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# Crystal structures and spectroscopic characterization of galactitol complexes of trivalent lanthanide and divalent alkaline earth chlorides

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**Abstract**—Crystal structures and FT-IR spectra of metal ion–galactitol ($C_6H_{14}O_6$, the ligand here abbreviated as L) complexes: $2LaCl_3 \cdot C_6H_{14}O_6 \cdot 10H_2O$ and $SrCl_2 \cdot C_6H_{14}O_6$ complexes are reported. Crystal data of lanthanide chlorides ($La^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Tb^{3+}$)–galactitol complexes and alkaline earth chlorides ($Ca^{2+}$, $Sr^{2+}$)–galactitol complexes published earlier are summarized. Unlike other lanthanide ion–galactitol complexes ($2MCl_3 \cdot C_6H_{14}O_6 \cdot 14H_2O$), lanthanum ions give rise to two different structures: $LaCl_3 \cdot C_6H_{14}O_6 \cdot 6H_2O$ (LaL1) and $2LaCl_3 \cdot C_6H_{14}O_6 \cdot 10H_2O$ (LaL2). $Sr^{2+}$–galactitol complexes also crystallized with two structures: $SrCl_2 \cdot C_6H_{14}O_6 \cdot 4H_2O$ (SrL1) and $SrCl_2 \cdot C_6H_{14}O_6$ (SrL2). These metal ions thus give different coordination structures with galactitol. The crystal structures and FT-IR spectra of lanthanide ion and alkaline earth ion–galactitol complexes were integrated to interpret the coordination modes of different metal ions. Similar IR spectra demonstrate the same coordination modes of the complexes.

*Keywords:* Crystal structure; Galactitol; Lanthanide; Alkaline earth

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## 1. Introduction

The interactions between saccharides and metal ions have been known since the turn of the 19th century when the first adduct of D-glucose with NaCl was reported.[1] The study of saccharide–metal ion interactions remains one of the main objectives of carbohydrate coordination chemistry, as such interactions are involved in many biochemical processes, including 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.[2–5]

Alditols constitute simple model oxygen–donor ligands. The complexation of metal cations by alditols has been extensively studied in the carbohydrate and cyclitol fields over the last four decades. Alditols are used as sweeteners in Europe and America. Galactitol as a metabolic product of galactose and an acylic alditol of biological importance has widespread distribution among plants.[6] It was isolated from the stems and leaves of *Fritillaria ussuriensis* (a Chinese traditional medicine).[7] In the clinic the presence of galactitol is related to a common genetic metabolic disease–galactose hematoma.[8]

Before 2000, only one crystal structure of a galactitol–lanthanide ion complex had been reported

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($2PrCl_3$·galactitol·$14H_2O$).[9] Crystallographic analyses are complicated by the difficulties in obtaining X-ray quality crystals of complexes containing sugars with free hydroxyl groups. Since the year 2000 our group has prepared a series of lanthanide ion– and alkaline earth ion–galactitol complexes.[10–15] The present contribution describes the coordination behavior of neutral, nonfunctionalized galactitol to alkaline earth and lanthanide ions, demonstrates the coordination differences of various metal ions, and improves our understanding of the correlation between structural and spectral manifestations. The interactions between metal ions and saccharides may provide an effective stereospecific mechanism for crosslinking carbohydrate chains in biological systems. We examine the crystal structures of a series of metal ion–galactitol complexes in an effort to clarify the structural factors controlling metal ion interactions with saccharides in aqueous and biological systems.

## 2. Results and discussion

### 2.1. Crystal structures of the $LaL_2$ complex

The crystal structure and the numbering of atoms for $2LaCl_3·C_6H_{14}O_6·10H_2O$ (LaL2) are shown in Figure 1 and the projection of the crystal cell in the structure of LaL2 is shown as Figure 2. Crystal data of LaL2 are listed in Table 1 and atomic parameters of this complex are given in Table 2. Selected bond lengths and bond angles are collected in Table 3. Hydrogen bonds are listed in Table 4.

LaL2 crystallized in a triclinic system, $P\bar{1}$ space group. Each $La^{3+}$ is coordinated to three hydroxyl groups of one galactitol, four water molecules (O-4, O-5, O-6, and O-7) and two chloride ions with La–O distances ranging from 2.515 to 2.621 Å and La–Cl distances from 2.9101 to 2.9287 Å. These two chloride ions are coordinated to another $La^{3+}$ at the same time to form two μ2

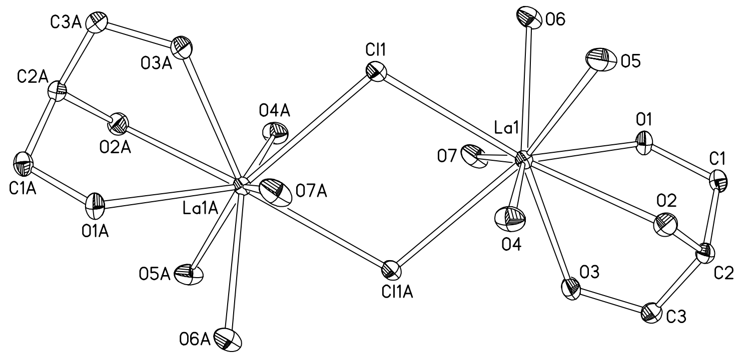

Figure 1. The structure and the numbering of atoms of $2LaCl_3·C_6H_{14}O_6·10H_2O$ (LaL2). Dimer unit of $La_2Cl_2(H_2O)_8$ ($C_6H_{14}O_6$), symmetry code: A, $-x, -y, -z$. La1 is in a tri-capped trigonal prism environment with Cl-1A, O-2, and O-6 as the caps.

