Inorg. Chem. **2007**, *46*, 5508–5517

Inorganic Chemistry
Article

Interaction between Metal Nitrates and Carbohydrates: The Topology Coordination Behavior of Galactitol with Trivalent Lanthanide and Divalent Alkaline Earth Ions

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Received July 28, 2006

It has long been known that metal ions and saccharides are involved in many biochemical processes. In this paper, metal nitrates were used as reactants to detect the coordination structures of the hydroxyl groups of galactitol in different environments. Three novel crystal structures and FT-IR spectra of metal nitrate–galactitol complexes of $La(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 4H_2O$, $2Ca(NO_3)_2 \cdot C_6H_{14}O_6 \cdot H_2O$, and $Sr(NO_3)_2 \cdot C_6H_{14}O_6$ were examined in an effort to clarify the structural factors that control metal ion interactions with saccharides in aqueous and biological systems. The coordination structures of galactitol with alkaline earth and lanthanide nitrates in the solid state were compared using FT-IR, Raman, and X-ray diffraction techniques to extensively discuss the coordination rules of different kinds of metal ions. Results provided a model of the coordination sites found in sugars and showed that the introduction of NO_3^- made the coordination modes of galactitol more diverse and complex than those of the corresponding chloride complexes. Specifically, new coordination modes of galactitol and complicated topology networks were found in $2Ca(NO_3)_2 \cdot C_6H_{14}O_6 \cdot H_2O$ and $Sr(NO_3)_2 \cdot C_6H_{14}O_6$. FT-IR results are consistent with the crystal structures and thus provide the possibility of using the similarity of IR spectra to speculate about unknown structures when the compounds are difficult to prepare as single crystals.

Introduction

Sugars, proteins, and nucleic acids are three essential materials for life. Many important biochemical activities involve the participation of sugars as the endogenesis material, which has the function of information transfer, energy transfer, and material transportation. The study of sugars may be traced back to the prominent work of the famous German scientist Fisher one hundred years ago. Compared to the study of proteins and nucleic acids, the study of sugars has dropped far behind because the structures of sugars are more difficult to obtain than those of the other two.

Biochemical processes such as the transport, storage, and calcification of metal ions, stabilization of membrane structures, adsorption between cells, binding of glycoproteins to cell surfaces, toxic metal metabolism, and the binding of proteins to sugars[1−7] may involve the sugar−metal ion interaction. Many biological functions of sugars, such as

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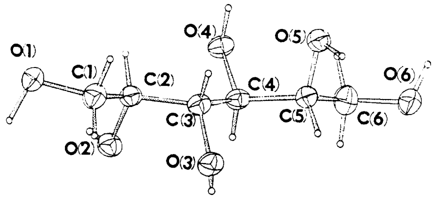
10.1021/ic061414h CCC: $37.00

Scheme 1. The Chemical Structure of Galactitol



those in chlorophyll and hemochrome, require binding with metal ions. The formation of a Ni^{2+}−carbohydrate complex in the human kidney was demonstrated in 1985.[8] The biological function of sugars may be understood on the basis of the cooperation among the chemical characteristics of the different hydroxyl groups of sugars. The interaction between carbohydrates and metal ions, as the model for studying the relation of different hydroxyl groups of sugars, may provide a good entry point for understanding the biological function of sugars more deeply.

Galactitol ($C_6H_{14}O_6$, shown in Scheme 1, the ligand abbreviated by L), the metabolic product of galactose and an acylic alditol of biological importance, has widespread distribution among plant life.[9] Before 2000, only one crystal structure of a galactitol−lanthanide ion complex was found in the literature ($2PrCl_3{\cdot}$galactitol$\cdot 14H_2O$).[10] Our group has prepared a series of lanthanide chloride− and alkaline earth chloride−galactitol complexes since 2000.[11−17] Most of the work on the crystal structures of metal ion−galactitol complexes is limited to the chloride system. Here, metal nitrates were used as reactants to detect the coordination structures of hydroxyl groups of carbohydrates in different environments. The Husson group reported the single-crystal structures of a series of lanthanide nitrate−*cis*,*cis*-1,3,5-cyclohexantriol and *cis*,*cis*-1,2,3-cyclohexantriol complexes.[18,19] The coordination numbers of the complexes were nine, ten, and eleven. The coordinated molecules included three hydroxyl groups of two ligands, a monodentate or bidentate nitrate group, and water molecules. Two different neodymium ion−galactitol complexes, $Nd(NO_3)_3{\cdot}C_6H_{14}O_6$ (NdLN1) and $2Nd(NO_3)_3{\cdot}C_6H_{14}O_6{\cdot}10H_2O$ (NdLN2), prepared by our group have been reported previously.[20] The contribution reported here, which summarized the diverse coordination behavior of neutral nonfunctionalized galactitol to alkaline earth and lanthanide nitrates, demonstrated the coordination differences of various metal ions and the formation of complicated networks and improved the understanding of the correlation between the structural and spectral manifestations.

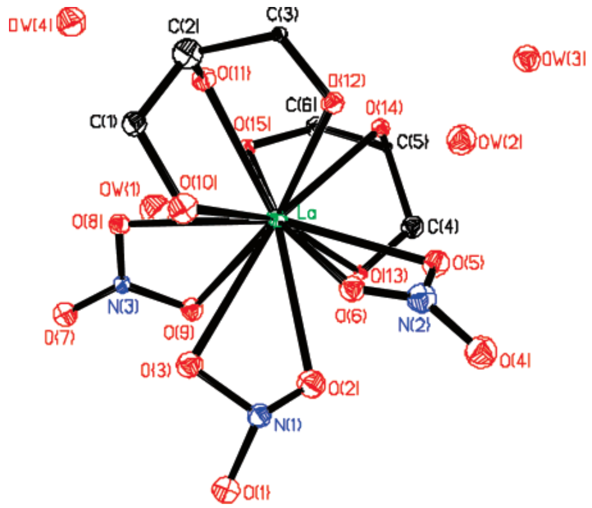


Figure 1. Structure and the numbering of atoms of $La(NO_3)_3{\cdot}C_6H_{14}O_6{\cdot}4H_2O$.

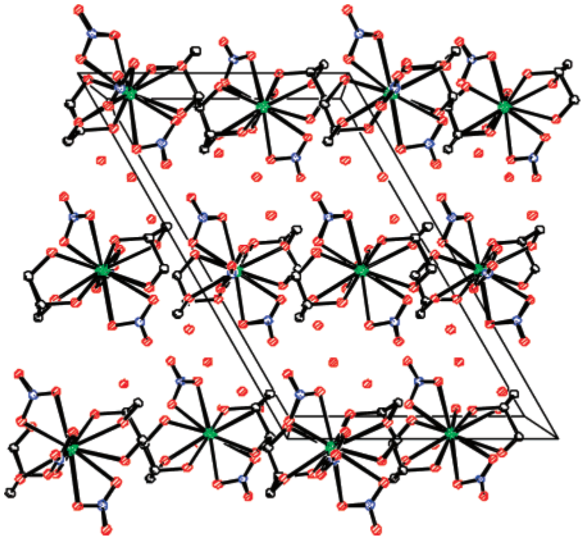


Figure 2. Projection of the crystal cell in the structure of LaLN.

