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Note

Sugar complexes with neodymium nitrate. Spectroscopic and structural studies of two $Nd(NO_3)_3$–galactitol complexes

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Abstract

Two different $Nd(NO_3)_3$–galactitol complexes, $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ and $Nd(NO_3)_3 \cdot C_6H_{14}O_6$ have been obtained and were characterized by FT-IR and X-ray diffraction techniques. The spectral differences of the two complexes were consistent with the crystal-structure data.

Keywords: Galactitol; Neodymium nitrate; FT-IR; Crystal structure

Carbohydrates and related compounds have long been known to form complexes with metal ions, and such complexes are of interest mainly because of the possible importance of such interactions in a variety of biological processes, for example, in the binding of metal ions to cell walls and the transport and storage of metal ions.[1–4]

Alditols and cyclitols, in contrast to aldoses and ketoses, constitute simpler systems for studying the ability of carbohydrates to coordinate with metal ions.[5] The coordination of metal cations by polyols (including alditols and cyclitols) in aqueous solution has been extensively studied during the past four decades,[6] but it is difficult to obtain metal ion–polyol single crystals from neutral solutions because the water molecule is a strong competitor for coordination with metal ions.

Galactitol, $C_6H_{14}O_6$, is widely distributed in plants. It occurs in seaweeds and is the sole constituent of Madagascar manna.[7] Lanthanide complexes are often used as shift reagents to probe metal-binding sites in solutions and they are used in agricultural fertilizers or as feed additives in animal husbandry.[8]

Before 2000 only one single crystal study of a lanthanide–alditol ($2PrCl_3 \cdot$galactitol$\cdot 14\ H_2O$) had been reported in the literature.[9] Recently our group has prepared a series of alkaline earth metal and lanthanide chloride–galactitol complexes,[10–14] as well as a series of lanthanide chloride–*myo*-inositol complexes.[15,16] This contribution describes two different crystal structures of the $Nd(NO_3)_3$–galactitol system, characterized by FT-IR spectroscopy and X-ray single crystal diffraction.

The structures and atom-numbering schemes of $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ (complex **I**) and $Nd(NO_3)_3 \cdot C_6H_{14}O_6$ (complex **II**) are shown in Fig. 1. The crystallographic data of the two complexes are summarized in Table 1. Selected bond lengths in complex **I** and **II** are collected in Table 2. Hydrogen bonds for complex **I** and **II** are listed in Tables 3 and 4, respectively.

The molar ratio of metal ion to galactitol is 2:1 and 1:1 for complex **I** and complex **II**, respectively. In the crystal structure of complex **I**, every Nd^{3+} is 10-fold coordinated by three hydroxyl groups from one galactitol, two bidentate nitrates and three water molecules with Nd–O distances from 2.462 to 2.727 Å. On the other hand, every Nd^{3+} in complex **II** is coordinated to the six hydroxyl groups of two molecules of galactitol,

