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Preparation and spectroscopic characterization of two HoCl₃–galactitol complexes and one ErCl₃–galactitol complex

Xiaohui Hua^a, Qinghua Pan^a, Lei Yu^a, Junhui Xue^a, Limin Yang^{b,*}, Yizhuang Xu^a, Guozhong Zhao^c, Weihong Li^a, Zheming Wang^a, Jinguang Wu^a, Kexin Liu^b, Jia'er Chen^b

^a The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China ^b State Key Laboratory of Nuclear Physics and Technology, Institute of Heavy Ion Physics, School of Physics, Peking University, Beijing 100871, China ^c Department of Physics, Capital Normal University, Beijing 100037, China

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ABSTRACT

The interactions between metal ions and hydroxyl groups of carbohydrates are important for their possible biological activities. Here two HoCl₃–galactitol complexes ([Ho(galac)(H₂O)₃)]Cl₃·0.5galac) (HoG(I)) and ([Ho₂(galac)(H₂O)₁₂)]Cl₆·2H₂O) (HoG(II))) and one ErCl₃–galactitol complex ([Er(galac)(H₂O)₃)] Cl₃·0.5galac)(ErG)) were prepared and characterized. The possible structures of HoG(I) and ErG were deduced from FTIR, elemental analysis, ESI-MS, FIR, THz and TGA results. It is suggested that Ho³⁺ or Er³⁺ is 9-coordinated with six hydroxyl groups from two galactitol molecules and three water molecules, and another galactitol molecule is hydrogen-bonded in HoG(I) and ErG and the ratio of metal to ligand is 1:1.5. The structure of HoG(II) was determined by FTIR and X-ray diffraction analyses. The results demonstrate that lanthanide ions with galactitol may form two compounds in a system and different topological structures can be obtained.

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1. Introduction

The interactions between metal ions and carbohydrates are involved in many biochemical processes, such as the transport of metal ions, storage or the regulation of metalloenzymes, stabilization of membrane structures, binding of glycoproteins to cell surfaces, toxic metal metabolism, and the binding of proteins to sugars [1–6]. There has been considerable interest in the development of carbohydrate-based pharmaceuticals as therapeutics for neurodegenerative diseases due to that they can easily pass the blood brain barrier, or as potent radiopharmaca and cancerostatica [7-10]. Metal-based glyconanoparticles (GNPs) are biofunctional nanomaterials having potential application in antiadhesion therapy and diagnosis [11]. Recently the investigation on the binding site of the interaction between mucin and calcium ions also show that when the concentration of Ca²⁺ is relatively low, Ca²⁺ prefers to coordinate with the carbohydrate moiety of mucin [12]. For a better understanding of the interactions involved in these events, models need to be designed that identify the coordination modes, the changes of conformations for sugars and hydrogen bond networks after complexation, etc.

The investigation on the interactions between metal ions and simple sugars can improve the understanding of metal ion interactions with sugar residues of biologically important compounds. Here galactitol ($C_6H_{14}O_6$, denoted as G or galac in formulas), one of the simplest representatives of carbohydrates, was chosen as a model to study the coordination of hydroxyl groups to metal ions.

Lanthanide ions are often used as probe of calcium ion, and have clinical pharmacology, for example, lanthanum carbonate is used in medicine as a phosphate binder [13]. Since the first crystal structure of galactitol 2PrCl₃·14H₂O has been reported by Angyal in 1993, some alkaline earth ion, lanthanide chloride or nitrate-galactitol complexes have been reported [14-18]. In the structures of these metal-galactitol complexes, galactitol has several coordination modes [14–18]: one is that three hydroxyl groups coordinated to one metal ion and the other three hydroxyl groups coordinate to another metal ion; or galactitol provides O-2, -3 to coordinate to one metal ion, and O-4, -5 with another metal ion, to form a chain structure; or galactitol provides O-1 to one metal ion, O-2, -3 to coordinate to the second metal ion, and O-4, -5 with the third metal ion, and O-6 to the fourth metal ion to form a network structure. And the coordination of chloride ions, water and nitrate ions make the complexation complicated.

