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Interactions between metal ions and carbohydrates. The coordination behavior of neutral erythritol to lanthanum and erbium ions

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Abstract—Lanthanide ions and erythritol form metal–alditol complexes with various structures. Lanthanum nitrate and erbium chloride coordinate to erythritol to give new coordination structures. The lanthanum nitrate–erythritol complex (LaEN), $2La(NO_3)_3 \cdot C_4H_{10}O_4 \cdot 8H_2O$, La^{3+} exhibits the coordination number of 11 (namely 11 polar atoms bound to one lanthanum) and is 11-coordinated to two hydroxyl groups from one erythritol molecule, six oxygen atoms from three nitrate ions and three water molecules. One erythritol molecule is coordinated to two La^{3+} ions and links the two metal ions together. The ratio of M:L is 2:1. The erbium chloride–erythritol complex (ErE), $ErCl_2 \cdot C_4H_9O_4 \cdot 2C_2H_5OH$ was obtained from $ErCl_3$ and erythritol in aqueous ethanol solution and the structure shows that deprotonation reaction occurs in the reaction process. The Er^{3+} cation is 8-coordinated with three hydroxyl groups of one erythritol molecule, two hydroxyl groups from another erythritol molecule, two ethanol molecules, and one chloride ion. Erythritol provides its three hydroxyl groups to one erbium cation and two hydroxyl groups to another erbium cation, that is, one hydroxyl group is coordinated to two metal ions and therefore loses its hydrogen atom and becomes a oxygen bridge. Another chloride ion is hydrogen bonded in the structure. The results indicate the complexity of metal–sugar coordination.
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Keywords: Lanthanum ion; Erbium ion; Erythritol; IR spectroscopy; Crystal structure

1. Introduction

The interactions between metal ions and carbohydrates, namely, the coordination of hydroxyl groups to metal ions, is important because they may be involved in such biochemical processes as the transport and storage of metal ions, stabilization of membrane structures, binding of glycoproteins to cell surfaces, toxic metal metabolism, and the binding of proteins to sugars.[1–7] 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. Aspects include the binding of hydroxyl or other groups, the exchange of hydrogen bonds, and characterization of the metal ion coordination of carbohydrates influencing the ligand conformation and configuration changes forced by the complexation process.[8,9] Therefore, erythritol ($C_4H_{10}O_4$, denoted as E), one of the simplest carbohydrates derivatives, was chosen as a model for study of the coordination of metal ions.

Erythritol, used as a sweetener, contains four hydroxyl groups and often provides two hydroxyl groups to

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one metal ion, and the other two hydroxyl groups to another metal ion, as two bidendate ligands for calcium and lanthanide chloride complexes, or as a tridendate ligand for some lanthanide nitrate–erythritol complexes, or as noncoordinated molecule in one of the copper chloride–erythritol complexes.[10–13] Deprotonated erythritol as a ligand coordinates with Cu^{2+} and the cuprate–erythritol complex, $Na_2[Cu(ErytH_{-4})]\cdot Eryt\cdot 12H_2O$ contains the fully deprotonated form of erythritol and the free, nondeprotonated erythritol molecule.[14] We report here the syntheses and structures of a new lanthanide nitrate–erythritol complex in which the ratio of metal to ligand is 2:1, and a new complex, an erbium chloride–erythritol complex, which has a unique structure completely different from other reported lanthanide chloride–erythritol complexes. This report describes the coordination behavior of neutral, nonfunctionalized erythritol toward lanthanide chlorides and nitrates, and demonstrates the coordination variations of different metal ions to a saccharide molecule.

2. Results and discussion

Single crystals of the lanthanum nitrate–erythritol complex LaEN and the erbium chloride–erythritol complex ErE, 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 complexes are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Tables 2 and 3. Selected bond lengths and bond angles of LaEN and ErE are given in Tables 4 and 5. The geometric parameters of hydrogen-bonding systems for the complex LaEN are listed in Table 6.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for LaEN

	x	*y*	*z*	*U*(eq)
La(1)	−5381(1)	2314(1)	2223(1)	19(1)
O(1)	−2476(5)	2801(3)	453(3)	28(1)
O(2)	−2650(4)	142(3)	717(3)	23(1)
O(3)	−9422(5)	3014(4)	2802(3)	39(1)
O(4)	−9006(5)	4935(4)	3341(4)	40(1)
O(5)	−12,039(5)	4851(4)	3869(4)	45(1)
O(6)	−4698(5)	−333(4)	3514(3)	33(1)
O(7)	−6659(5)	51(4)	2289(3)	35(1)
O(8)	−6000(6)	−1984(4)	3431(4)	48(1)
O(9)	−6925(5)	4325(3)	497(3)	33(1)
O(10)	−6600(5)	2066(3)	203(3)	31(1)
O(11)	−8064(6)	3833(4)	−990(4)	47(1)
OW1	−5000(5)	4738(4)	2700(4)	38(1)
OW2	−2358(5)	1599(4)	3141(3)	33(1)
OW3	−6825(6)	2545(4)	4707(3)	33(1)
OW4	−481(8)	−999(6)	4210(6)	90(2)
N(1)	−10,184(5)	4299(4)	3344(3)	29(1)
N(2)	−5795(5)	−781(4)	3081(3)	26(1)
N(3)	−7228(5)	3424(4)	−128(3)	26(1)
C(1)	−1501(6)	1872(4)	−715(4)	26(1)
C(2)	−911(6)	261(4)	−283(4)	21(1)