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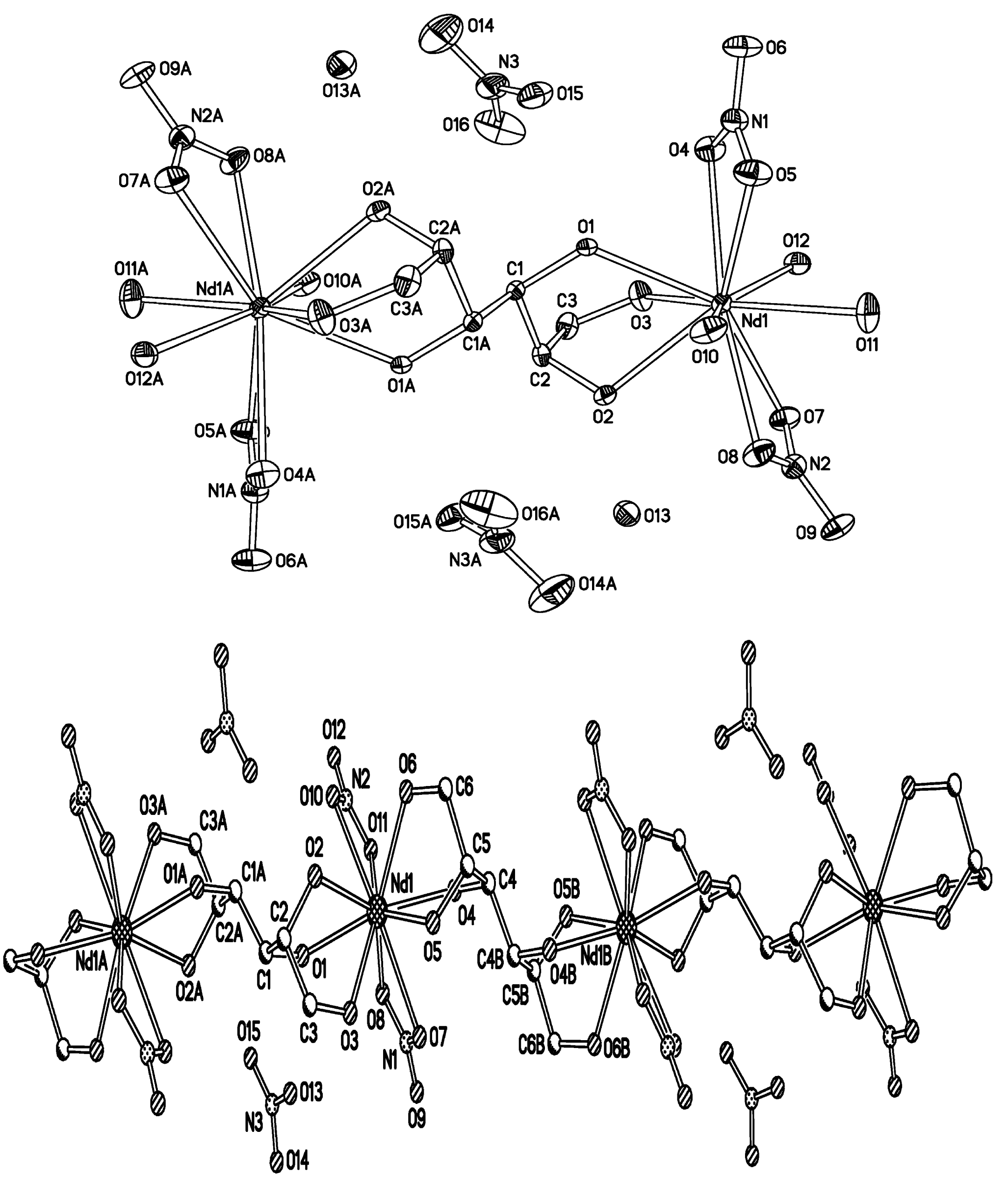

Fig. 1. The crystal structures and atom numbering schemes of $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ (upper) and $Nd(NO_3)_3 \cdot C_6H_{14}O_6$ (lower).

and the coordination sphere is completed to a coordination number of ten by two bidentate nitrates with Nd–O distances from 2.466 to 2.661 Å. In the literature we found another similar structure of $La[(L1)_2(NO_3)_2]$-(NO_3), L1 = *cis*,*cis*-1,3,5-trihydroxycyclohexane.[17] The coordination mode is just like complex **II** in which La is coordinated to two bidentate nitrate and six hydroxyl groups of two molecules of ligand.

In complex **I**, a dimer unit of $[[Nd(H_2O)_3(NO_3)_2]_2$-$(C_6H_{14}O_6)]$ is surrounded by free NO_3^- ions and water molecules (O-13), which are between the packing arrangement of the dimers in the lattice (down the *a* direction) and form numerous hydrogen bonds to the coordinated NO_3^-, H_2O, and hydroxyl groups of the dimers. Three hydroxyl groups of the ligand (O-1, O-2 and O-3) and four water molecules (O-10, O-11, O-12 and O-13) form two kinds of hydrogen bonds, respectively in complex **I** (seen in Table 3). In contrast, in complex **II**, a chain of $[Nd(NO_3)_2(C_6H_{14}O_6)]_\infty$ is surrounded by free NO_3^- ions, which are between the hexagonal packing arrangement of the chains in the lattice (down the *a*–*c* direction) and form hydrogen bonds to the chains. Complex **II** does not exhibit very strong H-bonds as compared with complex **I** because there are no water molecules in the structure of complex **II**. Only one sort of hydrogen bond is present in complex

Table 1
Crystal data and structure refinement for $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ and $Nd(NO_3)_3 \cdot C_6H_{14}O_6$

