

Interactions between Metal Ions and Carbohydrates. Coordination Behavior of Neutral Erythritol to Ca(II) and Lanthanide Ions

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The study of the sugar–metal ion interactions remains one of the main objectives of carbohydrate coordination chemistry because the interactions between metal ions and carbohydrates are involved in many biochemical processes. This paper presents a comparison of coordination structures of erythritol with alkaline-earth-metal and lanthanide chloride and nitrate in the solid state using FT-IR and X-ray diffraction. Neutral, nondeprotonated erythritol (E) reacts with CaCl_2 to give three CaCl_2 –erythritol (CaE(I), CaE(II), CaE(III)) complexes, showing that three of the five general features of calcium–carbohydrate complexes deduced in the reference encounter contrary examples. Different coordination structures have been observed for calcium and lanthanide chloride and nitrates. The coordination of carbohydrates to metal ions is complicated, and erythritol, chloride ions, nitrates, water molecules, and ethanol (crystallization medium and reaction solvents) have the chance to coordinate to metal ions. IR spectral results show that different lanthanide ions, from LaCl_3 to TbCl_3 , have similar coordination structures with erythritol. The results show that erythritol can act as two bidentate neutral ligands (CaE(I), CaE(II), CaE(III), CaEN, PrE, NdE) or as a three-hydroxyl donor (NdEN). The IR results are consistent with the crystal structures.

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 polyfunctional molecules and metal ions in living organisms, the modification of the biological function of both counterparts may be expected. Sugar–metal ion interaction is involved in many biochemical processes such as the transport and storage of metal ions,¹ stabilization of membrane structures,² binding of glycoproteins to cell surfaces,³ toxic metal metabolism,⁴ binding of protein to sugar,⁵ and so on. It is also regarded as an assembly of

carbohydrates around metal ions.⁶ The study of the sugar–metal ion interactions remains one of the dominant objectives of carbohydrate coordination chemistry.

The investigation of the interactions between metal ions and simple sugars can improve the understanding of metal ion interactions with sugar residues of biologically important compounds, which requires assignment of the binding hydroxyl or other groups and the change of hydrogen bonds and also characterization of the metal ion coordination of carbohydrates monitoring the ligand conformation and configuration changes forced by the complexation processes. The coordination of metal cations by polyols as chelate ligands in aqueous solution has been extensively studied in the carbohydrate and cyclitol fields over the past four decades.⁷ In aqueous solution metal ions coordinate with water molecules. The un-ionized hydroxyl groups of carbohydrates are weak competitors for metal ion coordination; therefore, complexes with functionalized and deprotonated carbo-

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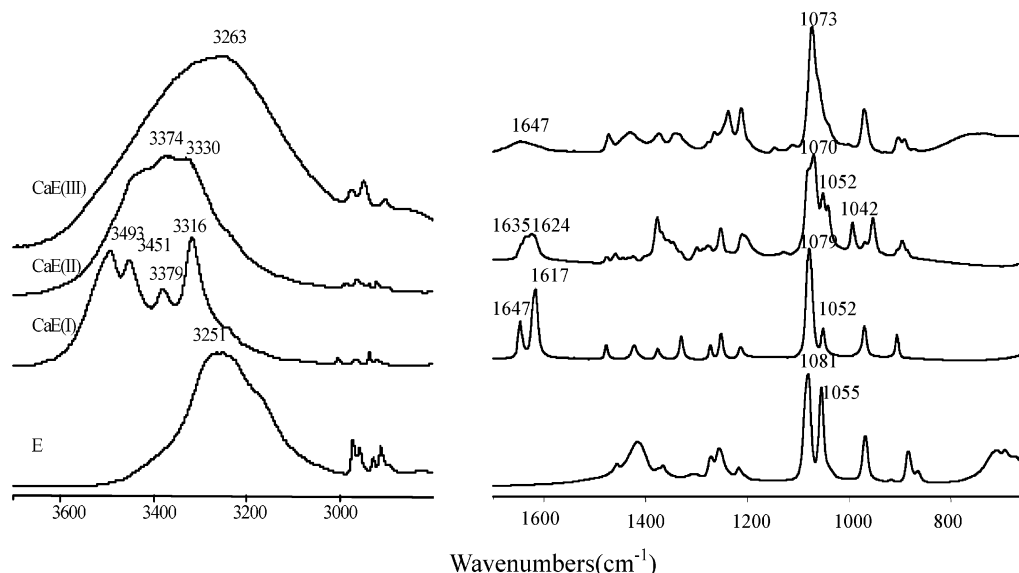


Figure 1. FT-IR spectra of three CaCl_2 -erythritol complexes in the 3700–2800 and 1700–650 cm^{-1} regions.

hydrate ligands are more common.⁸ Although coordination chemistry plays an important role, relatively few crystal structures of metal–sugar complexes have been reported, especially for neutral, nonfunctionalized mono- and disaccharides lacking anchor groups.⁹ There are only a few examples of sodium, calcium, and lanthanide complexes, and crystal structures are scarce for transition-metal–carbohydrate complexes.¹⁰ The binding sites of metal ions in monosaccharides were also studied by density functional theory (DFT) calculations.¹¹

Because a single crystal of the metal–sugar complex is very difficult to prepare, IR is also a useful technique to describe the complex formation and to deduce unknown structures.¹² Recently we have studied the coordination of galactitol, *myo*-inositol, and α -D-ribofuranose to lanthanide ions using X-ray single-crystal diffraction and FT-IR spectroscopy, which indicate that different carbohydrates have various coordination modes and some lanthanide ions may have similar coordination structures in many cases.¹³ The

investigation reported here describes the coordination behavior of neutral, nonfunctionalized erythritol to alkaline-earth-metal and lanthanide chlorides and nitrates and demonstrates the coordination variation of different metal ions to a saccharide.

Results and Discussion

Erythritol, being one of the simplest representatives of carbohydrates, is suitable as a building block for coordination polymers in which metal ions combine with hydroxyl groups to form extended structures. The crystal structures of metal ion-deprotonated erythritol complexes crystallized from alkaline solutions have been reported;¹⁴ however, there is no crystal structure reported for neutral erythritol–metal ion complexes in the literature, and the form with coordinated hydroxyl groups (OH) should be obviously different from the corresponding deprotonated form, O^- .

Structures of Alkaline-Earth-Metal Chloride–Erythritol and Alkaline-Earth-Metal Nitrate–Erythritol Complexes. The FT-IR spectra of the CaCl_2 -erythritol complexes indicate the formation of three metal complexes (Figure 1).

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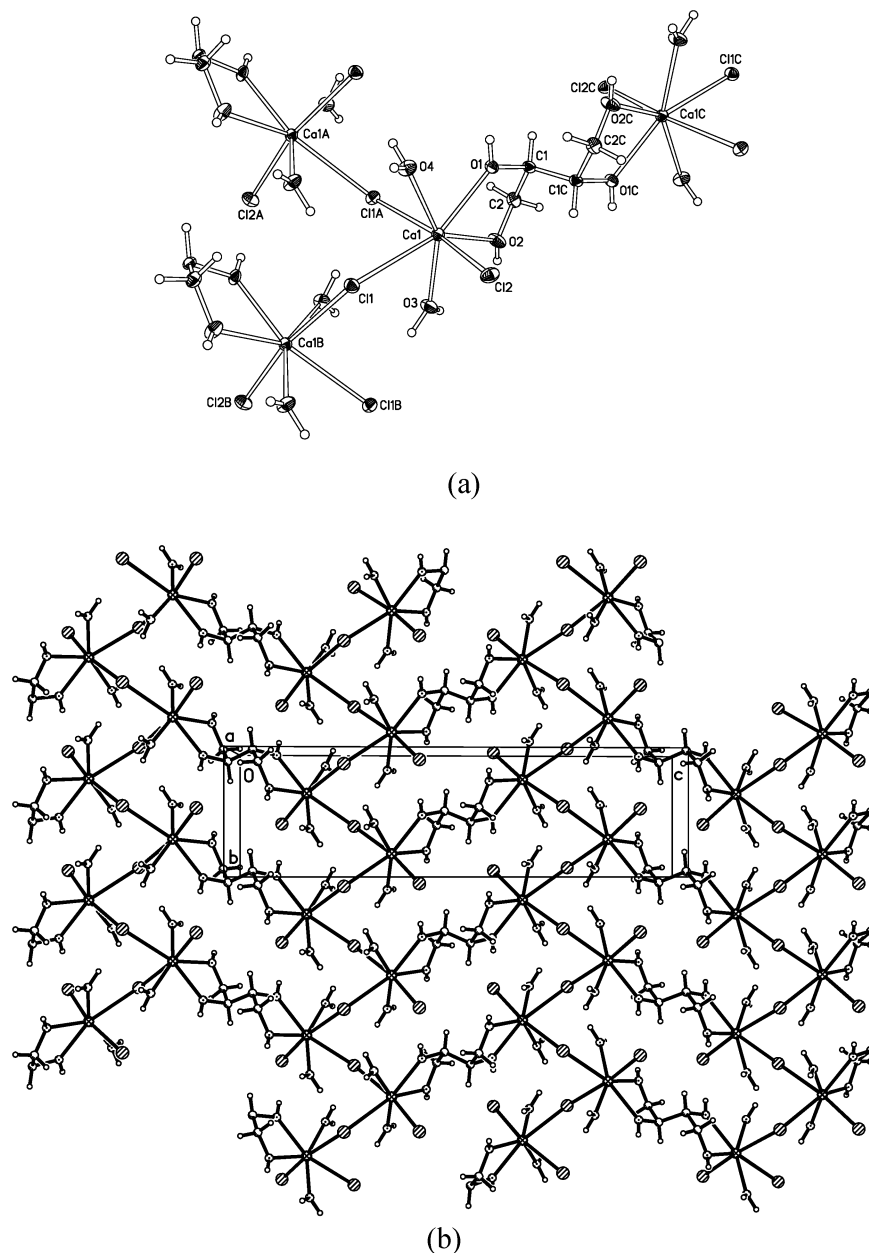


Figure 2. Crystal structures of CaE(I).