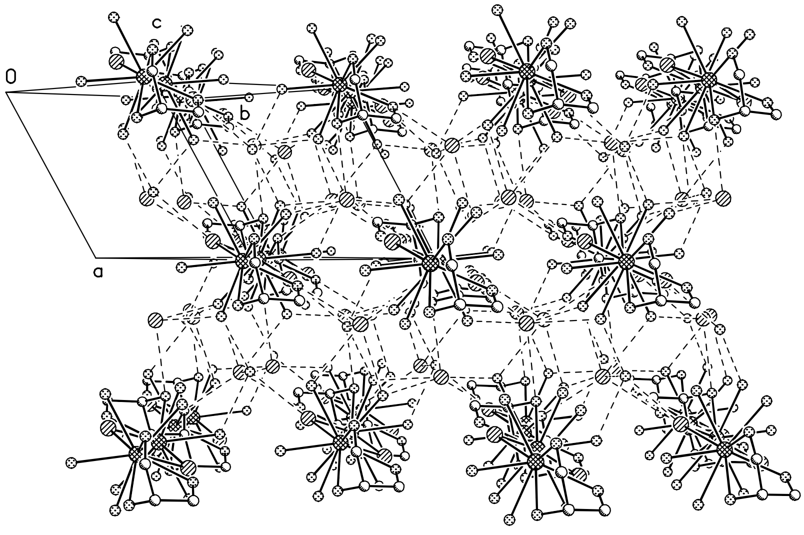

Figure 2. The projection of the crystal cell in the structure of LaL2. Hexagonal packing arrangement of the above chains in lattice (down the *b*–*c* direction), between them are Cl ions (Cl-2, Cl-3) and water molecules (O-8), which form numerous hydrogen bonds (dashed lines) to the chains.

**Table 1.** Crystal data and structure refinement for $2LaCl_3 \cdot C_6H_{14}O_6 \cdot 10H_2O$ (LaL2)

| | |
|---|---|
| Empirical formula | $C_6H_{34}Cl_6La_2O_{16}$ |
| Formula weight | 852.85 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Unit cell dimensions | $A = 8.2349(2)$ Å |
| | $\alpha = 78.4337(12)°$ |
| | $B = 8.9772(2)$ Å |
| | $\beta = 73.9809(14)°$ |
| | $C = 10.5483(3)$ Å |
| | $\gamma = 64.4630(11)°$ |
| Volume (Å$^3$) | 673.30(3) |
| $Z$, Calculated density (mg/m$^3$) | 1, 2.103 |
| Absorption coefficient (mm$^{-1}$) | 3.784 |
| $F(000)$ | 414 |
| Crystal size (mm) | $0.18 \times 0.20 \times 0.28$ |
| $\theta$ Range for data collection (°) | 3.79–27.47 |
| Index ranges | $-10 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 13$ |
| Reflections collected/unique | 13,695/3027 [$R(\mathrm{int}) = 0.0502$] |
| Completeness to $\theta = 27.48°$ | 98.0% |
| Max. and min. transmission | 0.511 and 0.436 |
| Data/restraints/parameters | 3027/21/178 |
| Goodness-of-fit on $F^2$ | 1.055 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0248$, $wR2 = 0.0568$ |
| $R$ indices (all data) | $R1 = 0.0307$, $wR2 = 0.0586$ |
| Extinction coefficient | 0.0138(10) |
| Largest diff. peak and hole (e Å$^{-3}$ ) | 0.635 and −1.165 |

**Table 2.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for LaL2

| | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| La(1) | 17(1) | −1989(1) | 1817(1) | 18(1) |
| Cl(1) | −1053(1) | −805(1) | −747(1) | 30(1) |
| Cl(2) | 3384(1) | −4485(1) | −2435(1) | 30(1) |
| Cl(3) | −6521(1) | 722(1) | 3539(1) | 36(1) |
| O(1) | −1196(3) | −2936(2) | 4232(2) | 23(1) |
| O(2) | 2358(3) | −4458(3) | 3052(2) | 25(1) |
| O(3) | 1352(4) | −1382(3) | 3486(2) | 38(1) |
| O(4) | 3079(3) | −3265(3) | 269(2) | 30(1) |
| O(5) | 350(3) | −4755(3) | 1290(2) | 33(1) |
| O(6) | −3154(3) | −2090(3) | 2023(2) | 29(1) |
| O(7) | −2538(3) | 596(3) | 2772(3) | 34(1) |
| O(8) | 6222(4) | −2592(3) | −620(3) | 40(1) |
| C(1) | 54(4) | −4173(3) | 5006(3) | 20(1) |
| C(2) | 1955(4) | −4188(4) | 4430(3) | 23(1) |
| C(3) | 2095(5) | −2580(4) | 4516(3) | 31(1) |