For different metal ions, especially lanthanide ions, they may form complexes with similar structures, for example, here HoG(II) has similar structure with $2PrCl_3 \cdot C_6H_{14}O_6 \cdot 14H_2O$ [14]. But for one metal ion and one ligand, several metal–ligand complexes can be obtained, for example, two NdCl₃, three CaCl₂ and two CuCl₂– erythritol complexes have been reported [19–21]. In this paper,

^{*} Corresponding author. Tel.: +86 10 62751889; fax: +86 10 62758849. *E-mail address*: yanglm@pku.edu.cn (L. Yang).

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Table 1

Crystal data and structure refinement for [Ho2(galac)(H2O)12)]Cl6·2H2O (HoG(II)).

Empirical formula	$C_{6}H_{42}Cl_{6}Ho_{2}O_{20} \cdot ([Ho_{2}(galac)(H_{2}O)_{12})]Cl_{6} \cdot 2H_{2}O)$
Formula weight	976.96
Temperature	293(2) K
Crystal system, space group	Triclinic, P Ī
Unit cell dimensions	a = 7.9469(2) Å, $b = 9.6209(4)$ Å, $c = 10.2728(5)$ Å $\alpha = 88.5028(14)^{\circ}$, $\beta = 72.1904(13)^{\circ}$, $\gamma = 87.363(3)^{\circ}$
Volume	746.93(5) Å ³
Refls. No. for cell measurement	14715
θ range for cell measurement	3.48-27.49°
Z, calculated density	4, 2.172 Mg/m^3
Absorption coefficient	5.866 mm^{-1}
$F(0 \ 0 \ 0)$	474
Crystal shape/crystal color	Block/pink
Crystal size	$0.20\times0.30\times0.30\ mm^3$
θ range for data collection	2.72-27.48°
Limiting indices	$-10 \le h \le 10, -12 \le k \le 12, -13 \le l \le 13$
Reflections collected/ unique	14715/3421 [<i>R</i> (int) = 0.0689]
Reflections with $I > 2\sigma(I)$	2382
Completeness to θ = 27.49	99.7%
Absorption correction	Empirical
Max. and min. transmission	0.583 and 0.198
Data/restraints/ parameters	3421/27/206
Goodness-of-fit on F^2	0.962
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0282, <i>wR</i> 2 = 0.0511
R indices (all data)	<i>R</i> 1 = 0.0434, <i>wR</i> 2 = 0.0532
Extinction coefficient	0.0498(10)
Largest diff. peak and hole	0.712 and -1.241 e Å ⁻³

the same phenomenon was observed. Two HoCl₃–galactitol complexes have been synthesized, one has the similar structure with PrCl₃–galactitol complex; and another has new structure. But unfortunately, although ErCl₃ and HoCl₃ with galactitol can form the same complexes having similar unknown structures, only powder samples, no single crystals can't be obtained for them. So we deduce their possible structures from elemental analysis, ESI-MS, IR, FIR, Terahertz (THz) and TGA measurements. Although the ligand is a simple molecule, it has several coordination modes [14–18] as shown in the references and may form different complexes with the same metal ion. The results demonstrated that various topological structures can be obtained for metal-sugar complexes.

2. Experimental

2.1. Materials

ErCl₃ was prepared and crystallized from corresponding rare earth oxide of high purity (99.99%). HoCl₃ was purchased from a chemical company in Shanghai. Galactitol was purchased from a chemical company in Beijing, and was used without further purification.

2.2. Preparation of two HoCl₃–galactitol complexes and ErCl₃–galactitol complex

Galactitol (3 mmol) and metal chlorides (6 mmol) were dissolved in H₂O/ethanol (2:3) and heated to prepare a concentrated solution and cooled down for crystallization. Small amount of EtOH (0.5 ml for each time) was kept being added into the solution during the heating process when the solution was about 4 ml to prolong the reaction time. For HoG(I), the elemental analysis results are as follows: C, 18.11; H, 4.53, so the formula of HoG(I) may be [Ho(galac)(H₂O)₃)]Cl₃·0.5galac (HoCl₃·1.5C₆H₁₄O₆·3H₂O). and Anal. Calcd. Data is C, 18.06; H, 4.55. Anal. Calcd. for HoG(II): [Ho₂(galac)(H₂O)₁₂)]Cl₆·2H₂O (2HoCl₃·C₆H₁₄O₆·14H₂O): C, 7.38; H, 4.33. Found: C, 7.78; H, 4.18. Anal. Calcd. for ErG: [Er(galac)(H₂O)₃)]Cl₃·0.5galac (ErCl₃·1.5C₆H₁₄O₆·3H₂O): C, 17.99; H, 4.53. Found: C, 18.19; H, 4.54.

