)
O(1)	3964(3)	7056(2)	2910(2)	37(1)
O(2)	1755(3)	7963(2)	2314(2)	35(1)
O(3)	4174(4)	8727(2)	2873(2)	51(1)
O(4)	3512(3)	5078(2)	3512(2)	32(1)
O(5)	1815(3)	4073(2)	2616(2)	34(1)
O(6)	3864(4)	3422(2)	3629(2)	53(1)
O(7)	-716(4)	5134(2)	1206(2)	39(1)
O(8)	-318(4)	6758(2)	1016(2)	39(1)
O(9)	-2007(4)	5906(3)	-16(2)	53(1)
O(10)	1315(3)	6710(2)	3951(1)	28(1)
O(11)	-1440(3)	6907(2)	2607(2)	27(1)
O(12)	-758(3)	5066(2)	3291(2)	27(1)
O(13)	-2745(4)	4242(2)	4529(2)	38(1)
O(14)	3049(3)	5544(2)	1424(2)	39(1)
N(1)	3340(4)	7943(2)	2708(2)	31(1)
N(2)	3089(4)	4169(2)	3262(2)	32(1)
N(3)	-1037(4)	5935(3)	715(2)	33(1)
C(1)	-236(5)	7190(3)	4134(2)	32(1)
C(2)	-1773(5)	6774(3)	3487(2)	28(1)
C(3)	-2159(4)	5635(3)	3562(2)	25(1)
C(4)	-2400(5)	5314(3)	4480(2)	31(1)
C(5)	4502(5)	5968(4)	1089(3)	39(1)
C(6)	3918(6)	6603(4)	286(3)	52(1)

<sup>a</sup> *U*<sub>eq</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

C–C–C–O, -59.9(1) and 58.4(1)° [21]. The C–O bond lengths of ZnEN are from 1.38 to 1.476 Å. In comparison with erythritol, significant differences can be observed on O–O–O angles, suggesting the influence of

Table 4  
Selected bond lengths (Å) and angles (°) for ZnEN<sup>a</sup>

Bond lengths			
Zn–O(4)#1	2.048(13)	O(1)–C(1)	1.406(16)
Zn–O(2)	2.079(11)	O(2)–C(2)	1.476(18)
Zn–O(8)	2.092(11)	O(3)–C(3)	1.38(2)
Zn–O(5)	2.121(11)	O(4)–C(4)	1.467(19)
Zn–O(1)	2.133(10)	O(5)–N(1)	1.244(17)
Zn–O(3)#1	2.135(11)	O(6)–N(1)	1.292(18)
O(3)–Zn#2	2.135(11)	O(7)–N(1)	1.20(2)
O(4)–Zn#2	2.048(13)	O(8)–N(2)	1.300(14)
C(1)–C(2)	1.50(2)	O(9)–N(2)	1.137(15)
C(2)–C(3)	1.505(10)	O(10)–N(2)	1.240(18)
C(3)–C(4)	1.518(16)		
Bond angles			
O(4)#1–Zn–O(2)	81.8(4)	C(4)–O(4)–Zn#2	112.9(8)
O(4)#1–Zn–O(8)	92.0(5)	N(1)–O(5)–Zn	114.1(11)
O(2)–Zn–O(8)	119.1(4)	N(2)–O(8)–Zn	108.8(7)
O(4)#1–Zn–O(5)	165.5(4)	O(7)–N(1)–O(5)	117.6(16)
O(2)–Zn–O(5)	86.5(4)	O(7)–N(1)–O(6)	124.5(16)
O(8)–Zn–O(5)	86.1(2)	O(5)–N(1)–O(6)	117.1(16)
O(4)#1–Zn–O(1)	97.1(2)	O(9)–N(2)–O(10)	122.0(13)
O(2)–Zn–O(1)	75.2(4)	O(9)–N(2)–O(8)	118.0(12)
O(8)–Zn–O(1)	164.2(4)	O(10)–N(2)–O(8)	119.3(13)
O(5)–Zn–O(1)	88.2(5)	O(1)–C(1)–C(2)	107.6(12)
O(4)#1–Zn–O(3)#1	76.3(4)	O(2)–C(2)–C(1)	106.4(12)
O(2)–Zn–O(3)#1	148.2(2)	O(2)–C(2)–C(3)	107.8(10)
O(8)–Zn–O(3)#1	84.8(5)	C(1)–C(2)–C(3)	113.3(10)
O(5)–Zn–O(3)#1	117.8(4)	O(3)–C(3)–C(2)	109.4(9)
O(1)–Zn–O(3)#1	84.8(5)	O(3)–C(3)–C(4)	109.1(12)
C(1)–O(1)–Zn	112.9(10)	C(2)–C(3)–C(4)	113.8(9)
C(2)–O(2)–Zn	117.7(9)	O(4)–C(4)–C(3)	103.8(11)
C(3)–O(3)–Zn#2	114.9(9)		

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1  $x, -y+1, z-1/2$ , #2  $x, -y+1, z+1/2$ .

metal coordination. The torsion angles of ZnEN are listed in Table 7. The torsion angle of C(1)–C(2)–C(3)–C(4) is 178.2(16), showing that the backbone of erythritol is nearly in a plane.

