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The coordination of lanthanide ions with picolinamide. The influence of different anions.

Jun-Hui Xue^{a,c}, Xiao-Hui Hua^a, Li-Min Yang^{*b}, Wei-Hong Li^a, Yi-Zhuang Xu^{*a}, Guo-Zhong Zhao^d, Gao-Hui Zhang^d, Ke-Xin Liu^b, Jia-Er Chen^b, Jin-Guang Wu^a

^a *Beijing National Laboratory for Molecular Sciences, State Key Laboratory for 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 Chemistry, Renmin University of China, Beijing 100872, China*

^d *Department of Physics, Capital Normal University, Beijing 100037, China*

* The corresponding author. Telephone: 86-10-62757951

Fax: 86-10-62751708 E-mail: xyz@pku.edu.cn, yanglm@pku.edu.cn

ABSTRACT

Four kinds of coordination structures formed by lanthanide-picolinamide complexes, including $[\text{La}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ (La-pa, Pr-pa, Nd-pa, Sm-pa and Gd-pa), $[\text{Er}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_4]\text{Cl}_3(\text{H}_2\text{O})$ (Er-pa), $[\text{Pr}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_5]\text{Br}_3$ (PrBr-pa) and $[\text{Nd}(\text{C}_6\text{H}_6\text{N}_2\text{O})_3(\text{NO}_3)_2](\text{C}_6\text{H}_6\text{N}_2\text{O})(\text{NO}_3)$ (NdN-pa) are reported. The crystal structures in the solid state are varied along with the changes of anions and lanthanide ions revealed by X-ray single crystal diffraction, FTIR, Raman, FIR and THz spectroscopy. In these crystal structures pyridyl nitrogen and carbonyl oxygen of picolinamide are coordinated to metal ions to form a five-membered ring structure or hydrogen-bonded. The results indicate the differences of the coordination of different lanthanide ions (Er ion is special for its small atom radius), the changes of hydrogen bonds and conformation of the ligands induced by complexation, and the influence of different anions. When nitrate ions are involved in the coordination structure, the coordination number of lanthanide ions is higher. Chloride and bromine ions do not coordinated to metal ions, so lanthanide bromine and lanthanide chloride-pa complexes have similar structures. The results provide models for the coordination structures of lanthanide ions with ligands having amide groups.

Keywords: Picolinamide; FT-IR; Complexation; Crystal structure; THz

Introduction

Lanthanide complexes have potential applications as luminescent and laser materials, efficient organic light emitting diodes (OLEDs) and polymer light emitting diodes (PLEDs),¹ as NMR shift reagents,² in analytical assays and as a modern antibody catalysts in biochemistry,³⁻⁶ or used in medicine, for example, lanthanum carbonate is used as a phosphate binder.^{7,8} Some of the applications are related to the interactions between lanthanide ions and biological ligands. The carboxamide group is an important part in the primary structure of proteins,^{9,10} so the study of the binding modes of lanthanide ions with

ligand having amide groups is of great interest. In addition, the interactions between amide groups and metal ions are also key issues in preparation of new materials. For example, when lanthanide complex is mixed with PA6 in melting spinning processes, the ultrafine filament of PA6, 0.5-1.0 Denier (denier is a unit of measure for the linear mass density of fibers; if the mass of a fiber whose length is 9000 m is 1.0 g, the linear mass density of the fiber is 1.0 denier) with excellent performance are prepared. It is due to that the coordination bonds of lanthanide ions with amide groups of PA6, and the chain structure of nylon varied to increase the stretching strength in the spinning process.¹¹⁻¹³

Picolinamide (2-pyridinecarboxamide; 2-NH₂COPY, denoted as pa) is selected as a model ligand to investigate the interactions between lanthanide ions and amide groups. It is an interesting ligand for inorganic chemistry,¹⁴⁻²³ and is also used for separation of actinide/lanthanide (An/Ln).²⁴ Picolinamide is often used as N, O-bidentate ligand to form a five-membered ring structure, or N, O, O-tridentate ligand as the carbonyl oxygen coordinates with two metal ions,¹⁴⁻²³ for example, supramolecular architecture via self-complementary amide hydrogen bonding in [Ag(picolinamide)₂](NO₃)·H₂O is observed.¹⁵ The structures of [Zn(H₂O)₂(picolinamide)₂]₂I₂, [Co(H₂O)₂(picolinamide)₂](NO₃)₂, [Co(H₂O)₂(picolinamide)₂]₂·Cl₂, [Cu_{1.5}(picolinamide)₃](H₂O)₆ and SrCl₂·C₆H₆N₂O·H₂O have been determined.^{14, 17, 22, 23}

Here we report the synthesis of the lanthanide ions complexes with pa, their structural characterization has been carried out by spectroscopic and X-ray diffraction analysis to compare the coordination differences of various lanthanide ions and the influence of anions. Four kinds of structures have been observed for different lanthanide ions and anions, which indicate the different coordination structures of lanthanide-amide complexes and suggested the complexity of characteristics of these compounds. It exhibits the potential basis of the extensive applications of lanthanide ions.

