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Complexation of trivalent lanthanide cations by erythritol in the solid state. The crystal structure and FT-IR study of $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$

Limin Yang,[a,b] Yizhuang Xu,[a] Xin Gao,[c] Shiwei Zhang[a] and Jinguang Wu[a,*]

[a] *The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[b] *Institute of Heavy Ion Physics, School of Physics, Peking University, Beijing 100871, China*
[c] *College of Arts and Science, Beijing Union University, Beijing 100038, China*

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Abstract—Erythritol was chosen to study the interactions between metal ions and carbohydrates. FTIR spectroscopy results indicate that a $EuCl_3$–erythritol complex different from a previously reported one was obtained. The crystal structure of $EuCl_3$–erythritol complex, $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$, $M_r = 443.49$, $a = 13.846(3)$ Å, $b = 7.4983(15)$ Å, $c = 14.140(3)$ Å, $\beta = 116.39(3)°$, $V = 1315.1(5)$ Å^3, $Z = 4$, $\mu = 5.394\,mm^{-1}$ and $R = 0.0395$ for 2965 observed reflections and 143 parameters, was determined. Characteristic of this complex is the presence of binuclear europium ions with different coordination structures. One Eu^{3+} ion is nine-coordinated, with five Eu–O bonds from water molecules, and four from hydroxyl groups of two erythritol molecules and another Eu^{3+} is eight-coordinated with two water molecules, two chloride ions, and four hydroxyl groups from two erythritol molecules. Erythritol provides two hydroxyl groups to one lanthanide ion and the other two to another rare earth ion. The OH, CO stretching and other vibrations are shifted in the IR spectra of the complexes and the results are consistent with the crystal structure.

Keywords: Lanthanide ion; Crystal structure; Complexation; Erythritol; FT-IR

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1. Introduction

The interactions between metal ions and carbohydrates are involved in many biochemical processes.[1–7] Erythritol ($C_4H_{10}O_4$, denoted as E) was chosen as a simple model to study the coordination of hydroxyl groups to metal ions.

The crystal structures of metal ion-deprotonated erythritol complexes crystallized from alkaline solutions have been reported,[8–11] however, the oxyanions existing in strong alkali obviously differ from the coordinated hydroxyl groups (OH) that neutral erythritol forms. Three complexes with calcium chloride, but only one kind of lanthanide–erythritol complex was obtained in our previous work.[12] Lanthanide ions often have higher coordination numbers and should afford more complex coordination structures with ligands as compared with calcium ions. Thus we have continued to synthesize lanthanide chloride–erythritol complexes, and another $EuCl_3$–erythritol complex was obtained and characterized by X-ray single crystal diffraction and FTIR spectroscopy. The results indicate that lanthanide ions also form several complexes with erythritol. Their coordination structures are complicated and different from calcium chloride–erythritol complexes.

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[*] Corresponding author. Tel.: +86-10-62757951; fax: +86-10-62751708; e-mail: wjg@chem.pku.edu.cn

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2. Experimental

2.1. Materials

Europium chloride ($EuCl_3$) was prepared and crystallized from the corresponding rare earth oxide of high purity (99.99%).[13] Erythritol was a commercial product, and was used without further purification.

2.2. Preparation of $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$

Erythritol (0.3663 g, 3 mmol) and an equivalent amount of $EuCl_3$ were dissolved in H_2O–EtOH and heated to prepare a concentrated solution that was cooled down for crystallization. Anal. Calcd for $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$: C, 10.83; H, 3.86. Found: C, 9.64; H, 4.82.

2.3. Physical measurements

Data collection of a block, colorless single crystal ($0.30\times0.20\times0.10\,mm^3$) of $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$ was made on a Rigaku RAXIS Rapid IP diffractometer using monochromatic MoKα radiation ($\lambda = 0.71073$ Å) in the θ range from 2.72° to 27.48° at 293(2) K. The final cycle of full-matrix least-squares refinement was based on 2965 observed reflections. The structure was resolved by direct methods with SHELX-97 and refined using the full-matrix least-squares on F^2 method. Empirical absorption corrections were applied and anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 233619. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [Fax: (internat) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

The mid-IR spectra were measured on a Nicolet Magna-IR 750 spectrometer using the micro-IR method, with 128 scans at $4\,cm^{-1}$ resolution. The FT-Raman spectra were recorded on a Nicolet FT-Raman 950 spectrometer at $8\,cm^{-1}$ resolution and 500 scans. Elemental analyses were carried out on a Elementar Vario EL spectrometer. The luminescence spectra were measured on a Hitachi F-4500 spectrometer with a 390 nm filter.

3. Results and discussion

3.1. IR spectra of erythritol and its complexes with $EuCl_3$

The FTIR spectra of erythritol and its two $EuCl_3$ complexes were shown in Figure 1. EuE(I) corresponds to $EuCl_3{\cdot}C_4H_{10}O_4{\cdot}6H_2O$ and EuE(II) is $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$. The FTIR spectrum of EuE(I) is similar to the spectrum of $PrCl_3{\cdot}C_4H_{10}O_4{\cdot}6H_2O$, whose structure has been determined.[12] The FTIR spectrum of EuE(II) is different from that of EuE(I), indicating that two $EuCl_3$–erythritol complexes have formed.