The ν_{OH} centered at 3251 cm^{-1} in the spectrum of erythritol is split into four evident peaks, 3493, 3451, 3379, and 3316 cm^{-1} , for CaE(I), becomes several bands located at 3374 and 3330 cm^{-1} for CaE(II), or is shifted to 3263 cm^{-1} for CaE(III). The ν_{CH} vibrations are shifted and the relative intensities are decreased in the $3000\text{--}2800\text{ cm}^{-1}$ region for the three complexes, and the bands in the $1500\text{--}650\text{ cm}^{-1}$ region in the IR spectra of the three complexes are different from one another and also that of the ligand erythritol, which confirms the formation of three different complexes. Especially the bands in the $1200\text{--}1000\text{ cm}^{-1}$ region related to C–O vibrations are shifted, which demonstrates the coordination of hydroxyl groups. The three molecular structures are shown in Figures 2–4. Selected bond lengths and angles are listed in Table 1. The molar ratio of metal ion to erythritol is 2:1, 1:1, and 1:2 for the three metal complexes CaE(I), CaE(II), and CaE(III), respectively. In the crystal structure

of CaE(I), Ca is 7-fold coordinated by three Cl ions, two water molecules, and half a $\text{C}_4\text{H}_{10}\text{O}_4$ group in a pentagonal bipyramid. Ca acts as a T-shaped node to connect three Ca ions via one bridging $\text{C}_4\text{H}_{10}\text{O}_4$ group and two $\mu\text{-Cl}$ (Cl1, Cl1A) ions. The coordination mode of CaE(II) is different from that of CaE(I) obviously: Ca^{2+} is coordinated to four hydroxyl groups from two erythritol molecules and four water molecules. Cl^- ions do not directly coordinate to Ca^{2+} and only participate in forming hydrogen bonds; thus, the wavelike cationic chain of $[\text{Ca}(\text{H}_2\text{O})_4(\text{C}_4\text{H}_{10}\text{O}_4)]_\infty$ has formed and Ca is 8-fold coordinated in a bicapped trigonal prism. But the environment of Ca^{2+} in the structure of CaE(III) is eight hydroxyl groups from four erythritol molecules. The Ca cation acts as a four-connecting node to link four neighbor Ca centers via $\text{C}_4\text{H}_{10}\text{O}_4$ ligands, and the Cl ions and water molecules locate in the rhombic channels of the diamond net built from Ca ions and bridging $\text{C}_4\text{H}_{10}\text{O}_4$ ligands. Average

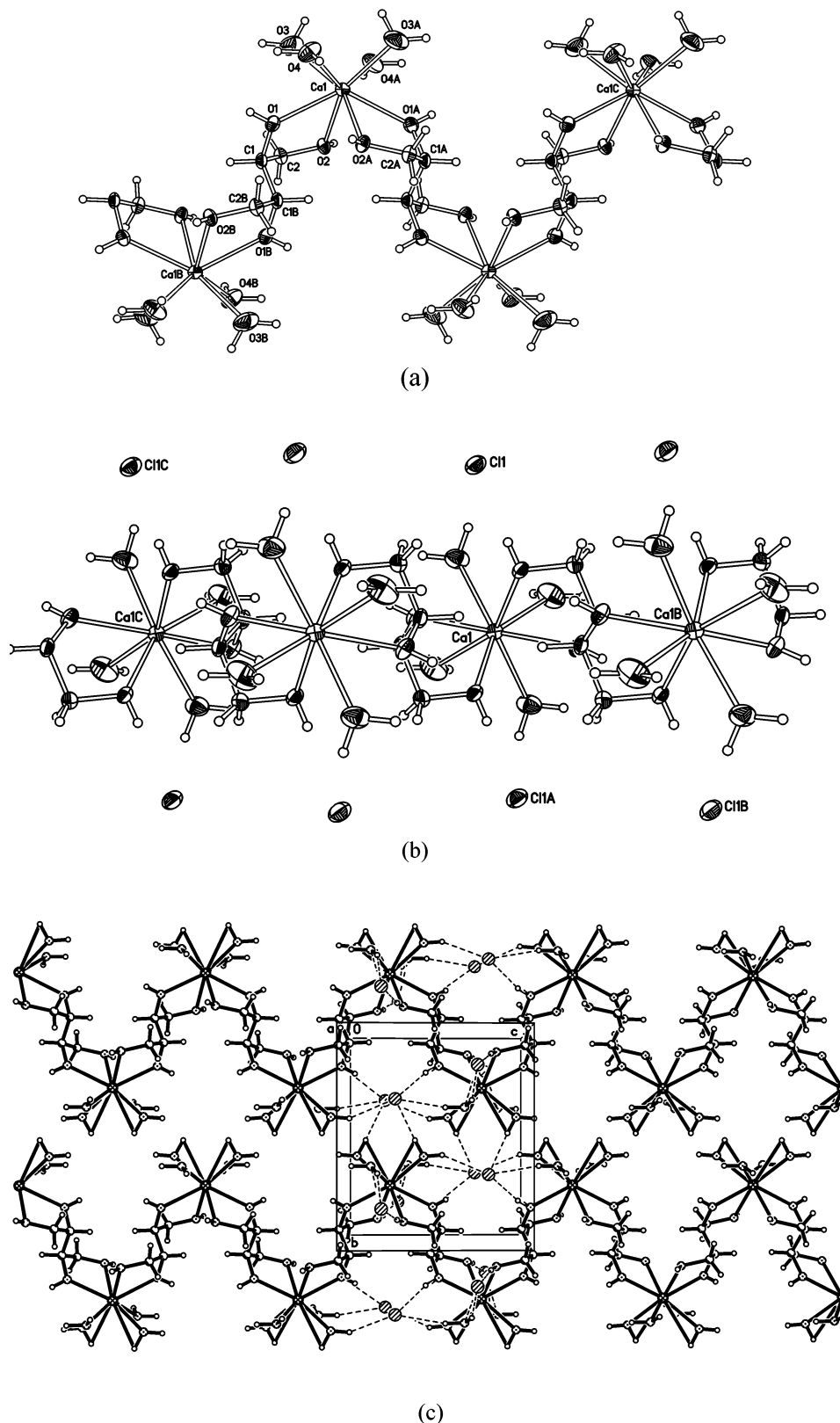


Figure 3. Crystal structure of CaE(II).

Ca–O distances are as follows: 2.403 Å (CaE(I)); 2.451 Å (CaE(II)); 2.435 Å (CaE(III)). Ca–Cl distances are from 2.7171 to 2.9567 Å for CaE(I). The hydrogen bond data listed in Table 2 show that there are different hydrogen bonds for the three complexes, which results in the variation of the OH stretching vibrations in their IR spectra. Many hydrogen

bonds are present in all these complexes as is common for crystalline adducts between polyols and inorganic salts according to the large quantity of donor and acceptor groups. There are O–H···Cl hydrogen bonds for CaE(I) and CaE(II) and O–H···Cl and O–H···O hydrogen bonds for CaE(III).

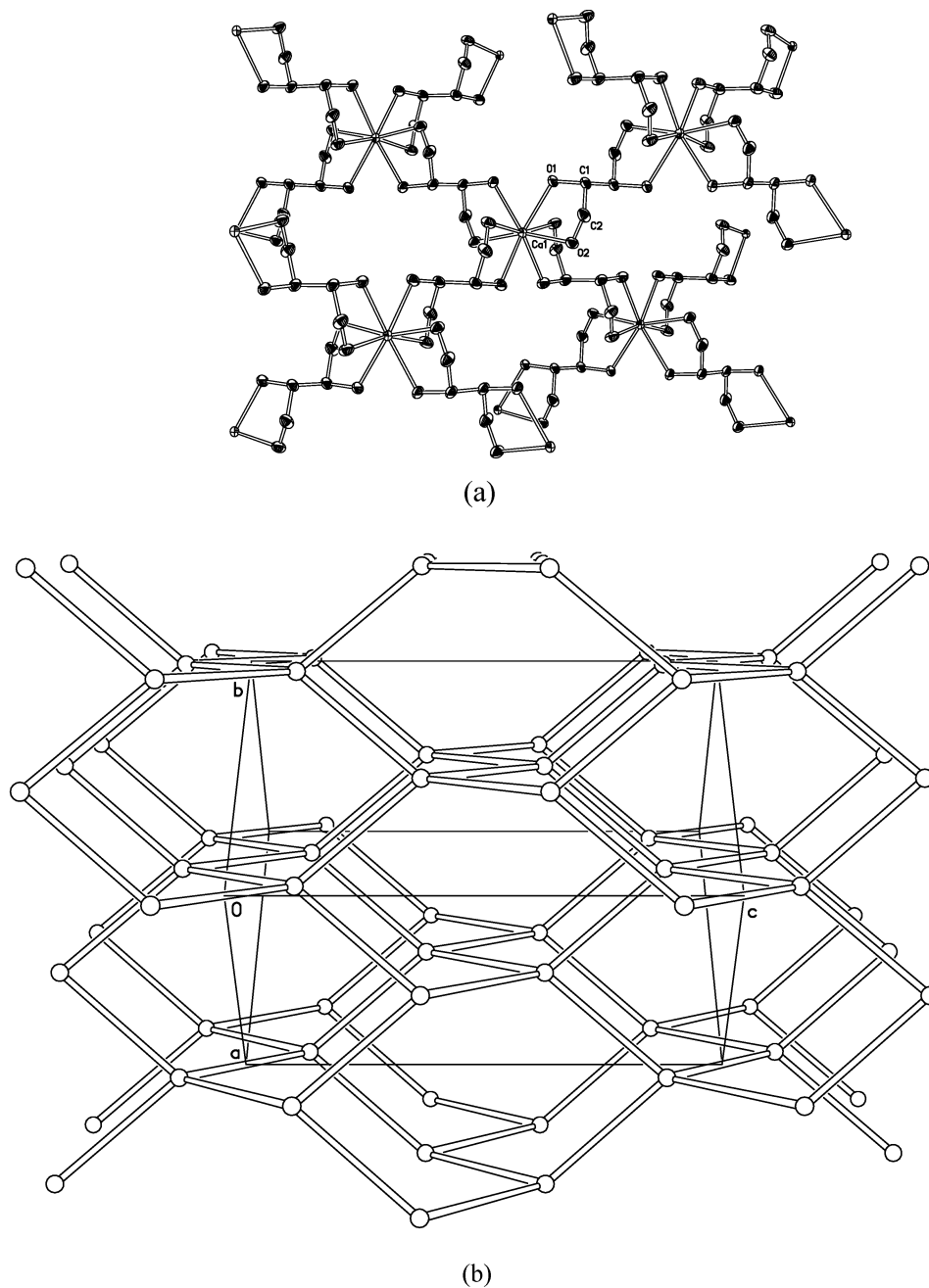


Figure 4. Crystal structures of CaE(III).

Although erythritol acts as two bidentate ligands in the three CaE complexes, the three conformations of erythritol have differences (Table 1 and Figures 1–4); for example, C–C and C–O bond lengths and C–C–O bond angles are changed after complexation: C–C = 1.51 Å, C–O = 1.47 or 1.39 Å, O1–C1–C2 = 107°, and C1–C2–C3 = 113° for erythritol;¹⁵ C–O is from 1.426 to 1.443 Å and C–C is from 1.504 to 1.530 Å for the three calcium complexes, which are shorter or longer than those of erythritol; O–C–C and C–C–C angles also have 1–2° differences with those of erythritol (Table 1).