2.3. Physical measurements

The mid-IR spectra were measured on a Nicolet Magna iN10 spectrometer using micro-IR method, 64 scans at 4 cm^{-1} resolution. Element analyses were carried out on an Elementar Vario EL spectrometer. The far-IR spectra of the molecules in the range of $650-50 \text{ cm}^{-1}$ were measured using common used Nujol mull method on a Nicolet Magna-IR 750 II spectrometer at room temperature and at 8 cm⁻¹ resolution, 128 scans. The THz absorption spectra were recorded at room temperature and 10 K for HoG(I) on the THz time-domain device of Capital Normal University of China, based on photoconductive switches for generation and electro-optical crystal detection of the far-infrared light. The experimental apparatus for terahertz transmission measurements has been discussed in detail elsewhere [22]. The preparation of the samples was by pressing mixed pellets with polyethylene powder, the thick of the samples are about 0.8 mm. The detection of THz



Fig. 1. the mid-IR spectra of HoG(I), HoG(II) and ErG complexes in the 3700–2400 and 1700–650 cm⁻¹ region.



Fig. 2. FIR spectra of HoG(I), HoG(II) and ErG.

absorption spectra was carried out at N₂ atmosphere to avoid the influence of water vapor. Effective spectrum range is 0.2–2.6 THz (\sim 7–87 cm⁻¹). The thermo gravimetric curve was measured on a

Q600SDT TGA–DTA–DSC equipment at N_2 environment and 10 °C/min from 27 to 600 °C. ESI-MS spectra of the samples were determined on a Bruker APEX IV Fourier Transform ion cyclotron resonance mass spectrometer.

The X-ray diffraction data of HoG(II) were collected on a NON-IUS KappaCCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the θ range from 3.48 to 27.49° at 293 K. A pink crystal with approximate dimensions of $0.20 \times 0.30 \times 0.30$ mm³ was selected for data collection. The structure was resolved by direct methods with SHELX-97 and refined using the full-matrix least-squares on F^2 method [23]. Empirical absorption corrections were applied and anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. The crystallographic data and structure refinement are listed in Table 1. Parameters in CIF format are available as Electronic Supplementary Publication from Cambridge Crystallographic Data Centre (CCDC number 788084).

3. Results and discussion

3.1. FTIR spectra of two HoCl₃-galactitol complexes and ErCl₃-galactitol complex

The FT-IR spectra of two HoCl₃–galactitol complexes and ErCl₃– galactitol complex were shown in Fig. 1. HoG(I) is [Ho(galac) (H₂O)₃)]Cl₃·0.5galac (i.e., HoCl₃·1.5C₆H₁₄O₆·3H₂O), ErG is [Er(galac) (H₂O)₃)]Cl₃·0.5galac (ErCl₃·1.5C₆H₁₄O₆·3H₂O) and HoG(II) corresponds to [Ho₂(galac)(H₂O)₁₂)]Cl₆·2H₂O (2HoCl₃·C₆H₁₄O₆·14H₂O), respectively. The FTIR spectrum of HoG(II) is similar to the spectra of 2PrCl₃·C₆H₁₄O₆·14H₂O and 2NdCl₃·C₆H₁₄O₆·14H₂O, whose structures were determined [14,24]. Therefore, the structure of HoG(II) should be similar to the structure of 2PrCl₃·C₆H₁₄O₆·14H₂O. And the FTIR spectrum of HoG(I) is different from the spectrum of Ho-



Fig. 3. THz absorption spectra of HoG(I), HoG(II) and ErG.

G(II), which indicate that two $HoCl_3$ -galactitol complexes have formed.

Comparing with the spectrum of free galactitol, the stretching vibrations of the OH groups of HoG(I), HoG(II) and ErG were changed upon salt formation. The vOH bands in the salt spectra were broadened. Mainly the bands at 3396, 3211 and 3134 cm⁻¹ for HoG(I), 3398, 3211 and 3126 cm⁻¹ for ErG, 3323 and 3241 cm⁻¹ for HoG(II) were observed. The OH stretching vibrations can be assigned to the H-bonds formed between the hydroxyl groups, water molecules and Cl⁻ ions. The broad bands in the region indicate the existence of complicated hydrogen bond networks in the complexes, and stronger hydrogen bonds exist in HoG(I) and ErG for

that the bands are shifted to lower wavenumbers compared to HoG(II).