The geometric parameters of hydrogen bonds in Table 6 indicate that the three oxygen atoms of each nitrate ion are not equivalent. According to the crystal structure data, one oxygen atom (O(8)) coordinates to metal ion, two oxygen atoms (O(8) and O(10)) participate in hydrogen bonds, the third oxygen atom (O(9)) is weakly hydrogen bonded to O(1). O(2) form hydrogen bond with O(8) of another molecule, not O(9) in the same molecule. The distance of H(O(2)) and O(8) is 1.82 Å, bond angle is 167.8°, but the distance of H(O(2)) with O(9) is 2.573 Å, bond angle is 93.9°. The distance of O(2) and O(8) is 2.753 Å. The distance of O(2) and O(9) is 2.801 Å, but bond angle is 93.9°, which is not suitable to form hydrogen bond. For another nitrate ion, the coordinated oxygen atom O(5) forms hydrogen bond with O(3); O(7) is hydrogen-bonded, O(6) is free. The six N–O bond lengths from nitrate are different from each other, indicating the breaking of the  $D_{3v}$  symmetry of nitrate. The highly distorted nitrate group is general for this kind of complexes. N–O dis-

tances are 1.20–1.292 Å and O–N–O bond angles are 117.1–124.5° for N(1), 1.14–1.30 Å and 118.0–122.0° for N(2) in ZnEN. Other reported complexes include Zn(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O: 1.22–1.30 Å and 118.1–123.3° for N(1), 1.23–1.28 Å and 118.0–121.3° for N(2) [13]; Zn(NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O: 1.25–1.27 Å and 117.8–122.5° for N [14]; Ca(NO<sub>3</sub>)<sub>2</sub>·C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>: 1.22–1.26 Å and 117.38–122.24° for N; Nd(NO<sub>3</sub>)<sub>3</sub>·C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>·C<sub>2</sub>H<sub>5</sub>OH: 1.215–1.274 Å and 115.7–122.2° for N(1), 1.216–1.263 Å and 116.9–122.1° for N(2), 1.224–1.268 Å and 116.7–122.4° for N(3) [12], etc.

The crystal structure of 2C-methyl-D-erythritol 2,4-cyclodiphosphate synthase was determined, which contains a Zn<sup>2+</sup> with tetrahedral coordination, including interaction with two histidines (N1 His-10, Nε2 His-42), the Asp-8 carboxylate Oδ2, and a CDP β-phosphate oxygen [22]. Here for Zn(NO<sub>3</sub>)<sub>2</sub>–erythritol complex, Zn<sup>2+</sup> adopts an octahedral environment by using oxygen ligands contributed from four hydroxyl groups of two erythritol molecules and two monodentate nitrate ions different from that binding of Zn<sup>2+</sup> in 2C-methyl-D-erythritol 2,4-cyclodiphosphate synthase.

For lanthanide nitrate–erythritol complex, EuEN, Eu<sup>3+</sup> is 10 coordinated by six oxygen atoms from three nitrate ions, three hydroxyl groups from one erythritol molecule and one hydroxyl group from ethanol (Fig. 2). The coordination number of Eu<sup>3+</sup> is 10 in EuEN, which is higher than the coordination number of rare earth ions in those lanthanide chloride–erythritol complexes [12]. The structure of EuEN is similar to the corresponding neodymium nitrate–erythritol complex, NdEN. Eu–O distances are from 2.421 to 2.600 Å, the average Eu–O distance is 2.49 Å, which is shorter than the Nd–O distances in NdEN, 2.455–2.620 Å and the average Nd–O distance, 2.53 Å. Each nitrate is bidentate ligand to coordinate to Eu<sup>3+</sup>, which is consistent with its binding to Ca<sup>2+</sup> and Nd<sup>3+</sup>. Three nitrate ions have nine N–O distances, which indicate that the symmetry of nitrate is decreased. For three nitrate ions, one nitrate ion (O(1), O(2), O(3)) provide two atoms to coordinate to metal ion (O(1), O(2)), one atom (O(2)) to form hydrogen bond with O(12), a hydroxyl group coordinated to Eu<sup>3+</sup>, and O(3) is free; two atoms (O(4), O(5)) of another nitrate ion (O(4), O(5), O(6)) are coordinated to Eu<sup>3+</sup>, and O(6) forms hydrogen bond with O(13), a non-coordinated hydroxyl group of erythritol. For the third nitrate ion (O(7), O(8), O(9)), O(7), O(8) are coordinated to Eu<sup>3+</sup>, and O(9) forms hydrogen bond with O(14), the hydroxyl group of ethanol. N–O distances and O–N–O bond angles of Eu(NO<sub>3</sub>)<sub>3</sub>·C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>·C<sub>2</sub>H<sub>5</sub>OH are as follows: 1.210–1.275 Å and 115.5–123.1° for N(1), 1.221–1.266 Å and 116.6–121.8° for N(2), 1.223–1.277 Å and 117.1–121.8° for N(3), which are similar to Nd(NO<sub>3</sub>)<sub>3</sub>·C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>·C<sub>2</sub>H<sub>5</sub>OH [12]. Erythritol is as three-hydroxyl donor and ethanol is also coordinated to metal ion. Extensive hydrogen bond network between