Erythritol is such a simple molecule and one of the simplest representatives of carbohydrates, but three CaCl₂–

erythritol complexes were isolated, which indicates the complexity of coordination of metal ions to carbohydrates. Calcium ion has several coordination structures derived from the various molar ratios of metal ion to erythritol. In the three CaCl₂–erythritol complexes Ca²⁺ is coordinated to two, four, and eight hydroxyl groups from one, two, and four erythritol molecules, respectively. Cl[–] ions or water molecules may bind to Ca²⁺ to reach the coordination number of Ca²⁺, 7 or 8. The results show that erythritol, water molecules, and chloride ions competitively coordinate to Ca²⁺ to form several complexes. Five general features were found for calcium–carbohydrate complexes in the review in ref 10a. The new results of CaCl₂–erythritol complexes show that some features are consistent: Ca ion is 7- or 8-coordinated, and the Ca–O distances fall within the range of 2.3–

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Table 1. Selected Bond Lengths and Angles for CaE(I), CaE(II), CaE(III), and CaEN^a

CaE(I)		CaE(II)		CaE(III)		CaEN	
Bond Lengths (Å)							
Ca1–O3	2.3954(18)	Ca1–O3	2.418(2)	Ca1–O2#1	2.416(2)	Ca–O2#1	2.3895(12)
Ca1–O4	2.3961(17)	Ca1–O3#1	2.418(2)	Ca1–O2	2.416(2)	Ca–O2	2.3895(12)
Ca1–O2	2.4021(18)	Ca1–O2#1	2.4584(15)	Ca1–O2#2	2.416(2)	Ca–O1#1	2.4004(14)
Ca1–O1	2.4184(17)	Ca1–O2	2.4584(15)	Ca1–O2#3	2.416(2)	Ca–O1	2.4004(14)
Ca1–Cl2	2.7171(8)	Ca1–O1#1	2.4626(16)	Ca1–O1	2.454(2)	Ca–O4	2.4708(12)
Ca1–Cl1#1	2.7994(8)	Ca1–O1	2.4626(16)	Ca1–O1#2	2.454(2)	Ca–O4#1	2.4708(12)
Ca1–Cl1	2.9567(8)	Ca1–O4	2.4647(19)	Ca1–O1#3	2.454(2)	Ca–O3	2.5824(13)
		Ca1–O4#1	2.4647(19)	Ca1–O1#1	2.454(2)	Ca–O3#1	2.5824(13)
O1–C1	1.443(3)	O1–C1	1.434(3)	O1–C1	1.437(3)	N–O5	1.2211(19)
O2–C2	1.432(3)	O2–C2	1.438(3)	O2–C2	1.426(4)	N–O4	1.2696(17)
C1–C2	1.504(3)	C1–C2	1.508(3)	C1–C2	1.506(4)	O1–C1	1.450(2)
C1–C1#3	1.524(5)	C1–C1#2	1.524(4)	C1–C1#4	1.530(7)	O2–C2	1.4389(18)
						C2–C2#2	1.533(3)
Bond Angles (deg)							
O3–Ca1–O4	152.82(7)	O3–Ca1–O3#1	105.55(13)	O2#1–Ca1–O2	161.84(11)	O2#1–Ca–O2	140.09(6)
O3–Ca1–O2	70.08(6)	O3–Ca1–O2#1	150.60(8)	O2#1–Ca1–O2#2	88.00(13)	O2#1–Ca–O1#1	65.82(4)
O4–Ca1–O2	134.78(6)	O3#1–Ca1–O2#1	89.31(7)	O2–Ca1–O2#2	94.86(13)	O2–Ca–O1#1	87.43(5)
O3–Ca1–O1	133.75(6)	O3–Ca1–O2	89.31(7)	O2#1–Ca1–O2#3	94.86(13)	O2#1–Ca–O1	87.43(5)
O4–Ca1–O1	71.68(6)	O3#1–Ca1–O2	150.60(8)	O2–Ca1–O2#3	88.00(13)	O2–Ca–O1	65.82(4)
O2–Ca1–O1	63.74(6)	O2#1–Ca1–O2	89.51(8)	O2#3–Ca1–O2#3	161.84(11)	O1#1–Ca–O1	96.52(7)
O3–Ca1–Cl2	96.04(6)	O3–Ca1–O1#1	142.82(8)	O2#1–Ca1–O1	133.46(7)	O2#1–Ca–O4	128.83(4)
O4–Ca1–Cl2	90.69(5)	O3#1–Ca1–O1#1	74.94(8)	O2–Ca1–O1	64.67(8)	O2–Ca–O4	84.91(4)
O2–Ca1–Cl2	98.97(6)	O2#1–Ca1–O1#1	65.05(5)	O2#2–Ca1–O1	81.85(9)	O1#1–Ca–O4	161.23(4)
O1–Ca1–Cl2	93.59(5)	O2–Ca1–O1#1	77.98(5)	O2#3–Ca1–O1	83.20(8)	O1–Ca–O4	95.92(5)
O3–Ca1–Cl1#1	86.44(6)	O3–Ca1–O1	74.94(8)	O2#1–Ca1–O1#2	83.20(8)	O2#1–Ca–O4#1	84.91(4)
O4–Ca1–Cl1#1	81.56(5)	O3#1–Ca1–O1	142.82(8)	O2–Ca1–O1#2	81.85(9)	O2–Ca–O4#1	128.83(4)
O2–Ca1–Cl1#1	93.91(5)	O2#1–Ca1–O1	77.98(5)	O2#2–Ca1–O1#2	64.67(8)	O1#1–Ca–O4#1	95.92(5)
O1–Ca1–Cl1#1	93.89(5)	O2–Ca1–O1	65.05(5)	O2#3–Ca1–O1#2	133.46(7)	O1–Ca–O4#1	161.23(4)
Cl2–Ca1–Cl1#1	166.96(3)	O1#1–Ca1–O1	127.32(8)	O1–Ca1–O1#2	130.21(11)	O4–Ca–O4#1	75.89(6)
O3–Ca1–Cl1	74.42(5)	O3–Ca1–O4	79.80(8)	O2#1–Ca1–O1#3	81.85(9)	O2#1–Ca–O3	78.82(4)
O4–Ca1–Cl1	80.28(5)	O3#1–Ca1–O4	71.85(9)	O2–Ca1–O1#3	83.20(8)	O2–Ca–O3	125.95(5)
O2–Ca1–Cl1	144.48(5)	O2#1–Ca1–O4	81.08(6)	O2#2–Ca1–O1#3	133.46(8)	O1#1–Ca–O3	144.10(4)
O1–Ca1–Cl1	151.77(4)	O2–Ca1–O4	136.77(6)	O2#3–Ca1–O1#3	64.67(8)	O1–Ca–O3	87.53(4)
Cl2–Ca1–Cl1	83.40(2)	O1#1–Ca1–O4	132.22(6)	O1–Ca1–O1#3	135.37(12)	O4–Ca–O3	50.50(4)
Cl1#1–Ca1–Cl1	84.964(19)	O1–Ca1–O4	71.72(7)	O1#2–Ca1–O1#3	69.06(10)	O4#1–Ca–O3	74.19(5)
Ca1#2–Cl1–Ca1	128.62(2)	O3–Ca1–O4#1	71.85(9)	O2#1–Ca1–O1#1	64.67(8)	O2#1–Ca–O3#1	125.95(5)
C1–O1–Ca1	123.75(13)	O3#1–Ca1–O4#1	79.80(8)	O2–Ca1–O1#1	133.46(8)	O2–Ca–O3#1	78.82(4)
C2–O2–Ca1	119.00(14)	O2#1–Ca1–O4#1	136.77(6)	O2#2–Ca1–O1#1	83.20(8)	O1#1–Ca–O3#1	87.53(4)
		O2–Ca1–O4#1	81.08(6)	O2#3–Ca1–O1#1	81.85(9)	O1–Ca–O3#1	144.10(4)
		O1#1–Ca1–O4#1	71.72(7)	O1–Ca1–O1#1	69.06(10)	O4–Ca–O3#1	74.19(5)
		O1–Ca1–O4#1	132.22(6)	O1#2–Ca1–O1#1	135.37(12)	O4#1–Ca–O3#1	50.50(4)
		O4–Ca1–O4#1	132.36(11)	O1#3–Ca1–O1#1	130.21(11)	O3–Ca–O3#1	109.66(6)
		C1–O1–Ca1	120.13(12)	C1–O1–Ca1	120.76(17)	C1–O1–Ca	118.36(10)
		C2–O2–Ca1	117.12(13)	C2–O2–Ca1	118.11(19)	C2–O2–Ca	122.16(9)
O1–C1–C2	105.8(2)	O1–C1–C2	107.80(17)	O1–C1–C2	106.0(2)	O1–C1–C2	107.88(13)
O1–C1–C1#3	109.3(2)	O1–C1–C1#2	108.3(2)	O1–C1–C1#4	108.8(3)	O2–C2–C1	107.56(11)
C2–C1–C1#3	113.4(2)	C2–C1–C1#2	113.5(2)	C2–C1–C1#4	113.6(3)	O2–C2–C2#2	108.16(14)
O2–C2–C1	106.96(19)	O2–C2–C1	107.28(17)	O2–C2–C1	107.5(3)	C1–C2–C2#2	112.79(16)

^a Symmetry transformations used to generate equivalent atoms: [CaE(I)] #1, $-x, y - 1/2, -z + 1/2$; #2, $-x, y + 1/2, -z + 1/2$; #3, $-x, -y + 1, -z + 1$; [CaE(II)] #1, $-x, y, -z + 1/2$; #2, $-x, -y + 1, -z$; [CaE(III)] #1, $-x + 1/4, y, -z + 1/4$; #2, $-x + 1/4, -y + 1/4, z$; #3, $x, -y + 1/4, -z + 1/4$; #4, $-x, -y, -z$; (CaEN) #1, $-x, y, -z + 3/2$; #2, $-x, -y + 1, -z + 1$.