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

**Table 3.** Coordinated bond lengths (Å) and angles (°) in complex LaL2 with estimated standard derivations

| | Bond length |
|---|---|
| La(1)–O(4) | 2.515(2) |
| La(1)–O(5) | 2.537(2) |
| La(1)–O(1) | 2.582(2) |
| La(1)–O(2) | 2.621(2) |
| La(1)–Cl(1) | 2.9287(7) |
| O(1)–C(1) | 1.440(3) |
| O(2)–C(2) | 1.445(4) |
| O(3)–C(3) | 1.430(4) |
| La(1)–O(7) | 2.527(2) |
| La(1)–O(3) | 2.564(2) |
| La(1)–O(6) | 2.600(2) |
| La(1)–Cl(1)#1 | 2.9101(7) |
| C(1)–C(2) | 1.510(4) |
| C(1)–C(1)#2 | 1.527(5) |
| C(2)–C(3) | 1.520(4) |
| | Bond angle |
| O(4)–La(1)–O(7) | 148.01(8) |
| O(4)–La(1)–Cl(1)#1 | 76.61(6) |
| Cl(1)#1–La(1)–Cl(1) | 73.34(2) |
| C(1)–O(1)–La(1) | 120.54(16) |
| O(1)–C(1)–C(2) | 108.4(2) |
| C(2)–C(1)–C(1)#2 | 113.6(3) |
| O(4)–La(1)–O(5) | 71.34(8) |
| O(7)–La(1)–Cl(1) | 89.73(6) |
| La(1)–Cl(1)–La(1) | 106.66(2) |
| C(2)–O(2)–La(1) | 110.18(17) |
| O(1)–C(1)–C(1)#2 | 107.7(3) |
| C(1)–C(2)–C(3) | 113.7(3) |

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

**Table 4.** Hydrogen bonds for LaL2 structure

| D–H···A | $d$(D–H) | $d$(H···A) | $d$(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O(1)–H(1)···Cl(3)#3 | 0.804(18) | 2.27(2) | 3.038(2) | 159(3) |
| O(2)–H(2)···Cl(2)#4 | 0.804(18) | 2.34(2) | 3.120(2) | 165(3) |
| O(3)–H(3)···Cl(3)#5 | 0.823(18) | 2.32(2) | 3.096(2) | 159(3) |
| O(4)–H(41)···O(8) | 0.945(18) | 1.85(2) | 2.779(3) | 167(3) |
| O(4)–H(42)···Cl(2) | 0.903(18) | 2.28(2) | 3.165(2) | 165(4) |
| O(5)–H(51)···Cl(2)#6 | 0.928(18) | 2.45(2) | 3.288(2) | 150(3) |
| O(5)–H(52)···O(8)#4 | 0.924(18) | 1.91(2) | 2.814(4) | 164(4) |
| O(6)–H(61)···Cl(3) | 0.922(18) | 2.204(19) | 3.123(2) | 175(4) |
| O(6)–H(62)···Cl(2)#6 | 0.929(18) | 2.20(2) | 3.098(2) | 162(4) |
| O(7)–H(71)···Cl(3) | 0.935(18) | 2.24(2) | 3.110(2) | 154(4) |
| O(7)–H(72)···Cl(2)#1 | 0.931(18) | 2.36(3) | 3.216(2) | 153(3) |
| O(8)–H(81)···O(6)#5 | 0.949(19) | 2.29(3) | 3.119(4) | 146(4) |
| O(8)–H(81)···Cl(1)#5 | 0.949(19) | 2.60(4) | 3.237(3) | 125(3) |
| O(8)–H(82)···Cl(3)#1 | 0.955(19) | 2.25(2) | 3.197(3) | 169(4) |

Symmetry transformations in LaL2 structure used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y-1, -z+1$; #3 $-x-1, -y, -z+1$; #4 $-x+1, -y-1, -z$; #5 $x+1, y, z$; #6 $-x, -y-1, -z$.

bridge bonds. These two chloride bridges connect the two $La^{3+}$ ions, resulting in a dimer unit of $La_2Cl_2$ $(H_2O)_8$ $(C_6H_{14}O_6)$, in which La-1 is in a tri-capped trigonal prism environment with Cl-1A, O-2, and O-6 as the caps (dimer1). In the lattice the dimer unit forms a chain of $[La_2Cl_2\ (H_2O)_8\ (C_6H_{14}O_6)]_\infty$ along the *bc* direction, which is surrounded by $Cl^-$ ions (Cl-2 and Cl-3) and lattice water molecules (O-8). These free $Cl^-$ and water molecules form numerous hydrogen bonds with the chain. As shown in Table 4 the main H-bonds are O–H···Cl except that one O(8)–H(81)···Cl(1)#5 (3.237 Å) is from a lattice water molecule (O-8) and a coordinated $Cl^-$, the other O–H···Cl hydrogen bonds are from hydroxyl groups of ligand or water molecules and free $Cl^-$. There are only three O–H···O hydrogen bonds: O(4)–H(41)···O(8) (2.779 Å), O(5)–H(52)···O(8)#4 (2.814 Å), O(8)–H(81)···O(6)#5 (3.119 Å) resulting from coordinated water and lattice water molecules.

The crystal structure of $LaCl_3{\cdot}C_6H_{14}O_6{\cdot}6H_2O$ (LaL1) has been reported in the literature.[14] In the structure of LaL1, the coordination number is 10 and no chloride ions take part in the coordination compared with the structure of LaL2. In our previously presented lanthanide ion (M)–galactitol complexes like $Nd^{3+}$–, $Sm^{3+}$–, $Eu^{3+}$–, $Tb^{3+}$–, and $Pr^{3+}$–galactitol[9–13] all have similar formulations: $2MCl_3{\cdot}$galactitol$\cdot 14H_2O$ (ML) and the coordination mode is different from those of LaL1 and LaL2. Each $M^{3+}$ is coordinated to nine oxygen atoms, three from galactitol and six from water molecules. Galactitol forms a proportion of the 1:2 complex having two cations attached to O-1, O-2, O-3 and O-4, O-5, O-6, respectively. Chloride ions do not participate in coordination in the $2MCl_3{\cdot}$galactitol$\cdot 14H_2O$ structure. In comparison to the chain structure of LaL1 and LaL2, every $M^{3+}$ is enclosed by one galactitol and six water molecules, forming a closed structure in the crystals of $2MCl_3{\cdot}$galactitol$\cdot 14H_2O$.