The bands in the 3000–2700 cm⁻¹ region can be assigned to the stretching vibrations of the CH group (ν CH). The bands positions were changed in the two Ho³⁺ salts and ErG and the intensities became weaker upon salt formation (Fig. 1). And the vibrations of OH have masked the CH bands.

The deformation vibrations of water molecules in the IR spectra of three complexes are located at 1642 cm⁻¹ for HoG(I) and ErG, 1631 cm⁻¹ for HoG(II), absent from the free ligand, corresponding to the water molecules in the structures. Usually δH_2O is located at ~1644 cm⁻¹ [25]. It has shifted to 1631 cm⁻¹ corresponding to



Fig. 4. TGA results of HoG(I) (a), ErG (b) and HoG(II) (c).

coordinated water molecules in HoG(II), which indicate that more coordinated water molecules exist in its structure.

The δ CH₂ vibration (1459 cm⁻¹ for galactitol) is shifted to 1469 or 1473 cm⁻¹ in the three salt spectra. Other bands in the 1500–650 cm⁻¹ region are shifted after complexation, and different changes occur for HoG(I) and HoG(II), which indicate the formation of two HoCl₃-galactitol complexes. The bands in the 1100–1000 cm⁻¹ region may be assigned mainly to CC, CO and OCH

vibrations [26]. Galactitol itself has six bands in this region at 1117, 1103, 1078, 1047, 1030 and 1001 cm⁻¹; the bands are shifted to 1071, 1053, 1019, 1009 and 981 cm⁻¹ for HoG(I), 1099, 1068, 1029 and 983 cm⁻¹ for HoG(II). The bands have different peak positions and relative intensities, which indicate that HoG(I) and HoG(II) have different structures and the IR spectra indicate the coordination of hydroxyl groups to metal ions. For example, 1089 cm^{-1} band in the calculation results for galactitol



Fig. 5. ESI spectra of HoG(I) (a), ErGb) and HoG(II) (c).



Fig. 6. Possible coordination structures of HoCl₃–galactitol complexes (a) possible coordination structure of HoG(1) (b) another possible coordination structure of HoCl₃–galactitol complex.

(1078 cm⁻¹ in the experimental results) was assigned to C101, O1C1H, C202, C303, O3C3H [26], the ${\sim}10~{\rm cm}^{-1}$ changes of peak positions after compexation indicate that the coordination of hydroxyl groups (O1H, O2H and O3H). And the bands in the region are similar for HoG(I) and ErG, which show that they should have similar structures.

The subtraction spectra of HoG(I) or ErG minus galactitol indicate the existence of uncoordinated galactitol molecule. When subtraction factor is \sim 0.12 after normalization, the subtraction spectra are nearly the same with the spectra of metal complexes, which demonstrate that the uncoordinated galactitol molecule exists in their structures.

The IR results indicate that the hydroxyl groups of galactitol took part in the metal–oxygen interaction; the hydrogen-bond network rearranged upon sugar metalation; the conformation of galactitol skeleton changed as a result of salt formation; two HoCl₃–galactitol complexes have formed and ErCl₃–galactiol can form similar complex with HoG(I). And uncoordinated galactitol molecule may exist in the structures of HoG(I) and ErG.

3.2. FIR and THz spectra of the metal complexes

The FIR and THz spectra of the metal complexes are shown in Figs. 2 and 3, respectively. FIR and THz are effective methods to

determine the formation of metal–ligand complexes [27–29]. Terahertz spectroscopy was regarded as the renaissance of far infrared spectroscopy [30]. HoG(I) and ErG have similar FIR spectra, which confirm the formation of metal complexes and they have similar structures. The FIR spectrum of HoG(II) is similar to PrG, NdG, SmG and different with galactitol itself in peak position and relative intensities because of the similarity of their structures. In the 650–100 cm⁻¹ region the peaks could be assigned to M–O vibrations: 209, 185, 175 cm⁻¹ for HoG(I) and 210, 188, 179 cm⁻¹ for ErG, 219 cm⁻¹ for HoG(II) according to the assignment in the reference [27,28]. Other bands in the region may be related to M–O vibration and δ OMO, etc. [28]. This is an important evidence of complex formation.