As compared with the spectrum of free erythritol, the stretching vibrations of the OH groups of EuE(I) and EuE(II) showed changes upon salt formation. The νOH bands in the salt spectra were broadened, and in particular two bands, at 3306, $3209\,cm^{-1}$ for EuE(II) and 3488, 3358, $3232\,cm^{-1}$ for EuE(I), were observed. The OH stretching vibrations can be assigned to the H bonds formed between the hydroxyl groups, water molecules, and Cl ions.

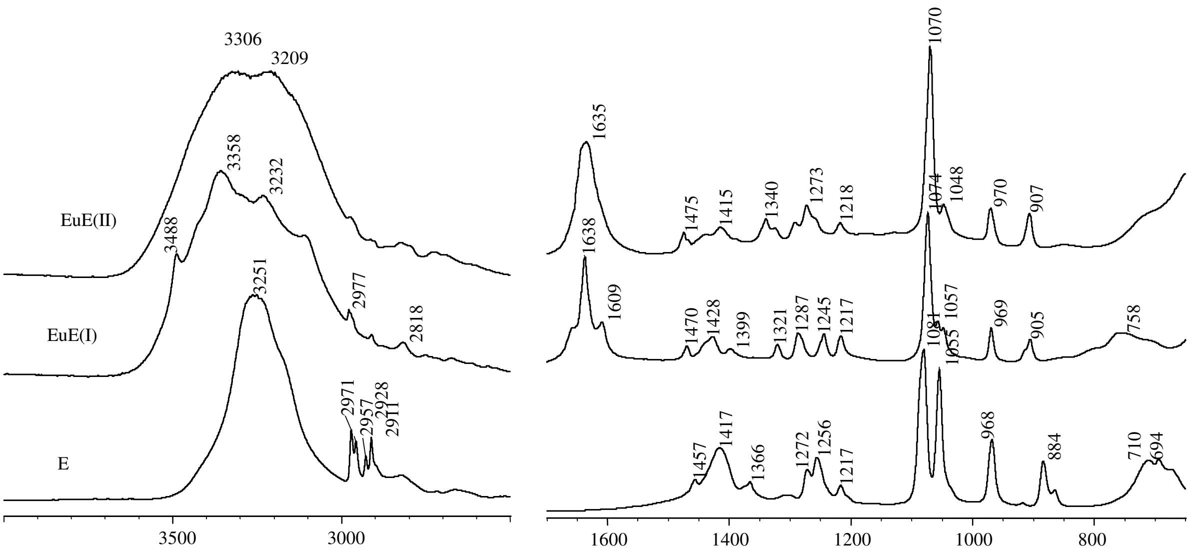

Figure 1. Mid-IR spectra of erythritol and two $EuCl_3$–erythritol complexes.

Free erythritol exhibited four bands at 2971, 2957, 2928, and 2911 cm^{-1}, assigned to the stretching vibrations of the CH group (νCH). These bands shifted in the two Eu^{3+} salts and the intensities became weaker upon salt formation (Fig. 1). The OH vibrations masked the CH bands.

The deformation vibrations of water molecules in the IR spectra of the two complexes, located at 1635 cm^{-1} for EuE(II) and 1638, 1609 cm^{-1} for EuE(I), and absent from the free ligand, and correspond to the water molecules in the complexes.

The CH_2 vibration (1457 cm^{-1} for erythritol) is shifted to 1475 or 1470 cm^{-1} in the spectra of the two salts. Other bands in the 1500–650 cm^{-1} region are shifted after complexation, and different changes occur for EuE(I) and EuE(II), confirming the formation of two metal–sugar complexes. In particular, the stronger bands in the region, 1081 and 1055 cm^{-1} bands assigned mainly to C–O stretching vibrations,[14] are shifted to 1074, 1057 cm^{-1} for EuE(I) and 1070, 1048 cm^{-1} for EuE(II), indicating the coordination of hydroxyl groups to metal ions.

The IR results indicate that the hydroxyl groups of erythritol take part in the metal–oxygen interaction; the hydrogen-bond network is rearranged upon sugar metalation; the conformation of the erythritol skeleton is changed as a result of salt formation, and two $EuCl_3$–erythritol complexes have formed.

3.2. X-Ray crystal structure

The crystal structure of the title compound is shown in Figures 2, and 3 is a projection of the crystal cell in the crystal structure of $2EuCl_3 \cdot 2C_4H_{10}O_4 \cdot 7H_2O$. The crystal data and structure refinement are listed in Table 1; atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2; selected bond lengths and angles are listed in Table 3, torsion angles in Table 4, and hydrogen bond data in Table 5, respectively.

For $2EuCl_3 \cdot 2C_4H_{10}O_4 \cdot 7H_2O$ (EuE(II)), the nine-coordinated Eu^{3+} binds to four hydroxyl groups of two erythritol molecules, five water molecules, and another Eu^{3+} is eight-coordinated with four hydroxyl groups of two erythritol molecules, two water molecules, and two chloride ions. Erythritol links two europium ions together to form a chain structure. Two chlorides are coordinated and another four chloride ions existing in the structure are not coordinated to europium ions. Eu–O distances are 2.412–2.516 Å for Eu-1 and Eu–O distances are 2.415–2.473 Å and the Eu–Cl distance is 2.7237 Å for Eu-2. O-7 is located at the symmetric axis. Erythritol is not symmetric after complexation with Eu^{3+} ion in EuE(II). The C–C, C–O distances, C–C–C, O–C–C bond angles, and torsion angles of EuE(II) and native erythritol[16] are listed in Table 6. The C–C, C–O distances, O–C–C bond angles, C–C–C bond angles, and especially the C–C–C–O torsion angles of EuE(II) show differences from those of erythritol itself.[15,16] The results show that the coordination of metal ions influences the conformation of erythritol, for example, the O(1)–C(1)–C(2) bond angle become smaller after complexation, and especially the changes of C–C–C–O torsion angles cause erythritol to provide two hydroxyl groups to one metal ion and the other two to another metal ion. There is an extensive hydrogen bond network in the structure of EuE(II) because of the existence of hydroxyl groups, water molecules and chloride ions (Table 5). The hydrogen bond data indicate that most of the hydrogen bonds are formed by O–H of erythritol and water molecules with chloride ions, namely O–H···Cl hydrogen bonds.