### 2.2. Crystal structures of SrL2

The structure and the numbering of atoms of $SrCl_2{\cdot}C_6H_{14}O_6$ (SrL2) are shown in Figure 3 and a projection of the crystal cell in the structure of SrL2 is shown in Figure 4. Crystal data of SrL2 is listed in Table 5. Atomic parameters of SrL2 complex are given in Table 6. Selected bond lengths and bond angles are collected in Table 7. Hydrogen bonds are listed in Table 8.

SrL2 crystallized in a monoclinic system, $C_2/c$ space group. Each $Sr^{2+}$ ion is coordinated to six oxygen atoms, three oxygen atoms from O-1, O-2, and O-3 of one galactitol, another three atoms from O-1A, O-2A, and O-3A of another galactitol and two chloride atoms. The Sr–O distances are from 2.5593 to 2.6041 Å and two Sr–Cl distances are both 2.9072 Å. The chain structure of $SrCl_2$ ($C_6H_{14}O_6$) is arranged along the *ac* diagonal direction in the hexagonal packing of the SrL2 lattice. In α-D-ribopyranose–lanthanide ion complexes such as $NdCl_3{\cdot}C_5H_{10}O_5{\cdot}5H_2O$,[16] one $Cl^-$ also takes part in the coordination with $Nd^{3+}$. The Nd–Cl distance is 2.819 Å, which is shorter than that of Sr–Cl (2.9072 Å). Because no water participates in the coordination, there is only one kind of hydrogen bond: O–H···Cl coming from the hydroxyl group of galactitol and coordinated $Cl^-$ in the structure of SrL2.

The crystal structure of $SrCl_2{\cdot}C_6H_{14}O_6{\cdot}4H_2O$ (SrL1) has been determined in the literature,[15] whose coordination mode is similar to that of $CaCl_2{\cdot}C_6H_{14}O_6{\cdot}4H_2O$ (CaL).[13] The coordination numbers of SrL1 and SrL2 are both eight, having a twofold axis. In the structure of SrL1, galactitol provides two adjacent hydroxyl groups, whereas in the structure of SrL2, galactitol provides three hydroxyl groups. As regards SrL1 and SrL2, every galactitol is coordinated to two $Sr^{2+}$ and thus $Sr^{2+}$ cations link galactitol together to form a chain structure.

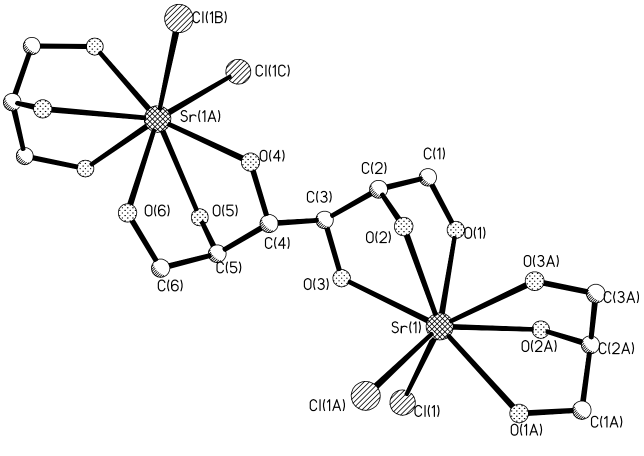

**Figure 3.** The structure and the numbering of atoms of $SrCl_2{\cdot}C_6H_{14}O_6$ (SrL2). Chain of $SrCl_2$ ($C_6H_{14}O_6$) running along *ac* diagonal direction. Symmetry code: A $-x+1, y, 1.5-z$; B $0.5-x, 0.5-y, -z+1$.

### 2.3. FT-IR study of LaL2

FT-IR spectra of Nd–, Sm–, Eu–, and Tb–galactitol complexes are shown in Figure 5. FT-IR spectra of LaL1, LaL2, and L are shown in Figure 6. The results of the spectral analyses are described as follows.

The IR spectra of Nd–, Sm–, Eu–, and Tb–galactitol complexes in the whole region (4000–650 $cm^{-1}$) are very similar, showing that these lanthanide ions have a similar coordination mode. The IR spectra of LaL1 and LaL2 are both different from those of the $Ln^{3+}$ complexes mentioned above, which are consistent with the crystal structure results.

In the 4000–3000 $cm^{-1}$ region, the broad band is assigned to the stretching vibrations of the OH groups of the galactitol and water, which is influenced by an extensive hydrogen-bonding network. When the complex forms, the νOH bands in the spectra of the two complexes are broadened and different from the peak positions of the free galactitol in this region.

In the region 3000–2800 $cm^{-1}$, the weak bands are the CH stretching vibrations, which are masked by OH vibrations. The relative intensities of the CH stretching vibrations are clearly decreased and peak positions are shifted in comparison with the spectrum of the free galactitol.