Experimental

Materials and methods

Praseodymium chloride and neodymium nitrate were purchased from Aladdin Reagent Company, China. Other lanthanide chlorides were prepared and crystallized from corresponding rare earth oxide of high purity (99.99%) with HCl. Picolinamide (98%) was purchased from J&K Company in China.

The preparation of these metal complexes was as follows: 3 mmol ligand and 3 or 6 mmol metal chlorides (praseodymium bromine or neodymium nitrate) were dissolved in H₂O/ethanol and heated on a water bath to prepare saturated solutions of metal-ligand complexes, then the concentrated solutions were filtered and cooled down for crystallization. Anal. Calcd for La-pa ($\text{LaCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 24.87; H, 3.82; N, 9.67. Found: C, 24.77; H, 3.80; N, 9.63. Anal. Calcd for Pr-pa ($\text{PrCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 24.78; H, 3.81; N, 9.63. Found: C, 24.71; H, 3.74; N, 9.56. Anal. Calcd for Nd-pa ($\text{NdCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 24.64; H, 3.79; N, 9.58. Found: C, 24.02; H, 3.86; N, 9.42. Anal. Calcd for Sm-pa ($\text{SmCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 24.38; H, 3.75; N, 9.48. Found: C, 24.35; H, 3.89; N, 9.38. Anal. Calcd for Gd-pa ($\text{GdCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 24.10; H, 3.71; N, 9.37. Found: C, 23.91; H, 3.66; N, 9.16. Anal. Calcd for Er-pa ($\text{ErCl}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 23.71; H, 3.65; N, 9.22. Found: C, 24.12; H, 3.49; N, 9.33. Anal. Calcd for PrBr-pa ($\text{PrBr}_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_2 \cdot 5\text{H}_2\text{O}$): C, 20.16; H, 3.10; N, 7.84. Found: C, 19.04; H, 3.04; N, 7.19. Anal. Calcd for NdN-pa ($\text{Nd}(\text{NO}_3)_3 \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_4$): C, 35.21; H, 2.95; N, 18.82. Found: C, 35.27; H, 2.98; N, 18.86. The elemental analyses are consistent with single crystal X-ray diffraction results, which indicate the purity of these lanthanide-pa complexes.

Physical measurements

X-Ray diffraction data for the metal complexes were collected on a Rigaku Saturn 724 spectrometer (Sm-pa, Gd-pa, PrBr-pa and NdN-pa) equipped with graphite-monochromatized

Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Saturn 724+ spectrometer using rotate target ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K (La-pa, Nd-pa, Pr-pa and Er-pa). The structures were resolved by direct methods with SHELX-97 and refined using the full-matrix least-squares on F^2 method. 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.²⁵

The mid-IR spectra were measured on a Nicolet Magna IN10 spectrometer using micro-IR method at 4 cm^{-1} resolution. Element analyses were carried out on an Elementar Vario EL spectrometer. The THz absorption spectra were recorded 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.²⁶ The far-IR spectra of the molecules in the $650\text{--}50 \text{ cm}^{-1}$ region were measured using commonly used Nujol mull method and were taken on a Nicolet Magna-IR 750 II Spectrometer at room temperature and at 8 cm^{-1} resolution and 128 scans. The Raman spectra were recorded on a Nicolet 6700 FTIR NXR FT-Raman module at 4 cm^{-1} resolution and 256 scans.

Results and Discussion

The results of four kinds of crystal structures

The crystal structures of La-pa ($[\text{La}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_5]\text{Cl}_3$), Er-pa ($[\text{Er}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_4]\text{Cl}_3(\text{H}_2\text{O})$), PrBr-pa ($[\text{Pr}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_5]\text{Br}_3$) and NdN-pa ($[\text{Nd}(\text{C}_6\text{H}_6\text{N}_2\text{O})_3(\text{NO}_3)_2](\text{C}_6\text{H}_6\text{N}_2\text{O})(\text{NO}_3)$) are shown in Fig. 1 representing the four kinds of crystal structures. Crystal data and structure refinements of these metal complexes are listed in Table 1. The selected bond lengths and bond angles are listed in Table S1.