Table 5  
Selected bond lengths (Å) and angles (°) for EuEN

<i>Bond lengths</i>			
Eu–O(10)	2.421(2)	O(4)–N(2)	1.265(4)
Eu–O(14)	2.427(2)	O(5)–N(2)	1.266(4)
Eu–O(11)	2.430(2)	O(6)–N(2)	1.221(4)
Eu–O(8)	2.483(3)	O(7)–N(3)	1.277(4)
Eu–O(4)	2.496(3)	O(8)–N(3)	1.252(4)
Eu–O(1)	2.499(3)	O(9)–N(3)	1.223(4)
Eu–O(7)	2.502(3)	O(10)–C(1)	1.446(4)
Eu–O(12)	2.538(2)	O(11)–C(2)	1.430(4)
Eu–O(2)	2.543(3)	O(12)–C(3)	1.454(4)
Eu–O(5)	2.600(3)	O(13)–C(4)	1.421(5)
Eu–N(3)	2.906(3)	O(14)–C(5)	1.451(4)
Eu–N(1)	2.955(3)	C(1)–C(2)	1.504(5)
O(1)–N(1)	1.266(4)	C(2)–C(3)	1.518(5)
O(2)–N(1)	1.275(4)	C(3)–C(4)	1.511(5)
O(3)–N(1)	1.210(4)	C(5)–C(6)	1.474(6)
<i>Bond angles</i>			
O(10)–Eu–O(14)	143.05(9)	O(2)–Eu–N(3)	92.67(9)
O(10)–Eu–O(11)	67.31(8)	O(5)–Eu–N(3)	95.78(9)
O(14)–Eu–O(11)	144.62(9)	O(10)–Eu–N(1)	70.88(8)
O(10)–Eu–O(8)	128.33(9)	O(14)–Eu–N(1)	85.17(8)
O(14)–Eu–O(8)	76.53(10)	O(11)–Eu–N(1)	94.53(9)
O(11)–Eu–O(8)	68.11(8)	O(8)–Eu–N(1)	88.07(9)
O(10)–Eu–O(4)	72.15(8)	O(4)–Eu–N(1)	91.23(9)
O(14)–Eu–O(4)	80.95(9)	O(1)–Eu–N(1)	25.09(8)
O(11)–Eu–O(4)	134.37(8)	O(7)–Eu–N(1)	137.25(9)
O(8)–Eu–O(4)	157.44(9)	O(12)–Eu–N(1)	137.77(8)
O(10)–Eu–O(1)	72.14(9)	O(2)–Eu–N(1)	25.42(8)
O(14)–Eu–O(1)	74.40(9)	O(5)–Eu–N(1)	136.34(9)
O(11)–Eu–O(1)	116.55(9)	N(3)–Eu–N(1)	112.63(9)
O(8)–Eu–O(1)	106.97(9)	N(1)–O(1)–Eu	98.04(19)
O(4)–Eu–O(1)	67.42(9)	N(1)–O(2)–Eu	95.7(2)
O(10)–Eu–O(7)	141.99(8)	N(2)–O(4)–Eu	99.2(2)
O(14)–Eu–O(7)	73.94(9)	N(2)–O(5)–Eu	94.18(19)
O(11)–Eu–O(7)	82.95(9)	N(3)–O(7)–Eu	95.0(2)
O(8)–Eu–O(7)	51.29(9)	N(3)–O(8)–Eu	96.6(2)
O(4)–Eu–O(7)	120.67(9)	C(1)–O(10)–Eu	117.87(19)
O(1)–Eu–O(7)	145.20(9)	C(2)–O(11)–Eu	110.62(19)
O(10)–Eu–O(12)	67.40(8)	C(3)–O(12)–Eu	117.73(19)
O(14)–Eu–O(12)	133.97(9)	C(5)–O(14)–Eu	137.5(2)
O(11)–Eu–O(12)	63.62(8)	O(3)–N(1)–O(1)	123.1(3)

Table 5 (continued)

<i>Bond angles</i>			
O(8)–Eu–O(12)	112.81(8)	O(3)–N(1)–O(2)	121.4(3)
O(4)–Eu–O(12)	82.29(8)	O(1)–N(1)–O(2)	115.5(3)
O(1)–Eu–O(12)	135.18(8)	O(3)–N(1)–Eu	174.9(3)
O(7)–Eu–O(12)	78.61(8)	O(1)–N(1)–Eu	56.87(17)
O(10)–Eu–O(2)	76.07(8)	O(2)–N(1)–Eu	58.89(17)
O(14)–Eu–O(2)	94.34(9)	O(6)–N(2)–O(4)	121.5(3)
O(11)–Eu–O(2)	73.47(9)	O(6)–N(2)–O(5)	121.8(3)
O(8)–Eu–O(2)	67.34(9)	O(4)–N(2)–O(5)	116.6(3)
O(4)–Eu–O(2)	116.08(8)	O(6)–N(2)–Eu	176.9(3)
O(1)–Eu–O(2)	50.42(8)	O(4)–N(2)–Eu	55.95(16)
O(7)–Eu–O(2)	118.63(9)	O(5)–N(2)–Eu	60.69(17)
O(12)–Eu–O(2)	131.41(8)	O(9)–N(3)–O(8)	121.1(3)
O(10)–Eu–O(5)	107.17(8)	O(9)–N(3)–O(7)	121.8(3)
O(14)–Eu–O(5)	71.29(9)	O(8)–N(3)–O(7)	117.1(3)
O(11)–Eu–O(5)	125.89(9)	O(9)–N(3)–Eu	178.7(3)
O(8)–Eu–O(5)	119.62(9)	O(8)–N(3)–Eu	58.07(17)
O(4)–Eu–O(5)	49.95(8)	O(7)–N(3)–Eu	59.07(17)
O(1)–Eu–O(5)	111.37(9)	O(10)–C(1)–C(2)	108.6(3)
O(7)–Eu–O(5)	71.11(9)	O(11)–C(2)–C(1)	107.5(3)
O(12)–Eu–O(5)	65.13(8)	O(11)–C(2)–C(3)	105.4(3)
O(2)–Eu–O(5)	160.43(9)	C(1)–C(2)–C(3)	116.6(3)
O(10)–Eu–N(3)	141.06(8)	O(11)–C(2)–Eu	44.86(14)
O(14)–Eu–N(3)	73.81(9)	C(1)–C(2)–Eu	81.51(19)
O(11)–Eu–N(3)	73.76(8)	C(3)–C(2)–Eu	85.83(19)
O(8)–Eu–N(3)	25.34(9)	O(12)–C(3)–C(4)	111.4(3)
O(4)–Eu–N(3)	143.04(9)	O(12)–C(3)–C(2)	107.4(3)
O(1)–Eu–N(3)	128.01(9)	C(4)–C(3)–C(2)	113.7(3)
O(7)–Eu–N(3)	25.96(9)	O(13)–C(4)–C(3)	112.3(3)
O(12)–Eu–N(3)	96.11(8)	O(14)–C(5)–C(6)	111.5(3)