From the similarity of the FTIR spectra of EuE(I) and $PrCl_3 \cdot C_4H_{10}O_4 \cdot 6H_2O$, the structure of EuE(I) was deduced in our previous paper[12]: it belongs to the monoclinic crystal system, $P\bar{1}$ space group. Eu^{3+} is nine-coordinated with four hydroxyl groups from two erythritol molecules, four water molecules and one chloride ion; An additional two water molecules are hydrogen-bonded with chloride ions and the two water molecules connect each other via a hydrogen bond. The unit dimensions of EuE(I) are deduced from powder X-ray diffraction results as follows: $a = 7.5509$ Å, $b = 10.2334$ Å, $c = 10.4693$ Å, $\alpha = 85.3680°$, $\beta = 84.2632°$,

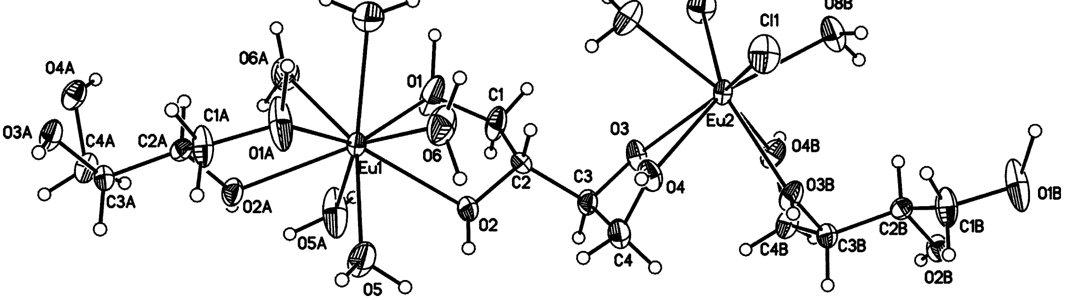

Figure 2. Structure and atom numbering scheme of $2EuCl_3 \cdot 2C_4H_{10}O_4 \cdot 7H_2O$.

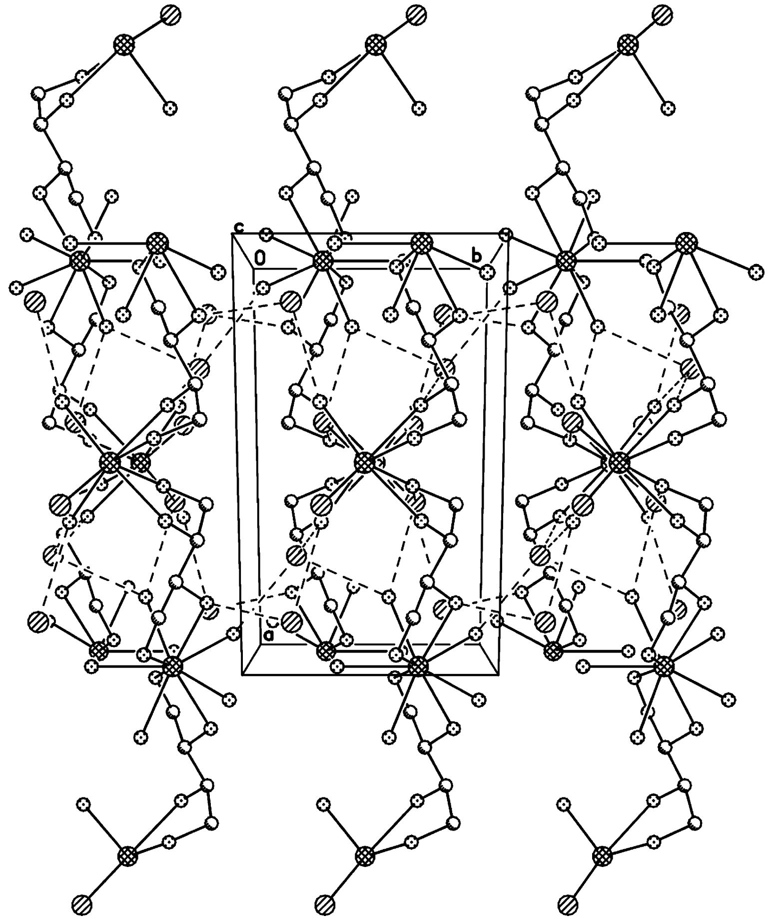

Figure 3. Projection of the crystal cell in the structure of $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$.

