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Facial and meridional isomers of holmium–nitrate N-tert-butylacetamide complexes

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ABSTRACT

Two Ho($C_6H_{13}NO)_3(NO_3)_3$ complexes formed by holmium nitrate and N-tert-butylacetamide (NtBA) (Ho-NtBA(I) in a Cc space group, and Ho-NtBA(II) in a $P2_1/c$ space group) are reported here to investigate the coordination of lanthanide ions with amide groups. Using X-ray single crystal diffraction, FTIR, Raman, FIR and THz methods the structures of the two complexes were identified, in which Ho^{3+} is 9-coordinated to three carbonyl oxygen atoms provided by three NtBA ligands and three bidentate nitrate ions to form the “facial” and “meridional” isomers. Their FTIR and Raman spectra indicate the formation of two holmium complexes, the variations of NtBA after holmium coordination and the spectra are similar for the isomers in some extent. Their FIR and THz spectroscopic results show the coordination of holmium ions and THz maybe more sensitive to isomers. The results demonstrate the coordination behaviors of holmium ions and NtBA ligand.

1. Introduction

The interaction between metal ions and amide groups is involved in bioinorganic chemistry for the relevance of amide group with protein and coordination chemistry, including reactivity aspects and the structural patterns, etc. [1,2] Lanthanide complexes are applied as luminescent or magnetic materials [3,4], contrast agents in magnetic resonance imaging [5], luminescent probes for biomedical analysis and imaging [6], or used in medicine [7], etc. The interactions between lanthanide ions and biological ligands may occur when lanthanide ions are involved in biomedical processes, so the binding modes of lanthanide ions with amide groups are investigated [8,9]. The lanthanide-amide interactions are also important in preparation of ultrafine filament of polyamide 6 (PA6), which is obtained by mixing lanthanide complex with PA6 in melting spinning processes. The key in the process is the formation of the coordination bonds of lanthanide ions with amide groups of PA6 [10,11]. So here N-tert-butylacetamide is selected as a model of PA6 to investigate the interactions between lanthanide ions and the ligands with amide groups because it has the structure of R1-C(=O)–N-R2 similar to PA6.

The structures of lanthanide complexes with 2,6-Bis(N-tert-butylacetamide)pyridine, 2,6-Bis(N-tert-butylacetamide)pyridine-N-oxide, TPPTAM (2, 2′,2″-(3,7,11-Triaza-1,5,9(2,6)–tripyridinacyclododecaphane-3,7,11-triyl)–triacetamide), benzyl-N,N-bis [(2′-furfuryl amino formyl) phenoxyl)ethyl]-amine, 2, 2′, 2″- nitrilotris-(N-phenylmethyl)-acetamide, 2, 2′, 2″- nitrilotris-(N-naphthalenemethyl)-acetamide and picolinamide, etc. are reported [12–19]. The single crystal results of metal–amide complexes indicate the varieties of coordination structures.

Here we report the synthesis of two holmium complexes with N-tert-butylacetamide (NtBA), whose structures have been

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revealed by X-ray single crystal diffraction, FTIR, FIR, Raman and THz spectroscopies. “Facial” and “meridional” isomers have been obtained. The corresponding FTIR and Raman spectra indicate the formation of two Ho-NtBA structures and the changes of NtBA after complexation, especially the variations of CH, amide group, nitrate ions and hydrogen bond systems, etc. FIR and THz results show the coordination of holmium ions and the formation of M−O bonds.

2. Experimental

2.1. Materials and methods

Holmium nitrate was purchased from Aladding Reagent Company, China. N-tert- butylacetamide (98%) was purchased from J&K Company, China.

3 mmol N-tert-butylacetamide and 6 mmol holmium nitrates were dissolved in H_2O/ethanol and heated on a water bath to prepare saturated solutions of the complexes, which were filtered and cooled down to room temperature. The single crystals of the holmium nitrates-N-tert-butylacetamide complexes were successfully grown by slow evaporation solution growth method.

Anal. Calcd for Ho-NtBA(I) ($Ho(C_6H_{13}NO)_3(NO_3)_3$): C, 31.04; H, 5.64; N, 12.07. Found: C, 30.57; H, 5.61; N, 12.03. Anal. Calcd for Ho-NtBA (II) ($Ho(C_6H_{13}NO)_3(NO_3)_3$): C, 31.04; H, 5.64; N, 12.07. Found: C, 30.90; H, 5.54; N, 12.00.

2.2. Physical measurements

A Rigaku Saturn 724 + spectrometer with rotate anode ($\lambda = 0.71073$ Å) at 173(2) K was used to get the X-ray diffraction data of the two holmium-N-tert-butylacetamide complexes. Direct methods with SHELX-97 and the full-matrix least-squares on F^2 method were adopted to resolve and refine the structures. Empirical absorption corrections and anisotropic thermal parameters were applied for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model [20].