Results and Discussion

Structure of the Lanthanide Nitrate−Galactitol Complexes. The crystal structure and the numbering of atoms of $La(NO_3)_3{\cdot}C_6H_{14}O_6{\cdot}4H_2O$ (LaLN) are shown in Figure 1, and the projection of the crystal cell in the structure of LaLN is shown in Figure 2. Crystal data and coordinated bond lengths and angles of LaLN are listed in Tables 1 and 2, respectively.

The crystal structure of LaLN belongs to the monoclinic system, *Cc* space group. Each La^{3+} is coordinated to twelve oxygen atoms: three oxygen atoms from O-10, O-11, O-12 of the hydroxyl groups of one galactitol (seen in Figure 1), another three atoms from O-13, O-14, O-15 of the hydroxyl groups of another galactitol (seen in Figure 1), and the other

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Table 1. Crystal Data and Structure Refinement for $La(NO_3)_3{\cdot}C_6H_{14}O_6{\cdot}4H_2O$

empirical formula	$C_6H_{22}LaN_3O_{19}$
fw	579.15
temp (K)	293(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	*Cc*
a (Å)	18.7018(11)
b (Å)	10.1221(4)
c (Å)	11.1991(7)
β (deg)	117.7810(14)
vol (Å^3)	1875.64(18)
Z	4
density calcd (mg/m^3)	2.001
abs coeff (mm^{-1})	2.378
F(000)	1096
cryst size (mm)	0.25 × 0.14 × 0.11
θ range (deg)	2.36−27.39
index ranges	$-23 \le h \le 24$ $-13 \le k \le 13$ $-14 \le l \le 14$
reflns collected/unique	4002/3999 [*R*(int) = 0.0545]
completeness to θ = 27.39°	99.5%
max. and min. transmission	0.7733 and 0.5890
refinement method	full-matrix least-squares on F^2
data/restraints/params	3999/260/263
GOF on F^2	0.506
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0346 wR2 = 0.0613
R indices (all data)	R1 = 0.0581 wR2 = 0.0650
absolute structure param	0.41(4)
largest diff. peak and hole (e Å^{-3})	0.749 and −0.551

Table 2. Selected Coordinated Bond Lengths (Å) and Angles (deg) in the LaLN Complex with Estimated Standard Derivations[a]

La−O(11)	2.547(12)	O(6)−N(2)	1.198(18)
La−O(13)	2.550(8)	O(7)−N(3)	1.249(15)
La−O(14)	2.587(11)	O(8)−N(3)	1.207(15)
La−O(10)	2.622(10)	O(9)−N(3)	1.299(17)
La−O(15)	2.641(8)	O(10)−C(1)	1.461(18)
La−O(9)	2.703(10)	O(11)−C(2)	1.412(18)
La−O(5)	2.707(10)	O(12)−C(3)	1.363(16)
La−O(8)	2.709(8)	O(13)−C(4)	1.421(18)
La−O(12)	2.727(9)	O(14)−C(5)	1.470(17)
La−O(2)	2.745(13)	O(15)−C(6)	1.571(17)
La−O(3)	2.808(13)	C(1)−C(2)	1.57(2)
La−O(6)	2.843(10)	C(2)−C(3)	1.59(2)
O(1)−N(1)	1.288(6)	C(3)−C(6)#1	1.530(6)
O(2)−N(1)	1.118(16)	C(4)−C(5)	1.47(2)
O(3)−N(1)	1.406(17)	C(5)−C(6)	1.44(2)
O(4)−N(2)	1.251(18)	C(6)−C(3)#2	1.530(6)
O(5)−N(2)	1.368(17)		
O(11)−La−O(13)	131.7(3)	O(11)−La−O(14)	80.39(14)
N(1)−O(2)−La	103.8(9)	N(1)−O(3)−La	92.8(6)
C(1)−O(10)−La	117.4(8)	C(2)−O(11)−La	110.3(9)
O(2)−N(1)−O(1)	140.3(13)	O(2)−N(1)−O(3)	116.7(6)
O(10)−C(1)−C(2)	106.6(12)	O(11)−C(2)−C(1)	115.1(13)
C(1)−C(2)−C(3)	107.1(12)	C(6)#1−C(3)−C(2)	110.8(9)
C(6)−C(5)−O(14)	105.1(10)	C(5)−C(6)−O(15)	110.1(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, −*y*, *z* + 1/2; #2 *x*, −*y*, *z* − 1/2.

six atoms from three bidentate nitrate groups (O-2, O-3; O-5, O-6; O-8, O-9 in Figure 1). The La−O distances are from 2.547 to 2.843 Å, in which the distances of La−O (galactitol) are shorter than those of La−O (NO_3^-) indicating that the hydroxyl group of galactitol has stronger interaction with La^{3+} than the nitrate group does. Four water molecules (OW-1, OW-2, OW-3, and OW-4) do not take part in the coordination, which involves all lattice water-forming hydrogen bonds with hydroxyl groups or nitrate groups. Each galactitol provides three hydroxyl groups to coordinate with one La^{3+} and another three hydroxyl groups to coordinate with another La^{3+}. At the same time, each La^{3+} is coordinated with two L ligands and thus La^{3+} links two galactitols together to form a chain structure $[La(NO_3)_3(C_6H_{14}O_6)]_\infty$ (Figure 2). The complex is in a bicapped pentagonal antiprism (trigonal icosahedron) configuration.

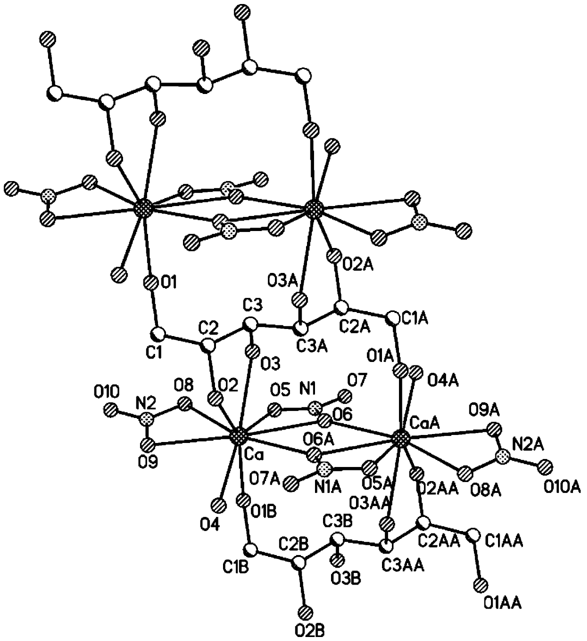

Figure 3. Structure and the numbering of atoms of $2Ca(NO_3)_2{\cdot}C_6H_{14}O_6{\cdot}H_2O$.

In two $LaCl_3$−galactitol complexes ($LaCl_3{\cdot}C_6H_{14}O_6{\cdot}6H_2O$ (LaL1)[15] and $2LaCl_3{\cdot}C_6H_{14}O_6{\cdot}10H_2O$ (LaL2)[17]), galactitol both provides three hydroxyl groups to La^{3+}, in which the coordination mode of galactitol is similar to that of LaLN and the chain structures are formed. In the structure of LaL1, each La^{3+} is coordinated to three hydroxyl groups of one galactitol, three hydroxyl groups of another galactitol, and four water molecules with La−O distances ranging from 2.5099 to 2.6916 Å. In the structure of LaL2, each La^{3+} is coordinated to three hydroxyl groups of one galactitol, four water molecules, and two chloride ions with La−O distances ranging from 2.515 to 2.621 Å.