Table 1. Crystal data for $2EuCl_3{\cdot}2C_4H_{10}O_4{\cdot}7H_2O$

Empirical formula	$C_4H_{17}C_{13}EuO_{7.50}$ ($EuCl_3{\cdot}C_4H_{10}O_4{\cdot}3.5H_2O$)
Formula weight	443.49
Temperature	293(2) K
Crystal system, space group	Monoclinic, P2/c
Unit cell dimensions	$a = 13.846(3)$ Å $b = 7.4983(15)$ Å $c = 14.140(3)$ Å $\alpha = 90°$ $\beta = 116.39(3)°$ $\gamma = 90°$
Volume	1315.1(5) $Å^3$
Refls. No. for cell measurement	9634
θ range for cell measurement	2.72–27.48°
Z, Calculated density	4, 2.240 mg/m^3
Absorption coefficient	5.394 mm^{-1}
$F(000)$	860
Crystal shape/crystal color	Block/colorless
Crystal size	$0.30 \times 0.20 \times 0.10\,mm^3$
θ range for data collection	2.72–27.48°
Limiting indices	$-17 \leqslant h \leqslant 17$, $-9 \leqslant k \leqslant 9$, $-18 \leqslant l \leqslant 16$
Reflections collected/unique	9643/2965 [R(int) = 0.0769]
Reflections with $I > 2\sigma$(I)	2382
Completeness to $\theta = 27.48$	97.9%
Absorption correction	Empirical
Max. and min. transmission	0.583 and 0.198
Data/restraints/parameters	2965/0/143
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0395$, $wR2 = 0.0970$
R indices (all data)	$R1 = 0.0524$, $wR2 = 0.0999$
Extinction coefficient	0.0016(3)
Largest diff. peak and hole	1.668 and −2.241 e·$Å^{-3}$
Max. and mean shift/sigma	0.000 and 0.000

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $2EuCl_3\cdot 2C_4H_{10}O_4\cdot 7H_2O$

	x	*y*	*z*	*U*(eq)
Eu(1)	0	3052(1)	2500	19(1)
Eu(2)	5000	5222(1)	2500	19(1)
Cl(1)	5978(1)	6871(2)	4413(1)	36(1)
Cl(2)	−1210(1)	8104(2)	3857(1)	35(1)
Cl(3)	−2697(1)	8034(2)	721(1)	38(1)
O(1)	411(3)	3979(8)	1056(4)	51(2)
O(2)	1605(3)	1577(6)	2440(3)	24(1)
O(3)	3629(3)	3015(6)	1584(3)	26(1)
O(4)	4436(3)	3309(6)	3591(3)	27(1)
O(5)	735(4)	655(8)	3757(5)	58(2)
O(6)	1668(3)	4246(7)	3878(4)	42(1)
O(7)	0	6351(10)	2500	52(2)
O(8)	3582(3)	6953(6)	2611(4)	36(1)
C(1)	1329(4)	3317(10)	926(5)	32(2)
C(2)	2139(4)	2735(7)	2026(4)	20(1)
C(3)	3151(4)	1843(8)	2061(5)	22(1)
C(4)	3996(4)	1574(9)	3197(5)	27(1)

U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

Table 3. Bond lengths [Å] and angles [°] for $2EuCl_3\cdot 2C_4H_{10}O_4\cdot 7H_2O$

Bond lengths		Bond lengths	
Eu(1)–O(5)#1	2.412(5)	Eu(2)–O(8)#2	2.417(4)
Eu(1)–O(5)	2.412(5)	Eu(2)–O(4)	2.473(4)
Eu(1)–O(6)	2.435(4)	Eu(2)–O4#2	2.473(4)
Eu(1)–O(6)#1	2.435(4)	Eu(2)–Cl(1)	2.7244(17)
Eu(1)–O(1)#1	2.451(4)	Eu(2)–Cl(1)#2	2.7244(17)
Eu(1)–O(1)	2.451(4)	O(1)–C(1)	1.450(6)
Eu(1)–O(7)	2.474(8)	O(2)–C(2)	1.425(6)
Eu(1)–O(2)#1	2.517(3)	O(3)–C(3)	1.436(6)
Eu(1)–O(2)	2.517(3)	O(4)–C(4)	1.439(7)
Eu(2)–O(3)	2.415(4)	C(1)–C(2)	1.523(8)
Eu(2)–O(3)#2	2.415(4)	C(2)–C(3)	1.533(7)
Eu(2)–O(8)	2.417(4)	C(3)–C(4)	1.524(8)
Bond angles		Bond angles	
O(5)#1–Eu(1)–O(5)	83.7(3)	O(6)#1–Eu(1)–O(1)	73.63(15)
O(5)#1–Eu(1)–O(6)	143.39(17)	O(1)#1–Eu(1)–O(1)	147.1(3)
O(5)–Eu(1)–O(6)	75.2(2)	O(5)#1–Eu(1)–O(7)	138.17(17)
O(5)#1–Eu(1)–O(6)#1	75.2(2)	O(5)–Eu(1)–O(7)	138.17(17)
O(5)–Eu(1)–O(6)#1	143.39(17)	O(6)–Eu(1)–O(7)	68.44(13)
O(6)–Eu(1)–O(6)#1	136.9(3)	O(6)#1–Eu(1)–O(7)	68.44(13)
O(5)#1–Eu(1)–O(1)#1	130.33(15)	O(1)#1–Eu(1)–O(7)	73.53(14)
O(5)–Eu(1)–O(1)#1	77.0(2)	O(1)–Eu(1)–O(7)	73.53(14)
O(6)–Eu(1)–O(1)#1	73.63(15)	O(5)#1–Eu(1)–O(2)#1	66.91(14)
O(6)#1–Eu(1)–O(1)#1	94.21(18)	O(5)–Eu(1)–O(2)#1	74.76(15)
O(5)#1–Eu(1)–O(1)	77.0(2)	O(6)–Eu(1)–O(2)#1	132.24(15)
O(5)–Eu(1)–O(1)	130.33(15)	O(6)#1–Eu(1)–O2#1	69.56(15)
O(6)–Eu(1)–O(1)	94.21(18)	O(1)#1–Eu(1)–O2#1	63.99(14)
O(1)–Eu(1)–O(2)	63.99(14)	O(1)–Eu(1)–O(2)#1	133.46(16)
O(7)–Eu(1)–O(2)	116.07(9)	O(7)–Eu1–O(2)#1	116.07(9)
O(2)#1–Eu(1)–O(2)	127.86(18)	O(5)#1–Eu(1)–O(2)	74.76(15)
O(3)–Eu(2)–O(3)#2	93.5(2)	O(5)–Eu(1)–O(2)	66.91(14)
O(3)–Eu(2)–O(8)	86.30(15)	O(6)–Eu(1)–O(2)	69.56(15)
O(3)#2–Eu(2)–O(8)	143.21(15)	O(6)#1–Eu(1)–O(2)	132.24(15)
O(3)–Eu(2)–O(8)#2	143.21(15)	O(1)#1–Eu(1)–O(2)	133.46(16)
O(3)#2–Eu(2)–O(8)#2	86.30(15)	O(8)–Eu(2)–O(4)#2	147.47(14)
O(8)–Eu(2)–O(8)#2	115.0(2)	O(8)#2–Eu(2)–O(4)#2	77.29(15)
O(3)–Eu(2)–O(4)	63.00(13)	O(4)–Eu(2)–O(4)#2	109.1(2)
O(3)#2–Eu(2)–O(4)	70.07(13)	O(3)–Eu(2)–Cl(1)	140.23(10)
O(8)–Eu(2)–O(4)	77.29(15)	O(3)#2–Eu(2)–Cl(1)	81.57(11)
O(8)#2–Eu(2)–O(4)	147.47(14)	O(8)–Eu(2)–Cl(1)	75.60(12)
O(3)–Eu(2)–O(4)#2	70.07(13)	O(8)#2–Eu(2)–Cl(1)	76.18(12)