hydroxyl groups of erythritol, ethanol and oxygen atoms of nitrate exists in the structure of EuEN (Table 6). Compared to the other metal–erythritol complexes, erythritol has different coordination mode, and the larger differences of C–C, C–O and C–C–C, C–C–O with erythritol itself have appeared [21], for example, C(1)–C(2)–C(3) is 116.6(3)°, O(13)–C(4)–C(3), 112.3(3)°, and O(12)–C(3)–C(4), 111.4(3)°, which is related the special binding site of erythritol different from others.

Table 6  
Hydrogen bond lengths (Å) and angles (°) in ZnEN and EuEN<sup>a</sup>

	D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
ZnEN	O(1)–HO1···O(10)#3	0.971(10)	1.799(18)	2.77(2)	177.2(8)
	O(2)–HO2···O(8)#4	0.95(12)	1.82(13)	2.753(15)	168(16)
	O(4)–HO4···O(7)#5	0.67(14)	2.15(14)	2.81(2)	173(17)
	O(3)–HO3···O(5)#6	0.967(13)	1.836(12)	2.709(18)	148.8(7)
	O(1)–HO1···N(2)#3	0.971(10)	2.494(10)	3.370(15)	149.9(6)
	O(1)–HO1···O(9)#3	0.971(10)	2.625(11)	3.296(15)	126.4(6)
	O(2)–HO2···N(2)#4	0.95(12)	2.66(14)	3.538(16)	154(12)
EuEN	O(10)–H(O10)···O(13)#1	1.021(2)	1.672(3)	2.674(4)	166.05(16)
	O(12)–H(O12)···O(2)#2	0.852(2)	2.107(3)	2.937(4)	164.72(17)
	O(13)–H(O13)···O(6)#3	0.79(4)	2.18(4)	2.950(5)	164(4)
	O(14)–H(O14)···O(9)#4	0.857(3)	2.064(3)	2.853(4)	152.8(2)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: ZnEN: #1  $x, -y+1, z-1/2$ , #2  $x, -y+1, z+1/2$ , #3  $x+1/2, y+1/2, z$ , #4  $x, -y, z+1/2, x-1/2, -y+1/2, z+1/2$ , #6  $x, y+1, z$ . EuEN: #1  $-x, -y+1, -z+1$ , #2  $-x, y-1/2, -z+1/2$ , #3  $x-1, y, z$ , #4  $-x, -y+1, -z$ .

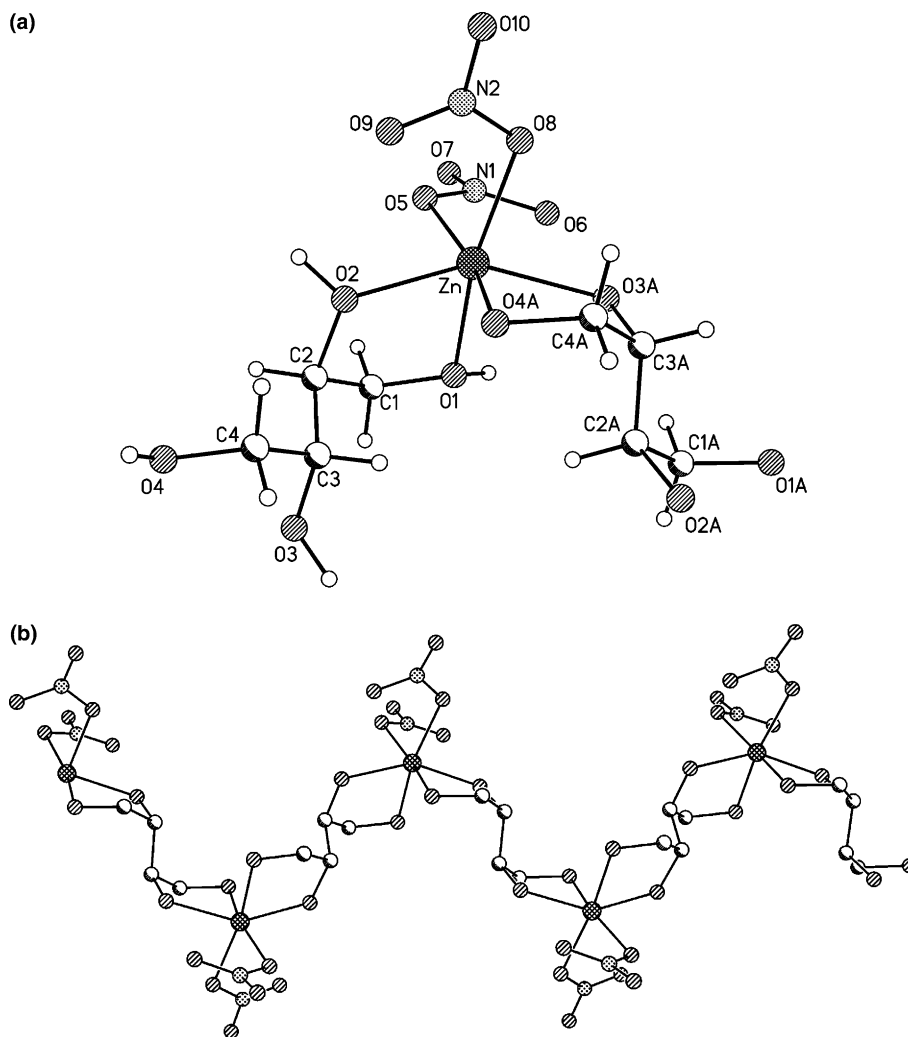


Fig. 1. Crystal structure of  $\text{Zn}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ : (a) the structure and atom numbering of ZnEN; (b) the zigzag chain of  $[\text{Zn}(\text{C}_4\text{H}_{10}\text{O}_4)(\text{NO}_3)_2]$ .