For La, Pr, Nd, Sm and Gd-pa complexes $[\text{Ln}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_5]\text{Cl}_3$, Ln^{3+} is 9-coordinated to two carbonyl oxygen atoms and two pyridyl nitrogen atoms from two pa ligands and five water molecules. Pa is N, O-bidentate ligand here to form a five-member

ring structure. Chloride ions are only involved in forming hydrogen bonds. The Ln–O distances are from 2.451 to 2.573 Å (La); from 2.424 to 2.542 Å (Pr); from 2.404 to 2.531 Å (Nd), from 2.370 to 2.520 Å (Sm) and from 2.362 to 2.487 Å (Gd). The average Ln–O distances from La to Gd are 2.522 (La), 2.491 (Pr), 2.473 (Nd), 2.446 (Sm) and 2.425 Å (Gd). The Ln–O distances, average Ln–O distances and the Ln–N distances decrease along with the increase of atom number, which are consistent with lanthanide contraction effect. The changes of the O–C–N angle in amide group are as follows: 121.7(6) and 122.2(6)° for La-pa, 121.4(4) and 122.3(4)° for Pr-pa, 121.8(3) and 121.6(3)° for Nd-pa, 123.0(10) and 123.0(11)° for Sm-pa, 121.5(5) and 122.0(5)° for Gd-pa. These O–C–N bond angles are from 121.4 to 123.0° and the bond angles are similar for different lanthanide ions.

The torsion angle results show that the pyridyl ring is nearly in a plane and amide group is also nearly in the plane, for example, for La-pa, O1–C6–C1–N1, -0.9(8)°; O2–C12–C7–N3, -1.6(8)°; for Pr-pa, O2–C12–C7–N3, -2.1(6)°; O1–C6–C1–N1, -2.4(6)°; C2–C3–C4–C5, 4.1(7)°; for Nd-pa, O2–C12–C7–N3, 1.9(3)°; N1–C1–C6–O1, 2.1(3)°; C1–C2–C3–C4, 2.4(4)°; C7–C8–C9–C10, 1.8(4)°; C11–C10–C9–C8, -3.2(4)° and C5–C4–C3–C2, -3.4(4)°. The deviations from the plane are a little different for various lanthanide ions. For Sm-pa, O1–C6–C1–N1, -2.0(14)°; O2–C12–C7–N3, -1.8(14)°; C7–C8–C9–C10, -2.2(17)°; C8–C9–C10–C11, 3.9(17)°; C5–C4–C3–C2, 4.0(16)°; C1–C2–C3–C4, -3.3(16)°. The torsion angles of O2–C12–C7–N3, O1–C6–C1–N1 and C2–C3–C4–C5 are 3.3(6), 1.4(6) and -3.3(8)° for Gd-pa. The results indicate the torsion angles are within 5°. Different lanthanide ions, from La to Gd, may cause the various deviations from the plane. As well as the hydrogen bonds in these lanthanide-pa complexes, for example, for La-pa complex, the coordinated water molecules are hydrogen-bonded with chloride ions, and the amino nitrogen atoms form hydrogen bonds with chloride ions and coordinated water molecule (O3). The

hydrogen bonds are the same for these complexes, but for the O–H...Cl, N–H...Cl or N–H...O hydrogen bonds, the distances between O and Cl (N and Cl, or N and O) and the corresponding bond angles have some differences.

For the second kind of lanthanide-pa complex (structure II), Er-pa, $[\text{Er}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_4]\text{Cl}_3(\text{H}_2\text{O})$, Er ion is 8-coordinated to two N, O-bidentate pa molecules and four water molecules. One water molecule and three chloride ions are hydrogen-bonded. Er–O distances are from 2.263 to 2.376 Å; the average Er–O distance is 2.324 Å; Er–N distances are 2.498(3) and 2.514(3) Å. The coordination mode of pa is the same with La-pa series complexes. The bond angle of O2–C12–N4 is 122.1(3)°; O1–C6–N2 is 120.7(3)°, which is similar to La-pa series complexes. The torsion angles of N3–C7–C12–O2 and N1–C1–C6–O1 related to coordinated amide group are 6.5(4) and 7.8(4)°, which are larger than La-pa series and indicate that the conformation of pa ligand is changed in different coordination structures.