Structures of Alkaline Earth Metal Nitrate−Galactitol Complexes. The crystal structure and the numbering of atoms of $2Ca(NO_3)_2{\cdot}C_6H_{14}O_6{\cdot}H_2O$ (CaLN) are shown in Figure 3, and the projection of the crystal cell in the structure of CaLN is shown in Figure 4. Crystal data, coordinated bond lengths and angles, and hydrogen bonds of CaLN are listed in Tables 3−5, respectively. The crystal structure and the numbering of atoms of $Sr(NO_3)_2{\cdot}C_6H_{14}O_6$ (SrLN) are shown in Figure 5, and the two-dimensional (2D (4,4)) net formed by Sr nodes and ligand nodes in the structure of SrLN is shown in Figure 6. Crystal data, coordinated bond lengths and angles, and hydrogen bonds of SrLN are listed in Tables 6−8, respectively.

The crystal structure of CaLN belongs to the monoclinic system, $P2_1/c$ space group. The structure of CaLN is

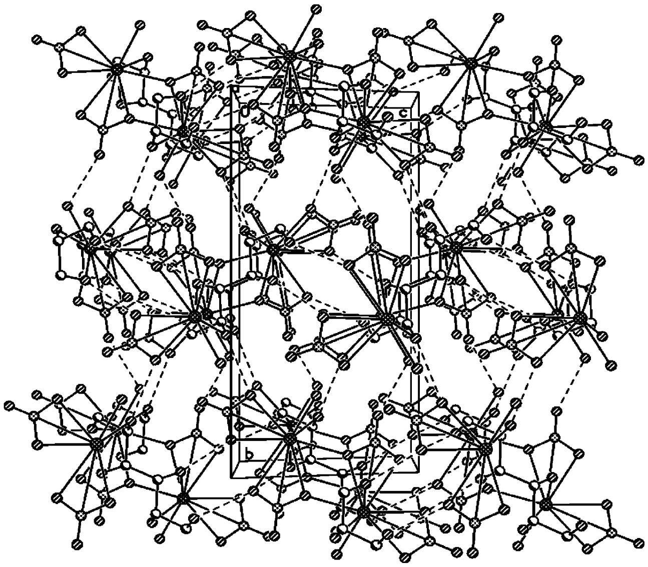

Figure 4. Projection of the crystal cell in the structure of CaLN.

Table 3. Crystal Data and Structure Refinement for $Ca(NO_3)_2 \cdot C_6H_{14}O_6 \cdot H_2O$

empirical formula	$C_6H_{16}Ca_2N_4O_{19}$
fw	528.37
temp (K)	293(2)
measurement device	Rigaku RAXIS RAPID IP
measurement method	oscillation
wavelength (Å)	0.71073
cryst syst, space group	monoclinic
space group	$P2_1/c$
a (Å)	7.2451(14)
b (Å)	17.063(3)
c (Å)	8.0827(16)
β (deg)	107.97(3)
vol (Å^3)	950.5(3)
Z	4
density calcd (mg/m^3)	1.909
abs coeff (mm^{-1})	0.713
F(000)	564
cryst shape/color	block/colorless
cryst size (mm)	0.35 × 0.30 × 0.10
θ range (deg)	2.91−27.48
index ranges	$-9 \leq h \leq 9$ $-22 \leq k \leq 22$ $-10 \leq l \leq 9$
reflns collected/unique	8455/2181 [R(int) = 0.0406]
reflns with $I > 2\sigma(I)$	1698
completeness to $\theta = 27.48°$	99.9%
abs correction	empirical
max. and min. transmission	0.931 and 0.606
method for primary solution	direct
method for secondary solution	Fourier difference map
hydrogen addition/treatment	hydrogen atoms are generated by HFIX/mixed
refinement method	full-matrix least-squares on F^2
data/restraints/params	2181/0/166
GOF on F^2	0.905
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0255 wR2 = 0.0512
R indices (all data)	R1 = 0.0393 wR2 = 0.0531
extinction coeff	0.0201(14)
largest diff. peak and hole (e Å^{-3})	0.372 and −0.263

Table 4. Coordinated Bond Lengths (Å) and Angles (deg) in the CaLN Complex with Estimated Standard Derivations[a]

Ca−O(1)#1	2.3821(12)	O(2)−C(2)	1.4400(16)
Ca−O(4)	2.3986(13)	O(3)−C(3)	1.4378(16)
Ca−O(3)	2.4118(11)	O(5)−N(1)	1.2427(15)
Ca−O(2)	2.4426(12)	O(6)−N(1)	1.2576(15)
Ca−O(6)#2	2.5316(13)	O(6)−Ca#2	2.5316(13)
Ca−O(8)	2.5341(14)	O(7)−N(1)	1.2290(16)
Ca−O(9)	2.5921(12)	O(8)−N(2)	1.2656(15)
Ca−O(6)	2.6491(11)	O(9)−N(2)	1.2559(16)
Ca−O(5)	2.7879(12)	O(10)−N(2)	1.2107(17)
Ca−N(2)	2.9864(5)	C(1)−C(2)	1.518(2)
Ca−N(1)	3.1519(14)	C(2)−C(3)	1.5242(18)
O(1)−C(1)	1.4339(17)	C(3)−C(3)#4	1.530(3)
O(1)−Ca#3	2.3821(12)		

O(1)#1−Ca−O(4)	76.17(4)	O(9)−Ca−N(2)	24.75(3)
O(1)#1−Ca−O(3)	143.29(4)	O(6)−Ca−N(2)	130.69(3)
O(4)−Ca−O(3)	140.32(4)	O(5)−Ca−N(2)	84.90(4)
O(1)#1−Ca−O(2)	152.21(4)	O(1)#1−Ca−N(1)	75.25(4)
O(4)−Ca−O(2)	76.68(4)	O(4)−Ca−N(1)	137.76(4)
O(3)−Ca−O(2)	64.36(4)	O(3)−Ca−N(1)	71.63(4)
O(1)#1−Ca−O(6)#2	98.06(4)	O(2)−Ca−N(1)	130.67(4)
O(4)−Ca−O(6)#2	73.38(5)	O(6)#2−Ca−N(1)	80.58(3)
O(3)−Ca−O(6)#2	91.79(4)	O(8)−Ca−N(1)	83.61(3)
O(2)−Ca−O(6)#2	79.64(4)	O(9)−Ca−N(1)	131.14(3)
O(1)#1−Ca−O(8)	83.47(4)	O(6)−Ca−N(1)	23.01(3)
O(4)−Ca−O(8)	122.99(5)	O(5)−Ca−N(1)	23.12(3)
O(3)−Ca−O(8)	77.61(4)	O(2)−Ca−O(8)	106.75(4)
C(1)−O(1)−Ca#3	138.47(9)	O(6)#2−Ca−O(8)	163.14(4)
C(2)−O(2)−Ca	120.51(8)	O(1)#1−Ca−O(9)	85.11(4)
C(3)−O(3)−Ca	121.74(8)	O(4)−Ca−O(9)	75.81(5)
O(3)−Ca−O(9)	105.08(4)	O(2)−Ca−O(9)	82.68(4)
O(6)#2−Ca−O(9)	147.23(3)	Ca#2−O(6)−Ca	122.36(4)
O(8)−Ca−O(9)	49.53(3)	O(1)#1−Ca−O(6)	82.25(4)
O(4)−Ca−O(6)	122.42(5)	O(7)−N(1)−O(5)	121.94(12)
O(3)−Ca−O(6)	73.45(4)	O(7)−N(1)−O(6)	121.01(12)
O(2)−Ca−O(6)	117.78(4)	O(5)−N(1)−O(6)	117.05(12)
O(6)#2−Ca−O(6)	57.64(4)	O(7)−N(1)−Ca	175.12(10)
O(8)−Ca−O(6)	106.25(3)	O(5)−N(1)−Ca	61.76(7)
O(9)−Ca−O(6)	154.00(3)	O(6)−N(1)−Ca	55.43(7)
O(4)−Ca−O(5)	144.09(4)	O(10)−N(2)−O(8)	121.08(13)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - 1, y, z$; #2 $-x, -y + 1, -z$; #3 $x + 1, y, z$; #4 $-x + 1, -y + 1, -z$.