Table 7  
The torsion angles in ZnEN<sup>a</sup>

Torsion angles			
O(4)#1–Zn–O(1)–C(1)	106.1(9)	O(3)#1–Zn–O(8)–N(2)	–146.9(9)
O(2)–Zn–O(1)–C(1)	26.6(9)	Zn–O(5)–N(1)–O(7)	165.0(14)
O(8)–Zn–O(1)–C(1)	–129.2(16)	Zn–O(5)–N(1)–O(6)	–5.9(18)
O(5)–Zn–O(1)–C(1)	–60.3(9)	Zn–O(8)–N(2)–O(9)	–17.5(15)
O(3)#1–Zn–O(1)–C(1)	–178.4(10)	Zn–O(8)–N(2)–O(10)	171.5(13)
O(4)#1–Zn–O(2)–C(2)	–99.2(11)	Zn–O(1)–C(1)–C(2)	–47.6(14)
O(8)–Zn–O(2)–C(2)	173.1(10)	Zn–O(2)–C(2)–C(1)	–24.6(16)
O(5)–Zn–O(2)–C(2)	89.5(11)	Zn–O(2)–C(2)–C(3)	97.3(9)
O(1)–Zn–O(2)–C(2)	0.5(11)	O(1)–C(1)–C(2)–O(2)	45.0(16)
O(3)#1–Zn–O(2)–C(2)	–52.6(18)	O(1)–C(1)–C(2)–C(3)	–73.3(12)
O(4)#1–Zn–O(5)–N(1)	169.3(16)	Zn#2–O(3)–C(3)–C(2)	–94.8(8)
O(2)–Zn–O(5)–N(1)	–154.4(11)	Zn#2–O(3)–C(3)–C(4)	30.2(15)
O(8)–Zn–O(5)–N(1)	86.2(11)	O(2)–C(2)–C(3)–O(3)	–177.0(14)
O(1)–Zn–O(5)–N(1)	–79.1(11)	C(1)–C(2)–C(3)–O(3)	–59.5(10)
O(3)#1–Zn–O(5)–N(1)	4.1(12)	O(2)–C(2)–C(3)–C(4)	60.7(13)
O(4)#1–Zn–O(8)–N(2)	–70.9(9)	C(1)–C(2)–C(3)–C(4)	178.2(16)
O(2)–Zn–O(8)–N(2)	10.8(10)	Zn#2–O(4)–C(4)–C(3)	48.3(14)
O(5)–Zn–O(8)–N(2)	94.6(8)	O(3)–C(3)–C(4)–O(4)	–49.3(15)
O(1)–Zn–O(8)–N(2)	163.8(15)	C(2)–C(3)–C(4)–O(4)	73.1(13)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms; #1  $x, -y+1, z-1/2$ , #2  $x, -y+1, z+1/2$ .

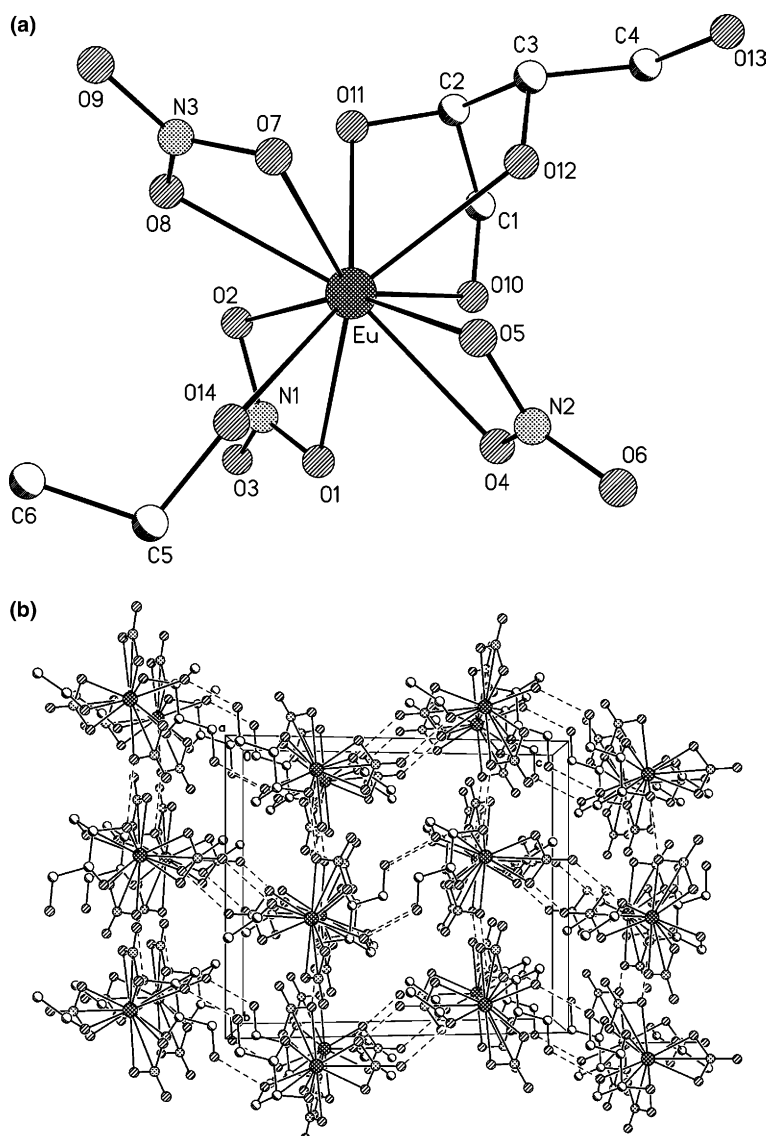


Fig. 2. Crystal structure of  $\text{Eu}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ : (a) the structure and atom numbering of EuEN; (b) the projection of the cell of  $\text{Eu}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ .

### 3.2. FTIR spectra of ZnEN and EuEN

The FT-IR spectra of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$  (ZnEN) are shown in Fig. 3. The stretching vibrations of OH in the region of  $3500\text{--}3000\text{ cm}^{-1}$  are shifted toward lower frequency after complexation. The peak positions of C–H stretching bands in the region of  $3000\text{--}2800\text{ cm}^{-1}$  are shifted and the relative intensities are changed. The variations of  $\nu\text{OH}$  and  $\nu\text{CH}$  indicate that both conformation of erythritol and the hydrogen bonding network exhibit significant changes when  $\text{Zn}(\text{NO}_3)_2$  is introduced. No water is involved in the obtained complex because no H–O–H bending vibration of water is observed between  $1700$  and  $1500\text{ cm}^{-1}$ . Furthermore, the strong bands of  $\text{NO}_3^-$ , including  $\nu_s\text{NO}_2$  ( $1300\text{--}1250\text{ cm}^{-1}$ ) and  $\nu_{\text{as}}\text{NO}_2$  ( $1530\text{--}1480\text{ cm}^{-1}$ ), undergo bandshift and split into several

peaks upon, suggesting that the symmetry around nitrate changes upon coordinating with erythritol [23]. The result is consistent with the variation of the symmetry of nitrate in the structure of ZnEN. Symmetric deformation vibration  $\delta_s\text{NO}_2$  at  $746\text{ cm}^{-1}$ , asymmetric deformation vibration  $\delta_a\text{NO}_2$  at  $710\text{ cm}^{-1}$  and out-of-plane bending vibration of nitrate at  $816\text{ cm}^{-1}$  appear in the IR spectrum of ZnEN [23].

The FT-IR spectra of erythritol and  $\text{Eu}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  (EuEN) are shown in Fig. 4. The change of OH vibrations of EuEN and NdEN is similar:  $3452, 3356\text{ cm}^{-1}$  (EuEN);  $3457, 3356\text{ cm}^{-1}$  (NdEN) and EuEN has broader OH band compared with NdEN [12]. The  $\nu\text{CH}$  vibrations of EuEN are shifted and masked by strong OH vibrations as compared with erythritol. In the structure of EuEN no water molecule appears, therefore, the weak band at  $1631\text{ cm}^{-1}$  may be the influence of

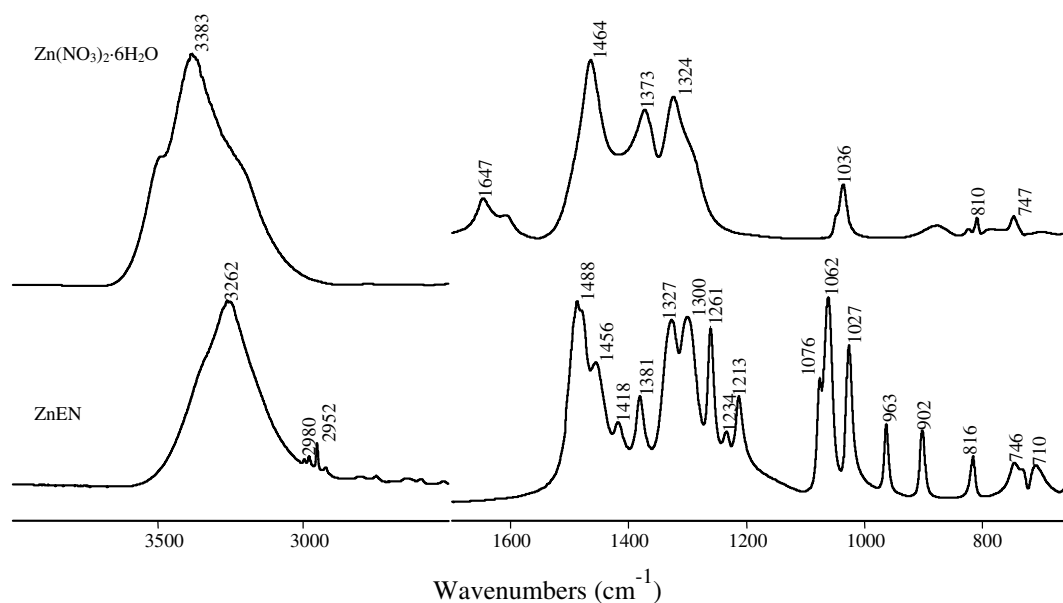


Fig. 3. FT-IR spectra of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ .

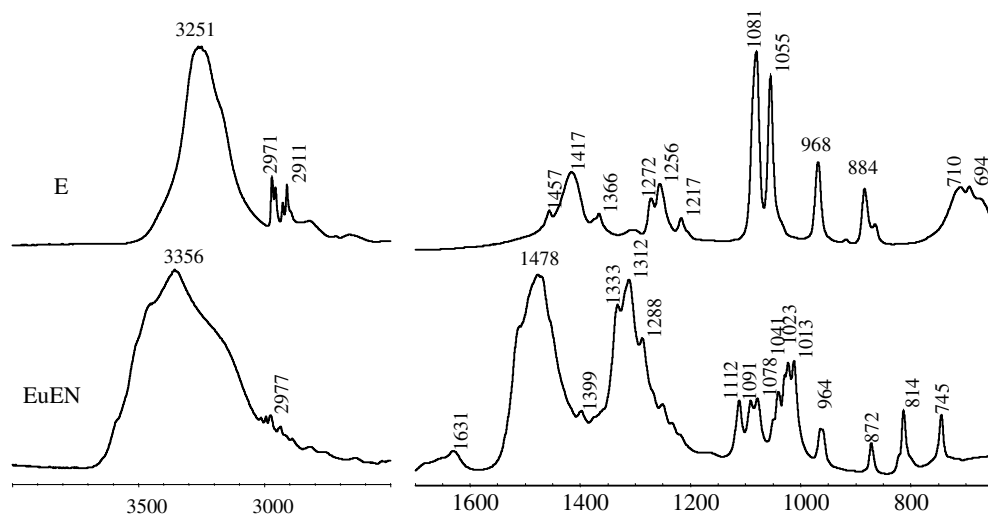


Fig. 4. FT-IR spectra of erythritol and  $\text{Eu}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  in the 4000–2500 and 1700–650  $\text{cm}^{-1}$  region.

adsorption water molecules. The peak positions in the 1530–1200  $\text{cm}^{-1}$  region of EuEN, including the vibrations of nitrate ions and  $\delta\text{CH}_2$  and other vibrations of erythritol, have a few wave number differences with NdEN, which indicate that the changes of bond length and angles of nitrate ions have differences. In the 1200–1000  $\text{cm}^{-1}$  region, the shifts of NO, CO stretching vibrations and skeletal vibrations of alditol show the coordination of erythritol and nitrate ions. The peak positions and relative intensities of NdEN and EuEN in the region are close: 1112(1112), 1090(1091), 1078(1078), 1041(1039), 1023(1023), 1012(1013)  $\text{cm}^{-1}$ , which shows the same coordination of erythritol. Symmetric deformation vibration  $\delta_s\text{NO}_2$  at 742(745)  $\text{cm}^{-1}$  and out-

of-plane bending vibration of nitrate at 873, 814 (872, 814)  $\text{cm}^{-1}$  appear in the IR spectra of NdEN and EuEN. The similarity of IR spectra of EuEN and NdEN are consistent with their single crystal structure results, which is in a good agreement with our previous conclusion deduced from the results of lanthanide–galactitol, *myo*-inositol and *D*-ribose complexes that similar FTIR spectra correspond to analogous crystal structures [24–29].

### 3.3. Raman spectroscopic study of ZnEN and EuEN

The Raman spectra of erythritol, ZnEN and EuEN are shown in Fig. 5, which also indicate the formation of



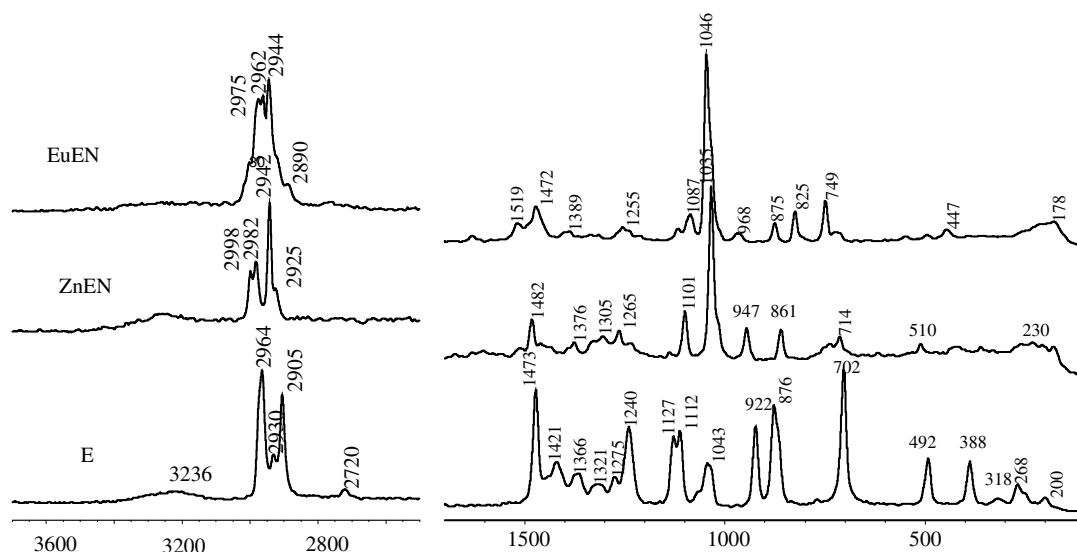


Fig. 5. The Raman spectra of erythritol,  $\text{Zn}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$  and  $\text{Eu}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  in the  $3700\text{--}2500\text{ cm}^{-1}$  and  $1700\text{--}100\text{ cm}^{-1}$  region.

the two metal complexes.  $\nu\text{OH}$  vibrations become weak band and  $\nu\text{CH}$  bands shift and become strong in their Raman spectra.  $\nu\text{NO}$  bands of nitrate ions are located at  $1046\text{ cm}^{-1}$  (EuEN);  $1035\text{ cm}^{-1}$  (ZnEN). The other peaks also have shifted compared with erythritol. In the  $650\text{--}100\text{ cm}^{-1}$  region the peaks could be assigned to M–O vibrations:  $178\text{ cm}^{-1}$  for EuEN,  $230\text{ cm}^{-1}$  for ZnEN [30]. This is an important evidence of complex formation.