The medium bands at ∼1640 $cm^{-1}$ (due to the water bending mode), which are absent in the spectrum of the free galactitol, are assigned to the bonded $H_2O$ molecules. The peak positions for the two complexes are 1651, 1624 $cm^{-1}$ (LaL1); 1669, 1657, 1632 $cm^{-1}$

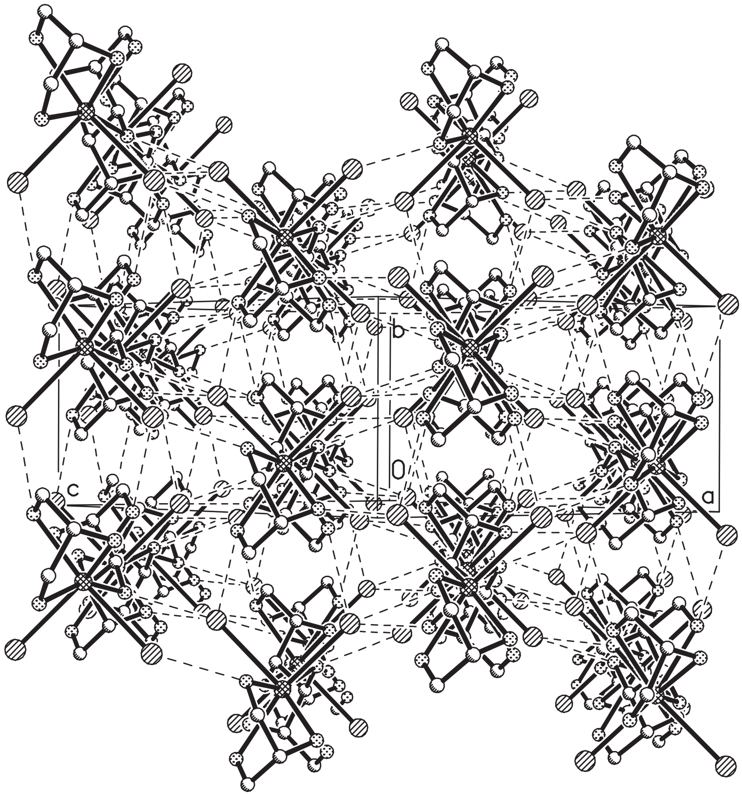

**Figure 4.** The projection of the crystal cell in the structure of SrL2. Hexagonal packing of the chains viewed down the *ac* direction, dashed lines are O–H···Cl H-bonds.

(LaL2) corresponding to many bonded water molecules in the two structures.

Bands in the region 1200–950 $cm^{-1}$ could be assigned mainly to CO stretching vibration: 1107, 1091, 1076, 1028, 995, 977 $cm^{-1}$ (LaL1), 1094, 1070, 1019, 981, 945 $cm^{-1}$ (LaL2) corresponding to 1118, 1104, 1079, 1049, 1031, 1001 $cm^{-1}$(L).[17] The peak positions in the spectra of the two complexes are similar because the coordination modes of galactitol in the structures of LaL1 and LaL2 are both providing three hydroxyl groups to $La^{3+}$.

### 2.4. FT-IR study of SrL2

FT-IR spectra of SrL1, SrL2, and L are shown in Figure 7. FT-IR spectra of SrL1 and SrL2 are completely different, which are consistent with their crystal structure results. There are three main points of difference between the two complexes. In 4000–3000 $cm^{-1}$ region the half-band width of the OH stretching vibration in SrL2 complex is narrower than that of SrL1 complex. No water takes part in the coordination in the structure of SrL2 and only the hydroxyl groups of galactitol forms hydrogen bonds. Additionally, the deformational vibrations of $H_2O$ located at 1635 and 1618 $cm^{-1}$ appear in the spectrum of SrL1 and no δHOH band appears in the spectrum of SrL2 complex. This is another proof that no coordinated or free water molecules exist in the structure of SrL2 complex. Bands in the region 1200–950 $cm^{-1}$ could be assigned to CO stretching vibration: 1099, 1071, 1050, 1026 $cm^{-1}$ (SrL1), 1102, 1076, 1039, 971, 944 $cm^{-1}$ (SrL2) corresponding to 1118, 1104, 1079, 1049, 1031, 1001 $cm^{-1}$(L). The peak positions and appearances of the two complexes are different because the coordination modes of galactitol are providing either two adjacent hydroxyl groups in SrL1 or three hydroxyl groups in SrL2.

The observation that no δ HOH band can be observed in the IR spectrum of SrL2, which correlates with the X-ray structure is a significant finding since IR spectra are much easier to obtain than X-ray diffraction measurement of a single crystal. IR spectroscopy is an effective technique to evaluate metal–carbohydrate complexes formation. These results may prove useful in assigning structures of complexes where the crystal structure of X-ray determination is not available.

## 3. Conclusions

The crystallographic studies demonstrate that, in hydrated solid-state environments, neutral sugars chelate metal ions through sets of hydroxyl groups. These results indicate that metal ions, in conjunction with water