(*continued on next page*)

Table 3 (*continued*)

Bond lengths		Bond lengths	
O(3)#2–Eu(2)–O(4)#2	63.00(14)	O(4)–Eu(2)–Cl(1)	78.44(10)
O(3)#2–Eu(2)–Cl(1)#2	140.23(10)	O(4)#2–Eu(2)–Cl(1)	136.62(9)
O(8)–Eu(2)–Cl(1)#2	76.18(12)	O(3)–Eu(2)–Cl(1)#2	81.57(11)
O(8)#2–Eu(2)–Cl(1)#2	75.60(12)	O(2)–C(2)–C(1)	108.3(4)
O(4)–Eu(2)–Cl(1)#2	136.62(9)	C(3)–C(2)–C(1)	113.9(4)
O(4)#2–Eu(2)–Cl(1)#2	78.44(10)	O(3)–C(3)–C(2)	108.9(4)
Cl(1)–Eu(2)–Cl(1)#2	126.01(8)	O(3)–C(3)–C(4)	106.1(4)
C(1)–O(1)–Eu(1)	123.3(3)	C(2)–C(3)–C(4)	110.7(5)
C(2)–O(2)–Eu(1)	111.9(3)	O(4)–C(4)–C(3)	106.4(5)
C(3)–O(3)–Eu(2)	125.8(3)	O(1)–C(1)–C(2)	104.9(4)
C(4)–O(4)–Eu(2)	118.7(3)	O(2)–C(2)–C(3)	110.8(4)

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

Table 4. Torsion angles [°] for $2EuCl_3\cdot 2C_4H_{10}O_4\cdot 7H_2O$

Torsion angles		Torsion angles	
O(5)#1–Eu(1)–O(1)–C(1)	−81.6(5)	Cl(1)#2–Eu(2)–O(3)–C(3)	−150.7(4)
O(5)–Eu(1)–O(1)–C(1)	−11.7(6)	O(3)–Eu(2)–O(4)–C(4)	25.5(3)
O(6)–Eu(1)–O(1)–C(1)	62.4(5)	O(3)#2–Eu(2)–O(4)–C(4)	−79.4(3)
O(6)#1–Eu(1)–O(1)–C(1)	−159.8(6)	O(8)–Eu(2)–O(4)–C(4)	117.9(4)
O(1)#1–Eu(1)–O(1)–C(1)	128.5(5)	O(8)#2–Eu(2)–O(4)–C(4)	−125.2(4)
O(7)–Eu(1)–O(1)–C(1)	128.5(5)	O(4)#2–Eu(2)–O(4)–C(4)	−28.9(3)
O(2)#1–Eu(1)–O(1)–C(1)	−121.0(5)	Cl(1)–Eu(2)–O(4)–C(4)	−164.5(3)
O(2)–Eu(1)–O(1)–C(1)	−2.4(5)	Cl(1)#2–Eu(2)–O(4)–C(4)	64.4(4)
O(5)#1–Eu(1)–O(2)–C(2)	114.8(4)	Eu(1)–O(1)–C(1)–C(2)	−24.3(7)
O(5)–Eu(1)–O(2)–C2	−155.7(4)	Eu(1)–O(2)–C(2)–C(3)	176.6(3)
O(6)–Eu(1)–O(2)–C(2)	−73.6(4)	Eu(1)–O(2)–C(2)–C(1)	−57.8(5)
O(6)#1–Eu(1)–O(2)–C(2)	62.0(4)	O(1)–C(1)–C(2)–O(2)	51.7(6)
O(1)#1–Eu(1)–O(2)–C(2)	−113.4(4)	O(1)–C(1)–C(2)–C(3)	175.4(5)
O(1)–Eu(1)–O(2)–C(2)	32.0(3)	Eu(2)–O(3)–C(3)–C(2)	91.3(5)
O(7)–Eu(1)–O(2)–C(2)	−21.8(4)	Eu(2)–O(3)–C(3)–C(4)	−27.9(5)
O(2)#1–Eu(1)–O(2)–C(2)	158.2(4)	O(2)–C(2)–C(3)–O(3)	176.9(4)
O(3)#2–Eu(2)–O(3)–C(3)	69.0(4)	C(1)–C(2)–C(3)–O(3)	54.6(6)
O(8)–Eu(2)–O(3)–C(3)	−74.1(4)	O(2)–C(2)–C(3)–C(4)	−66.9(6)
O(8)#2–Eu(2)–O(3)–C(3)	157.5(4)	C(1)–C(2)–C(3)–C(4)	170.8(5)
O(4)–Eu(2)–O(3)–C(3)	3.5(3)	Eu(2)–O(4)–C(4)–C(3)	−48.0(5)
O(4)#2–Eu(2)–O(3)–C(3)	128.6(4)	O(3)–C(3)–C(4)–O(4)	44.8(5)
Cl(1)–Eu(2)–O(3)–C(3)	−12.0(5)	C(2)–C(3)–C(4)–O(4)	−73.2(5)