Table 5. Hydrogen Bonds for the Structure of the CaLN Complex[a]

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
O(1)−H(1)···O(5)#5	0.785(18)	2.003(18)	2.7688(16)	165.1(18)
O(2)−H(2)···O(9)#6	0.732(17)	2.181(18)	2.9067(16)	170.8(19)
O(3)−H(3)···O(8)#5	0.761(17)	2.023(18)	2.7810(16)	173.7(18)
O(4)−H(4A)···O(7)#7	0.79(2)	2.03(2)	2.8050(18)	166(2)
O(4)−H(4B)···O(7)#2	0.76(3)	2.12(3)	2.790(2)	148(2)

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

interesting. Each Ca^{2+} is coordinated to nine oxygen atoms: two from O-2, O-3 of the hydroxyl group of one galactitol, one from O-1B of the hydroxyl group of another galactitol, four from two bidentate nitrate groups (O-5, O-6; O-8, O-9), one from the third nitrate group (O-6A), and one from water molecule (O-4). The Ca−O distances range from 2.3821 to 2.7879 Å. For O-6 and O-6A from two nitrate groups, they are coordinated with another Ca^{2+} at the same time, forming two μ_3 bridge bonds. These two nitrate groups are coordinated with two Ca^{2+} ions at the same time to form bidentate coordination. Each Ca^{2+} is coordinated with two neighbor hydroxyl groups of one L ligand (O-2 and O-3 in Figure 3) and one hydroxyl group of another L ligand (O-18 in Figure 3). Each Ca^{2+} is coordinated with two L ligands; each L ligand provides O-2 and O-3 for one Ca^{2+}, O-1 for the second Ca^{2+}, O-2A and O-3A for the third Ca^{2+}, and O-1A for the fourth Ca^{2+}. Each L ligand is coordinated with four Ca^{2+}. Each Ca^{2+} is coordinated with two L ligands to form a 1:2

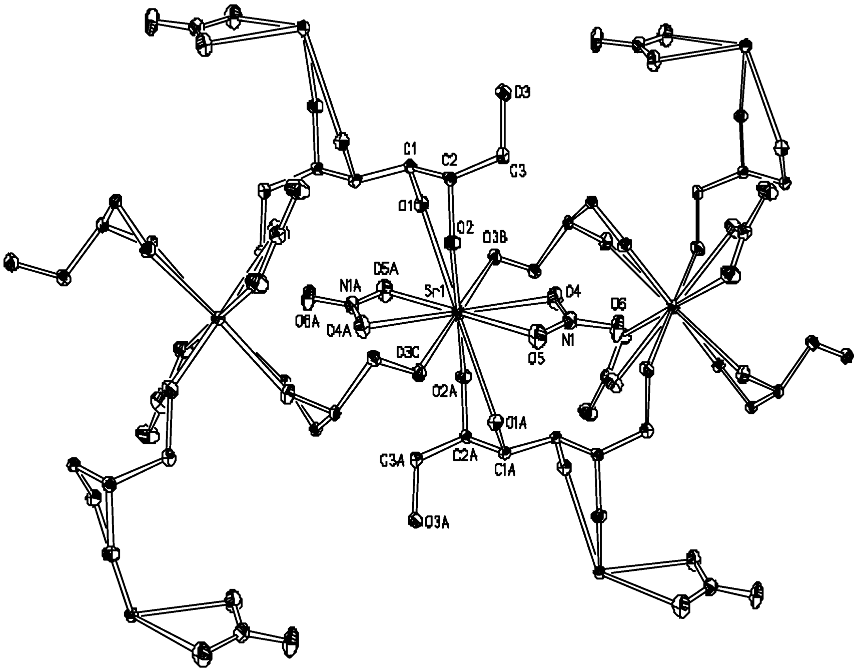

Figure 5. Structure and the numbering of atoms of $Sr(NO_3)_2 \cdot C_6H_{14}O_6$.

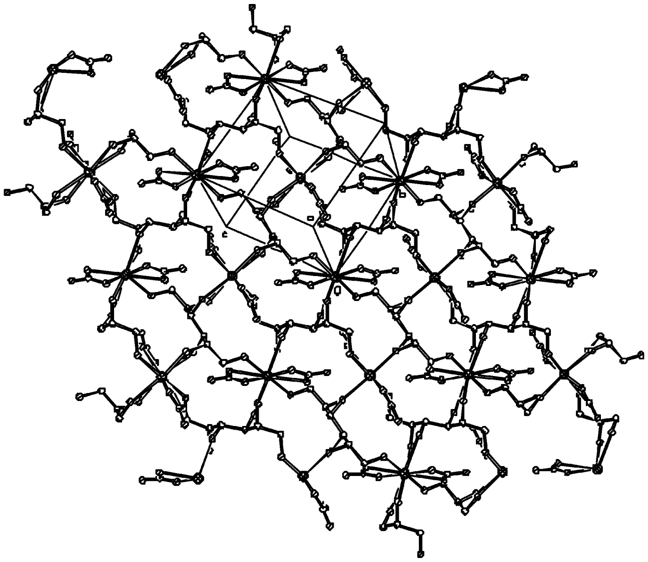

Figure 6. Projection of the crystal cell in the structure of SrLN.

complex. Galactitol links the Ca^{2+} ions together to form a chain structure and two chains are connected together by oxygen bridges (O-6 and O-6A in Figure 3) formed by two nitrate groups like a ladder structure. From Table 5, four nitrate groups and a water molecule all take part in the coordination, only five hydrogen bonds form in the structure. Three hydrogen bonds are between hydroxyl groups of the L ligand and the coordinated oxygen atoms of nitrate groups: O(1)−H(1)···O(5)#5 (2.7688 Å), O(2)−H(2)···O(9)#6 (2.9067 Å), and O(3)−H(3)···O(8)#5 (2.7810 Å). The other two are between the hydroxyl group of water molecules and the uncoordinated oxygen atoms (O7): O(4)−H(4A)···O(7)#7 (2.8050 Å) and O(4)−H(4B)···O(7)#2 (2.790 Å).