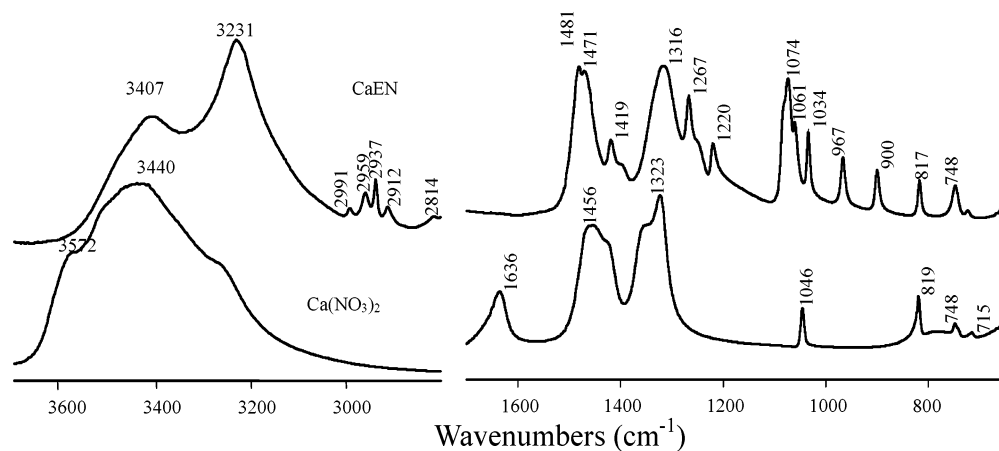
2.6 Å. However, three of the five general features encounter contrary examples: no water molecule coordinates to Ca²⁺ for CaE(III), chloride anions also coordinate to Ca²⁺, and the calcium ion is only coordinated to one erythritol molecule for CaE(I), which indicates that the coordination of metal ions to carbohydrates is complicated. Chloride anions also have the chance to coordinate to metal ions to reach the coordination numbers of metal ions. It has to be mentioned that the crystals of CaE(I) and CaE(II) were taken from the same bottle. Three calcium chloride–erythritol complexes have been characterized. Among them the single crystals of two CaCl₂–erythritol complexes were grown in a bottle and obtained from the same equimolar solution, and two crystal structure results show that the molar ratios of metal to sugar are 1:1 and 2:1. The preparation of the three CaCl₂–erythritol

complexes was via similar processes, and the original molar ratio of CaCl₂ to erythritol is 1:1 for the three complexes. Therefore, there should be an equilibrium of several coordinations in solution, and maybe the products in the solid state will be one or two of them. Two single crystals of CaE(I) and CaE(II) having different shapes were obtained in a bottle in our experiment, but one was isolated earlier, the other later. The single crystal of CaE(III) was prepared in another experiment. Erythritol is able to form several complexes with metal ions, and they were obtained together, which indicates that different metal–sugar complexes should have similar energies and show the high reactivity and complexity of carbohydrate coordination to metal ions. Various coordination structures exist in the metal–sugar adduct systems for a simple alditol, which implies that the

Table 2. Hydrogen Bond Data for the Structures of Three CaCl_2 - and $\text{Ca}(\text{NO}_3)_2$ -Erythritol Complexes^a

	D-H...A	$d(\text{D}-\text{H})$ (Å)	$d(\text{H}\cdots\text{A})$ (Å)	$d(\text{D}\cdots\text{A})$ (Å)	$\angle(\text{D}-\text{H}\cdots\text{A})$ (deg)
CaE(I)	O1-H1...Cl2#4	0.817(16)	2.299(17)	3.1104(17)	173(2)
	O2-H2...Cl2#5	0.792(17)	2.350(19)	3.1312(18)	169(4)
	O3-H31...Cl1#2	0.921(16)	2.351(18)	3.2627(19)	171(3)
	O3-H32...Cl2#5	0.928(17)	2.386(18)	3.2746(19)	160(3)
	O4-H41...Cl1#6	0.933(16)	2.290(18)	3.1950(18)	163(2)
CaE(II)	O4-H42...Cl1#4	0.902(17)	2.468(18)	3.3658(19)	174(3)
	O1-H1...Cl1#3	0.821(18)	2.384(16)	3.1855(16)	166(3)
	O2-H2...Cl1	0.814(18)	2.341(19)	3.1500(16)	172(5)
	O3-H31...Cl1#4	0.921(18)	2.44(2)	3.329(3)	163(4)
	O3-H32...Cl1#5	0.919(18)	2.62(3)	3.411(3)	145(4)
CaE(III)	O4-H41...Cl1#1	0.964(19)	2.30(3)	3.180(2)	152(4)
	O4-H42...Cl1#3	0.956(18)	2.50(2)	3.432(2)	166(4)
	O1-H1...Cl1	0.826(19)	2.287(17)	3.086(3)	163(3)
	O2-H2...OW	0.798(19)	1.95(2)	2.725(6)	164(4)
CaEN	OW-HW1...OW#5	0.974(19)	2.57(5)	2.803(13)	94(4)
	OW-HW2...OW#6	0.936(19)	2.02(4)	2.772(12)	136(4)
	O1-HO1...O3#3	0.78(2)	2.23(2)	2.9966(18)	171(2)
	O2-HO2...O4#4	0.78(2)	1.96(2)	2.7305(17)	169(2)

^a Symmetry transformations used to generate equivalent atoms: [CaE(I)] #1, $-x, y - 1/2, -z + 1/2$; #2, $-x, y + 1/2, -z + 1/2$; #3, $-x, -y + 1, -z + 1$; #4, $x, y - 1, z$; #5, $x - 1, y, z$; #6, $-x + 1, y - 1/2, -z + 1/2$; [CaE(II)] #1, $-x, y, -z + 1/2$; #2, $-x, -y + 1, -z$; #3, $x + 1/2, -y + 1/2, z - 1/2$; #4, $-x - 1/2, y - 1/2, -z + 1/2$; #5, $-x - 1/2, -y + 1/2, -z$; [CaE(III)] #1, $-x + 1/4, y, -z + 1/4$; #2, $-x + 1/4, y, -z + 1/4, z$; #3, $x, -y + 1/4, -z + 1/4$; #4, $-x, -y, -z$; #5, $-x - 1/2, -y + 1/2, -z$; #6, $-x - 1/4, -y + 3/4, z$; (CaEN) #1, $-x, y, -z + 3/2$; #2, $-x, -y + 1, -z + 1$; #3, $-x - 1/2, y + 1/2, -z + 3/2$; #4, $-x, -y, -z + 1$.

**Figure 5.** FT-IR spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$.

interactions between metal ions and the sugar residue of biomolecules will be more complicated. Compared with another Ca^{2+} -alditol complex, $\text{CaCl}_2 \cdot \text{galactitol} \cdot 4\text{H}_2\text{O}$, galactitol ($\text{C}_6\text{H}_{14}\text{O}_6$) provides O2,3 to coordinate with one Ca^{2+} , and O4,5 to coordinate with another Ca^{2+} .^{13h} It has been shown that alditol molecules often use two adjacent hydroxyl groups to coordinate with Ca^{2+} .

Most of the works about crystal structures of metal ion–sugar complexes are limited to the chloride solution system. Here metal nitrates were used as reactants to detect the coordination structures of hydroxyl groups of saccharides in different environments. The FT-IR spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ (CaEN) are shown in Figure 5. After complexation OH vibrations of water molecules for $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ located at 3572 and 3440 cm^{-1} have shifted to lower frequencies, 3407 and 3231 cm^{-1} , assigned to the ν_{OH} of erythritol. The appearance of CH stretching vibrations (2991, 2959, 2937, 2912, and 2814 cm^{-1}) and the absent of $\delta_{\text{H}_2\text{O}}$ vibrations (1636 cm^{-1} for $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) indicate the coordination of the saccharide and that no water exists in the structure. Furthermore, the presence of bands at 1074

and 1061 cm^{-1} (mainly C–O stretching vibrations of the saccharide) and other bands indicates the coordination of erythritol. For the alkaline-earth-metal nitrate–erythritol complex, Ca^{2+} is coordinated to four hydroxyl groups from two erythritol molecules and four oxygen atoms from two nitrate ions. The coordination number (CN) of Ca^{2+} is 8 (Figure 6). Selected bond lengths and angles are listed in Table 1. Ca–O distances are from 2.3895 to 2.5824 Å, and the average Ca–O distance is 2.461 Å, which is longer than those of the three calcium chloride complexes. Each nitrate is a bidentate ligand and provides two oxygens to coordinate to Ca^{2+} . Each erythritol molecule provides two hydroxyl groups to coordinate to one Ca^{2+} , and two to another Ca^{2+} ; thus, a chain has formed and an extensive hydrogen bond network exists in the structure via two hydrogen bonds: O1–HO1...O3#3, 2.9966 Å; O2–HO2...O4#4, 2.7305 Å (Table 2). It is obvious that the two OH stretching vibrations, 3407 and 3231 cm^{-1} , are related to the two hydrogen bonds, 2.9966 and 2.7305 Å. For nitrate and chloride systems, erythritol has the same coordination manner, but different hydrogen bond networks have formed, and various 3D

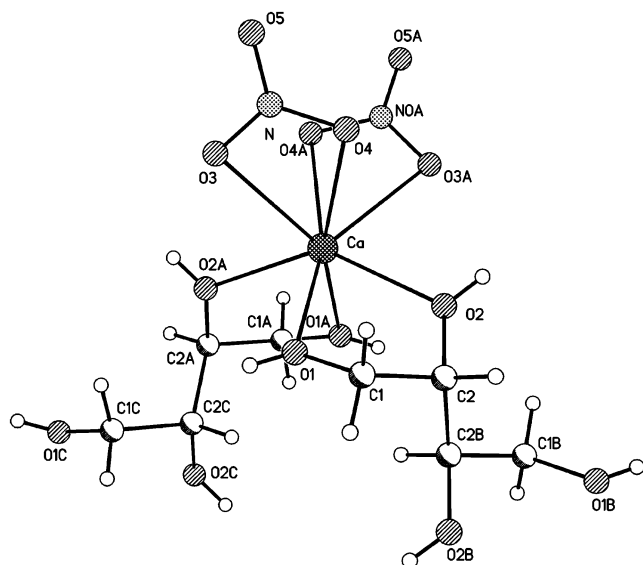


Figure 6. Structure and atom numbering scheme of CaEN.

structures have been found. The 3D structures are as follows: The chain of $[\text{Ca}(\text{NO}_3)_2(\text{C}_4\text{H}_{10}\text{O}_4)]_\infty$ forms a layer, and then the 3D structure for CaEN is formed by the above layers via hydrogen bonds. The T-shaped Ca nodes build a herringbone-like 2D net, and then the 3D structure is built by the above layers. Between the layers are numerous $\text{O}-\text{H}\cdots\text{Cl}$ H-bonds for CaE(I). The layer is built by the wavelike cationic chain of $[\text{Ca}(\text{H}_2\text{O})_4(\text{C}_4\text{H}_{10}\text{O}_4)]_\infty$ via $\text{O}-\text{H}\cdots\text{Cl}$ H-bonds and the 3D structures are built by the chains and Cl ions via $\text{O}-\text{H}\cdots\text{Cl}$ H-bonds for CaE(II). The diamond net is built from Ca ions and bridging $\text{C}_4\text{H}_{10}\text{O}_4$ ligands and the Cl ions and water molecules locate in the rhombic channels of the diamond net for CaE(III). Erythritol is a chain molecule, and it is suitable to use two hydroxyl

groups to coordinate to one metal ion and the other two to another metal ion; thus, a chain structure may be formed. The layer will form by the above chain and 3D structures will be built via hydrogen bonds, for example, for CaEN and CaE(II), but CaE(I) and CaE(III) have different 3D structures.