The coordination number of Er is 8, which is smaller than the coordination number of La-pa series complexes. The difference of Er-pa and La-pa is the number of coordinated water molecules. The complicated hydrogen bonds in Er-pa are also different with La-pa series complexes. Uncoordinated water molecule (O7) forms hydrogen bonds with Cl1 and Cl3, coordinated water molecule (O4) forms hydrogen bond with uncoordinated water molecule (O7). Amino nitrogen atoms of pa form hydrogen bonds with chloride ions (N4 with Cl1, N2 with Cl3), amino nitrogen atom N2 of pa also form hydrogen bonds with coordinated water molecules (O1 and O5). Coordinated water molecules form hydrogen bonds with chloride ions (O3 with Cl2, O5 with Cl3, O4 with Cl2, O6 with Cl2 and O5 with Cl1). Most of the hydrogen bonds are formed via some symmetric operations. Er ion sometimes has different coordination structure with some ligand, for example, Er-erythritol complex has a special coordination structure.²⁷

The third structure is related to PrBr-pa complex, structure III. The coordination of Pr³⁺

in PrBr-pa is similar to the one in Pr-pa complex. Pr³⁺ is 9-coordinated to two pa molecules and five water molecules. Three bromine ions, similar to three chloride ions, are hydrogen-bonded. Pr–O distances are from 2.421 to 2.566 Å, the average Pr–O distance is 2.492 Å. Pr–N distances are 2.709(7) and 2.725(8) Å, which indicate that the binding of Pr–O is stronger than Pr–N. The Pr–O distances are from 2.424 to 2.542 Å and the average Pr–O distance is 2.491 Å, Pr–N distances are 2.671(3) and 2.702(4) Å in Pr-pa complex. The Pr–O distances are similar in Pr-pa and PrBr-pa complexes and Pr–N distances are larger in PrBr-pa complex.

The bond angles of O1–C6–N2 and O2–C12–N4 related to coordinated amide groups are 121.5(10) and 119.5(9)°. The torsion angle of N3–C7–C12–O2 and O1–C6–C1–N1 are 5.3(13) and 1.8(14)°. The torsion angle of O–C–C–N, 5.3(13)° is larger than Pr-pa complex, which indicate the influence of bromine ion. The C–C–C–C torsion angles are similar to Pr-pa complex, which indicate that the pyridyl rings are nearly in a plane in Pr-pa and PrBr-pa complexes. Most of the hydrogen bonds are O–H···Br and N–H···Br. Coordinated water molecules form hydrogen bonds with bromine ions, amino nitrogen atoms of pa form hydrogen bonds with bromine and coordinated water molecule.

The fourth structure is NdN-pa complex, [Nd(C₆H₆N₂O)₃(NO₃)₂] (C₆H₆N₂O) (NO₃) (structure IV). Nd³⁺ is 10-coordinated to three pa molecules and two bidentate nitrate ions. One nitrate ion and one pa molecule are hydrogen-bonded. Nd–O distances are from 2.427 to 2.641 Å; the average Nd–O distances is 2.526 Å; the Nd–N distances are 2.664(4), 2.678(4) and 2.688(4) Å, respectively. The Nd–O distances are from 2.404 to 2.531 Å and the average Nd–O distance is 2.473 Å in Nd-pa complex, which is smaller than the one in NdN-pa complex; Nd–N distances are 2.657(2) and 2.683(2) Å in Nd-pa complex, which is similar to NdN-pa complex. Here pa appears to be a bidentate ligand or hydrogen-bonded. It is not

common for pa as hydrogen-bonded ligand, but it is common for other ligands, for example, in the structure of CuCl_2 -erythritol complex, non-coordinated erythritol unit exist side by side in the crystal.²⁸ The presence of uncoordinated pa is belonging to one coordination mode of pa in metal-pa complexes, which is not related to any impurity in the crystal.

The torsion angles of C2–C3–C4–C5 and C1–N1–C5–C4 are $-0.2(7)$ and $1.4(6)^\circ$, which indicate that the pyridyl ring is nearly in a plane. The torsion angles of N3–C11–C12–O2 and N1–C5–C6–O1 related to coordinated amide group are $24.6(5)$ and $-11.8(5)^\circ$, which indicate the change of pa conformation different with the other three kinds of lanthanide-pa complexes. For the hydrogen-bonded pa molecule, the torsion angle of N9–C23–C24–O10, C22–C23–C24–O10, N9–C23–C24–N10, C22–C23–C24–N10 are $-162.7(4)$, $15.8(7)$, $16.3(6)$ and $-165.2(4)^\circ$, which is different from the coordinated pa molecule. There are N–H...O hydrogen bonds formed by amino nitrogen atom with oxygen atoms from nitrate ions, or carbonyl oxygen atoms of hydrogen-bonded pa molecule; N10, the amino nitrogen atom in the uncoordinated pa molecule, forms hydrogen bonds with O10 (the carbonyl oxygen atom in another uncoordinated pa molecule) and O7 (an oxygen atom from one coordinated nitrate ion). The high coordination number of Nd^{3+} is related to the influences of nitrate ions. One nitrate ion provides two oxygen atoms to coordinate to metal ion, which make the coordination number high. Similarly, for lanthanide nitrate and lanthanide chloride-galactitol complexes, lanthanide ions have higher coordination numbers (12) in lanthanide nitrate complexes.²⁹