The crystal structure of $Sr(NO_3)_2 \cdot C_6H_{14}O_6$ belongs to the monoclinic system, $P2_1/n$ space group. The coordination

Table 6. Crystal Data and Structure Refinement for $Sr(NO_3)_2 \cdot C_6H_{14}O_6$

empirical formula	$C_6H_{14}N_2O_{12}Sr$
fw	393.81
temp (K)	293(2)
wavelength (Å)	0.71073
program for structure solution	SHELXS-97 (Sheldrick 1997)
program for structure refinement	SHELXL-97 (Sheldrick 1997)
program for molecular graphics	Bruker SHELXTL, version 5.1 (Sheldrick 1998)
program for publication material	SHELXL-97 (Sheldrick 1997)
cryst syst,	monoclinic
space group	$P2_1/n$
a (Å)	8.6712(2)
b (Å)	7.7620(2)
c (Å)	10.2841(3)
α (deg)	90
β (deg)	109.6903(10)
γ (deg)	90
vol (Å^3)	651.71(3)
Z	2
density calcd (mg/m^3)	2.007
abs coeff (mm^{-1})	4.206
F(000)	396
cryst shape/color	block/colorless
cryst size (mm)	0.32 × 0.15 × 0.15
θ range (deg)	3.62−27.48
limiting indices	$-11 \leq h \leq 11$ $-9 \leq k \leq 10$ $-13 \leq l \leq 13$
reflns collected/unique	11 409/1482 [R(int) = 0.0607]
reflns with $I > 2\sigma(I)$	1194
completeness to $2\theta = 30.03°$	99.3%
abs correction	empirical
max. and min. transmission	0.542 and 0.423
method for primary solution	direct
method for secondary solution	Fourier difference map
hydrogen addition/treatment	geometry/mixed
refinement method	full-matrix least-squares on F^2
data/restraints/params	1482/6/108
GOF on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0261 wR2 = 0.0579
R indices (all data)	R1 = 0.0405 wR2 = 0.0630
extinction coeff	0.075(3)
largest diff. peak and hole (e Å^{-3})	0.574 and −0.744

Table 7. Selected Coordinated Bond Lengths (Å) and Angles (deg) in the SrLN Complex with Estimated Standard Derivations[a]

Sr(1)−O(2)#1	2.5996(15)	O(2)−H(2)	0.810(16)
Sr(1)−O(2)	2.5996(15)	O(3)−C(3)	1.427(3)
Sr(1)−O(4)#1	2.6184(17)	O(3)−Sr(1)#4	2.6639(16)
Sr(1)−O(4)	2.6184(17)	O(3)−H(3)	0.803(16)
Sr(1)−O(3)#2	2.6639(16)	O(4)−N(1)	1.269(2)
Sr(1)−O(3)#3	2.6639(16)	O(5)−N(1)	1.223(3)
Sr(1)−O(1)	2.7012(12)	O(6)−N(1)	1.253(3)
Sr(1)−O(1)#1	2.7012(16)	C(1)−C(2)	1.516(3)
Sr(1)−O(5)	3.0490(18)	C(1)−C(1)#5	1.528(4)
Sr(1)−O(5)#1	3.0490(18)	C(1)-H(1A)	0.9800
Sr(1)−N(1)	3.2439(19)	C(2)−C(3)	1.525(3)
Sr(1)−N(1)#1	3.2439(19)	C(2)−H(2A)	0.9800
O(1)−C(1)	1.436(2)	C(3)−H(3A)	0.9700
O(1)−H(1)	0.795(16)	C(3)−H(3B)	0.9700
O(2)−C(2)	1.431(2)		

O(2)#1−Sr(1)−O(2)	180.00(7)	O(1)−Sr(1)−N(1)	114.53(5)
O(2)#1−Sr(1)−O(4)#1	83.78(5)	O(1)#1−Sr(1)−N(1)	65.47(5)
O(4)#1−Sr(1)−O(4)	180.00(11)	O(2)−Sr(1)−N(1)#1	05.37(5)
O(2)#1−Sr(1)−O(1)	120.49(5)	C(1)−O(1)−Sr(1)	120.83(11)
O(2)−Sr(1)−O(1)	59.51(5)	C(1)−O(1)−H(1)	110.2(16)
O(4)#1−Sr(1)−O(1)	75.24(5)	Sr(1)−O(1)−H(1)	114.7(19)
O(4)−Sr(1)−O(1)	104.76(5)	C(2)−O(2)−Sr(1)	123.24(12)
O(3)#2−Sr(1)−O(1)	112.55(5)	C(2)−O(2)−H(2)	109.4(16)
O(3)#3−Sr(1)−O(1)	67.45(5)	Sr(1)−O(2)−H(2)	125.3(16)
O(4)#1−Sr(1)−O(1)#1	104.76(5)	Sr(1)#4−O(3)−H(3)	119.7(17)
O(4)#1−Sr(1)−O(5)	136.20(5)	O(6)−N(1)−Sr(1)	164.97(15)
O(4)−Sr(1)−O(5)	43.80(5)	O(4)−N(1)−Sr(1)	50.13(11)
O(3)#2−Sr(1)−O(5)	66.79(5)	O(1)−C(1)−C(2)	108.46(17)
O(3)#3−Sr(1)−O(5)	113.21(5)	O(1)−C(1)−C(1)#5	107.5(2)
O(1)−Sr(1)−O(5)	117.34(5)	C(2)−C(1)−C(1)#5	113.1(2)
O(4)−Sr(1)−O(5)#1	136.20(5)	O(2)−C(2)−C(3)	108.13(17)
O(1)−Sr(1)−O(5)#1	62.66(5)	C(1)−C(2)−H(2A)	109.8
O(1)#1−Sr(1)−O(5)#1	117.34(5)	C(3)−C(2)−H(2A)	109.8
O(5)−Sr(1)−O(5)#1	180.00(9)	O(3)−C(3)−C(2)	112.23(17)
O(2)#1−Sr(1)−N(1)	105.37(5)	O(3)−C(3)−H(3A)	109.2
O(4)#1−Sr(1)−N(1)	158.16(5)	O(3)−C(3)−H(3B)	109.2
O(3)#2−Sr(1)−N(1)	88.45(5)	H(3A)−C(3)−H(3B)	107.9
O(3)#3−Sr(1)−N(1)	91.55(5)		

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

Table 8. Hydrogen Bonds for the Structure of the SrLN Complex[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1)−H(1)···O(4)#4	0.795(16)	2.03(2)	2.773(2)	155(2)
O(2)−H(2)···O(6)#6	0.810(16)	2.047(17)	2.846(2)	169(3)
O(3)−H(3)···O(6)#7	0.803(16)	2.125(19)	2.911(2)	166(3)

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

structure is very special: each Sr^{2+} is coordinated with ten oxygen atoms from four ligands and two nitrate groups. Two ligands provide O-1 and O-2 of two hydroxyl groups (O-1, O-2; O-1A, O-2A in Figure 5), another two ligands provide O-3 of one hydroxyl group (O-3B, O-3C in Figure 5); two bidendate nitrate groups provide O-4 and O-5 (O-4, O-5; O-4A, O-5A in Figure 5). As shown in Table 7, the bond lengths of the Sr−O bonds range from 2.5996 to 3.0490 Å, and the bond length of Sr−O(5) at 3.0490 Å is longer than that of the usual M−O bond. As shown in Figure 6, the Sr cation acts as a four−connecting node to link four neighbor Sr cation centers via galactitol ligands, forming a diamond net (2D (4,4)) built from Sr^{2+} ions and bridging galactitol-ligands. A similar diamond structure was found in the $CaCl_2\cdot 2C_4H_{10}O_4\cdot 4H_2O$ complex prepared by our group.[21] The rhombic channels of the diamond net are built from Ca cations and bridging $C_4H_{10}O_4$ (erythritol) ligands. Because no water takes part in the coordination of SrLN, very few hydrogen bonds form: O(1)−H(1)···O(4)#4 (2.773 Å), O(2)−H(2)···O(6)#6 (2.846 Å), and O(3)−H(3)···O(6)#7 (2.911 Å), which are from the hydroxyl groups of the L ligand and the coordinated atom (O-4) or uncoordinated atom (O-6) of a nitrate group (seen in Figure 5 and Table 8).