Structures of Lanthanide Chlorides and Nitrate–Erythritol Complexes. Lanthanide complexes are used for numerous applications, as catalysts for the cleavage of RNA and DNA or as luminescence probes in biology and medicine. Since the applications are related to the interaction between lanthanide ions and biological ligands, the study of the binding modes of lanthanide ions with carbohydrates is of interest. The IR spectra of lanthanide–erythritol complexes are shown in Figure 7. All of the bands are shifted compared with the IR spectrum of the erythritol molecule, including the strong broad ν_{OH} bands, ν_{CH} with decreased intensities, and the bands related to skeletal vibrations in the $1500\text{--}650\text{ cm}^{-1}$ region, which reveal that the hydroxyl groups of erythritol are involved in the coordination to metal ions. The hydrogen bond networks rearrange after complexation. The conformation of the erythritol skeleton is changed upon sugar metalation. The existence of three bending vibrations of water molecules indicates the coordination of water molecules to metal ions. These lanthanide complexes, from La to Tb, have similar spectra in the whole region, which indicates they have analogous structures. The molecular structure of PrE is shown in Figure 8. Pr^{3+} is coordinated to four hydroxyl groups from two erythritol molecules, four water molecules, and a chloride ion, and thus, the coordination number of Pr^{3+} is 9. The chain of $[\text{Pr}(\text{H}_2\text{O})_4(\text{C}_4\text{H}_{10}\text{O}_4)\text{Cl}]_\infty$ and the surrounding Cl ions (Cl2, Cl3) and water (O9, O10) are shown in Figure 8b. The chain runs along the body-

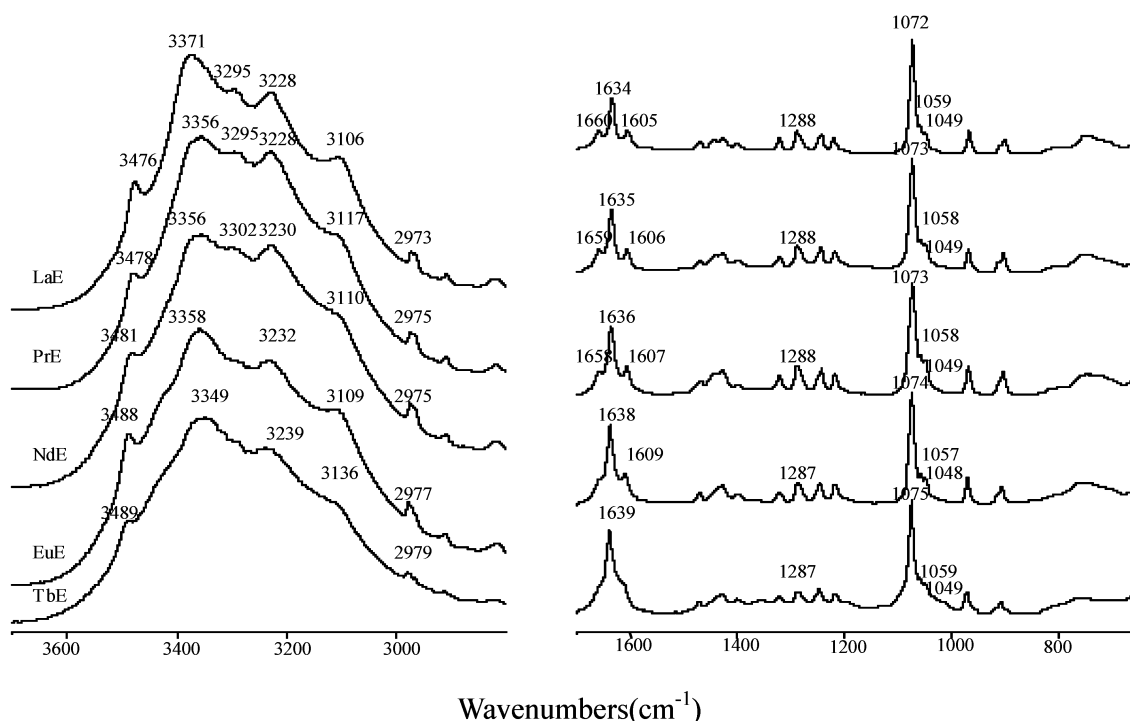


Figure 7. FT-IR spectra of lanthanide–erythritol complexes in the $3700\text{--}2800$ and $1700\text{--}650\text{ cm}^{-1}$ regions.

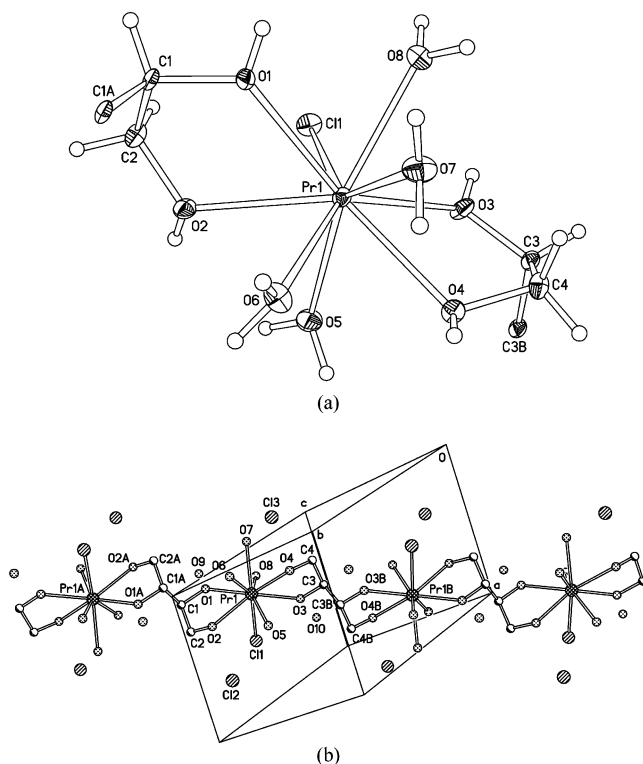


Figure 8. Structure and atom numbering scheme of PrE.

diagonal direction $b + c - a$. Thus, a hexagonal packing arrangement of the above chains is formed in the lattice; between them are Cl ions (Cl2, Cl3) and water molecules (O9, O10), which form numerous hydrogen bonds to the chains. NdE and PrE are isomorphous, which confirm the conclusion of the IR spectra. The results show that calcium and lanthanide ions have different coordination structures and lanthanide ions have a larger coordination number. Selected bond lengths and angles of PrE and NdE are listed in Table 3. Hydrogen bond data in the structures are listed in Table 4. Pr–O distances are from 2.436 to 2.568 Å for PrE. Nd–O distances are from 2.423 to 2.552 Å for NdE. The Pr–Cl distance is 2.9227, and the Nd–Cl distance is shorter, 2.9060 Å. Pr–O and Pr–Cl distances are longer than

Nd–O and Nd–Cl, which is consistent with the so-called lanthanoid contraction. Each OH forms a hydrogen bond with Cl[−] or water molecules; thus, the hydrogen bonds of lanthanide–erythritol complexes are more complicated than those of the three calcium chloride complexes. ν_{OH} vibrations of lanthanide complexes are strong broad bands in the IR spectra, which is consistent with the extensive hydrogen bond networks in the structures.

The FT-IR spectra of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ (NdEN) are shown in Figure 9. The change of OH vibrations, the existence of ν_{CH} vibrations, the absence of $\delta_{\text{H}_2\text{O}}$, the appearance of several bands in the 1200–1000 cm^{-1} region, and the shift of NO_3^- stretching vibrations show the coordination of the saccharide and nitrate ions. The crystal structure shown in Figure 10 confirms the above results of the IR spectra. Nd^{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. The coordination number of Nd^{3+} is 10 in NdEN, which is higher than the coordination number of rare-earth-metal ions in the lanthanide chloride–erythritol complexes. Nd–O distances are from 2.455 to 2.620 Å for NdEN, which is longer than the Nd–O distances in NdE. Each nitrate is a bidentate ligand coordinated to Nd^{3+} , which is consistent with its binding to Ca^{2+} . Erythritol serves as two bidentate ligands in the other six complexes, but here it serves as a three-hydroxyl donor, and ethanol also coordinates to the metal ion. Selected bond lengths and angles are listed in Table 3. An extensive hydrogen bond network between the hydroxyl groups of erythritol and ethanol and oxygen atoms of nitrate exists in the structure of NdEN, which is different from lanthanide chloride–erythritol complexes (Table 4). For three nitrate ions, two of them provide one oxygen atom to form hydrogen bonds, O6 and O13, respectively; another nitrate ion has more hydrogen bonds. Compared to the other metal–erythritol complexes, erythritol has a different coordination mode, and larger differences of C–C, C–O, C–C–C, and C–C–O have appeared; for example, C1–C2–C3 is 106.5°, O3–C3–C4 is 111.2°, O4–C4–C3 is 111.7°, and

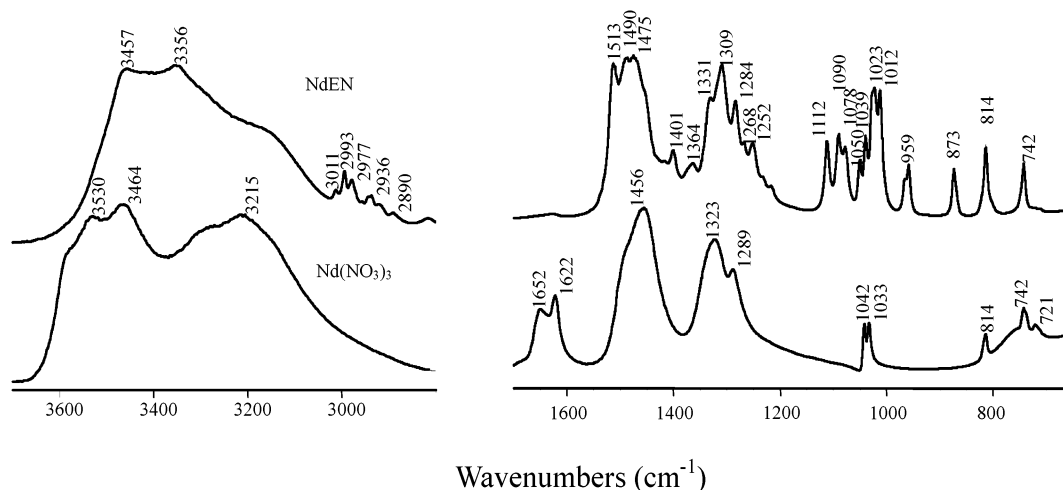


Figure 9. FT-IR spectra of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$.