The changes of THz spectra also indicate the formation of metal–sugar complexes. For HoG(II), a weak broad band at 1.61 THz was observed. HoG(I) and ErG have similar THz bands. Relatively broad bands at 1.38 and 2.11 THz for HoG(I); 1.43 and 2.12 THz for ErG were observed and the two spectra are different with galactitol itself [29]. At low temperature, 0.76, 1.00, 1.26 THz band was emphasized for HoG(I). These bands are related to crystal lattice vibration and hydrogen bonds, etc. At low temperature the bands have shift or some new bands appear. For these metal complexes, the bands become broader, maybe because after complexation the coordination structures are complicated, extensive hydrogen bond networks formed and some of them may be similar, so the bands become broader. The FIR and THz spectra confirm the formation of metal complexes and the similarity of the spectra of ErG and HoG(I) indicate that they should have similar structures.

3.3. TGA spectra of HoG(I), HoG(II) and ErG

The TGA spectrum of HoG(I), HoG(II) and ErG are shown in Fig. 4. For HoG(I), the first broad peak may be related to water molecules, including absorbed and three coordinated water molecules. Other weight losses (\sim 35%) are related to galactitol molecules. Elemental analyses were done for the residuals (\sim 53%) after TGA experiments, the results are C 26.82%, H 1.56%. And no obvious weight loss can be observed in the region of 600–1000 °C. For ErG, the weight losses are 12% (corresponding to the loss of water), 35% (the loss of galactitol), and C 27.16%, H 1.48% were observed for 51% residuals. For HoG(II), the first two peaks are related to the weight losses of water molecules, the third and fourth peak maybe related to galactitol, respectively.

3.4. ESI-MS spectra of HoG(I), HoG(II) and ErG

The ESI-MS spectra of HoG(I), HoG(II) and ErG are shown in Fig. 5. In fact, some peaks are similar in the ESI spectra of HoG(I) and HoG(II) in some extent, for example, 391, 437 and 527 molecular ion peaks are the same. There is no peaks corresponding to molecular weight in HoG(II). For HoG(I), 943 is corresponding to $2HoCl_3 \cdot 2C_6H_{14}O_6 \cdot 2H_2O_1$, indicate that there is a chain structure formed by Ho ions and galactitol ligands. Other molecular ion peaks, are related to the loss of water, or fragment of galactitol etc. compared to $2HoCl_3 \cdot 2C_6H_{14}O_6 \cdot 2H_2O$. For example, 391 may be related to HoCl₃·C₄H₈O₄, 437 may be related to HoCl₃·C₆H₁₄O₅, 527 may be related to HoCl₃·C₆H₁₄O₆·4H₂O, and 563 may be related to HoCl₃·C₆H₁₄O₆·6H₂O. For ErG, the molecular ion peaks are similar to HoG(I). For comparison, the ESI spectrum of galactitol also has been measured. And 183.1 peak is corresponding to galactitol, but 205.1 peak is the strongest peak in the ESI spectrum of galactitol, corresponding to fragment of galactitol molecules.

And according to above results, the possible structure of HoG(I) may be as follows: Ho^{3+} ion is 9-coordinated with six hydroxyl groups from two galactitol molecules and three water molecules, and uncoordinated galactitol molecule is hydrogen-bonded. The



Fig. 7. The crystal structure of HoG(II) (a) the crystal structure of HoG(II), with H-atoms omitted for clarity. Symmetry code: A 2 - x, -y, -z. (b) The projection of the crystal cell in the structure of HoG(II) as viewed along *a* axis.

possible coordination structure was shown in Fig. 6a. Galactitol provide three hydroxyl groups to one metal ion and another three hydroxyl groups to another metal ion and links two Ho ions together. It is possible that the chloride ions exist in the structure and do not coordinate to Ho ion in HoG(I) as in HoG(II). But this is only a preliminary deduced possible structure. According to the coordination mode of galactitol, there are still other possible coordination structures, for example, Fig. 6b, Ho is 9-coordinated with six hydroxyl groups of galactitol and three water molecules to form metal to ligand 1:1 complex. It is also a resonable structure according to the coordination modes of metal ion and ligand.