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

Table 5. Hydrogen bonds for $2EuCl_3\cdot 2C_4H_{10}O_4\cdot 7H_2O$ [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠ DHA
O(1)–H(O1)···Cl(2)#1	1.211(5)	2.2804(16)	3.268(6)	136.6(2)
O(1)–H(O1)···O(1)#3	1.211(5)	2.334(5)	3.088(9)	117.7(2)
O(2)–H(O2)···Cl(3)#4	1.075(4)	2.5722(17)	3.551(4)	151.1(2)
O(3)–H(O3)···Cl(3)#3	0.826(4)	2.2123(18)	3.028(4)	169.8(3)
O(4)–H(O4)···Cl(1)#5	0.994(4)	2.2172(16)	3.123(4)	150.8(2)
O(5)–H(O5A)···Cl(3)#4	0.992(4)	2.2455(16)	3.163(5)	153.3(3)
O(5)–H(O5B)···Cl(2)#6	1.431(5)	1.9493(17)	3.272(6)	150.6(2)
O(6)–H(O6A)···Cl(1)#5	1.097(5)	2.3696(18)	3.188(5)	130.1(2)
O(6)–H(O6B)···Cl(3)#1	0.936(5)	2.2206(19)	3.114(5)	159.4(3)
O(7)–H(O7)···Cl(2)	0.961(3)	2.3887(17)	3.327(3)	165.39(17)
O(8)–H(O8A)···Cl(2)#1	0.977(5)	2.3664(16)	3.128(5)	134.2(2)
O(8)–H(O8B)···Cl(3)#1	0.961(5)	2.6809(17)	3.207(5)	115.0(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$; #2 $-x+1, y, -z+1/2$; #3 $-x, -y+1, -z$; #4 $-x, y-1, -z+1/2$; #5 $-x+1, -y+1, -z+1$; #6 $-x, -y+1, -z+1$.

$\gamma = 78.7033°$, being thus similar to PrE. The results indicate that the two $EuCl_3$–erythritol complexes have the same M:L ratio (1:1), but they have different structures, eight- and nine-coordinated Eu^{3+} exist in the

Table 6. The C-C, C-O distances, C-C-C, O-C-C bond angles and torsion angles of EuE(II) and erythritol[16]

EuE(II)		Erythritol[16]	
O(1)–C(1)	1.450(6)	O(1)–C(1)	1.425(1)
O(2)–C(2)	1.425(6)	O(2)–C(2)	1.433(1)
O(3)–C(3)	1.436(6)		
O(4)–C(4)	1.439(7)		
C(1)–C(2)	1.523(8)	C(1)–C(2)	1.523(1)
C(2)–C(3)	1.533(7)	C(2)–C(2′)	1.539(1)
C(3)–C(4)	1.524(8)		
O(2)–C(2)–C(1)	108.3(4)	O(2)–C(2)–C(1)	107.7(1)
C(3)–C(2)–C(1)	113.9(4)	C(1)–C(2)–C(2′)	112.9(1)
O(3)–C(3)–C(2)	108.9(4)		
O(3)–C(3)–C(4)	106.1(4)		
C(2)–C(3)–C(4)	110.7(5)		
O(4)–C(4)–C(3)	106.4(5)		
O(1)–C(1)–C(2)	104.9(4)	O(1)–C(1)–C(2)	112.2(1)
O(2)–C(2)–C(3)	110.8(4)	O(2)–C(2)–C(2′)	109.7(1)
O(1)–C(1)–C(2)–O(2)	51.7(6)	O(1)–C(1)–C(2)–O(2)	62.9(1)
O(1)–C(1)–C(2)–C(3)	175.4(5)		
O(2)–C(2)–C(3)–O(3)	176.9(4)		
C(1)–C(2)–C(3)–O(3)	54.6(6)	C(1)–C(2)–C(2′)–O(2′)	−59.9(1)
O(2)–C(2)–C(3)–C(4)	−66.9(6)		
C(1)–C(2)–C(3)–C(4)	170.8(5)		
O(3)–C(3)–C(4)–O(4)	44.8(5)		
C(2)–C(3)–C(4)–O(4)	−73.2(5)	C(2)-C(2′)–C(1′)–O(1′)	58.4(1)

structure of EuE(II). Erythritol provides two hydroxyl groups to one metal ion and the other two to another metal ion, but the changes of bond distances and angles should be different in the two complexes because of the differences of their IR spectra.