Table 3. Selected Bond Lengths and Angles for PrE, NdE, and NdEN^a

PrE		NdE		NdEN	
Bond Lengths (Å)					
Pr1–O5	2.436(3)	Nd1–O5	2.423(4)	Nd1–O1	2.455(3)
Pr1–O6	2.457(4)	Nd1–O6	2.449(4)	Nd1–O5	2.458(3)
Pr1–O3	2.511(3)	Nd1–O3	2.492(4)	Nd1–O2	2.462(3)
Pr1–O1	2.514(3)	Nd1–O1	2.500(4)	Nd1–O12	2.515(3)
Pr1–O4	2.535(3)	Nd1–O4	2.520(4)	Nd1–O7	2.537(3)
Pr1–O8	2.540(3)	Nd1–O8	2.528(4)	Nd1–O9	2.541(3)
Pr1–O2	2.552(3)	Nd1–O2	2.529(4)	Nd1–O14	2.550(3)
Pr1–O7	2.568(4)	Nd1–O7	2.552(4)	Nd1–O3	2.569(3)
Pr1–Cl1	2.9227(14)	Nd1–Cl1	2.9060(15)	Nd1–O6	2.571(3)
O1–C1	1.453(6)	O1–C1	1.446(6)	Nd1–O10	2.620(3)
O2–C2	1.428(6)	O2–C2	1.433(6)	O1–C1	1.442(5)
O3–C3	1.435(6)	O3–C3	1.451(6)	O2–C2	1.432(5)
O4–C4	1.440(6)	O4–C4	1.442(6)	O3–C3	1.450(5)
C1–C2	1.507(7)	C1–C2	1.513(8)	O4–C4	1.420(5)
C1–C1#1	1.543(10)	C1–C1#1	1.527(11)	C1–C2	1.505(6)
C3–C4	1.496(7)	C3–C4	1.500(8)	C2–C3	1.524(6)
C3–C3#2	1.532(9)	C3–C3#2	1.538(11)	C3–C4	1.512(6)
Bond Angles (deg)					
O5–Pr1–O6	74.90(13)	O5–Nd1–O6	74.56(15)	O1–Nd1–O5	143.30(11)
O5–Pr1–O3	80.33(13)	O5–Nd1–O3	80.55(14)	O1–Nd1–O2	66.57(10)
O6–Pr1–O3	132.02(12)	O6–Nd1–O3	132.13(14)	O5–Nd1–O2	145.05(12)
O5–Pr1–O1	131.30(12)	O5–Nd1–O1	131.44(13)	O1–Nd1–O12	127.49(10)
O6–Pr1–O1	87.05(12)	O6–Nd1–O1	87.13(14)	O5–Nd1–O12	77.44(12)
O3–Pr1–O1	138.45(11)	O3–Nd1–O1	138.25(13)	O2–Nd1–O12	67.62(10)
O5–Pr1–O4	69.67(12)	O5–Nd1–O4	69.60(13)	O1–Nd1–O7	72.24(11)
O6–Pr1–O4	72.44(12)	O6–Nd1–O4	72.21(14)	O5–Nd1–O7	74.48(11)
O3–Pr1–O4	60.53(11)	O3–Nd1–O4	60.89(12)	O2–Nd1–O7	116.22(10)
O1–Pr1–O4	146.14(12)	O1–Nd1–O4	145.84(13)	O12–Nd1–O7	107.64(11)
O5–Pr1–O8	149.11(13)	O5–Nd1–O8	149.19(15)	O1–Nd1–O9	72.52(10)
O6–Pr1–O8	134.51(12)	O6–Nd1–O8	134.71(14)	O5–Nd1–O9	80.91(12)
O3–Pr1–O8	71.88(12)	O3–Nd1–O8	71.61(14)	O2–Nd1–O9	133.98(10)
O1–Pr1–O8	69.30(11)	O1–Nd1–O8	69.34(13)	O12–Nd1–O9	158.28(11)
O4–Pr1–O8	106.31(12)	O4–Nd1–O8	106.27(13)	O7–Nd1–O9	67.62(10)
O5–Pr1–O2	70.16(12)	O5–Nd1–O2	70.22(13)	O1–Nd1–O14	142.14(10)
O6–Pr1–O2	70.04(12)	O6–Nd1–O2	70.21(13)	O5–Nd1–O14	73.75(11)
O3–Pr1–O2	136.57(12)	O3–Nd1–O2	136.43(14)	O2–Nd1–O14	83.13(10)
O1–Pr1–O2	61.16(11)	O1–Nd1–O2	61.25(12)	O12–Nd1–O14	50.19(11)
O1–C1–C2	106.9(4)	O1–C1–C2	105.8(4)	O1–C1–C2	109.0(3)
O1–C1–C1#1	107.3(5)	O1–C1–C1#1	108.0(5)	O2–C2–C1	108.2(3)
C2–C1–C1#1	114.1(5)	C2–C1–C1#1	113.7(6)	O2–C2–C3	104.6(3)
O2–C2–C1	106.9(4)	O2–C2–C1	107.2(4)	C1–C2–C3	116.5(4)
O3–C3–C4	105.8(4)	O3–C3–C4	105.1(4)	O3–C3–C4	111.2(4)
O3–C3–C3#2	108.8(5)	O3–C3–C3#2	108.0(5)	O3–C3–C2	107.0(3)
C4–C3–C3#2	113.9(5)	C4–C3–C3#2	113.9(6)	C4–C3–C2	113.0(4)
O4–C4–C3	106.0(4)	O4–C4–C3	106.3(4)	O4–C4–C3	111.7(4)
				O5–C5–C6	111.1(4)

^a Symmetry transformations used to generate equivalent atoms: (PrE) #1, $-x, -y + 2, -z + 2$; #2, $-x + 1, -y + 1, -z + 1$; (NdE) #1, $-x, -y + 2, -z + 2$; #2, $-x + 1, -y + 1, -z + 1$; (NdEN) #1, $-x, -y + 1, -z + 1$; #2, $-x, y - 1/2, -z + 1/2$; #3, $-x, y + 1/2, -z + 1/2$; #4, $x - 1, y, z$; #5, $-x, -y + 1, -z$.

O2–C2–C3 is 104.6(3)°, which is related to the special binding site of erythritol being different from the others.

The first single-crystal structure of a lanthanide–saccharide complex (2PrCl₃·galactitol·14H₂O) was reported in 1993.¹⁶ Since then a series of crystal structures of lanthanide ion–galactitol, *-myo*-inositol, and *-D*-ribose complexes have been reported in the literature.^{13a–g} Lanthanide ions often have higher coordination numbers; the CN is 9 and 10 here, which is consistent with previously reported results. Some lanthanide ions, for instance, Pr³⁺, Nd³⁺, and Sm³⁺, would have coordination modes similar to those of galactitol, *myo*-inositol, and α -*D*-ribofuranose. Here these lanthanide ions, from LaCl₃ to TbCl₃, may have similar coordination modes with erythritol, but it is not true that all of the lanthanide ions have similar coordination to carbohydrates;

for example, two lanthanum–galactitol complexes different from other lanthanide–galactitol complexes have been characterized,¹³ⁱ which reflects the coordination variety of lanthanide ions. Compared with the results previously reported, different saccharides have various coordination structures: *D*-ribose provides *ax*–*eq*–*ax* hydroxyl groups to coordinate to metal ions; *myo*-inositol uses two adjacent hydroxyl groups to bind to metal ions; galactitol usually supplies three hydroxyl groups to one metal ion and the other three to another. Here the results of metal ion–erythritol complexes indicate that the bindings of metal ions to carbohydrates are very complicated: metal ions may bind to carbohydrates to form complexes with different M:L molar ratios, and sugars may have various binding sites; for example, two binding modes of erythritol to metal ions have been found (Figure 11). Table 5 is the summary of coordina-

(16) Angyal S. J.; Craig D. C. *Carbohydr. Res.* **1993**, *241*, 1–8.

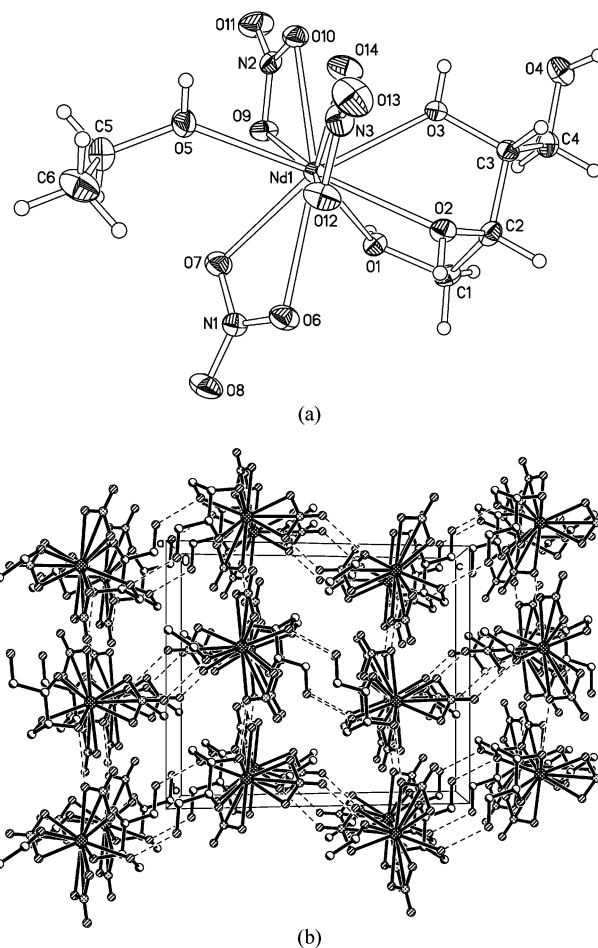
Table 4. Hydrogen Bond Data for the Structures of PrE, NdE, and NdEN^a