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

Table 1. Crystal and structure refinement for LaEN and ErE

	LaEN	ErE
Empirical formula	$C_4H_{26}La_2N_6O_{30}$ ($2La(NO_3)_3\cdot C_4H_{10}O_4\cdot 8H_2O$)	$C_8H_{21}Er_1Cl_2O_6$ ($ErCl_2\cdot C_4H_9O_4\cdot 2C_2H_5OH$)
Formula weight	916.08	451.41
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
Unit cell dimensions	$a = 7.3612(15)$ Å $\alpha = 84.12(3)°$	$a = 17.050(3)$ Å $\beta = 106.79(3)°$
	$b = 9.6056(19)$ Å $\beta = 72.79(3)°$	$b = 9.3352(19)$ Å
	$c = 10.750(2)$ Å $\gamma = 67.83(3)°$	$c = 19.271(4)$ Å
Volume	672.4(2) $Å^3$	2936.6(10) $Å^3$
Refls. no. for cell measurement	6338	8794
θ Range for cell measurement	2.29–27.48°	2.50–27.53°
Z, Calculated density	1, 2.183 Mg/m^3	8, 2.042 Mg/m^3
Absorption coefficient	3.255 mm^{-1}	6.090 mm^{-1}
$F(000)$	430	1752
Crystal shape/crystal color	Block/colorless	Block/colorless
Crystal size	$0.40 \times 0.25 \times 0.20$ mm^3	$0.40 \times 0.25 \times 0.20$ mm^3
Limiting indices	$-9 \leqslant h \leqslant 8$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$	$-22 \leqslant h \leqslant 20$, $-10 \leqslant k \leqslant 12$, $-24 \leqslant l \leqslant 25$
Reflections collected/unique	6338/3043 [R(int) = 0.0411]	8794/3236 [R(int) = 0.0928]
Reflections with $I > 2\sigma(I)$	2818	2143
Completeness to $\theta = 27.48$	98.4%	95.7%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.522 and 0.272	0.296 and 0.066
Data/restraints/parameters	3043/0/199	3236/2/163
Goodness-of-fit on F^2	1.052	0.919
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0349$, $wR2 = 0.0844$	$R1 = 0.0523$, $wR2 = 0.1146$
R indices (all data)	$R1 = 0.0379$, $wR2 = 0.0856$	$R1 = 0.0790$, $wR2 = 0.1204$
Largest diff. peak and hole	1.670 and −2.676 e A^{-3}	1.991 and −2.872 e A^{-3}
Max. and mean shift/σ	0.001 and 0.000	0.009 and 0.000

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for ErE

	x	*y*	*z*	*U*(eq)
Er(1)	502(1)	4235(1)	4340(1)	26(1)
Cl(1)	1174(2)	3391(3)	3316(1)	39(1)
Cl(2)	−1387(2)	877(3)	4953(2)	50(1)
O(1)	−550(4)	4744(9)	3220(3)	42(2)
O(2)	−636(4)	4970(12)	4558(3)	64(3)
O(3)	−1935(4)	5274(9)	4967(4)	48(2)
O(4)	−1158(5)	7648(8)	4856(4)	58(2)
O(5)	805(5)	6572(8)	4042(4)	49(2)
O(6)	−292(5)	2095(9)	4045(4)	53(2)
C(1)	−1273(6)	5435(12)	3311(5)	39(3)
C(2)	−1429(7)	4920(17)	3982(7)	61(3)
C(3)	−2094(7)	5869(13)	4283(6)	53(3)
C(4)	−1846(6)	7293(13)	4270(6)	46(3)
C(5)	918(8)	7164(14)	3379(6)	59(3)
C(6)	1780(8)	7284(17)	3444(7)	73(4)
C(7)	−354(11)	975(18)	3502(9)	91(5)
C(8)	−1153(12)	600(20)	3087(7)	119(8)

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

2.1. Crystal structure of LaEN

The structure of LaEN ($2La(NO_3)_3 \cdot C_4H_{10}O_4 \cdot 8H_2O$) is shown in Figures 1 and 2. The crystal of LaEN is triclinic with the $P\bar{1}$ space group. La^{3+} is 11-coordinated to two hydroxyl groups from one erythritol molecule, six oxygen atoms from three nitrate ions, and three water molecules. Erythritol provides its 1- and 2-hydroxyl groups to coordinate with one La^{3+} and its 3- and 4-hydroxyl groups coordinate another La^{3+}. Thus, two La^{3+} ions are connected by one erythritol molecule. The molar ratio between metal ion and erythritol is 2:1 in LaEN. The elemental analysis for carbon deviates from acceptable values, maybe the purity of the complex is not as high as the single crystal used for X-ray diffraction measurement.

The bond lengths and bond angles data show that La–O bond lengths are from 2.531 to 2.925 Å, C–C bond lengths are from 1.505 to 1.527 Å, C–O bond lengths are from 1.442 to 1.449 Å, O–C–C bond angles are 107.0–108.2°, and the C–C–C bond angle is 113.6° (Table 4). For erythritol itself, C–C bond lengths are 1.51 Å, C–O bond lengths are 1.39 and 1.47 Å, O–C–C bond angles are 107°, and the C–C–C bond angle is 113°.[15] After complexation, the C–C bond lengths are close to those of crystalline erythritol itself,[15] the O–C bond lengths changes somewhat, and the O–C–C bond angles show some small changes, indicating that the coordination of the metal ion has influenced the conformation of the ligand.