3.5. X-ray crystal structure of [Ho₂(galac)(H₂O)₁₂)]Cl₆·2H₂O (HoG(II))

The crystal structure of [Ho₂(galac)(H₂O)₁₂)]Cl₆·2H₂O is shown in Fig. 7. For HoG(II), the 9-coordinated Ho³⁺ binds to three hydroxyl groups of one galactitol molecule and six water molecules. Galactitol links two Ho ions together. The chloride ions do not coordinate to Ho ion and only participate to form hydrogen bonds. Ho–O distances are from 2.356 to 2.459 Å. Some selected bond distances and bond angles are listed in Table 2 and hydrogen bond data are listed in Table 3, respectively. Compared to other reported lanthanide–galactitol complexes with similar structures, Pr–O distances from 2.473 to 2.571 Å; Nd–O distances from 2.461 to 2.552 Å; Sm–O distances from 2.417 to 2.520 Å; Eu–O distances are from 2.412 to 2.515 Å; Tb–O distances are from 2.386 to 2.484 Å. These are consistent with the sequence of ion radius and electrons of lanthanide ions, i.e., in a good agreement with lanthanide contraction. There is an extensive hydrogen bond network in the structure of HoG(II) because of the existence of hydroxyl groups, water molecules and chloride ions. The hydrogen bond data indicate that most of the hydrogen bonds are formed by hydroxyl groups of galactitol and water molecules with chloride ions, $O \cdots CI$ hydrogen bonds.

For metal–sugar complexes, different metal ions, anion (for example, chloride ion or nitrate ion), solvents (water or ethanol), different ligands, and the environment (including pH or temperature), have influences on the coordination behavior of metal ions, so the coordination between metal ions and carbohydrates are complicated. Compared to the structure of galactitol, the coordination of galactitol. Compared to Pr, Nd, Sm, Eu and Tb chloride–galactitol complexes with the structure $[Ln_2(galac)(H_2O)_{12})]Cl_6·2H_2O$, the changes induced by metal ions are similar, for example, the angle of C(3)-C(2)-C(1) and C(2)-C(1)-C(1)#1 after complexation are close for these lanthanide–galactitol complexes, which show that they have similar coordination structures.

In conclusion, the FTIR, FIR, THz, TGA, ESI and X-ray single crystal diffraction spectra results indicate that Ho ion with galactitol can form two complexes in the same environment. The saccharide, chloride ions and water molecules can competitively coordinate with metal ions and form two different complexes, which indicate the high reactivity of galactitol and complexity of the interactions between metal ions and carbohydrates, i.e., solvent, anion ions and other factors may have effect on the coordination of metal ions and different topological structures can be obtained. But the coordination mode of galactitol to lanthanide ions as three hydroxyl group donor may be the same because lanthanide ions have large coordi-

Table 3

Table 2			
Selected bond	lengths (Å) an	d angles (°)	for HoG(II).

Bond lengths		Bond lengths	
Ho(1)-O(6)	2.356(3)	Ho(1)-O(3)	2.464(3)
Ho(1)-O(8)	2.363(3)	C(1) - O(1)	1.437(5)
Ho(1)-O(7)	2.367(3)	C(1) - C(2)	1.519(5)
Ho(1) - O(1)	2.377(3)	C(1)-C(1)#1	1.522(8)
Ho(1)-O(9)	2.397(3)	C(2) - O(2)	1.435(5)
Ho(1)-O(5)	2.403(3)	C(2) - C(3)	1.509(6)
Ho(1) - O(4)	2.419(3)	C(3)-O(3)	1.428(5)
Ho(1)-O(2)	2.459(3)		
Bond angles		Bond angles	
O(6)-Ho(1)-O(8)	83.51(12)	O(1)-Ho(1)-O(5)	135.60(11)
O(6)-Ho(1)-O(7)	77.91(11)	O(9)-Ho(1)-O(5)	124.82(10)
O(8)-Ho(1)-O(7)	70.69(10)	O(6)-Ho(1)-O(4)	87.38(12)
O(6)-Ho(1)-O(1)	140.77(10)	O(8)-Ho(1)-O(4)	139.04(10)
O(8)-Ho(1)-O(1)	84.81(11)	O(7) - Ho(1) - O(4)	145.35(11)
O(7) - Ho(1) - O(1)	132.03(10)	O(1)-Ho(1)-O(4)	77.47(10)
O(6)-Ho(1)-O(9)	70.97(11)	O(9)-Ho(1)-O(4)	68.75(11)
O(8)-Ho(1)-O(9)	70.51(11)	O(5)-Ho(1)-O(4)	72.37(11)
O(7)-Ho(1)-O(9)	132.19(11)	O(6)-Ho(1)-O(2)	143.23(12)
O(1)-Ho(1)-O(9)	69.82(10)	O(8)-Ho(1)-O(2)	71.11(10)
O(6)-Ho(1)-O(5)	69.63(11)	O(7)-Ho(1)-O(2)	68.93(10)
O(8)-Ho(1)-O(5)	138.52(11)	O(1)-Ho(1)-O(2)	64.22(9)
O(7) - Ho(1) - O(5)	73.11(11)	O(9) - Ho(1) - O(2)	121.45(10)
O(6)-Ho(1)-O(3)	138.92(11)	O(5)-Ho(1)-O(2)	113.31(10)
O(8)-Ho(1)-O(3)	134.23(10)	O(4) - Ho(1) - O(2)	129.16(11)
O(7) - Ho(1) - O(3)	97.85(11)	O(5)-Ho(1)-O(3)	70.09(11)
O(1) - Ho(1) - O(3)	70.42(10)	O(4) - Ho(1) - O(3)	73.11(11)
O(9)-Ho(1)-O(3)	129.38(12)	O(2) - Ho(1) - O(3)	63.59(10)
O(1)-C(1)-C(2)	106.0(3)	C(3)-C(2)-C(1)	114.3(4)
O(1)-C(1)-C(1)#1	108.2(4)	O(3)-C(3)-C(2)	108.3(3)
C(2)-C(1)-C(1)#1	113.0(4)	C(1)-O(1)-Ho(1)	123.1(2)
O(2)-C(2)-C(3)	108.7(3)	C(2) - O(2) - Ho(1)	110.2(2)
O(2)-C(2)-C(1)	104.5(3)	C(3) - O(3) - Ho(1)	121.1(3)