Empirical formula	$C_6H_{30}N_6Nd_2O_{32}$	$C_6H_{14}N_3NdO_{15}$
Formula weight	986.84	512.44
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	9.2488(3)	9.2571(2)
b (Å)	14.1674(4)	14.1541(4)
c (Å)	11.2674(4)	11.6317(2)
β (°)	94.4894(12)	92.6418(18)
V (Å^3)	1471.85(8)	1522.43(6)
Z	2	4
D_{calcd} (g cm^{-3})	2.227	2.236
Absorption coefficient (mm^{-1})	3.621	3.501
F(000)	968	1004
Crystal shape/crystal colour	Block/light purple	Column/light purple
Crystal size (mm)	$0.35 \times 0.35 \times 0.40$	$0.40 \times 0.23 \times 0.12$
θ range for data collection (°)	3.40–27.48	3.51–27.11
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 18$, $-14 \le l \le 14$	$-11 \le h \le 11$, $-17 \le k \le 18$, $-13 \le l \le 14$
Reflections collected/unique	24030/3340 [$R_{int} = 0.0748$]	27123/3340 [$R_{int} = 0.0714$]
Reflections with $I > 2\sigma(I)$	2028	2690
Completeness to $\theta = 27.48°$	99.3%	99.3%
Max and Min transmission	0.302 and 0.223	0.662 and 0.504
Hydrogen addition/treatment	geometry/mixed	geometry/mixed
Data/restraints/parameters	3340/18/244	3340/12/246
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290$, $wR_2 = 0.0565$	$R_1 = 0.0293$, $wR_2 = 0.0578$
R indices (all data)	$R_1 = 0.0711$, $wR_2 = 0.0658$	$R_1 = 0.0475$, $wR_2 = 0.0629$
Goodness-of-fit on F^2	1.016	1.020
Extinction coefficient	0.0117(4)	0.0034(3)
Largest difference peak and hole (e Å^{-3})	0.821 and −0.785	0.972 and −1.049

II: six hydroxyl groups of the two molecules of ligands (O-1, O-2, O-3 and O-4, O-5, O-6) form eight H-bonds (seen in Table 4).

FT-IR spectra of the two complexes and of galactitol are shown in Fig. 2. The results of the spectral analysis are described as follows.

Compared to the spectrum of free galactitol, the stretching vibrations of the OH groups in the region of 4000–3000 cm^{-1} are broadened in the spectrum of complex **I** corresponding to numerous hydrogen bonds formed between the hydroxyl groups of galactitol and the water molecules in its crystal structure. In compar-

Table 2
Selected bond lengths (Å) in complexes **I** and **II** with estimated standard deviations

Complex **I** [$2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$]		Complex **II** [$Nd(NO_3)_3 \cdot C_6H_{14}O_6$]	
Bond lengths			
Nd(1)–O(12)	2.462(3)	Nd(1)–O(5)	2.466(2)
Nd(1)–O(10)	2.464(3)	Nd(1)–O(3)	2.475(3)
Nd(1)–O(3)	2.469(3)	Nd(1)–O(6)	2.484(3)
Nd(1)–O(11)	2.476(3)	Nd(1)–O(8)	2.490(3)
Nd(1)–O(1)	2.489(3)	Nd(1)–O(1)	2.505(2)
Nd(1)–O(2)	2.508(3)	Nd(1)–O(4)	2.511(2)
Nd(1)–O(5)	2.545(3)	Nd(1)–O(2)	2.529(2)
Nd(1)–O(7)	2.622(3)	Nd(1)–O(11)	2.546(3)
Nd(1)–O(8)	2.634(3)	Nd(1)–O(10)	2.621(2)
Nd(1)–O(4)	2.727(3)	Nd(1)–O(7)	2.661(3)

Table 3
Hydrogen bonds for complex **I**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1)–H(1)···O(15)	0.801(18)	1.88(2)	2.663(4)	168(4)
O(2)–H(2)···O(13)	0.808(19)	1.89(2)	2.669(4)	163(5)
O(3)–H(3)···O(9)#2	0.796(18)	2.14(2)	2.923(4)	169(3)
O(10)–H(101)···O(9)#3	0.923(19)	2.00(2)	2.914(4)	172(4)
O(10)–H(102)···O(4)#4	0.924(19)	1.97(2)	2.885(4)	170(4)
O(11)–H(111)···O(16)#4	0.919(18)	1.91(2)	2.823(5)	170(5)
O(11)–H(112)···O(13)#5	0.920(19)	1.87(2)	2.782(5)	170(5)
O(12)–H(121)···O(15)#6	0.903(18)	1.90(2)	2.796(4)	175(4)
O(12)–H(122)···O(14)#7	0.901(18)	2.10(3)	2.918(5)	150(4)
O(13)–H(131)···O(14)#8	0.949(19)	1.84(3)	2.742(5)	157(5)
O(13)–H(132)···O(5)#6	0.940(19)	1.91(3)	2.770(4)	152(5)
O(10)–H(102)···O(6)#4	0.924(19)	2.65(4)	3.211(5)	120(3)
O(12)–H(121)···O(14)#6	0.903(18)	2.62(4)	3.191(6)	122(3)
O(13)–H(132)···O(6)#6	0.940(19)	2.52(4)	3.187(5)	128(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z+2$; #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 $-x+1/2,y-1/2,-z+3/2$; #6 $x+1/2,-y+1/2,z-1/2$; #7 $-x+1/2,y-1/2,-z+5/2$; #8 $x,y,z-1$.