Table 4. Selected bond lengths (Å) and angles (°) for LaEN

Bond lengths		Bond lengths	
La(1)–OW2	2.531(3)	O(2)–C(2)	1.442(5)
La(1)–O(1)	2.564(3)	O(3)–N(1)	1.269(5)
La(1)–OW3	2.565(3)	O(4)–N(1)	1.234(5)
La(1)–OW1	2.566(3)	O(5)–N(1)	1.234(5)
La(1)–O(2)	2.572(3)	O(6)–N(2)	1.256(5)
La(1)–O(10)	2.646(3)	O(7)–N(2)	1.251(5)
La(1)–O(7)	2.662(3)	O(8)–N(2)	1.229(5)
La(1)–O(3)	2.678(3)	O(9)–N(3)	1.266(4)
La(1)–O(9)	2.706(3)	O(10)–N(3)	1.261(4)
La(1)–O(6)	2.715(3)	O(11)–N(3)	1.213(5)
La(1)–O(4)	2.925(4)	C(1)–C(2)	1.505(5)
O(1)–C(1)	1.449(5)	C(2)–C(2)#1	1.527(7)
Bond angles		**Bond angles**	
OW2–La(1)–O(1)	72.53(10)	OW3–La(1)–O(6)	64.76(10)
OW2–La(1)–OW3	73.32(11)	OW1–La(1)–O(6)	130.31(11)
O(1)–La(1)–OW3	138.02(11)	O(2)–La(1)–O(6)	69.41(10)
OW2–La(1)–OW1	71.79(11)	O(10)–La(1)–O(6)	107.86(9)
O(1)–La(1)–OW1	68.83(11)	O(7)–La(1)–O(6)	46.86(9)
OW3–La(1)–OW1	77.84(12)	O(3)–La(1)–O(6)	94.36(11)
OW2–La(1)–O(2)	77.03(10)	O(9)–La(1)–O(6)	153.70(10)
O(1)–La(1)–O(2)	60.52(9)	OW2–La(1)–O(4)	118.16(10)
OW3–La(1)–O(2)	132.15(10)	O(1)–La(1)–O(4)	117.18(10)
OW1–La(1)–O(2)	126.28(10)	OW3–La(1)–O(4)	61.30(11)
OW2–La(1)–O(10)	145.34(10)	OW1–La(1)–O(4)	59.88(10)
O(1)–La(1)–O(10)	83.01(10)	O(2)–La(1)–O(4)	164.06(10)
OW3–La(1)–O(10)	137.71(11)	O(10)–La(1)–O(4)	94.62(10)
OW1–La(1)–O(10)	121.83(11)	O(7)–La(1)–O(4)	106.57(10)
O(2)–La(1)–O(10)	69.57(10)	O(3)–La(1)–O(4)	44.67(10)
OW2–La(1)–O(7)	112.34(10)	O(9)–La(1)–O(4)	64.07(10)
O(1)–La(1)–O(7)	126.72(10)	O(6)–La(1)–O(4)	119.48(10)
OW3–La(1)–O(7)	88.78(11)	C(1)–O(1)–La(1)	119.5(2)
OW1–La(1)–O(7)	164.36(12)	C(2)–O(2)–La(1)	124.7(2)
O(2)–La(1)–O(7)	68.95(10)	N(1)–O(3)–La(1)	104.3(3)
O(10)–La(1)–O(7)	63.94(9)	N(1)–O(4)–La(1)	93.0(2)
OW2–La(1)–O(3)	145.21(10)	N(2)–O(6)–La(1)	96.6(2)
O(1)–La(1)–O(3)	139.82(11)	N(2)–O(7)–La(1)	99.4(2)
OW3–La(1)–O(3)	72.12(11)	N(3)–O(9)–La(1)	97.0(2)
OW1–La(1)–O(3)	104.39(11)	N(3)–O(10)–La(1)	100.1(2)
O(2)–La(1)–O(3)	125.38(10)	O(4)–N(1)–O(5)	122.7(4)
O(10)–La(1)–O(3)	66.91(10)	O(4)–N(1)–O(3)	117.6(4)
O(7)–La(1)–O(3)	63.21(11)	O(5)–N(1)–O(3)	119.7(4)
OW2–La(1)–O(9)	136.90(10)	O(8)–N(2)–O(7)	122.2(4)
O(1)–La(1)–O(9)	70.10(10)	O(8)–N(2)–O(6)	120.8(4)
OW3–La(1)–O(9)	125.37(11)	O(7)–N(2)–O(6)	117.1(3)
OW1–La(1)–O(9)	75.27(11)	O(11)–N(3)–O(10)	121.9(4)
O(2)–La(1)–O(9)	101.91(9)	O(11)–N(3)–O(9)	122.6(4)
O(10)–La(1)–O(9)	47.07(9)	O(10)–N(3)–O(9)	115.5(3)
O(7)–La(1)–O(9)	106.92(9)	O(1)–C(1)–C(2)	107.0(3)
O(3)–La(1)–O(9)	69.92(11)	O(2)–C(2)–C(1)	107.0(3)
OW2–La(1)–O(6)	67.06(10)	O(2)–C(2)–C(2)#1	108.2(4)
O(1)–La(1)–O(6)	120.77(10)	C(1)–C(2)–C(2)#1	113.6(4)

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

There is an extensive hydrogen-bond network formed by hydroxyl groups of erythritol, oxygen atoms of nitrate ions and water molecules. For example, the hydrogen-bond data show that the hydroxyl groups of erythritol, coordinated water molecules, and oxygen atoms of nitrate ions form hydrogen bonds, coordinated and hydrogen-bonded water molecules form hydrogen bonds (OW2–H(13B)···OW4), that make an extensive hydrogen-bond network (Table 6). Three nitrate ions form different hydrogen bonds. Two oxygen atoms of one nitrate ion participate in coordination and formation of hydrogen bonds [O(9), O(10)], but the third