Compared the four kinds of lanthanide-pa complexes, lanthanide chloride-pa complexes have two kinds of structures, the coordination numbers are 9 for La to Gd, 8 for Er ion, respectively, maybe the atom radius of Er is smaller than other lanthanide ions, so the coordination number is lower, which make the one water difference. When the anion is bromine ion, because it is hydrogen-bonded, the coordination structure is similar to chloride

ion (structure I). The influence of nitrate ion is reflected at the coordination number of lanthanide ion and the hydrogen bonds, because nitrate ions are involved in the coordination, and in the structure one pa molecule and one nitrate ion are hydrogen-bonded.

The FTIR and Raman results of four kinds of lanthanide–pa complexes

The FTIR spectra of pa and its eight lanthanide complexes are shown in Fig. 2. Corresponding to four kinds of crystal structures, four kinds of IR spectra are observed. For the ligand pa, the ν_{NH} and ν_{CH} vibrations are located at 3420, 3277, 3187 and 3061 cm^{-1} . After complexation, from La to Gd, the ν_{NH} , ν_{OH} and ν_{CH} vibrations are broad bands, and peak widths at half height are similar, which indicate the existence of extensive hydrogen bond networks in these complexes and water molecules may involve in the coordination. The bands are located nearly at 3304, 3212 and 3188 cm^{-1} , and little shifts are observed from La to Gd, for example, 3304 cm^{-1} for La and 3312 cm^{-1} for Gd, which reflect the minor difference of intensity of hydrogen bonds. The bands are located at 3346 cm^{-1} for Sm-pa, which is a little different with other lanthanide ions. The ν_{CO} vibrations are located at 1662 cm^{-1} for pa,^{30–32} and it is shifted to 1665, 1666 or 1667 cm^{-1} after coordination, which indicate the coordination of C=O group. $\nu_{\text{NH}_2\text{scis}}$ are located at 1605 cm^{-1} for pa, and it is shifted to 1613, 1614 or 1616 cm^{-1} after complexation. Other bands are similar for these metal complexes, for example, ν_{ring} are located at 1588 and 1569 cm^{-1} for pa, and they are located at 1583 and 1568 cm^{-1} for La, Pr and Nd-pa, 1584 and 1568 cm^{-1} for Sm-pa, 1585 and 1569 cm^{-1} for Gd-pa complex, which indicate the changes of the rings. ν_{CN} is located at 1393 cm^{-1} for pa, and it is shifted to 1434 cm^{-1} for La-pa, 1435 cm^{-1} for Pr-pa, 1436 cm^{-1} for Nd and Sm-pa, 1437 cm^{-1} for Gd-pa, which indicate the coordination of pyridyl nitrogen.¹⁷ The IR results indicate that these lanthanide ions, from La to Gd, form complexes having similar structures with pa.

In the FTIR spectrum of Er-pa complex (structure II), the νNH and νOH vibrations are located at 3469, 3351 and 3184 cm^{-1} , which indicate that its hydrogen bonds are different with those complexes having structure I, especially longer hydrogen bond related to 3469 cm^{-1} band exists. The νCO vibration is shifted to 1681 cm^{-1} in Er-pa, which show the coordination of C=O group. The ν_{ring} are located at 1581 and 1567 cm^{-1} for Er-pa (1585 and 1569 cm^{-1} for Gd-pa complex). δCH vibrations are located at 1491, 1492, 1493 and 1494 cm^{-1} for La-pa series complexes, but at 1505 cm^{-1} for Er-pa. νCN is shifted to 1433 cm^{-1} , which indicate the coordination of pyridyl nitrogen. δ_{ring} are located at 785, 786, 787, 788 and 789 cm^{-1} from La to Gd-pa, but 794 and 786 cm^{-1} for Er-pa, which indicate the different change of the ring and pa conformation.