**Table 5.** Crystal data and structure refinement for $SrCl_2 \cdot C_6H_{14}O_6$ (SrL2)

| | |
|---|---|
| Empirical formula | $C_6H_{14}Cl_2O_6Sr$ |
| Formula weight | 340.69 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| *a* (Å) | 14.2182(4) |
| *b* (Å) | 6.7701(2) |
| *c* (Å) | 13.0191(3) |
| β (°) | 109.8711(19) |
| Volume (Å$^3$) | 1178.58(6) |
| *Z*, Calculated density (mg/m$^3$) | 4, 1.920 |
| Absorption coefficient (mm$^{-1}$) | 5.033 |
| *F*(000) | 680 |
| Crystal shape/crystal color | block/colorless |
| Crystal size (mm) | $0.40 \times 0.35 \times 0.30$ |
| $\theta$ Range for data collection | 3.52–27.50° |
| Limiting indices | $-18 \leqslant h \leqslant 18$, $-8 \leqslant k \leqslant 8$, $-16 \leqslant l \leqslant 16$ |
| Reflections collected/unique | 10109/1340 [$R(\mathrm{int}) = 0.0513$] |
| Reflections with $I > 2\sigma(I)$ | 1199 |
| Completeness to $2\theta = 30.03$ | 99.3% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.246 and 0.179 |
| Hydrogen addition/treatment | geometry /mixed |
| Data/restraints/parameters | 1340/6/80 |
| Goodness-of-fit on $F^2$ | 1.068 |
| Final *R* indices [$I > 2\sigma(I)$] | $R1 = 0.0219$, $wR2 = 0.0478$ |
| *R* indices (all data) | $R1 = 0.0269$, $wR2 = 0.0496$ |
| Extinction coefficient | 0.0096(6) |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.280 and −0.458 |

**Table 6.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for SrL2

| | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| Sr(1) | 5000 | 2512(1) | 7500 | 19(1) |
| Cl(1) | 6103(1) | −467(1) | 6767(1) | 33(1) |
| O(1) | 3826(1) | 1823(2) | 5509(1) | 25(1) |
| O(2) | 3317(1) | 4413(2) | 6842(1) | 25(1) |
| O(3) | 4899(1) | 5445(2) | 6227(1) | 30(1) |
| C(1) | 2972(1) | 3076(3) | 5028(2) | 22(1) |
| C(2) | 3112(1) | 4942(3) | 5718(2) | 23(1) |
| C(3) | 3943(2) | 6295(3) | 5665(2) | 30(1) |

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

**Table 7.** Coordinated bond lengths (Å) and angles (°) in complexes SrL2 with estimated standard derivations

| | Bond length |
|---|---|
| Sr(1)–O(3)#1 | 2.5593(15) |
| Sr(1)–O(2)#1 | 2.5928(14) |
| Sr(1)–O(1) | 2.6041(14) |
| Sr(1)–Cl(1)#1 | 2.9072(5) |
| O(1)–C(1) | 1.438(2) |
| O(2)–C(2) | 1.436(2) |
| O(3)–C(3) | 1.428(3) |
| Sr(1)–O(3) | 2.5593(15) |
| Sr(1)–O(2) | 2.5928(14) |
| Sr(1)–O(1)#1 | 2.6041(14) |
| Sr(1)–Cl(1) | 2.9072(5) |
| C(1)–C(2) | 1.523(3) |
| C(1)–C(1)#2 | 1.533(4) |
| C(2)–C(3) | 1.515(3) |
| | Bond angle |
| O(3)#1–Sr(1)–O(3) | 78.21(7) |
| O(1)–Sr(1)–C(2) | 45.72(5) |
| Cl(1)#1–Sr(1)–C(2) | 100.06(4) |
| C(1)–O(1)–Sr(1) | 119.25(11) |
| O(3)#1–Sr(1)–Cl(1)#1 | 104.09(4) |
| O(1)–C(1)–C(2) | 108.10(15) |
| C(2)–C(1)–C(1)#2 | 112.8(2) |
| C(3)–C(2)–Sr(1) | 82.76(11) |
| O(2)–C(2)–Sr(1) | 47.93(8) |
| Cl(1)#1–Sr(1)–Cl(1) | 92.17(2) |
| O(3)#1–Sr(1)–O(2)#1 | 63.80(5) |
| O(1)#1–Sr(1)–C(2) | 151.07(5) |
| Cl(1)–Sr(1)–C(2) | 120.78(4) |
| C(2)–O(21)–Sr(1) | 107.79(10) |
| O(3)–Sr(1)–Cl(1)#1 | 146.42(3) |
| O(1)–C(1)–C(1)#2 | 108.44(19) |
| C(3)–C(2)–C(1) | 114.97(17) |
| C(1)–C(2)–Sr(1) | 85.05(10) |
| C(2)#1–Sr(1)–C(2) | 120.69(4) |

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

**Table 8.** Hydrogen bonds for SrL2 structure

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O(1)–H(1)···Cl(1)#3 | 0.808(16) | 2.37(2) | 3.1371(15) | 158(2) |
| O(2)–H(2)···Cl(1)#4 | 0.807(16) | 2.339(19) | 3.1178(14) | 162(2) |
| O(3)–H(3)···Cl(1)#5 | 0.804(16) | 2.429(19) | 3.2036(16) | 162(2) |

Symmetry transformations in SrL2 structure used to generate equivalent atoms: #1 $-x+1, y, -z+3/2$; #2 $-x+1/2, -y+1/2, -z+1$; #3 $-x+1, -y, -z+1$; #4 $x-1/2, y+1/2, z$; #5 $x, y+1, z$.

molecules, can bind simultaneously to several uncharged sugar residues and thereby form hydrated carbohydrate–metal ion–carbohydrate bridges.

The coordination modes of CaL, SrL1, SrL2, LaL1, LaL2, and ML are summarized in Table 9. In general the coordination numbers of lanthanide ions ($La^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, and $Tb^{3+}$) are 9 or 10, which are close to the summation of the numbers of 6s, 6p, and 5d orbits. However, the coordination number of alkaline earth ions is generally eight that is lower than those of lanthanide ions. The difference in coordination modes stems from the difference of radius and charge between lanthanide ions and alkaline earth ions. The larger the radius or the higher the charge of metal ion is, the larger the coordination number is.