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

Bond lengths		Bond lengths	
Er(1)–O(2)#1	2.200(7)	O(3)–C(3)	1.383(13)
Er(1)–O(2)	2.210(7)	O(3)–Er(1)#1	2.466(7)
Er(1)–O(5)	2.351(7)	O(4)–C(4)	1.413(11)
Er(1)–O(6)	2.388(8)	O(4)–Er(1)#1	2.396(7)
Er(1)–O(4)#1	2.396(7)	O(5)–C(5)	1.455(14)
Er(1)–O(1)	2.421(6)	O(6)–C(7)	1.462(16)
Er(1)–O(3)#1	2.466(7)	C(1)–C(2)	1.472(16)
Er(1)–Cl(1)	2.669(2)	C(2)–C(3)	1.670(18)
O(1)–C(1)	1.445(11)	C(3)–C(4)	1.397(16)
O(2)–C(2)	1.482(13)	C(5)–C(6)	1.443(16)
O(2)–Er(1)#1	2.200(7)	C(7)–C(8)	1.41(2)
Bond angles		Bond angles	
O(2)#1–Er(1)–O(2)	64.1(3)	O(3)#1–Er(1)–Cl(1)	83.45(19)
O(2)#1–Er(1)–O(5)	87.3(4)	O(2)#1–Er(1)–Er(1)#1	32.12(18)
O(2)–Er(1)–O(5)	91.4(4)	O(2)–Er(1)–Er(1)#1	31.96(17)
O(2)#1–Er(1)–O(6)	113.9(4)	O(5)–Er(1)–Er(1)#1	89.27(19)
O(2)–Er(1)–O(6)	80.6(4)	O(6)–Er(1)–Er(1)#1	98.1(2)
O(5)–Er(1)–O(6)	150.2(3)	O(4)#1–Er(1)–Er(1)#1	93.4(2)
O(2)#1–Er(1)–O(4)#1	74.0(3)	O(1)–Er(1)–Er(1)#1	99.44(16)
O(2)–Er(1)–O(4)#1	112.1(3)	O(3)#1–Er(1)–Er(1)#1	97.87(19)
O(5)–Er(1)–O(4)#1	138.1(3)	Cl(1)–Er(1)–Er(1)#1	174.04(6)
O(6)–Er(1)–O(4)#1	70.5(3)	C(1)–O(1)–Er(1)	114.7(5)
O(2)#1–Er(1)–O(1)	129.6(3)	C(2)–O(2)–Er(1)#1	123.5(7)
O(2)–Er(1)–O(1)	69.1(2)	C(2)–O(2)–Er(1)	120.6(6)
O(5)–Er(1)–O(1)	76.0(3)	Er(1)#1–O(2)–Er(1)	115.9(3)
O(6)–Er(1)–O(1)	74.3(3)	C(3)–O(3)–Er(1)#1	109.4(6)
O(4)#1–Er(1)–O(1)	143.9(3)	C(4)–O(4)–Er(1)#1	118.0(7)
O(2)#1–Er(1)–O(3)#1	66.7(3)	C(5)–O(5)–Er(1)	131.4(7)
O(2)–Er(1)–O(3)#1	128.8(3)	C(7)–O(6)–Er(1)	133.4(8)
O(5)–Er(1)–O(3)#1	72.9(3)	O(1)–C(1)–C(2)	109.7(8)
O(6)–Er(1)–O(3)#1	133.6(3)	C(1)–C(2)–O(2)	106.8(9)
O(4)#1–Er(1)–O(3)#1	65.3(3)	C(1)–C(2)–C(3)	116.4(11)
O(1)–Er(1)–O(3)#1	144.1(3)	O(2)–C(2)–C(3)	106.7(9)
O(2)#1–Er(1)–Cl(1)	150.1(2)	O(3)–C(3)–C(4)	115.0(10)
O(2)–Er(1)–Cl(1)	145.06(17)	O(3)–C(3)–C(2)	98.8(9)
O(5)–Er(1)–Cl(1)	85.6(2)	C(4)–C(3)–C(2)	105.1(10)
O(6)–Er(1)–Cl(1)	85.0(2)	C(3)–C(4)–O(4)	113.2(10)
O(4)#1–Er(1)–Cl(1)	92.4(2)	C(6)–C(5)–O(5)	110.1(10)
O(1)–Er(1)–Cl(1)	76.45(16)	C(8)–C(7)–O(6)	116.3(14)

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

Table 6. Hydrogen-bond lengths (Å) and angles (°) in LaEN

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(1)–HO1···O(9)#2	0.88	1.89	2.762(4)	172.0
O(2)–HO2···O(10)#3	0.78	1.96	2.723(4)	166.7
OW1–H(12A)···O(5)#4	0.91	2.02	2.858(5)	152.2
OW2–H(13A)···O(3)#4	0.85	2.14	2.882(5)	146.0
OW1–H(12B)···O(8)#5	0.85	2.58	3.081(5)	118.9
OW3–H(14A)···O(6)#6	0.73	2.40	2.841(4)	120.6
OW3–H(14B)···O(5)#7	1.01	1.80	2.783(5)	163.0
OW2–H(13B)···OW4	0.98	1.72	2.684(5)	167.9
OW1–H(12B)···O(4)	0.85	2.31	2.758(5)	113.1

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x-1, -y+1, -z$; #3 $-x-1, -y, -z$; #4 $x+1, y, z$; #5 $x, y+1, z$; #6 $-x-1, -y, -z+1$; #7 $-x-2, -y+1, -z+1$.