Erythritol is an open-chain molecule. The structures of ZnEN and EuEN indicate that erythritol may be two bidentate ligands or three hydroxyl group donor. The OH groups of erythritol, on the one hand, act as ligand to coordinate to metal ions and, on the other hand, they form hydrogen bonds network to build three-dimensional structures. Nitrate ions may be monodentate or bidentate ligands. The above results provide us clear evidences to support that versatile structural features can be observed in metal saccharides complexes. This implies that complex and diverse structures are expected in the supra-molecular complexes between metal ion and bio-molecules with residue that is composed of various saccharides. The variety of coordination feature may serve as information storage and transmission in biological activities. FTIR and Raman results indicate the coordination of hydroxyl groups of erythritol to metal ions, which are consistent with single crystal structure results.

### Acknowledgements

We gratefully acknowledge the financial support by the National Natural Science Foundation of China for the grants (Nos. 50203001, 30371604), the State Key Project for Fundamental Research of MOST

(G1998061307, 2002CCA01900, 2002CB713600) and project of Education Ministry Ph.D candidate program to support this work.

### References

- [1] D.M. Templeton, B. Sarkar, *Biochem. J.* 230 (1985) 35–42.
- [2] P.F. Predki, D.M. Whitfield, B. Sarkar, *Biochem. J.* 281 (1992) 835–841.
- [3] W.I. Weis, K. Drickamer, W.A. Hendrickson, *Nature* 360 (1992) 127–134.
- [4] K. Drickamer, *Nature* 360 (1992) 183.
- [5] B. Gyurcsik, L. Nagy, *Coord. Chem. Rev.* 203 (2000) 81–149.
- [6] J.F. Verchere, S. Chapelle, F. Xin, D.C. Crans, *Progr. Inorg. Chem.* 47 (1998) 837–945.
- [7] S. Yano, M. Otsuka, in: H. Sigel (Ed.), *Metal Ions in Biological Systems*, 32, 1996, pp. 27–60.
- [8] S.J. Angyal, *Aust. J. Chem.* 27 (1974) 1447–1456.
- [9] P. Klüfers, T. Kunte, *Angew. Chem. Int. Ed. Engl.* 40 (22) (2001) 4210–4212.
- [10] J. Burger, P. Klüfers, *Angew. Chem. Int. Ed. Engl.* 36 (7) (1997) 776–779.
- [11] P. Klüfers, J. Schuhmacher, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1742–1744.
- [12] L.M. Yang, Y.L. Su, Y.Z. Xu, Z.H. Guo, Z.M. Wang, S.F. Weng, C.H. Yan, S.W. Zhang, J.G. Wu, *Inorg. Chem.* 42 (19) (2003) 5844–5856.
- [13] B. Ribar, W. Nowacki, M. Sljukic, F. Gabela, B. Matkovic, *Z. Kristallogr.* 131 (1970) 175–185.
- [14] D. Petrovic, B. Ribar, *Acta Cryst. B* 31 (1975) 1795–1796.
- [15] B. Ribar, M. Sljukic, B. Matrovic, F. Gabela, E. Girt, *Acta Cryst.* 23 (1967) 1113.
- [16] B. Ribar, W. Nowacki, M. Sljukic, F. Gabela, B. Matkovic, *Z. Kristallogr.* 129 (1969) 305–317.
- [17] C.J. O'Connor, E. Sinn, R.L. Carlin, *Inorg. Chem.* 16 (1977) 3314–3320.
- [18] W. van de Giesen, C.H. Stam, *Cryst. Struct. Commun.* 1 (1972) 257–260.
- [19] I. Persson, *Acta Chem. Scand. A* 36 (1982) 7–12.
- [20] B. Muller, H. Vahrenkamp, *Eur. J. Inorg. Chem.* (1999) 117–127.

- [21] A. Bekoe, H.M. Powell, Proc. R. Soc. London Ser. A 250 (1959) 301–315.
- [22] L.E. Kemp, C.S. Bond, W.N. Hunter, Proc. Natl. Acad. Sci. USA 99 (10) (2002) 6591–6596.
- [23] J.G. Wu, Modern Fourier Transform Spectroscopic Techniques and its Applications II, Science and Technology References Press, Beijing, 1994, pp. 262–263.
- [24] L.M. Yang, Y.L. Su, W. Liu, X.L. Jin, J.G. Wu, Carbohydr. Res. 337 (16) (2002) 1485–1493.
- [25] L.M. Yang, J.G. Wu, S.F. Weng, X.L. Jin, J. Mol. Struct. 612 (1) (2002) 49–57.
- [26] L.M. Yang, Y. Zhao, Y.Z. Xu, X.L. Jin, W. Tian, S.F. Weng, J.G. Wu, G.X. Xu, Carbohydr. Res. 334 (2001) 91–95.
- [27] Y.L. Su, L.M. Yang, X.L. Jin, S.F. Weng, J.G. Wu, J. Mol. Struct. 616 (1–3) (2002) 221–230.
- [28] Y.L. Su, L.M. Yang, S.F. Weng, J.G. Wu, J. Rare Earths 20 (5) (2002) 339–342.
- [29] Y.L. Su, L.M. Yang, Z.M. Wang, C.H. Yan, S.F. Weng, J.G. Wu, Carbohydr. Res. 338 (19) (2003) 2029–2034.
- [30] L.Q. Yang, J.G. Wu, Q. Zhou, J. Bian, Y.M. Yang, D.F. Xu, G.X. Xu, Microchim. Acta 14 (1997) 251–252.