Galactitol coordinates with one or two metal ions at the same time to form 1:1 (CaL, SrL1, SrL2, LaL1) and 1:2 (ML, LaL2) proportion complexes, respectively. In general 1:1 complexes form a chain structure and 1:2 complexes form a closed structure except that LaL2 also

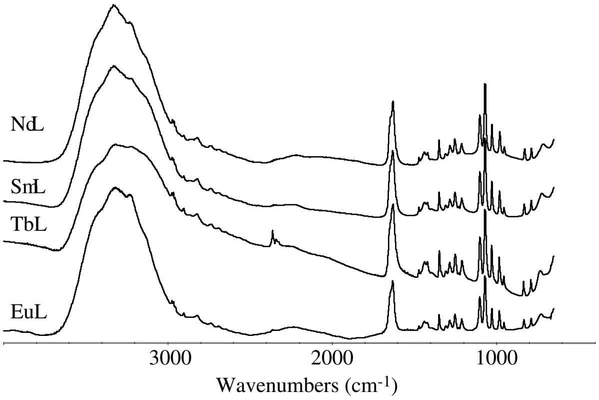

**Figure 5.** FT-IR spectra of NdL, SmL, EuL, and TbL (4000–650 $cm^{-1}$).

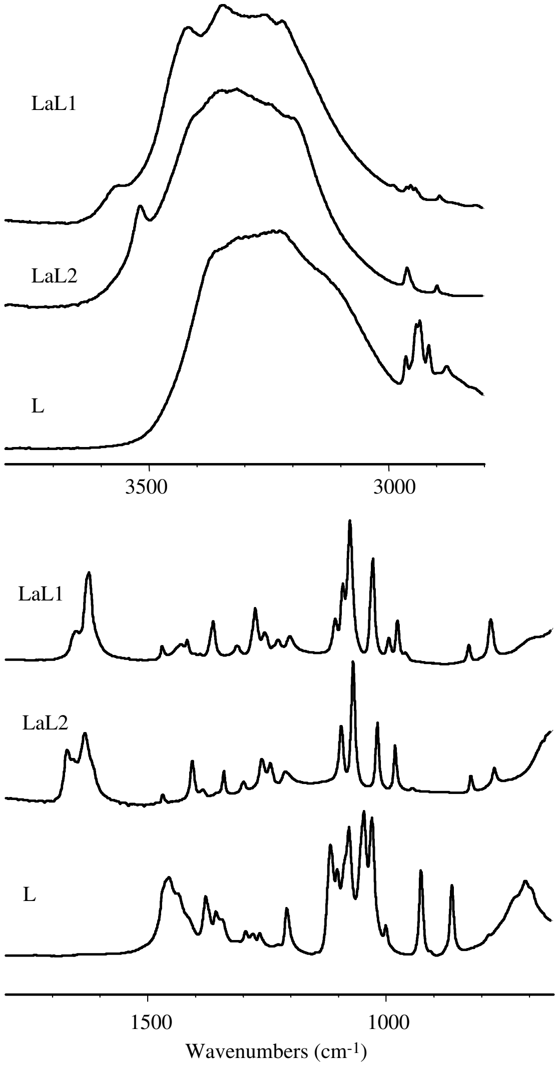

**Figure 6.** FT-IR spectra of LaL1, LaL2, and L (4000–650 $cm^{-1}$).

has a chain structure because of two μ2 chloride bridge bonds. Galactitol has two kinds of coordination modes: providing two adjacent hydroxyl groups or three hydroxyl groups to metal ions (shown in Fig. 8). CaL and SrL1 belong to the first kind of coordination mode; whereas SrL2, LaL1, LaL2, and ML belong to the second kind of coordination mode.

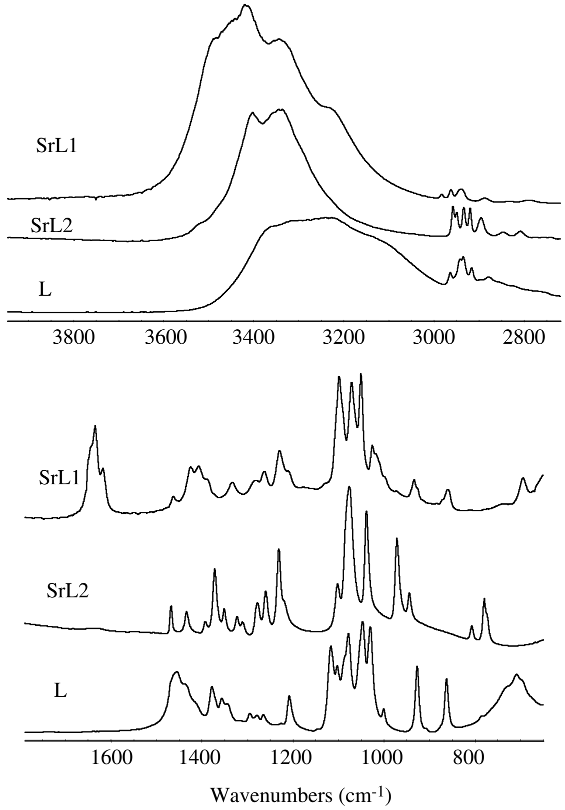

**Figure 7.** FT-IR spectra of SrL1, SrL2, and L (4000–650 $cm^{-1}$).

These versatile structural features can be observed in other metal–alditol complexes. Three erythritol–$Ca^{2+}$ complexes have also been prepared by our group via a similar process: $2CaCl_2{\cdot}C_4H_{10}O_4{\cdot}4H_2O$, $CaCl_2{\cdot}C_4H_{10}O_4{\cdot}4H_2O$, and $CaCl_2{\cdot}2C_4H_{10}O_4{\cdot}4H_2O$,[18] which indicate that different metal–sugar complexes should have similar energies and show the 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 interactions between metal ions and the sugar residue of biomolecules will be more complicated. There exists equilibrium of several coordinations in the solution of metal ion and alditol and the products in the solid state will be one or two of them.