It is not usual for two metal ions to exist in a metal–sugar complex structure. Another example is $[La(L1)_2(NO_3)_2][LaL1(NO_3)_4]$ (L1 = 1,3,5-trihydroxycyclohexane) in which two La^{3+} ions are 10- and 11-coordinated.[17] The results indicate the complexity of metal ion–sugar interactions. In the crystal structure of $2EuCl_3 \cdot galactitol \cdot 14H_2O$,[18] galactitol ($C_6H_{14}O_6$) provides three hydroxyl groups to one lanthanide ion and the other three to another lanthanide ion; Eu^{3+} is coordinated to three hydroxyl groups and six water molecules, and M:L ratio is 2:1. However, two complexes with M:L 1:1 were obtained for erythritol. The results indicate that Eu^{3+} should form various coordination structures with different carbohydrates.

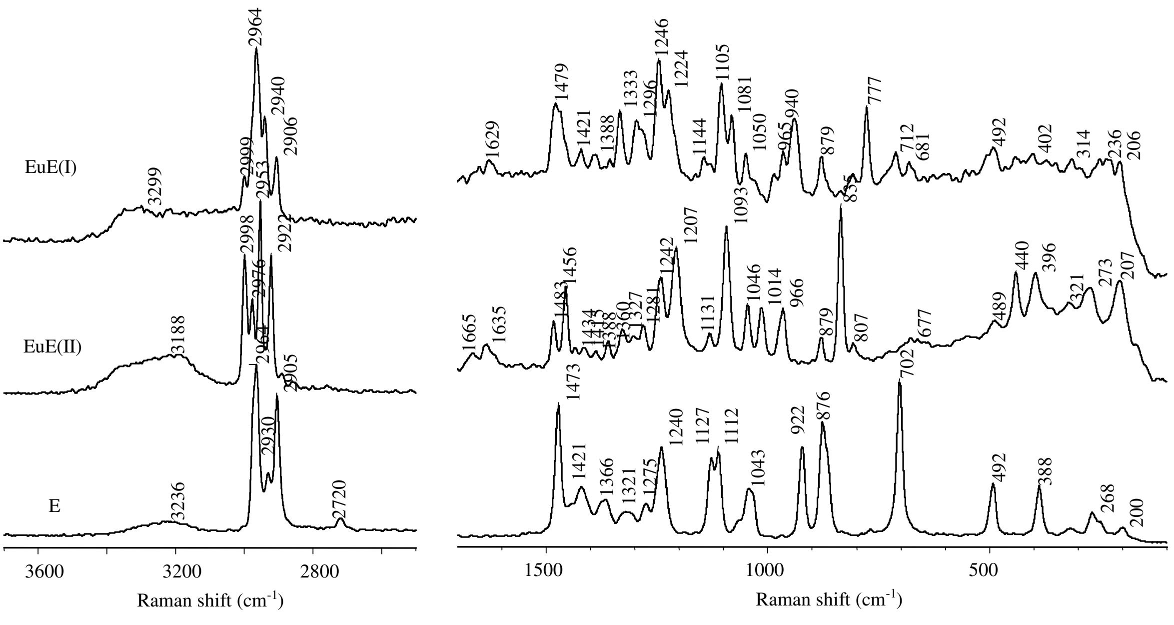

Figure 4. Raman spectra of erythritol and its two complexes, EuE(I) and EuE(II) in the 3700–2500 and 1700–100 cm^{-1} region.

3.3. Raman spectra of EuE(I) and EuE(II)

The FT-Raman spectra of erythritol and its two EuCl$_3$ complexes are shown in Figure 4. IR and Raman spectra can complement each other and offer additional information. Here, the Raman spectra of the two EuCl$_3$ complexes also show differences in peak positions and relative intensities. The OH stretching vibrations appear in the 3700–3000 cm^{-1} region: 3299, 3216 cm^{-1} for EuE(I) and 3188 cm^{-1} for EuE(II), and the CH stretching vibrations are 2999, 2964, 2940, 2906 cm^{-1} for EuE(I); 2998, 2976, 2953, 2922 cm^{-1} for EuE(II), respectively. The νCH bands are strong in the Raman spectra. In the 1700–1500 cm^{-1} region, the following peaks could be assigned to the deformational vibration of water [coordinated waters for EuE(II); coordinated and hydrogen-bonded waters for EuE(I)]: 1629 cm^{-1} for EuE(I), and 1665, 1635 cm^{-1} for EuE(II). In the 1500–650 cm^{-1} region the bands assigned to CC, CO, COH, CCH, CCO, OCH vibrations are shifted to higher or lower wavenumbers in the two Raman spectra.[19] The shift to higher or lower wavenumber depends on the change in the structures related to the vibrational mode of the peak. In the 650–100 cm^{-1} region the peaks could be assigned to M–O vibrations: 206 cm^{-1} for EuE(I), and 207 cm^{-1} for EuE(II).[20] This is an important evidence of complex formation.