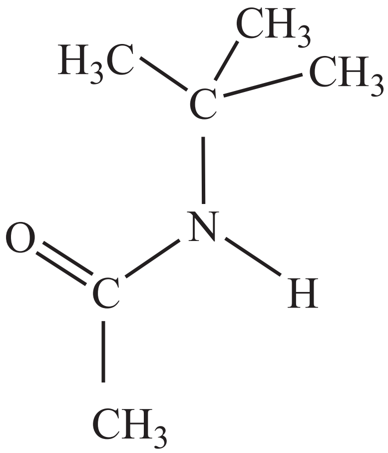
The mid-IR spectra were determined using micro-IR method at 4 cm^{-1} resolution on a Nicolet Magna IN10 spectrometer. Element analyses of the two complexes were performed on an Elementar Vario EL spectrometer. The THz absorption spectra were measured on the THz time-domain device of Capital Normal University, China [21]. Their far-IR spectra in the 650–50 cm^{-1} region were taken using Nujol mull method at 8 cm^{-1} resolution and 128 scans on a Nicolet Magna-IR 750 II Spectrometer. The corresponding Raman spectra were recorded at 4 cm^{-1} resolution and 256 scans on a Nicolet 6700 FTIR NXR FT-Raman module.

3. Results and discussion

3.1. The results of two kinds of crystal structures

The structure of N-tert-butylacetamide ($CH_3CONHC(CH_3)_3$, denoted as NtBA) is shown in Scheme 1. The crystal structures of Ho-NtBA(I) ($Ho(C_6H_{13}NO)_3(NO_3)_3$) and Ho-NtBA (II) ($Ho(C_6H_{13}NO)_3(NO_3)_3$) are shown in Fig. 1. Related crystal data and structure refinements of Ho-NtBA(I) and Ho-NtBA(II) are listed in Table 1, the selected bond lengths and bond angles in Table S1, respectively.

For Ho-NtBA(I) $Ho(C_6H_{13}NO)_3(NO_3)_3$ in a Cc space group, Ho^{3+} is 9-coordinated to three carbonyl oxygen atoms from three NtBA molecules and six oxygen atoms from three bidentate nitrate ions. NtBA is O-monodentate ligand here. Ho−O distances are from 2.277 to 2.546 Å; the average Ho−O distance is 2.399 Å. The bond angles of amide groups, O1−C1−N1, O2−C7−N2 and O3−C13−N3 are 123.3, 123.0 and 123.2°, respectively.



Scheme 1. Scheme of molecular structure of N-tert-butylacetamide.

In the Ho-NtBA (I) complex three N−H⋯O hydrogen bonds are formed. The hydrogen bonds are as follows: N3−H3⋯O6 [x-1, y, z] (174.45°, 3.040 Å); N2−H2⋯O6 [x-1/2, -y+1/2, z-1/2] (170.73°, 2.967 Å); N1−H1⋯O8 [x, -y, z+1/2] (154.58°, 3.131 Å); N1−H1⋯O9 [x, -y, z+1/2] (149.07°, 3.173 Å); N1−H1⋯N5 [x, -y, z+1/2] (172.92°, 3.567 Å).

For the Ho-NtBA (II) complex, Ho^{3+} is 9-coordinated to three O-monodentate NtBA molecules and six oxygen atoms from three bidentate nitrate ions. The coordination mode of NtBA is the same with Ho-NtBA (I) complex. In fact, they are isomers, one is facial and the other one is meridional. The Ho−O distances are from 2.263 to 2.529 Å, and the average Ho−O distance is 2.398 Å. The bond angles related to amide groups, O1−C1−N1, O2−C7−N2 and O3−C13−N3 are 122.3, 122.4 and 122.4°, respectively, which are smaller than Ho-NtBA (I).

The hydrogen bond data of Ho-NtBA(II) are as follows: N3−H3⋯O10 [x, -y+1/2, z-1/2] (170.01°, 2.971 Å); N2−H2⋯O6 [-x+1, y+1/2, -z+3/2] (158.27°, 3.086 Å) and N1−H1⋯O6 [x+1, y, z] (143.72°, 3.036 Å). The three coordinated NtBA molecules form hydrogen bonds with two nitrate ions.

The hydrogen bond networks of Ho-NtBA(II) have minor differences with Ho-NtBA (I) complex, The main differences are weak N1−H1⋯O9 and N1−H1⋯N5 hydrogen bonds appear in Ho-NtBA(I), and the three ∠NHO for N3−H3⋯O6, N2−H2⋯O6 and N1−H1⋯O8 is 174.45, 170.73 and 154.58° for Ho-NtBA(I), but 170.01, 158.27 and 143.72° for Ho-NtBA(II).

The results indicate that the isomers are formed for Ho-NtBA complexes and they are facial and meridional isomers. Here Ho-NtBA complexes have two coordination structures. It is not strange that several coordination structures formed for the same metal and same ligand system. For example, three lanthanum chloride-erythritol complexes, two $CuCl_2$-erythritol complexes (isomers) and three $CaCl_2$-erythritol complexes have been obtained [22–24]. The coordination numbers of lanthanide ions usually are 6–12, and the ligand and solvents compete to coordinate to metal ions, so several stable structures can be obtained for one lanthanide-ligand system. Another example of lanthanide-ligand isomers likes $Ce(NO_3)(Pic)$ $(H_2O)_2(EO_3)](Pic)$ complex isomers (the ligands are triethylene glycol (EO_3) and picrate anion (Pic)), in which Ce^{3+} ions have different coordination numbers, 9 and 10, respectively [25]. Here NtBA has the same coordination mode, but the two Ho complexes are corresponding to $P2_1/c$ and Cc space group, they belong to “facial” and “meridional” isomers.

“Facial” and “meridional” usually is related to 6-coordinatiod octahedral geometries. For lanthanide ions, 6-coordinated