oxygen atom [O(11)] does not take part in coordination and formation of hydrogen bonds; one oxygen atom of another nitrate ion [O(6)] takes part in coordination and forms a hydrogen bond with a coordinated water molecule (OW3). One oxygen atom [O(7)] only participates in coordination and is not involved in a hydrogen-bond network, one oxygen atom [O(8)] only forms a hydrogen bond with a coordinated water molecule (OW1); two oxygen atoms of the third nitrate ions [O(3), O(4)] take part in coordination and form hydrogen bonds with coordinated water molecules OW2 and OW1, respectively [OW2–H(13A)···O(3)#4 (2.882 Å) and OW1–H(12B)···O(4) (2.758 Å)]; and the third oxygen atom [O(5)] forms two hydrogen bonds with two coordinated water molecules [OW1–H(12A)···O(5)#4 and OW3–H(14A)···O(6)#6]. Two N–O bond lengths are identical [O(4)–N(1) and O(5)–N(1), 1.234(5) Å], the other seven N–O bond lengths are different, which indicates that the symmetry of nitrate ions decreases. The crystal-structure results thus provide evidence of metal–sugar

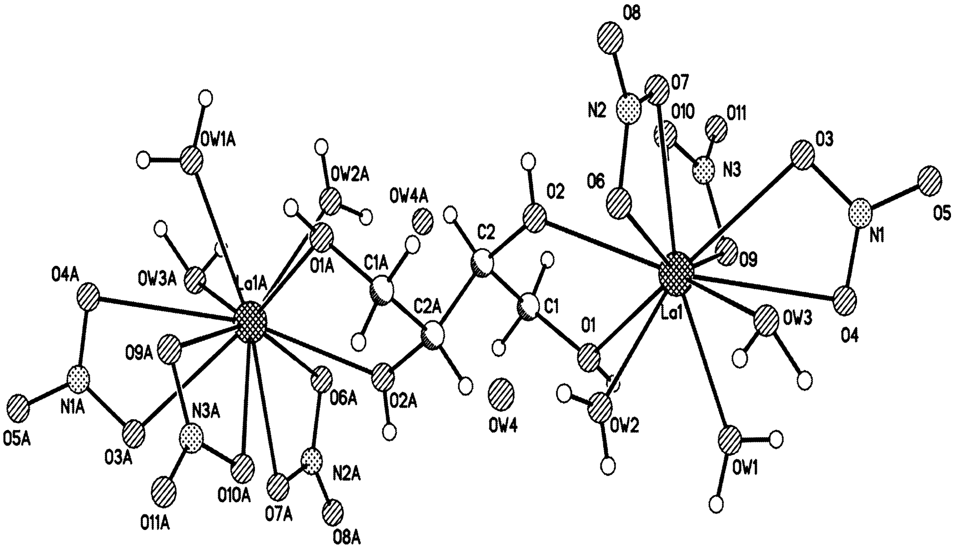

Figure 1. Crystal structure of $2La(NO_3)_3{\cdot}C_4H_{10}O_4{\cdot}8H_2O$.

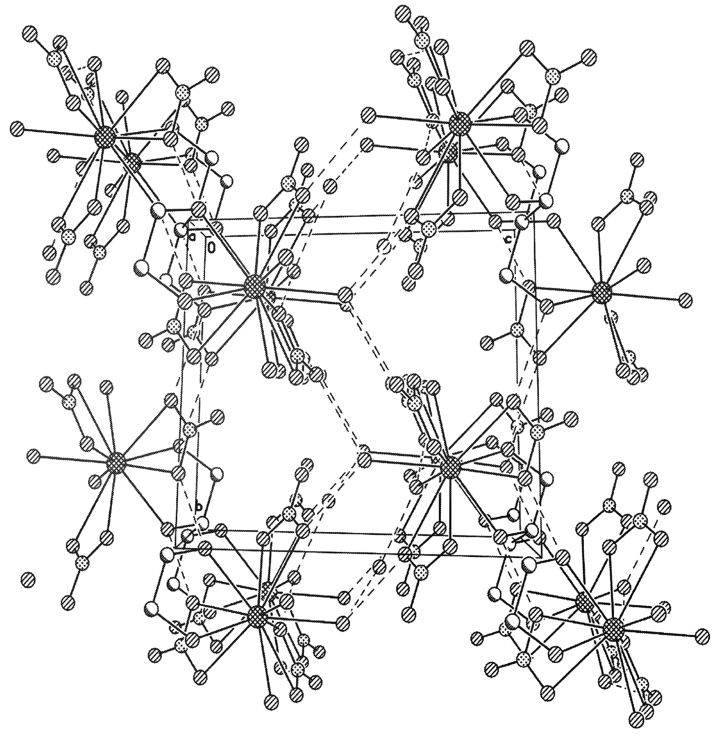

Figure 2. The projection of the cell of $2La(NO_3)_3{\cdot}C_4H_{10}O_4{\cdot}8H_2O$.

interaction and the coordination of hydroxyl groups of carbohydrates to metal ion.

Other lanthanide nitrate–erythritol complexes, NdEN and EuEN, $Ln(NO_3)_3{\cdot}C_4H_{10}O_4{\cdot}C_2H_5OH$ were obtained and their structures were determined.[10] Their structures belong to the triclinic system with $P\bar{1}$ space group. Each Ln^{3+} ion is 10-coordinated to three hydroxyl groups from an erythritol molecule, six oxygen atoms from three nitrate ions, and one hydroxyl group from ethanol. The ratio of metal to ligand in NdEN and EuEN is 1:1. Erythritol provides 1,2,3-hydroxyl groups to coordinate to one metal ion. One of the differences between LaEN and NdEN (EuEN) is that water molecule is involved in coordination of erythritol to La^{3+}, but a water molecule is absent from the coordination of NdEN (EuEN).