In the FTIR spectrum of PrBr-pa, structure III, the νNH and νOH vibrations are located at 3380, 3354, 3299, 3214, 3180 and 3169 cm^{-1} , and the peak width at half height is similar to structure I, which is from the similar coordination structures. The νCO vibration is located at 1660 cm^{-1} in PrBr-pa related to the coordination of carbonyl oxygen of pa. Some bands are similar for Pr-pa and PrBr-pa, for example, 1583(1581), 1568(1568), 1492(1492), 1435(1434), 1309(1308), 1261(1260), 1222(1217), 1164 (1164), 1119(1119), 1056(1056), 1010 (1009), 820(818), 786(784), 756(753), 656(656), 633(633) cm^{-1} [Pr-pa(PrBr-pa)], which should be related to the similar topological structures. The different bands are located at (1450 cm^{-1}), 1081 (1092 and 1076 cm^{-1}), (720 cm^{-1}) [Pr-pa(PrBr-pa)], which are related to δCH , $\text{NH}_{2\text{rock}}$, $\gamma(\text{CO})$ and reflect the various changes of pa conformation. The νCN vibration at 1393 cm^{-1} of free pa changes quite consistently for all complexes because the coordination of pyridyl nitrogen and the influence of the pyridyl ring. The ring vibration at about 1588 and 1569 cm^{-1} only have small changes compared to pa because the pyridyl ring has no obvious changes after complexation.

In the FTIR spectrum of NdN-pa, structure IV, the νNH and νCH vibrations are located at 3384, 3357, 3288, 3181 and 3092 cm^{-1} , and the peak width at half height is larger. The νCO vibration is shifted to 1675 cm^{-1} in NdN-pa, which indicate the coordination of carbonyl oxygen of pa. The νCO vibration is located at 1665 cm^{-1} in Nd-pa complex. The 10 cm^{-1} difference (1675 and 1665) may be resulted from the different torsion angles related to amide groups (24.6 and 11.8° for NdN-pa, 1.9 and 2.1° for Nd-pa). For Nd-pa and other lanthanide complexes with structure I, the change of conformation of pa is relatively small, so the νCO vibrations only have little shifts compared to pa. In addition, in the structure of Nd-pa complex, formed hydrogen bonds between water molecules and carbonyl group different with NdN-pa complex also result in the small shift of νCO . The δCH vibrations and $\nu_{\text{as}}(\text{NO}_2)$ are at 1493 and 1482 cm^{-1} in NdN-pa (δCH at 1493 cm^{-1} for Nd-pa), which show the difference of the pyridyl ring and the influence of nitrate ions. The bands at 1445, 1432, 1410, 1346, 1327, 1308 and 1296 cm^{-1} also should be related to the coordinated and uncoordinated nitrate ions, δCH_2 and δCOH , etc. Similar bands appear for lanthanide nitrate-galactitol complexes where coordinated and uncoordinated nitrate ions present.³³ The bands at 1259, 1223 and 1009 cm^{-1} in NdN-pa (1261, 1222 and 1011 cm^{-1} in Nd-pa) are similar, but most of the bands have differences, for example, 1178 and 1158 (1164), 1116 (1120), 1091 (1082), 1040, 997, 829 and 816 (820), 784(787), 762, 754 and 744(756), 651(658), 630(633), 616 (614) cm^{-1} for NdN-pa and Nd-pa, which are related to ν_{ring} , δCH , $\chi(\text{CH})$, δ_{ring} , τ_{ring} and $\chi(\text{CO})$ and show the various changes of pa conformation. The FTIR results indicate that four kinds of structures are obtained, which are consistent with crystal structures.

The Raman results shown in Fig. 3 also indicate the formation of four kinds of metal-pa complexes. The intensities of νNH and νOH vibrations are decreased compared to corresponding FTIR spectra and νCH vibrations become stronger in the Raman spectra. The