Table 4
Hydrogen bonds for complex **II**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1)–H(1)···O(13)	0.803(18)	1.95(2)	2.706(4)	158(3)
O(2)–H(2)···O(15)#1	0.803(18)	2.32(3)	3.006(4)	144(4)
O(3)–H(3)···O(9)#3	0.795(18)	1.95(2)	2.728(4)	165(3)
O(4)–H(4)···O(14)#4	0.802(18)	1.948(18)	2.746(4)	173(4)
O(5)–H(5)···O(15)#5	0.803(18)	2.000(16)	2.786(4)	166(3)
O(6)–H(6)···O(10)#6	0.794(18)	2.01(2)	2.799(3)	170(3)
O(5)–H(5)···O(14)#5	0.803(18)	2.58(3)	3.175(4)	132(4)
O(6)–H(6)···O(12)#6	0.794(18)	2.66(3)	3.195(5)	127(3)

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

ison with complex **I**, there is only one narrow ν(OH) band in the spectrum of complex **II**. Because no water molecules participate in the coordination reaction, only the hydroxyl groups form hydrogen bonds in the structure of complex **II**.

In the 3000–2500 cm^{-1} region, the weak bands are characteristic of CH stretching vibrations which are masked by OH vibrations. In the spectra of the two complexes 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 peak at 1633 cm^{-1}(due to the water deformational vibration), which is absent in the spectra of the free galactitol and complex **II**, is attributed to the bonded H_2O molecules in the spectrum of complex **I**. This is consistent with the crystal result that no water molecules exist in the structure of complex **II**.

The strong asymmetric and symmetric stretching codes of NO_2 are located in the 1530–1480 and 1300–1250 cm^{-1} regions, respectively.[18] In the spectrum of complex **I**, the two strong bands are located at 1497 cm^{-1} ($\nu_{\mathrm{asNO_2}}$) and 1297 cm^{-1} ($\nu_{\mathrm{sNO_2}}$), respectively, corresponding to 1506 cm^{-1} ($\nu_{\mathrm{asNO_2}}$) and a weak band at 1308 cm^{-1} ($\nu_{\mathrm{sNO_2}}$) in the spectrum of complex **II**. The peak positions of the two complexes were similar and the differences were less than 10 cm^{-1}. From the crystal structures we found that NO_3^- were in the same coordination mode through bidentate nitrate in the two complexes. We could conclude that the same bidentate coordination mode result in the similar band positions in IR spectra.