Other reported crystal structures of lanthanum complexes with hydroxyl-group coordination include two lanthanum complexes with *cis*,*cis*-1,3,5-trihydroxycyclohexane and one lanthanum chloride–galactitol complex.[16,17] For the two lanthanum-*cis*,*cis*-1,3,5-trihydroxycyclohexane complexes, La^{3+} is 11-coordinated to three hydroxyl groups from one ligand and eight oxygen atoms from four nitrate ions; or La^{3+} ion is 10-coordinated to six hydroxyl group from two molecules of ligands and four oxygen atoms from two nitrate ions.[16] For the lanthanum chloride–galactitol complex, each La^{3+} ion in the unit cell is 10-coordinated, three hydroxyl groups from one alditol, three from another alditol, and four from water molecules, with La–O distances from 2.5099 to 2.6916 Å.[17] For different ligands, La^{3+} has various coordination structures.

2.2. Crystal structure of ErE

The single crystal of the erbium chloride–erythritol complex, $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$ was obtained from $ErCl_3$ and erythritol in aqueous ethanol solution, and the result indicates that deprotonation occurs in the reaction process. The crystal structure shows that the erbium chloride–erythritol complex (Fig. 3) is composed of discrete coordinated Er^{3+} dimers. Fig. 4 is a projection of the unit cell of $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$. In the dinuclear complex, the Er^{3+} cation is 8-coordinated with three hydroxyl groups of one erythritol molecule, two hydroxyl groups from another erythritol molecule, two ethanol molecules, and one chloride ion. The coordination number of erbium cation, 8 is the smallest among the reported lanthanide–carbohydrate complexes.[17–24] Water is not involved in the coordination. Erythritol provides its three hydroxyl groups to one erbium cation and two hydroxyl groups to another erbium cation, that is, one hydroxyl group is coordinated to two metal ions, becoming an oxygen bridge and therefore losing its hydrogen atom. Erythritol becomes $C_4H_9O_4$. Two oxygen bridges from two erythritol molecules link two erbium ions together. Another chloride ion is hydrogen bonded in the structure.

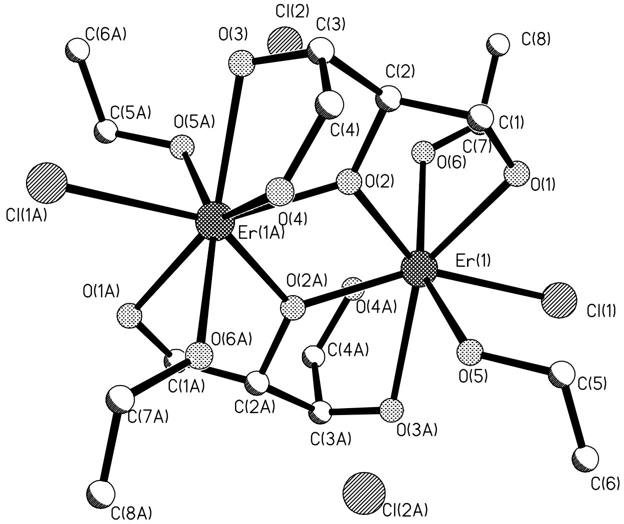

Figure 3. The structure and atom numbering of $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$.

The structure of the erbium chloride–erythritol complex, $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$ obtained from $ErCl_3$

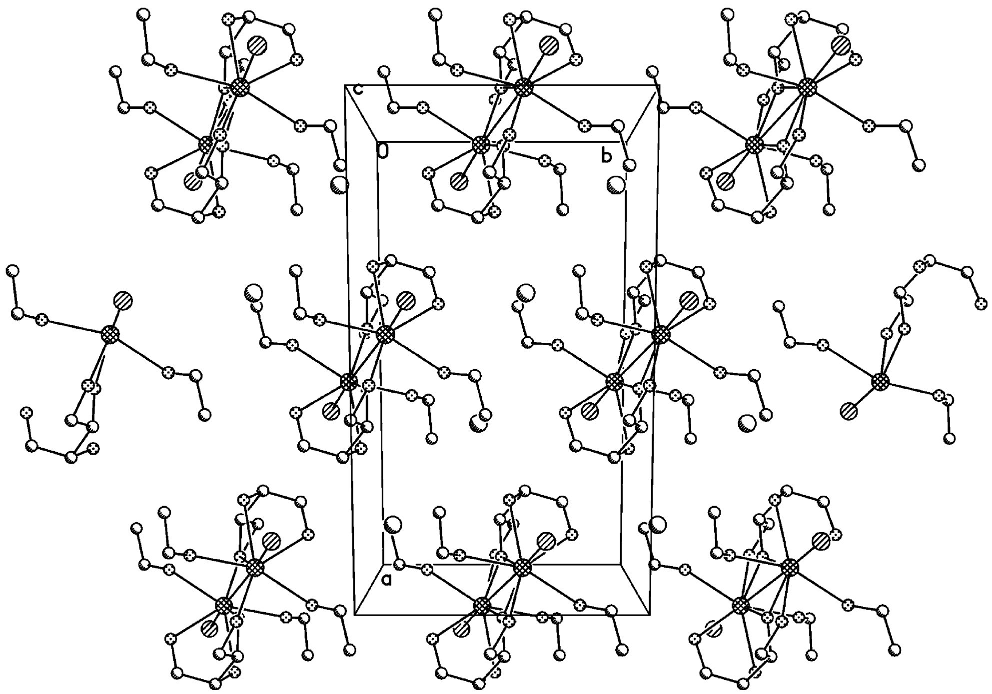

Figure 4. The projection of the cell of $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$.