In the crystal structures of $CaCl_2\cdot C_6H_{14}O_6\cdot 4H_2O$ (CaL)[14] and two $SrCl_2$−galactitol complexes ($SrCl_2\cdot C_6H_{14}O_6\cdot 4H_2O$ (SrL1)[16] and $SrCl_2\cdot C_6H_{14}O_6$ (SrL2)[17]), every galactitol is coordinated two metal ions, and thus, the cations link galactitol together to form a chain structure, which is different from the ladder structure of CaLN and the diamond net structure of SrLN. In the two similar structures of CaL and SrL, each Ca^{2+}/Sr^{2+} is coordinated to two adjacent hydroxyl groups of one galactitol, two hydroxyl groups of another galactitol, and four water molecules with Ca−O distances ranging from 2.414 to 2.542 Å and Sr−O distances from 2.5420 to 2.6359 Å. In the structure of SrL2, each Sr^{2+} ion is coordinated to three hydroxyl groups of one galactitol, another three hydroxyl groups of another galactitol, and two chloride atoms with Sr−O distances ranging from 2.5593 to 2.6041 Å.

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

FT-IR and Raman Comparative Study of LaLN, CaLN, and SrLN. FT-IR spectra of LaLN, CaLN, SrLN, and galactitol are shown in Figure 7. CaLN is a 2:1 complex; SrLN and LaLN are 1:1 complexes, in which the SrLN complex does not contain water molecules. The three complexes have different structures corresponding to different FT-IR spectra. The results of the spectral analysis are divided into six regions between 4000 and 650 cm^{-1} and are discussed as follows.

Compared with the spectrum of pure galactitol and metal chloride−carbohydrate hydration complexes,[17] the OH stretching vibrations do not form a broad band but are divided into several peaks. The band for νOH in the CaLN complex is divided into four peaks: 3598, 3486, 3359, and 3267 cm^{-1}. The one for LaLN is divided into 3533, 3491, 3333, and 3205 cm^{-1}. Because no water molecule exists in the structure of SrLN, the band for νOH is obviously narrower than those of CaLN and LaLN and is divided into two individual peaks: 3441 and 3364 cm^{-1}. The features of the νOH band are affected by the numbers of hydrogen bonds in the crystal structures. For a larger number of hydrogen bonds, more peaks appear in the IR spectra. For example, SrLN has three

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(21) Yang, L. M.; Su, Y. L.; Xu, Y. Z.; Wang, Z. M.; Guo, Z. H.; Weng, S. F.; Yan, C. H.; Zhang, S. W.; Wu, J. G. *Inorg. Chem.* **2003**, *42*, 5844−5856.

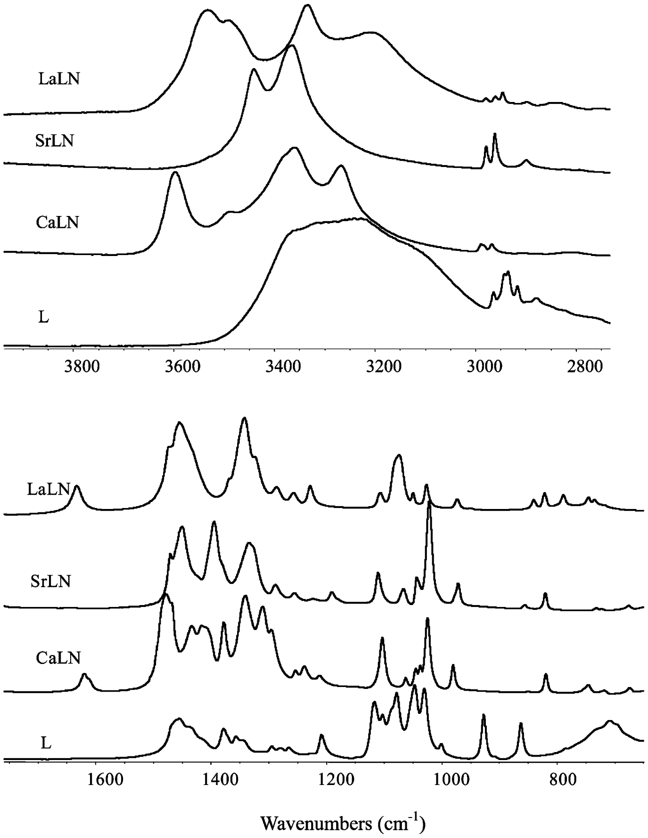

Figure 7. FT-IR spectra of LaLN, CaLN, SrLN, and galactitol (4000−650 cm^{-1}).

hydrogen bonds corresponding to two νOH peaks, and CaLN has five hydrogen bonds corresponding to four νOH peaks.

The CH stretching vibrations are very weak in the spectrum of CaLN, which is masked by the OH stretching vibrations, and there are two low-intensity peaks: 2988 and 2967 cm^{-1}. The CH stretching vibrations in the spectrum of LaLN are also very weak: 2979, 2960, 2946, 2897, and 2833 cm^{-1}. The νCH bands of SrLN (2987, 2961, and 2899 cm^{-1}) are not masked by the νOH bands and are stronger than those of CaLN and LaLN.

In the spectrum of CaLN, the deformational vibration of water is located at 1621 cm^{-1}, which indicates the existence of a water molecule in the structure. For SrLN, no δHOH band appears at 1640 cm^{-1} indicating that no water is present in the structure of SrLN. In general, the absorption bands of lattice water are located at 3550−3200 (OH stretching vibration) and 1630−1600 cm^{-1}(HOH deformational vibration).[22] From the result of the crystal structure of LaLN, the four water molecules are all lattice waters. In the spectrum of LaLN, the νOH band is located in the 3533−3205 cm^{-1} region, and the δHOH peak is located at 1633 cm^{-1}, which is in agreement with the expected result for lattice water.