S	vmmetry	transformations	used to	generate e	quivalent	atoms: #1	-x + 2,	$-v_{1}$ -	-z.
				0				~ /	

Hydrogen bonds with $H \cdot \cdot A < r(A) + 2.000 \text{ Å}$ and $\angle DHA > 110^{\circ}$ for HoG(II) (Å and °).

$D{-}H{\cdot}{\cdot}{\cdot}A$	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdots A)$	∠DHA
01-H1···010	0.931	1.745	2.664	169.14
O2–H2···Cl1#1	0.931	2.146	3.034	159.19
O3–H3···Cl(3)	0.926	2.268	3.177	167.04
04-H41···01	0.916	2.391	3.001	124.06
04-H41···010	0.916	2.540	3.445	169.75
04-H42···010#2	0.928	2.146	3.039	161.23
05–H51…Cl(2)	0.944	2.249	3.159	161.59
05-H52···Cl3	0.943	2.269	3.155	156.33
O6-H61Cl2#3	0.918	2.268	3.139	158.06
06-H62···Cl3#4	0.925	2.416	3.302	160.27
07–H71…Cl1	0.936	2.167	3.101	175.77
07–H72···Cl2#4	0.921	2.261	3.118	154.48
08-H81Cl1#5	0.942	2.254	3.153	159.46
O8−H82…Cl2#6	0.937	2.266	3.167	161.31
O9–H91…Cl1#5	0.926	2.189	3.101	168.08
09-H92···Cl3	0.931	2.184	3.109	172.40
010-H101···Cl2#2	0.943	2.248	3.123	153.91
010-H102···Cl3#2	0.937	2.483	3.284	143.62

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

nation numbers. Different lanthanide ions may have similar coordination structures with ligands because of their similarities, here ErG and HoG(I) having similar structures, HoG(II) having resemble structure with NdG are new examples.