and erythritol in aqueous ethanol, thus indicates that deprotonation occurs in the reaction process:

$$ErCl_3+C_4H_{10}O_4+2C_2H_5OH \rightarrow ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH+HCl$$

The erbium chloride–erythritol complex differs from other lanthanide chloride–erythritol complexes where erythritol provides two hydroxyl groups to one lanthanide ion and another two hydroxyl groups to another lanthanide ion.[10,11] It also differs from some lanthanide nitrate–erythritol complexes, in which erythritol provides three hydroxyl groups to one metal ion.[10] Here, the special coordination of erythritol results in the unique structure of erbium chloride–erythritol complex. Coordination of the erbium ion makes a hydroxyl group of erythritol lose a hydrogen atom and become an oxygen bridge, which connects with two carbon atoms and two erbium cations. Because one chloride ion is lost, the oxygen bridge also plays a role in charge balance. This result is unexpected because the complex was prepared from a neutral reactant solution. Those reported lanthanide–erythritol complexes prepared using the same experimental methods contain the free, nondeprotonated ligand.[10] In the literature the deprotonated ligand was obtained only in strongly alkaline solution, when metal sodium or potassium was added.[25,26] Here the deprotonated ligand is produced in neutral solution because of coordination of the erbium cation.

The atomic coordinates and equivalent isotropic displacement parameters are listed in Tables 3 and 5 lists selected bond lengths and angle data for $ErCl_2{\cdot}C_4H_9O_4{\cdot}2C_2H_5OH$. The average Er–O bond length is 2.347 Å; Er–O bond lengths are 2.200–2.466 Å, which are shorter than the corresponding Pr–O and Nd–O bond lengths in praseodymium chloride–erythritol and neodymium chloride–erythritol complex. The Er–Cl bond length is 2.669 Å, which is also shorter than Pr–Cl and Nd–Cl bond lengths in praseodymium chloride–erythritol and neodymium chloride–erythritol complexes. As compared with the structure of erythritol itself,[15] the C(2)–C(3) bond length becomes longer because O(2) is a bridge. The O–C–C bond angles are from 98.8 to 115° for the erbium–erythritol complex (107° for erythritol itself), and the C–C–C bond angles are 105.1 and 116.4° (113° for erythritol itself). In the erbium complex, the erythritol has a bent chain and the torsion angle of C(1)–C(2)–C(3)–C(4) is about −48.43°, but the torsion angle of C(1)–C(2)–C(2)#1–C(1)#1 is 180° for LaEN. The torsion angle of O(1)–C(1)–C(2)–O(2) is 46.1° for LaEN, 46.66° for ErE, the two torsion angles are close; and the torsion angle of O(1)–C(1)–C(2)–C(2)#1 is −73.2° for LaEN, but the torsion angle of O(1)–C(1)–C(2)–C(3) is 165.67° for ErE, and the results show that the conformation of erythritol in the two complexes are different. There is also a hydrogen-bond network between hydroxyl groups of erythritol or ethanol and chloride ions for ErE. The results indicate changes of erythritol after complexation, as related to its coordination to erbium cation. For other reported lanthanide chloride–erythritol complexes, Ln^{3+} is coordinated to four hydroxyl groups from two erythritol molecules, four water molecules, and a chloride ion, and thus the coordination number of Ln^{3+} is 9.[10] The unique coordination structure of the erbium–erythritol complex differs from other lanthanide chloride–erythritol complexes and indicates that the structures of metal–carbohydrate complexes are complicated. Lanthanide ions often have high coordination numbers, and the erythritol molecule has several coordination modes, therefore, various structures have been observed. Unfortunately, the amount of erbium chloride–erythritol complex sample prepared was not large enough for further characterization.

Erythritol is centro-symmetric and is not inherently chiral, and the results for its metal complexes seem also to be centro-symmetric. For example, one of the three calcium chloride–erythritol complexes CaE(I), the europium nitrate–erythritol complex EuEN, and the neodymium chloride–erythritol complex NdEN belong to the $P2_1/c$ space group, CaE(II), one of the two copper chloride–erythritol complexes CuE(I), the manganese chloride–erythritol complex MnE, the calcium nitrate–erythritol complex CaEN and ErE belong to the $C2/C$ space group, and the europium chloride–erythritol complex EuE belongs to the $P2/c$ space group. The foregoing crystal structures have $C2h$ symmetry and therefore have a symmetric center; the praseodymium chloride–erythritol complex PrE, the neodymium chloride–erythritol complex NdE, CuE(II), and the lanthanum nitrate–erythritol complex LaEN belong to $P\bar{1}$ space group; CaE(III) has $D2h$ symmetry and has a symmetric center, and the zinc nitrate–erythritol complex ZnEN also has symmetric center. The results show that the metal complexes have symmetric centers, but the symmetric center may not be the erythritol molecule, because erythritol has various coordination modes.