3.4. Luminescence spectra of EuE(I) and EuE(II)

The luminescence spectra are shown in Figure 5, including exciting and emission spectra of EuE(I) and EuE(II). The exciting spectra are similar, and the two emission spectra show some differences for the two complexes. The assignments of the peaks in the emission spectra are as follows: 536 nm ($^5D_1 \rightarrow {}^7F_1$), 556 nm ($^5D_1 \rightarrow {}^7F_2$), 592 nm ($^5D_0 \rightarrow {}^7F_1$), 615 nm ($^5D_0 \rightarrow {}^7F_2$), 692 nm ($^5D_0 \rightarrow {}^7F_4$).[21] The strongest peak is at 616 nm in many cases, but a 592 nm band is the strongest peak for the two complexes, indicating that the transition probability of $^5D_0 \rightarrow {}^7F_1$ over $^5D_0 \rightarrow {}^7F_2$ is because of the influence of different coordination environments. I_{592}/I_{616} is $\sim$1.27 for EuE(I) and $\sim$2.2 for EuE(II). The 536 nm band is relatively

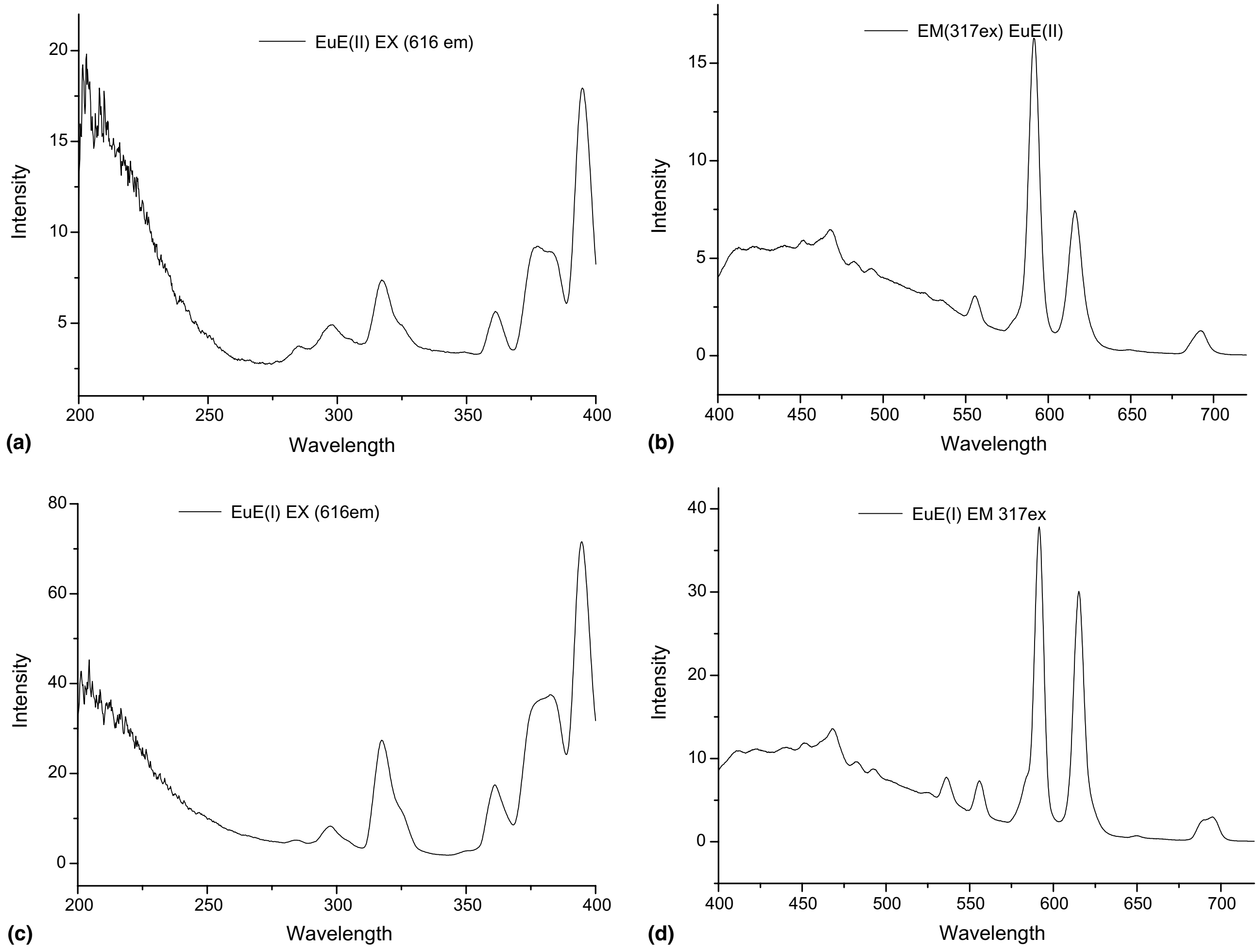

Figure 5. Luminescence spectra of EuE(I) and EuE(II).

stronger in EuE(I) and weaker in EuE(II). The results indicate that lanthanide–erythritol complexes have luminescence properties, but the luminescence is weaker than most of other lanthanide chelates.

In conclusion, the FTIR, X-ray single crystal diffraction, FT-Raman, and luminescence spectra results indicate that lanthanide ions form several complexes with erythritol, one of these having two rare earth ions with 8- and 9-coordination. The saccharide, chloride ions, and water molecules coordinate competitively with metal ions and form two different complexes, EuE(I) and EuE(II), respectively, indicating the high reactivity of erythritol and the complexity of the interactions between metal ions and carbohydrates.

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