	D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(D—H···A) (deg)
PrE	O1—H1···O9	0.816(19)	1.91(2)	2.721(5)	173(5)
	O2—H2···C12	0.813(19)	2.320(19)	3.131(4)	174(5)
	O3—H3···O10	0.823(19)	1.85(2)	2.671(5)	174(5)
	O4—H4···C13	0.822(19)	2.20(2)	3.011(4)	168(5)
	O5—H51···C12	0.949(19)	2.21(3)	3.126(4)	162(6)
	O5—H52···C12#3	0.954(19)	2.31(2)	3.265(4)	174(5)
	O6—H61···C12#4	0.951(19)	2.22(2)	3.153(4)	168(5)
	O6—H62···C13#5	0.945(19)	2.18(2)	3.117(4)	169(5)
	O7—H71···C13	0.973(19)	2.41(3)	3.290(4)	151(5)
	O7—H72···C11#4	0.95(2)	2.27(2)	3.209(4)	169(6)
O8—H81···O9#6	0.932(19)	1.93(3)	2.799(5)	155(6)	
O8—H82···C11#7	0.930(19)	2.40(2)	3.325(4)	170(5)	
O9—H91···O10#7	0.96(2)	2.03(5)	2.844(6)	142(6)	
O9—H92···C13#8	0.940(19)	2.22(3)	3.110(4)	158(6)	
O10—H101···C11#7	0.952(19)	2.25(2)	3.196(4)	174(6)	
O10—H102···C12#9	0.960(19)	2.15(2)	3.107(4)	175(7)	
NdE	O1—H1···O9	0.83(2)	1.90(3)	2.721(6)	170(8)
	O2—H2···C12	0.82(2)	2.315(19)	3.130(4)	174(4)
	O3—H3···O10	0.82(2)	2.12(7)	2.677(6)	125(7)
	O4—H4···C13	0.82(2)	2.24(4)	3.005(4)	156(7)
	O5—H51···C12	0.94(2)	2.21(3)	3.133(4)	167(7)
	O5—H52···C12#3	0.949(19)	2.42(5)	3.250(5)	146(6)
	O6—H61···C12#4	0.96(2)	2.21(3)	3.151(4)	165(6)
	O6—H62···C13#5	0.96(2)	2.18(3)	3.106(4)	163(6)
	O7—H71···C13	0.95(2)	2.36(2)	3.305(5)	178(6)
	O7—H72···C11#4	0.95(2)	2.28(3)	3.208(4)	165(6)
O8—H81···O9#6	0.946(19)	1.86(3)	2.794(6)	168(6)	
O8—H82···C11#7	0.94(2)	2.41(3)	3.331(4)	166(6)	
O9—H91···O10#7	0.95(2)	1.94(5)	2.841(7)	158(10)	
O9—H92···C13#8	0.95(2)	2.20(4)	3.116(5)	162(8)	
O10—H101···C11#7	0.96(2)	2.24(2)	3.194(5)	172(8)	
O10—H102···C12#9	0.96(2)	2.21(6)	3.098(4)	153(9)	
NdEN	O1—H1···O4#1	0.795(18)	1.91(2)	2.692(4)	171(3)
	O2—H2···O10#2	0.783(18)	2.08(2)	2.848(4)	166(3)
	O2—H2···O11#2	0.783(18)	2.57(4)	3.119(5)	128(5)
	O3—H3···O6#3	0.803(18)	2.140(19)	2.935(4)	170(5)
	O4—H4···O11#4	0.82	2.17	2.962(5)	161.8
O4—H4···O9#4	0.82	2.54	3.221(5)	141.0	
O5—H5···O13#5	0.807(18)	2.05(2)	2.839(5)	165(3)	

^a Symmetry transformations used to generate equivalent atoms: (PrE) #1, $-x, -y + 2, -z + 2$; #2, $-x + 1, -y + 1, -z + 1$; #3, $-x + 1, -y + 2, -z + 1$; #4, $x - 1, y, z$; #5, $-x, -y + 2, -z + 1$; #6, $-x, -y + 1, -z + 2$; #7, $-x + 1, -y + 1, -z + 2$; #8, $x, y, z + 1$; #9, $x, y - 1, z$; (NdE) #1, $-x, -y + 2, -z + 2$; #2, $-x + 1, -y + 1, -z + 1$; #3, $-x + 1, -y + 2, -z + 1$; #4, $x - 1, y, z$; #5, $-x, -y + 2, -z + 1$; #6, $-x, -y + 1, -z + 2$; #7, $-x + 1, -y + 1, -z + 2$; #8, $x, y, z + 1$; #9, $x, y - 1, z$; (NdEN) #1, $-x, -y + 1, -z + 1$; #2, $-x, y - 1/2, -z + 1/2$; #3, $-x, y + 1/2, -z + 1/2$; #4, $x - 1, y, z$; #5, $-x, -y + 1, -z$.

tion of metal ions to erythritol, which shows the different coordinations of calcium and lanthanide ions. Although lanthanide ions are often used as probes of calcium ion, they have different coordination structures to carbohydrates and various hydrogen bond networks in the solid state. While they coordinate to the same carbohydrate molecule, different coordination numbers may be observed. When the reactants are metal nitrates, Ca²⁺ and Nd³⁺ also have different coordinations because of the alteration of their charge and radius.

FT-IR spectroscopy is used to characterize the formation of metal–carbohydrate complexes and deduce unknown structures from the similarity of the IR spectra here. According to the X-ray diffraction and IR spectroscopy results for alkaline-earth-metal and rare-earth-metal ion–erythritol complexes, different metal ions have various coordination modes. It is often difficult to know whether the compounds isolated and structurally characterized were

**Figure 10.** Structure and atom numbering scheme of NdEN.**Figure 11.** Binding mode of erythritol to metal ions.

indeed the major species present in solution, especially when mixtures of complexes are obtained. Maybe the structures in solution are not the same as those in the solid state, but the results in this paper give us a model to understand the coordination of metal ions to carbohydrates in solution.

Conclusions

The results presented here serve as a comparison of how carbohydrate coordinates to various metal ions using X-ray diffraction and FT-IR spectroscopy. Because sugar residues have a crucial role in biochemical processes (molecular recognition and so on), the interactions between metal ions and carbohydrates are important, but they are also complicated since various coordination structures may occur; for instance, three CaCl₂–erythritol complexes have been obtained here, showing that metal ions may bind to carbohydrates to form complexes with different M:L molar ratios and sugars may have various binding sites. It has been shown that a saccharide lacking anchor groups can be bound as two bidentate chelating ligands or as a three-hydroxyl donor,

Table 5. Chelation Data for the Metal Shell of Metal Complexes of Uncharged Erythritol

stoichiometry	space group	no. of OH groups	no. of E molecules	no. of H ₂ O molecules	no. of Cl ⁻ ions	no. of NO ₃ ⁻ ions	CN	M–O distance (Å)	M–Cl distance (Å)
2CaCl ₂ ·C ₄ H ₁₀ O ₄ ·4H ₂ O	<i>P2₁/c</i>	2	1	2	3 ^a		7	2.3954–2.4184	2.7171–2.9567
CaCl ₂ ·C ₄ H ₁₀ O ₄ ·4H ₂ O	<i>C2/c</i>	4	2	4	0		8	2.418–2.4647	
CaCl ₂ ·2C ₄ H ₁₀ O ₄ ·4H ₂ O	<i>Fddd</i>	8	4	0	0		8	2.416, 2.454	
PrCl ₃ ·C ₄ H ₁₀ O ₄ ·6H ₂ O	<i>P1</i>	4	2	4	1		9	2.436–2.568	2.9227
NdCl ₃ ·C ₄ H ₁₀ O ₄ ·6H ₂ O	<i>P1</i>	4	2	4	1		9	2.423–2.552	2.9060
Ca(NO ₃) ₂ ·C ₄ H ₁₀ O ₄	<i>C2/c</i>	4	2	0		2	8	2.3895–2.5824	
Nd(NO ₃) ₃ ·C ₄ H ₁₀ O ₄ ·C ₂ H ₅ OH	<i>P2₁/c</i>	3	1	0		3	10	2.455–2.620	

^a 2- μ -Cl.

which is neither oxidized nor deprotonated upon complexation. When the reactants are metal chloride or nitrates, the products are related to the saccharide, chloride ions, nitrates, water molecules, and ethanol (crystallization medium and reaction solvents), which competitively coordinate with metal ions. Alkaline-earth-metal and lanthanide ions have different coordination structures.

Experimental Section

Physical Measurements. Infrared spectra were measured on a Nicolet Magna-IR 750 spectrometer using the micro-IR method with 64 scans at 4 cm⁻¹ resolution. Elemental analyses were carried out with an Elementar Vario EL elemental analyzer.

Synthesis. Erythritol (Sigma) and the other reagents were obtained from commercial sources and were used as supplied. Lanthanide chlorides were prepared and crystallized from the corresponding RE oxide of high purity (99.99%). MCl₂·*x*C₄H₁₀O₄·*n*H₂O complexes were prepared by mixing erythritol (3 mmol) and metal chlorides (6 or 3 mmol) in H₂O/EtOH solvents and heating with the addition of EtOH to make a concentrated solution, which was cooled for crystallization at room temperature. The metal nitrate–erythritol complexes Ca(NO₃)₂·C₄H₁₀O₄ and Nd(NO₃)₃·C₄H₁₀O₄·C₂H₅OH were synthesized following the same procedure, and metal chlorides were replaced by metal nitrates. The elemental analysis results are as follows. Anal. Calcd for LaCl₃·C₄H₁₀O₄·6H₂O (LaE): C, 10.10; H, 4.77. Found: C, 10.12; H, 4.77. Anal. Calcd for PrCl₃·C₄H₁₀O₄·6H₂O (PrE): C, 10.06; H, 4.64. Found: C, 10.19; H, 4.79. Anal. Calcd for NdCl₃·C₄H₁₀O₄·6H₂O (NdE): C, 9.99; H 3.93. Found: C, 10.00; H, 4.38. Anal. Calcd for Ca(NO₃)₂·C₄H₁₀O₄ (CaEN): C, 16.78; H, 3.52; N, 9.79. Found: C, 16.55; H, 3.557; N, 8.37. Anal. Calcd for Nd(NO₃)₃·C₄H₁₀O₄·C₂H₅OH (NdEN): C, 14.45; H, 3.24; N, 8.43. Found: C, 14.53; H, 3.24; N, 7.68. Anal. Calcd for 2CaCl₂·C₄H₁₀O₄·4H₂O (CaE(I)): C, 11.54; H, 4.36. Found: C, 15.26; H, 4.20. Anal. Calcd for CaCl₂·2C₄H₁₀O₄·4H₂O (CaE(III)): C, 22.49; H, 6.60. Found: C, 25.30; H, 5.94.