2.3. FTIR spectrum of LaEN

The FTIR spectra of $La(NO_3)_3{\cdot}6H_2O$ and LaEN are shown in Figure 5. After complex formation, the spectrum of LaEN differs from $La(NO_3)_3{\cdot}6H_2O$ itself. The νOH vibrations of water molecules in $La(NO_3)_3{\cdot}6H_2O$ are located at 3499, 3450, 3405, 3249 cm^{-1}, but 3567 and 3321 cm^{-1} bands appear for the $La(NO_3)_3$–erythritol complex. The νCH vibrations are located at 2992, 2978, and 2933 cm^{-1}, and their relative intensities are decreased as compared with erythritol itself. The appearance of the bending vibration of water molecules located at 1633 cm^{-1} indicates that water molecules are present in the structure of the $La(NO_3)_3$–erythritol

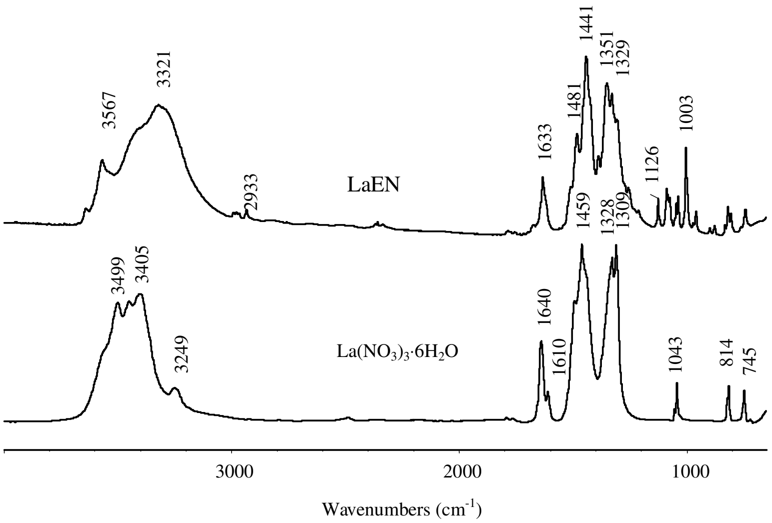

Figure 5. The FTIR spectra of $La(NO_3)_3{\cdot}6H_2O$ and its erythritol complex LaEN in the 4000–650 cm^{-1} region.

complex, which is consistent with the crystal-structure results.

In the 1500–1200 cm^{-1} region the bands related to nitrate ions, including 1459 cm^{-1} ($\nu asNO_2$), and 1328, 1309 cm^{-1} (νsNO_2)[27] shift and are split into several bands after complexation (Fig. 5), indicating the coordination of nitrate ions and the decrease of nitrate ion symmetry. The appearance of the bands in the 1200–900 cm^{-1} region different from erythritol itself and related to C–O and skeleton vibrations of erythritol and N–O vibrations of nitrate ions also indicates the formation of a lanthanum nitrate–erythritol complex. The FTIR spectrum of LaEN is different from the spectra of other reported lanthanide nitrate–erythritol complexes,[10] indicating that LaEN has a new structure. The FTIR spectrum indicates the formation of a metal–sugar complex having a structure different from reported lanthanide nitrate–erythritol complexes, and is consistent with the single-crystal X-ray diffraction results.

In conclusion, the FTIR and X-ray single crystal diffraction results of LaEN and ErE indicate that lanthanide ions and erythritol form metal–alditol complexes with various structures, and especially the deprotonated ligand is formed from neutral reactants because of coordination of the erbium cation. The characteristics of the two new structures are as follows: for LaEN, its M:L ratio 2:1 is different from other reported lanthanide nitrate–erythritol complexes; and ErE is a new dinuclear, di-bridged complex, the deprotonated ligand being present in the complex. The results indicate the complexity of metal–sugar coordination. Although erythritol is a simple molecule, it exhibits various coordination modes to metal ions. Lanthanide ions have high coordination numbers, and therefore, many lanthanide–erythritol complexes having various structures have been observed.

3. Experimental

3.1. Materials and methods

Erythritol ($C_4H_{10}O_4$, Sigma) and the other reagents were obtained commercially and used as supplied. Lanthanide chlorides and nitrates were prepared and crystallized from corresponding lanthanide oxides of high purity, La_2O_3 and Er_2O_3 (99.99%). The procedure for preparing the lanthanum nitrate–erythritol complex (LaEN) is as follows: 3 mmol of erythritol (0.3663 g) and 3 mmol of $La(NO_3)_3{\cdot}6H_2O$ (~1.2999 g) were dissolved in a 1:1 H_2O–EtOH (10 mL) mixture. The solution was put in a water bath at about 80 °C. Small aliquots of EtOH (Analytical Reagent) were periodically added to the solution during the heating process to prolong the reaction time, leading to the formation of the complex. The resultant concentrated solution was filtered and cooled for crystallization at room temperature. The procedure for preparing the erbium chloride–erythritol complex was as before, with 3 mmol of erythritol and 3 mmol of erbium chloride dissolved in 1:1 H_2O–EtOH (10 mL). The amount of single crystal obtained was sufficient only for single-crystal X-ray analysis. We had to use the poly-crystal obtained from the same container where the single crystal was produced to perform elemental analysis. Anal. Calcd for $2La(NO_3)_3{\cdot}C_4H_{10}O_4{\cdot}8H_2O$: C, 5.24; N, 9.17; H, 2.86. Found: C, 7.11; N, 9.42; H, 3.04.

3.2. Physical measurements

Data for the lanthanum nitrate–erythritol complex, LaEN, and the erbium chloride–erythritol complex, ErE, were collected on a Rigaku RAXIS RAPID IP spectrometer with graphite monochromatized Mo Kα

radiation ($\lambda = 0.71073$ Å) at room temperature (293 K). The structures were 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 structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 273169 and 273170. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat) +44-1223/336033; email: deposit@ccdc.cam.ac.uk].

The infrared spectrum of the LaEN complex was measured on a NIC-plan infrared microscope attached on a Nicolet Magna-IR 750 II FT-IR spectrometer at a resolution of 4 cm^{-1} and 64 scans were co-added. Elemental analysis of the sample LaEN was carried out on an Elementar Vario EL elemental analyzer.

Acknowledgments

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