The asymmetric and symmetric stretching vibrations of NO_2 are located at 1530−1480 and 1300−1250 cm^{-1}, respectively. The bending vibrations of CH_2 (1500−1300 cm^{-1}) are also located in this spectral region and are coupled with the strong NO_2 stretching vibrations. Many strong peaks at 1530−1250 cm^{-1} are observed in the spectra of the three complexes in comparison with several weak peaks in the spectrum of galactitol. In the complex, free NO_3^- peak is located at 1384 cm^{-1}, and the characteristic bands belonging to bidentate nitrate group are located at 743, 809, 1069, 1288, and 1522 cm^{-1}. However, the complication of NO_2/CH_2 vibrational coupling prevented any detailed analysis. The bands in the 1200−950 cm^{-1} region are mainly assigned to CO stretching vibrations, and a medium intensity NO stretching vibration is located at 1040−970 cm^{-1}, which is masked by CO stretching vibrations. There are several characteristic νCO peaks (1103, 1062, 1045, 1037, 1024, and 980 cm^{-1} (CaLN); 1110, 1066, 1043, 1022, and 971 cm^{-1} (SrLN); and 1107, 1074, 1050, 1026 ,and 973 cm^{-1} (LaLN)), corresponding to the 1117, 1103, 1078, 1047, 1030, and 1001 cm^{-1} peaks in the spectrum of galactitol. Compared with pure galactitol, the peaks related to C−O vibrations in the spectra of the three complexes are shifted, which demonstrates the coordination of the hydroxyl groups. The bond lengths of the C−O bonds in the L ligand are different in the three complexes: there are six kinds of C−O bonds in LaLN, 1.461, 1.412, 1.363, 1.421, 1.470, and 1.571 Å, corresponding to three kinds of C−O bonds in both the CaLN (1.4339, 1.4440, and 1.4378 Å) and SrLN (1.436, 1.431, and 1.427 Å) complexes. The various coordination modes of galactitol in the three complexes result in different peaks in the region of the C−O stretching vibrations.

The weak NO_3^- out-of-plane bending vibration is located at 820−780 cm^{-1}. In the spectra of CaLN, SrLN, and LaLN, the δNO_3^- peaks are located at 819, 820, and 821 cm^{-1}, respectively. Weak asymmetric and symmetric bending vibrations of NO_2 are located at about 739 and 713 cm^{-1}, respectively. In the spectrum of CaLN, the $\delta_{as}NO_2$ and δ_s-NO_2 peaks are located at 745 and 718 cm^{-1}, respectively. In the spectrum of SrLN, the band of δNO_2 is very weak and could not be observed. In the spectrum of LaLN, the $\delta_{as}NO_2$ peak is located at 745 cm^{-1}.

Although the nitrate groups all act as bidentate ligands in the three complexes, the bond lengths of the N−O bonds are different, resulting from the difference in the symmetry of the nitrate groups. For LaLN, the bond lengths of the three nitrate groups are completely different: N(1)−O = 1.288, 1.118, 1.406 Å; N(2)−O = 1.251, 1.368, 1.198 Å; and N(3)−O = 1.249, 1.207, 1.299 Å. For CaLN, the bond lengths of the two nitrate groups are different: N(1)−O = 1.2427, 1.2576, 1.2290 Å and N(2)−O = 1.2656, 1.2559, 1.2107 Å. For SrLN, the bond lengths of the two nitrate groups are the same: N(1)−O = 1.269, 1.223, 1.253 Å. Because the number of N−O bonds in the LaLN complex is the largest of the three complexes, there are many broad peaks in the vibration region of the NO_2 group that could not be separated completely.

FT-Raman spectra of CaLN, SrLN, and LaLN are shown in Figure 8. The νOH band becomes very weak and could not be observed in the Raman spectrum. The νCH bands become strong and the peaks are located at 2991, 2968, 2940, 2919 (CaLN); 2980, 2957, 2903 (SrLN); and 2982, 2970,

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(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Chemical Industry Press: Beijing, 1991.

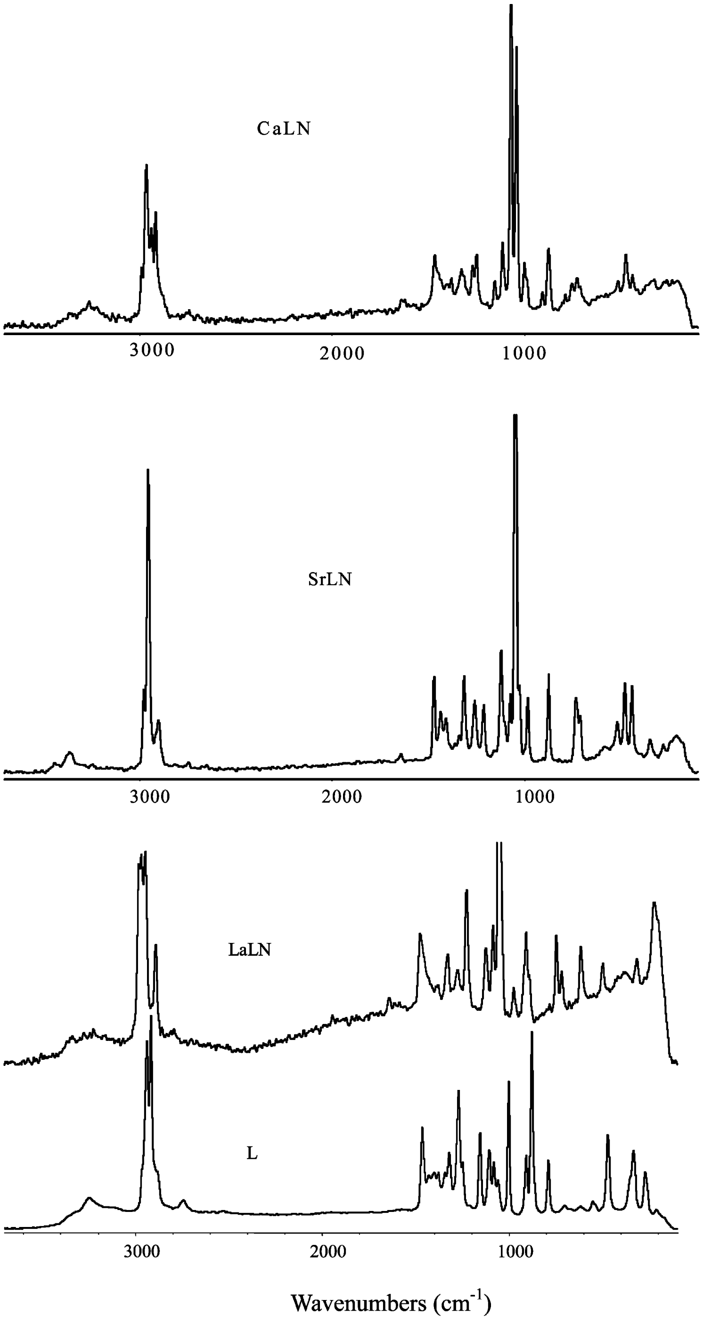

Figure 8. FT-Raman spectra of LaLN, CaLN, SrLN, and galactitol (3700−100 cm^{-1}).

2949, 2893 cm^{-1} (LaLN). The deformational vibration of water (1640 cm^{-1}) is very weak and nearly could not be observed in the spectra of CaLN and LaLN. In the lower frequency of the Raman spectra region (650−100 cm^{-1}), the broad band in the 250−200 cm^{-1} region is assigned as the vibration of the metal−oxygen bond: 232 (CaLN); 210 (SrLN); 222 (LaLN), providing the best evidence for the formation of the metal ion-sugar complex.

Conclusions

The coordination modes of the five crystal structures of metal nitrate−galactitol complexes are summarized in Table 9. NO_3^- has three N−O bonds, which are easier to coordinate to the metal ions than the chloride ion is. In addition the N−O bonds are easier to form H-bonds with the hydroxyl groups of the ligand than the chloride ion is. The introduction of NO_3^- increases the chance of metal ion coordination with galactitol and makes the coordination number larger than that of the corresponding metal chloride−galactitol complexes. For example, the coordination numbers of alkaline earth−carbohydrate complexes are generally seven or eight. In the CaLN complex, it is nine, and in the SrLN complex it is ten, which is unusual.