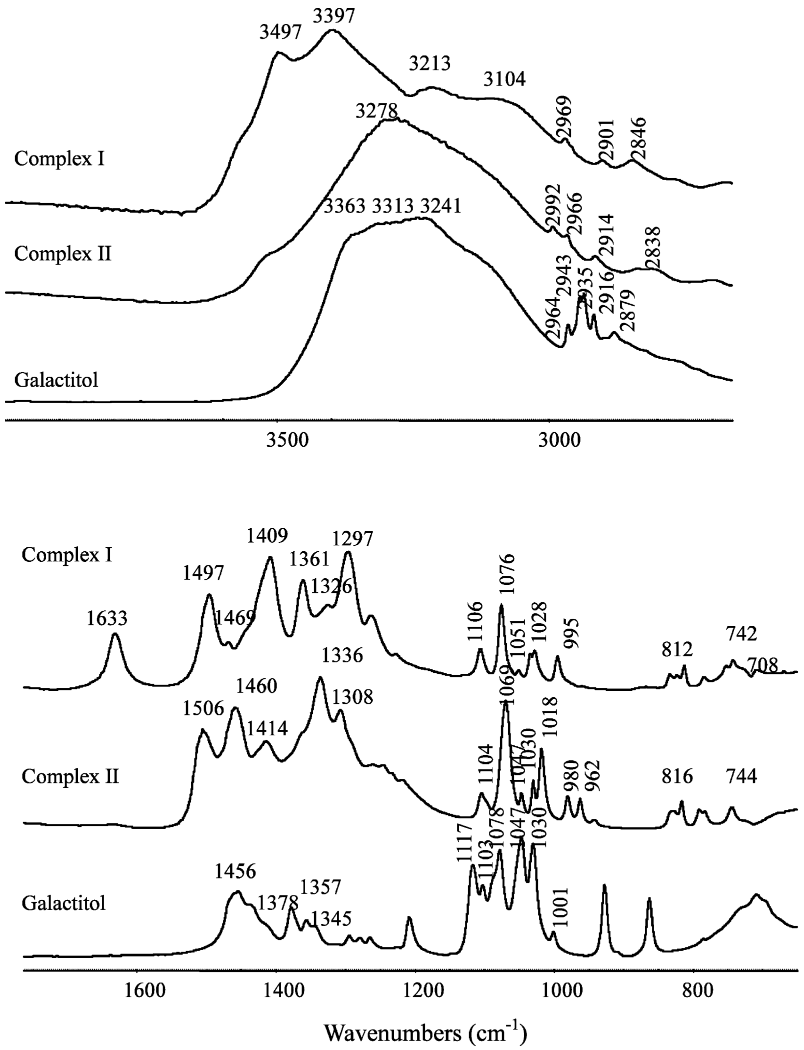

Fig. 2. The mid-IR spectra of $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ (complex **I**) and $Nd(NO_3)_3 \cdot C_6H_{14}O_6$ (complex **II**) and galactitol (4000–650 cm^{-1}).

There are major contributions from C–O stretching vibration in the 1200–950 cm^{-1} region. There also exists a medium N–O stretching vibration in the 1040–970 cm^{-1} region that are masked by C–O stretching vibrations. Several characteristic peaks (1117, 1103, 1078, 1047, 1030, 1001 cm^{-1}) appear in the spectrum of galactitol, corresponding to 1106, 1076, 1051, 1028, 995 cm^{-1} in the spectrum of complex **I** and 1104, 1069, 1047, 1030, 1018, 980, 962 cm^{-1} in the spectrum of complex **II**, respectively. The spectral changes of the sugar C–O stretching vibrations evidently result from the metal–sugar binding via sugar hydroxyl groups.

The two neodymium nitrate–galactitol complexes have similar complexing structures in that every neodymium atom only coordinates with oxygen atoms from either hydroxyl groups of galactitol, nitrate group, or water molecules. The major difference between complex **I** and **II** is that three hydroxyl groups replace three water molecules in complex **II**. So the minor difference of the two structures results in similar peak positions in FT-IR spectra.

In 1974 Craig and co-workers reported that $CaCl_2$ coordinated with β-D-fructose in 1:1 and 1:2 proportion to form two kinds of crystals.[19,20] In our study, $Nd(NO_3)_3$ complexes with galactitol in 2:1 and 1:1 proportion to form two different crystal structures. We conclude that one kind of metal ion may form crystals of different complexes with a saccharide under the same conditions.

1. Experimental

1.1. Material

Crystal of $Nd(NO_3)_3 \cdot 6\ H_2O$ were prepared from high purity Nd_2O_3 (99.99%) and HNO_3 in aqueous solution.

Galactitol (AR) was purchased from a chemical factory, Beijing, China, and was used as supplied.

1.2. Preparation of galactitol complexes

The single crystals of $Nd(NO_3)_3$–galactitol complexes used for X-ray and infrared analysis were grown from concentrated solution in a sealed flask which was prepared by dissolving 3 mmol of galactitol with 6 mmol of $Nd(NO_3)_3 \cdot 6\ H_2O$ in a mixed water–EtOH solvent. The amount of Nd^{3+} is greater than that of galactitol in order to form the sugar–metal ion complex easily. Under the same reaction conditions two different crystals were obtained from two separate flasks. The two $Nd(NO_3)_3$–galactitol complexes were first found by two different FT-IR spectra. Then their crystal structures were determined by X-ray single crystal diffraction method.

Elemental analyses of the neodymium nitrate complexes were run on an Elementar Vario EL II with CHN mode. Anal. Calcd for $2Nd(NO_3)_3 \cdot C_6H_{14}O_6 \cdot 8\ H_2O$ (complex **I**): C, 7.300; H, 3.041; N, 8.514. Found: C, 7.578; H, 3.313; N, 7.456. Anal. Calcd for $Nd(NO_3)_3 \cdot C_6H_{14}O_6$ (complex **II**): C, 14.26; H, 2.994; N, 7.266. Found: C, 14.05; H, 2.732; N, 8.197.

1.3. Physical measurement

Microscope IR spectra of two complexes (4000–650 cm^{-1}) were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan microscope at a spectral resolution of 4 cm^{-1} by coadding the results of 128 scans. A mercury cadmium telluride detector was used.

The two crystal structures were determined by X-ray analysis on a Nonius KappaCCD Diffractometer using monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å) at 293(2) K. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares refinement. The structure was solved by SHELXS-97 and refined by SHELXL-97.

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