Metal ions may bind carbohydrates to form complexes with different metal:ligand molar ratios and saccharides may have various binding sites. This implies that complexes with diverse structures are expected in the sugar–molecular complexes between metal ion and biomolecules. This variety of coordination feature may serve as information storage and transmission in biological activities.

**Table 9.** Summary of coordination modes of metal chlorides–galactitol complexes

| Structure formula | C.N. | C.W. | L.W. | Coordination mode of L | Coordination mode of $Cl^-$ |
|---|---|---|---|---|---|
| $CaCl_2 \cdot C_6H_{14}O_6 \cdot 4H_2O$ | 8 | 4 | 0 | O-2, O-3, O-2A, O-3A | |
| $SrCl_2 \cdot C_6H_{14}O_6 \cdot 4H_2O$ (SrL1) | 8 | 4 | 0 | O-2, O-3, O-2A, O-3A | |
| $SrCl_2 \cdot C_6H_{14}O_6$ (SrL2) | 8 | 0 | 0 | O-1, O-2, O-3, O-1A, O-2A, O-3A | Cl-1, Cl-1A |
| $LaCl_3 \cdot C_6H_{14}O_6 \cdot 6H_2O$ (LaL1) | 10 | 4 | 2 | O-1, O-2, O-3, O-4, O-5, O-6 | |
| $2LaCl_3 \cdot C_6H_{14}O_6 \cdot 10H_2O$ (LaL2) | 9 | 4 (each $La^{3+}$) | 1 (each $La^{3+}$) | O-1, O-2, O-3 | Cl-1, Cl-1A bridge bonds |
| $2LnCl_3 \cdot C_6H_{14}O_6 \cdot 14H_2O$ ($Ln = Pr, Nd, Sm, Eu, Tb$) | 9 | 6 (each $M^{3+}$) | 1 (each $M^{3+}$) | O-1, O-2, O-3 | |

Abbreviation: C.N.: coordination number, C.W.: coordinated water, L.W.: lattice water.

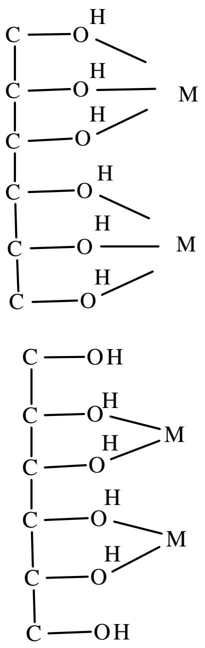

**Figure 8.** Two coordination modes of galactitol to metal ions.

## 4. Experimental

### 4.1. Syntheses and characterizations of the complexes

Lanthanide chlorides were prepared and crystallized from corresponding oxides of high purity (99.99%). 1:1 (v/v) $HCl/H_2O$ was added to dissolve the $La_2O_3$ powder. The solution was heated and stirred to drive off the acid and brought to a pH 4–5. $SrCl_2$ and galactitol (AR) were purchased from chemical factories, Beijing, China, and were used as supplied. Galactitol (3 mmol) and 2 equiv of metal chlorides were dissolved in water–ethanol mixtures and heated to make a concentrated solution. The flask was then sealed until the complex crystallized. Interestingly, the two colorless complexes of SrL1 and SrL2 were obtained in different batches. Complexes of LaL1 and LaL2 were obtained by a similar procedure. The two complexes of $La^{3+}$ or $Sr^{2+}$ were first identified by two different FT-IR spectra. Then their crystal structures were determined by the X-ray single crystal diffraction technique.

### 4.2. X-ray crystallographic analyses of complexes

All crystals were determined on a Nonius KappaCCD diffractometer using monochromatic MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures of all complexes were solved by the SHELX-97 program and refined using full-matrix least-squares and the $F^2$ method. The direct method was used for primary solution and difference Fourier maps for secondary solution. Empirical absorption corrections were made, and the addition and treatment of hydrogen atoms were according to the geometric and mixed methods.

The CCDC 268325 for LaL2 and CCDC 268326 for SrL2 entries contain the supplementary crystallographic data for this paper. These data may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

### 4.3. Physical measurements

Elemental analysis of lanthanum complexes were run on an Elementar Vario EL II with CHN mode. Anal. Calcd for $2LaCl_3 \cdot C_6H_{14}O_6 \cdot 10H_2O$ (LaL2): C, 8.44; H, 3.99. Found: C, 8.51; H, 3.58. Anal. Calcd for $SrCl_2 \cdot C_6H_{14}O_6$ (SrL2): C, 21.13; H, 4.11. Found: C, 20.49; H, 4.05.

The microscopic FT-IR spectra (4000–650 $cm^{-1}$) were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan microscope at a resolution of 4 $cm^{-1}$ by co-adding the results of 64 scans. A mercury cadmium telluride detector was used.

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