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*-inositiol uses two adjacent hydroxyl groups to bind with metal ions; erythritol usually supplies three hydroxyl

Table 9. Summary of the Coordination Modes of the Five Metal Nitrate−Galactitol Complexes[a]

structure formula	CN	CW	LW	coordination mode of G	coordination mode of NO_3^-
$2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8H_2O$	10	3 for each Nd^{3+}	1 for each Nd^{3+}	O1, O2, O3	two bidentate coordinated NO_3^-
$Nd(NO_3)_3 \cdot C_6H_{14}O_6$	10	0	0	O1, O2, O3 O4, O5, O6	two bidentate coordinated NO_3^-
$La(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 4H_2O$	12	0	4	O1, O2, O3 O4, O5, O6	three bidentate coordinated NO_3^-
$2Ca(NO_3)_2 \cdot C_6H_{14}O_6 \cdot H_2O$	9	1	0	O2, O3, O1B	two bidentate coordinated NO_3^-, one O of NO_3^- coordinated with another Ca^{2+} to form bridge
$Sr(NO_3)_2 \cdot C_6H_{14}O_6$	10	0	0	O1, O2, O1A, O2A, O3B, O3C	two bidentate coordinated NO_3^-

[a] Abbreviation: CN, coordination number; CW, coordinated water; LW, lattice water.

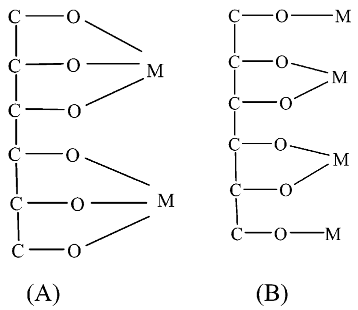

Figure 9. Two coordination modes of galactitol with metal nitrates

groups to one metal ion or two hydroxyl groups to one metal ion and two hydroxyl groups to another. In the metal chloride−galactitol complexes, galactitol provides two adjacent hydroxyl groups or three hydroxyl groups to metal ions.

Galactitol coordinates with one or two metal ions at the same time to form 1:1 (NdLN1, LaLN, SrLN) and 1:2 (NdLN2, CaLN) proportion complexes, respectively. In the 1:1 nitrate−galactitol complex, galactitol has two kinds of coordination modes: one mode is as two tridendate donors providing three hydroxyl groups O-1, O-2, and O-3 to two metal ions (shown in Figure 9A). Each L ligand is coordinated with two metal ions, and each metal ion is coordinated with two L ligands forming a chain structure such as in NdLN1 and LaLN. The other mode can be observed in the structure of SrLN. Galactitol provides O-1 to the first Sr^{2+}, O-2 and O-3 with the second Sr^{2+}, O-4 and O-5 with the third Sr^{2+}, and O-6 with the fourth Sr^{2+} (shown in Figure 9B). Each Sr^{2+} is coordinated with four L ligands (O1, O2; O1A, O2A; O3B, O3C in Figure 5) at the same time to form a net structure (shown in Figure 6). In the 2:1 nitrate−galactitol complex, galactitol also has two kinds of coordination modes similar to those of the 1:1 complex: one mode is shown in Figure 9A. Each L ligand is coordinated with two metal ions, and each metal ion is coordinated with one L ligand in which the L ligand is surrounded by two metal ions forming a closed structure such as in NdLN2.[20] The other mode can be observed in the structure of CaLN in which the coordination mode of galactitol is shown in Figure 9B. Each galactitol is coordinated with four Ca^{2+} (O1; O2, O3; O3A; O2A; O1A in Figure 3), and each Ca^{2+} is coordinated with two L ligands forming a chain structure (shown in Figure 4).

Galactitol is such a simple molecule and one of the simplest representatives of carbohydrates. The structure of galactitol is centrosymmetric and easy to form complexes with metal ions. But the structures of the metal ion−galactitol complexes manifest an unusual complexity. First, the chemical composition is changeable. The solvent and anion compete with the sugar ligand for the coordination. The complexing ratio between the sugar molecule and metal ions may change between 1:1 and 1:2. Second, the coordination modes and the topology structures of the complexes are diverse. Third, the same cause may bring on different results (two different structures of the complexes belonging to the same system).

Experimental Section

Materials and Synthesis of the Complexes. Lanthanum nitrates were prepared and crystallized from the corresponding oxide of high purity (99.99%); $Ca(NO_3)_2$ was prepared from $CaCl_2$ and HNO_3, and $Sr(NO_3)_2$ and galactitol (AR) were purchased from Beijing chemical factories, China, and were used as supplied. Three millimoles of galactitol and 2 equiv (6 mmol) of the metal nitrates ($La(NO_3)_3$, $Ca(NO_3)_2$, and $Sr(NO_3)_2$) were dissolved in a water−ethanol mixed solvent and heated with the addition of ethanol to make a concentrated solution. Then the flask was cooled, and the mixture was filtered into a sealed 25 × 40 mm glass vial for crystallization at room temperature. Three colorless single crystals were prepared, and the structures were determined by X-ray single-crystal diffraction, FT-IR, and Raman techniques.

X-ray Crystallographic Analyses of the Complexes. The $2Ca(NO_3)_2 \cdot C_6H_{14}O_6 \cdot H_2O$ crystal structure was determined on a Rigaku RAXIS RAPID IP diffractometer, and the other two crystal structures were determined on a Nonius KappaCCD diffractometer using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2)K. The structures of all complexes were solved by the SHELX-97 program and refined using a full-matrix least-squares on F^2 method. A suitable trial structure was obtained by the direct method through numerical absorption correction. The secondary solution was completed by use of Fourier difference maps. All non-hydrogen atoms were anistropically refined on F^2, and the hydrogen atoms were isotropically refined.

Physical Measurements. Elemental analyses of metal nitrate−galactitol complexes were run on an Elementar Vario EL II with

CHN mode. Anal. Calcd for $La(NO_3)_3{\cdot}C_6H_{14}O_6{\cdot}4H_2O$ (LaLN): C, 12.43; H, 3.799; N, 7.252. Found: C, 12.45; H, 4.042; N, 5.709. Anal. Calcd for $2Ca(NO_3)_2{\cdot}C_6H_{14}O_6{\cdot}H_2O$ (CaLN): C, 13.63; H, 3.028, N, 10.22. Found: C, 13.40; H, 3.648; N, 8.606. Anal. Calcd for $Sr(NO_3)_2{\cdot}C_6H_{14}O_6$ (SrLN): C, 18.38; H, 3.555; N, 7.110. Found: C, 18.08; H, 3.551; N, 6.695.

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 coaddition of the results of 64 scans. A mercury cadmium telluride detector was used. FT-Raman spectra (3700−100 cm^{-1}) were recorded on a Nicolet FT-Raman 950 spectrometer at a resolution of 8 cm^{-1} by coadding the results of 1000 scans.

Acknowledgment. The authors thank the National Natural Science Foundation of China for grants (30371604, 39730160, 50203001, and 20171004), the State Key Project for Fundamental Research of MOST (2002CCA01900), and the project of the Education Ministry PhD candidate program for support of this work.

IC061414H