Structural Analysis of Seven Complexes, CaE(I), CaE(II), CaE(III), CaEN, PrE, NdE, and NdEN. X-ray crystallographic data of three CaCl₂–erythritol complexes, two LnCl₃–erythritol and Nd(NO₃)₃·C₄H₁₀O₄·C₂H₅OH complexes were collected on a NON-IUS KappaCCD diffractometer, and the data for Ca(NO₃)₂·C₄H₁₀O₄ were collected on a Rigaku RAXIS RAPID IP spectrometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073\text{Å}$) at room temperature (293 K). The structures of all seven compounds were solved with SHELX-97 and refined using the full-matrix least-squares on *F*² method. The direct method was used for primary solution and difmap for secondary solution. Empirical absorption corrections have been done, and the addition and treatment of hydrogen atoms are according to the geometric and mixed methods.

Crystal Data for CaE(I). 2CaCl₂·C₄H₁₀O₄·4H₂O, fw = 416.14; colorless block, 0.45 × 0.37 × 0.33 mm³; monoclinic, *P2₁/c*; *a* = 6.1950(2) Å, *b* = 5.9745(2) Å, *c* = 21.3602(10) Å, $\alpha = 90^\circ$, $\beta = 92.4364(14)^\circ$, $\gamma = 90^\circ$, *Z* = 2, *V* = 0.789.87(5) Å³; *D_c* = 1.750 g/cm³; $\mu = 1.420\text{ mm}^{-1}$; maximum and minimum transmission factors, 0.632 and 0.558; θ range for cell measurement and data collection, 3.54–27.39°; completeness to $\theta = 27.39^\circ$, 99.3%; limiting indices, $-8 \leq h \leq +8$, $-7 \leq k \leq +7$, $-27 \leq l \leq +27$; 9253 reflections collected, 1782 unique [*R*(int) = 0.0809]; number of data/restraints/parameters, 1782/10/102; final GOF, 0.971; *R*1 = 0.0350 [1194 reflections, *I* > 2 σ (*I*)], *wR*2 = 0.0533; *R* indices (all data), *R*1 = 0.0753, *wR*2 = 0.0605; extinction coefficient, 0.231(5); largest diffraction peak and hole, 0.325 and $-0.339\text{ e} \cdot \text{Å}^{-3}$.

Crystal Data for CaE(II). CaCl₂·C₄H₁₀O₄·4H₂O, fw = 305.16; colorless column, 0.40 × 0.15 × 0.12 mm³; monoclinic, *C2/c*; *a* = 12.8561(5) Å, *b* = 10.6094(5) Å, *c* = 9.1925(4) Å, $\alpha = 90^\circ$, $\beta = 92.930(3)^\circ$, $\gamma = 90^\circ$, *Z* = 4, *V* = 0.1252.18(9) Å³; *D_c* = 1.619 g/cm³; $\mu = 0.947\text{ mm}^{-1}$; maximum and minimum transmission factors, 0.898 and 0.846; θ range for cell measurement and data collection, 3.84–27.46°; completeness to $\theta = 27.46^\circ$, 98.1%; limiting indices, $-16 \leq h \leq +16$, $-13 \leq k \leq +13$, $-11 \leq l \leq +11$; 12195 reflections collected, 1403 unique [*R*(int) = 0.0597]; number of data/restraints/parameters, 1403/10/89; final GOF, 1.034; *R*1 = 0.0341 [1048 reflections, *I* > 2 σ (*I*)], *wR*2 = 0.0774; *R* indices (all data), *R*1 = 0.0571, *wR*2 = 0.0857; extinction coefficient, 0.0171(15); largest diffraction peak and hole, 0.259 and $-0.238\text{ e} \cdot \text{Å}^{-3}$.

Crystal Data for CaE(III). CaCl₂·2C₄H₁₀O₄·4H₂O, fw = 427.28; colorless block, 0.50 × 0.40 × 0.22 mm³; orthorhombic, *Fddd*; *a* = 11.6282(3) Å, *b* = 15.3443(4) Å, *c* = 22.2933(7) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *Z* = 8, *V* = 0.3977.72(19) Å³; *D_c* = 1.427 g/cm³; $\mu = 0.633\text{ mm}^{-1}$; maximum and minimum transmission factors, 0.875 and 0.798; θ range for cell measurement and data collection, 3.51–27.45°; completeness to $\theta = 27.45^\circ$, 99.8%; limiting indices, $-15 \leq h \leq +15$, $-19 \leq k \leq +19$, $-28 \leq l \leq +28$; 19225 reflections collected, 1141 unique [*R*(int) = 0.0496]; number of data/restraints/parameters, 1141/7/69; final GOF, 1.085; *R*1 = 0.0631 [970 reflections, *I* > 2 σ (*I*)], *wR*2 = 0.1919; *R* indices (all data), *R*1 = 0.0711, *wR*2 = 0.1990; extinction coefficient, 0.0032(8); largest diffraction peak and hole, 0.707 and $-0.542\text{ e} \cdot \text{Å}^{-3}$.

Crystal Data for CaEN. Ca(NO₃)₂·C₄H₁₀O₄, fw = 286.22; colorless block, 0.35 × 0.3 × 0.3 mm³; monoclinic, *C2/c*; *a* = 12.602(3) Å, *b* = 8.0889(16) Å, *c* = 10.521(2) Å, $\beta = 99.49(3)^\circ$, *Z* = 2, *V* = 1057.8(4) Å³; *D_c* = 0.899 g/cm³; $\mu = 0.323\text{ mm}^{-1}$; maximum and minimum transmission factors, 0.908 and 0.596; θ range for cell measurement and data collection, 3.00–27.48°; completeness to $\theta = 27.48^\circ$, 98.3%; limiting indices, $-16 \leq h \leq +16$, $-10 \leq k \leq +10$, $-13 \leq l \leq +13$; 3977 reflections collected, 1201 unique [*R*(int) = 0.0686]; number of data/restraints/

parameters, 1201/0/87; final GOF, 1.053; $R1 = 0.0346$ [1021 reflections, $I > 2\sigma(I)$], $wR2 = 0.0903$; R indices (all data), $R1 = 0.0445$, $wR2 = 0.0959$; extinction coefficient, 0.065(4); largest diffraction peak and hole, 0.434 and $-0.376 \text{ e} \cdot \text{\AA}^{-3}$.

Crystal Data for PrE. $\text{PrCl}_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot 6\text{H}_2\text{O}$, $fw = 477.48$; light green block, $0.40 \times 0.28 \times 0.23 \text{ mm}^3$; triclinic, $P\bar{1}$; $a = 7.5099(3) \text{ \AA}$, $b = 10.1860(3) \text{ \AA}$, $c = 10.4213(3) \text{ \AA}$, $\alpha = 85.3935(14)^\circ$, $\beta = 84.2916(14)^\circ$, $\gamma = 78.6868(14)^\circ$, $Z = 2$, $V = 776.31(4) \text{ \AA}^3$; $D_c = 2.043 \text{ g/cm}^3$; $\mu = 3.689 \text{ mm}^{-1}$; maximum and minimum transmission factors, 0.885 and 0.705; θ range for cell measurement and data collection, $3.49\text{--}27.19^\circ$; completeness to $\theta = 27.19^\circ$, 98.2%; limiting indices, $-9 \leq h \leq +9$, $-13 \leq k \leq +13$, $-13 \leq l \leq +13$; 15745 reflections collected, 3409 unique [$R(\text{int}) = 0.0878$]; number of data/restraints/parameters, 3409/26/214; final GOF, 0.993; $R1 = 0.0368$ [2675 reflections, $I > 2\sigma(I)$], $wR2 = 0.0734$; R indices (all data), $R1 = 0.0578$, $wR2 = 0.0798$; extinction coefficient, 0.097(3); largest diffraction peak and hole, 0.878 and $-1.874 \text{ e} \cdot \text{\AA}^{-3}$.

Crystal Data for NdE. $\text{NdCl}_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot 6\text{H}_2\text{O}$, $fw = 480.81$; light purple block, $0.45 \times 0.45 \times 0.21 \text{ mm}^3$; triclinic, $P\bar{1}$; $a = 7.5056(3) \text{ \AA}$, $b = 10.1631(4) \text{ \AA}$, $c = 10.3943(4) \text{ \AA}$, $\alpha = 85.399(2)^\circ$, $\beta = 84.2317(17)^\circ$, $\gamma = 78.6292(15)^\circ$, $Z = 2$, $V = 771.90(5) \text{ \AA}^3$; $D_c = 2.069 \text{ g/cm}^3$; $\mu = 3.917 \text{ mm}^{-1}$; maximum and minimum transmission factors, 0.458 and 0.340; θ range for cell measurement and data collection, $3.39\text{--}27.48^\circ$; completeness to $\theta = 27.48^\circ$, 98.0%; limiting indices, $-9 \leq h \leq +9$, $-13 \leq k \leq +13$, $-13 \leq l \leq +13$; 14114 reflections collected, 3467 unique [$R(\text{int}) = 0.0768$]; number of data/restraints/parameters, 3467/26/214; final GOF, 1.002; $R1 = 0.0414$ [2729 reflections, $I > 2\sigma(I)$], $wR2 = 0.0863$; R indices (all data), $R1 = 0.0619$, $wR2 = 0.0932$;

extinction coefficient, 0.0261(14); largest diffraction peak and hole, 1.705 and $-2.234 \text{ e} \cdot \text{\AA}^{-3}$.

Crystal Data for NdEN. $\text{Nd}(\text{NO}_3)_3 \cdot \text{C}_4\text{H}_{10}\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$, $fw = 498.46$; light purple column, $0.40 \times 0.35 \times 0.16 \text{ mm}^3$; monoclinic, $P2_1/c$; $a = 7.9385(2) \text{ \AA}$, $b = 13.0140(3) \text{ \AA}$, $c = 15.3331(5) \text{ \AA}$, $\beta = 101.5721(11)^\circ$, $Z = 4$, $V = 1551.89(7) \text{ \AA}^3$; $D_c = 2.133 \text{ g/cm}^3$; $\mu = 3.426 \text{ mm}^{-1}$; maximum and minimum transmission factors, 0.591 and 0.357; θ range for cell measurement and data collection, $3.41\text{--}27.48^\circ$; completeness to $\theta = 27.48^\circ$, 99.0%; limiting indices, $-10 \leq h \leq +10$, $-16 \leq k \leq +16$, $-19 \leq l \leq +19$; 25427 reflections collected, 3528 unique [$R(\text{int}) = 0.1164$]; number of data/restraints/parameters, 3528/8/233; final GOF, 0.956; $R1 = 0.0348$ [2382 reflections, $I > 2\sigma(I)$], $wR2 = 0.0571$; R indices (all data), $R1 = 0.0761$, $wR2 = 0.0654$; extinction coefficient, 0.0329(7); largest diffraction peak and hole, 1.167 and $-1.618 \text{ e} \cdot \text{\AA}^{-3}$.

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Supporting Information Available: X-ray crystallographic file containing full details of the structural analysis of the seven structures (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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