νNH and νOH vibrations are located at 3363, 3193 and 3144 cm^{-1} in La-pa, 3375 cm^{-1} in Pr-pa, 3302 cm^{-1} in Nd-pa, 3386 cm^{-1} in Sm-pa, 3296 cm^{-1} for Gd-pa complexes, 3380 cm^{-1} in PrBr-pa, respectively (The spectra of Pr-pa, Sm-pa and PrBr-pa show the luminescence effect). The νCH vibrations are located at 3072 and 3064 cm^{-1} for pa, after complexation they are shifted to 3072 and 3063 cm^{-1} (La), 3068 cm^{-1} (Pr), 3072 cm^{-1} (Sm), 3078 and 3064 cm^{-1} (Gd), 3078 cm^{-1} (NdN-pa), 3078 and 3063 cm^{-1} (Nd-pa), 3065 cm^{-1} (PrBr-pa), 3085, 3074 and 3059 cm^{-1} (Er-pa), which indicate the changes of the pyridyl ring. The νCO vibration of pa is located at 1664 cm^{-1} , after coordination the bands at 1655 and 1614 cm^{-1} (La), 1654 and 1608 cm^{-1} (Pr), 1675, 1644 and 1614 cm^{-1} (Nd), 1672 and 1610 cm^{-1} (Sm), 1677 and 1615 cm^{-1} (Gd), 1695, 1644 and 1608 cm^{-1} (Er), 1666 and 1606 cm^{-1} (PrBr-pa) and 1613 cm^{-1} (NdN-pa) are related to amide groups, including νCO and $\text{NH}_{2\text{scis}}$.³² For the complexes of Nd with pa, Nd-pa and NdN-pa, the electronic enhanced Raman spectra are observed in the 2200–1700 cm^{-1} region.³⁴ The various bands of Nd-pa and NdN-pa assigned to the $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{11/2}$ transition of Nd reflect the different coordination environment of Nd^{3+} .

The band positions and relative intensities in the 1500–400 cm^{-1} region are similar for the complexes with structure I and structure III. For Er-pa and NdN-pa (structure II and structure IV), although some of the band positions are similar in some extent, the relative intensities have differences. Four kinds of structures also can be identified using Raman spectroscopy. The bands in the 400–100 cm^{-1} region are related to $\nu\text{M-O}$, $\nu\text{M-N}$ and ring deformation, etc.³⁵ These bands have different band positions and relative intensities, which reflect the coordination differences of various lanthanide ions and anions.

The FIR and THz results of four kinds of lanthanide-pa complexes

The FIR and THz results are shown in Fig. 4 and Fig. S1. The FIR spectrum of pa has the bands at 649, 630, 609, 519, 420, 385, 252, 177, 135, 76 and 54 cm^{-1} assigned to δ_{ring} ,

δCO , $\text{NH}_{2\text{twist}}$, δCN , τ_{ring} , ν_{CC} , $\text{NH}_{2\text{wag}}$, δCC , γCC and τCCCO , etc.³² After complexation, the band positions and relative intensities for the complexes with structure I are similar, which are consistent with that they have the similar coordination structures. The bands at 293, 249, 212, 186 and 128 cm^{-1} for La-pa, at 286, 260, 218, 142, 133 and 102 cm^{-1} for Pr-pa, 286, 265, 218, 143, 132 and 104 cm^{-1} for Nd-pa, 287, 271, 230, 217, 143 and 106 cm^{-1} for Sm-pa, 291, 237, 220, 164, 137 and 94 cm^{-1} for Gd-pa, can be assigned to $\nu_{\text{Ln-O}}$, $\nu_{\text{Ln-N}}$ and ring deformation, etc.³⁵ The FIR spectrum of Er-pa is similar to La-pa series in some extent. The FIR spectra of PrBr-pa and NdN-pa have larger differences with other lanthanide ions. The different band positions and relative intensities in the FIR spectra indicate the formation of four kinds of metal-pa complexes.

The bands in the THz region are related to lattice vibrations, intermolecular hydrogen bonds, collective modes, etc.^{36,37} The THz bands are located at 1.23, 1.49, 1.64, 1.87 and 2.25 THz for pa at room temperature.²³ For La-pa series, the THz bands are located near 1.90 THz, and the bands are shifted a little for different lanthanide ions. For Er-pa, the bands are located at 1.06, 1.40, 1.70, 2.02 and 2.13 THz, and the relative intensities have obvious differences with other lanthanide ions. For NdN-pa, the band at 1.88 THz is similar to 1.87 THz in Nd-pa. The THz spectrum of PrBr-pa has larger difference with Pr-pa. The THz spectra are different for various lanthanide ions, which indicate that maybe THz is more sensitive to different metal ions.

Conclusion

For different lanthanide ions and anions, four kinds of Ln-pa complexes have been observed. When anion is chloride ion, two structures have been obtained for different lanthanide ions. Er ion is special for that its small atom radius results in lower coordination number. The coordination structures of Pr-pa and PrBr-pa complexes are similar. The coordination of nitrate ions makes the coordination number of lanthanide ions higher.