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References

- [1] S.J. Angyal, Adv. Carbohydr. Chem. Biochem. 47 (1989) 1.
- [2] K. Burger, L. Nagy, in: Biocoordination Chemistry: Coordination Equilibria in Biologically Active Systems, 1990, p. 236.
- [3] P. Umberto, F. Carlo, Progr. Inorg. Chem. 46 (1997) 393.
- [4] B. Gyurcsik, L. Nagy, Coord. Chem. Rev. 203 (2000) 81.
- [5] S. Yano, M. Otsuka, Metal Ions Biol. Syst. 32 (1996) 27.
 [6] M. Gottschaldt, U.S. Schubert, Chem. Eur. J. 15 (2009) 1548.
- [7] C. Vetter, P. Pornsuriyasak, J. Schmidt, N.P. Rath, T. Ruffer, A.V. Demchenko, D. Steinborn, Dalton Trans. 39 (2010) 6327.
- G.H. Li, A. Badkar, H. Kalluri, A.K. Banga, J. Pharm. Sci. 99 (2010) 1931.
- T. Storr, M. Merkel, G.X. Song-Zhao, L.E. Scott, D.E. Green, M.L. Bowen, K.H. [9] Thompson, B.O. Patrick, H.J. Schugar, C. Orvig, J. Am. Chem. Soc. 129 (2007) 7453
- [10] C.G. Hartinger, A.A. Nazarov, S.M. Ashraf, P.J. Dyson, B.K. Keppler, Curr. Med. Chem. 15 (2008) 2574.
- [11] I. Garcia, M. Marradi, S. Penades, Nanomedicine 5 (2010) 777.
- [12] Y.L. Su, Y.Z. Xu, L.M. Yang, S.F. Weng, R.D. Soloway, D.J. Wang, J.G. Wu, J. Mol. Struct. 920 (2009) 8.
- [13] M.P. Curran, D.M. Robinson, Drugs 69 (2009) 2329.
- [14] S.J. Angyal, D.C. Craig, Carbohyd. Res. 241 (1993) 1.
- [15] Y.L. Su, L.M. Yang, Y.Z. Xu, Z.M. Wang, S.F. Weng, C.H. Yan, D.J. Wang, J.G. Wu, Inorg. Chem. 46 (2007) 5508.
- [16] Y.L. Su, L.M. Yang, Z.M. Wang, X.L. Jin, S.F. Weng, C.H. Yan, Z.W. Yu, J.G. Wu, Carbohyd. Res. 341 (2006) 75.
- [17] S. Herdin, P. Klufers, T. Kunte, H. Piotrowski, Z. Anorg. Allg. Chem. 630 (2004) 701.
- [18] Y.L. Su, L.M. Yang, Z.M. Wang, C.H. Yan, S.F. Weng, J.G. Wu, Carbohyd. Res. 338 (2003) 2029.
- [19] L.M. Yang, D.T. Xie, Y.Z. Xu, Y.L. Wang, S.W. Zhang, S.F. Weng, K. Zhao, J.G. Wu, J. Inorg. Biochem. 99 (2005) 1090.
- [20] L.M. Yang, Y.L. Su, Y.Z. Xu, Z.M. Wang, Z.H. Guo, S.F. Weng, C.H. Yan, S.W. Zhang, J.G. Wu, Inorg. Chem. 42 (2003) 5844.
- [21] L.M. Yang, W. Tian, Y.Z. Xu, Y.L. Su, S. Gao, Z.M. Wang, S.F. Weng, C.H. Yan, J.G. Wu, J. Inorg. Biochem. 98 (2004) 1284.
- [22] Y. Hu, X.H. Wang, L.T. Guo, C.L. Zhang, H.B. Liu, X.C. Zhang, Acta Phys. Sin. 54 (2005) 4124 (in Chinese).
- [23] G.M. Sheldrick, SHELXS97, SHELXL97, Programs for Crystal Structures Solution and Refinement, University of Gottingen, Gottingen, Germany, 1997.
- [24] L.M. Yang, Y. Zhao, W. Tian, X.L. Jin, S.F. Weng, J.G. Wu, Carbohyd. Res. 330 (2001) 125.
- [25] J.G. Wu, Modern Fourier Transform Spectroscopic Techniques and Its Applications, Science and Technology References Press, Beijing, 1994.
- [26] R.G. Zhbankov, V.M. Andrianov, H. Ratajczak, M. Marchewka, J. Struct. Chem. 36 (1995) 392
- [27] L.Q. Yang, J.G. Wu, Q. Zhou, J. Bian, Y.M. Yang, D.F. Xu, G.X. Xu, Microchim. Acta 14 (1997) 251.
- [28] S.F. Weng, Fourier Transform Infrared Spectrometer, Chemical Industry Press, Beijing, 2005. p. 270.
- [29] L.M. Yang, H.Q. Sun, S.F. Weng, K. Zhao, L.L. Zhang, G.Z. Zhao, Y.G. Wang, Y.Z. Xu, X.Y. Lu, C.L. Zhang, J.G. Wu, J.E. Chen, Spectrochim. Acta A 69 (2008) 160.
- [30] H.H. Mantsch, D. Naumann, J. Mol. Struct. 964 (2010) 1.