Chloride ion, bromine ion and nitrate ions have different influences on the coordination structures of lanthanide-pa complexes. Pyridyl nitrogen and carbonyl oxygen of picolinamide are coordinated to metal ions to form a five-membered ring structure or hydrogen-bonded. FTIR and Raman spectra indicate the formation of four kinds of structures. The electronic enhanced Raman spectra of Nd-pa and NdN-pa complexes are observed, which reflect the difference of Nd coordination environment. FIR and THz absorption spectra show the vibrations of M–O, M–N and ring deformation, etc. These experimental results provide models for the coordination modes of lanthanide ions with ligands having amide groups.

Supplementary material

Crystallographic data as .cif files for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. CCDC numbers are 841635 and 918184–918187, 918190–918192. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

Financial support from National Natural Science Foundation of China for the grants (21001009 and 50973003), the State Key Project for Fundamental Research of MOST (2011CB808304), National High-tech R&D Program of China (863 Program) of MOST (2010AA03A406), and the Scientific Research Project of Beijing Municipal Commission of Education and Beijing Natural Science Foundation (Grant No. KZ201310028032) are gratefully acknowledged. The authors thank Prof. Xiang Hao, Tongling Liang and Lin Wang (Institute of Chemistry, Chinese Academy of Sciences) for invaluable assistance with the X-ray crystallography.

References

- 1 K. Binnemans, *Rare-earth beta-diketonates*, in: Jr. K.A. Gschneidner; J.-C.G. Bunzli; V. K. Pecharsky,(Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Amsterdam, 2005, 35 (225), 107.
- 2 T. J. Wenzel, in: *Lanthanide Shift Reagents in Stereochemical Analysis*, T.C. Morill, (ed.), VCH Publishers, Weinheim, 1986, 5, 151.
- 3 A. K. Hagan, T. Zuchner, *Anal. Bioanal. Chem.* 2011, **400**, 2847.
- 4 Y. Y. Song, Y. Z. Xu, S. F. Weng, L. B. Wang, X. F. Li, T. F. Zhang, J. G. Wu, *Biospectroscopy* 1999, **5**, 371.
- 5 A. Kuzuya, K. Machida, T. Sasayama, Y. Shi, R. Mizoquchi, M. Komiyama. *J. Alloy. Compd.* 2006, **408**, 396.
- 6 Y. L. Su, Y. Z. Xu, L. M. Yang, J. Yang, S. F. Weng, Z. W. Yu, J. G. Wu, *Anal. Biochem.* 2005, **347**, 89.
- 7 F. Albaaj, A. J. Hutchison, *Int. J. Clin. Pract.* 2005, **59**, 1091.
- 8 M. P. Curran, D. M. Robinson, *Drugs* 2009, **69**, 2329.
- 9 K. B. Girma, V. Lorenz, S. Blaurock, F. T. Edelman, *Coord. Chem. Rev.* 2005, **249**, 1283.
- 10 R. C. Dunbar, J. D. Steill, J. Oomens, *J. Am. Chem. Soc.* 2011, **133**, 1212.
- 11 Y. J. Wu, Y. Z. Xu, D. J. Wang, Y. Zhao, S. F. Weng, D. F. Xu, J. G. Wu, *J. Appl. Polym. Sci.* 2004, **91**, 2869.
- 12 S. X. Liu, C. F. Zhang, Y. H. Liu, Y. Zhao, Y. Z. Xu, Y. Ozaki, J. G. Wu, *J. Mol. Struct.* 2012, **1021**, 63.
- 13 W. X. Sun, X. B. Hu, Y. Z. Xu, L. W. Qu, Z. L. Yang, D. J. Wang, X. X. Liu, F. X. Guo, S. F. Weng, J. G. Wu, D. F. Xu, *Acta Chimica Sinica* 2000, **58**, 1602.
- 14 Q. Y. Du, L. Y. Xin, Y. P. Li, D. S. Cao, *Chinese J. Struct. Chem.* 2006, **25**, 295.

- 15 M. Dakovic, M. Benko, Z. Popovic, *J Chem Crystallogr.* 2011, **41**, 343.
- 16 M. Dakovic, D. Vila-Vicosa, M. J. Calhorda, Z. Popovic, *Cryst. Eng. Comm.* 2011, **13**, 5863.
- 17 H. Pasaoglu, S. Guven, Z. Heren, O. Buyukgungor, *J. Mol. Struct.* 2006, **794**, 270.
- 18 E. Bugella-Altamirano, J. M. Gonzalez-Perez, D. Choquesillo-Lazarte, J. Niclos-Gutierrez, A. Castineiras-Campos, *Z. Anorg. Allg. Chem.* 2000, **626**, 930.
- 19 M. M. Reinoso-García, A. Dijkman, W. Verboom, D. N. Reinhoudt, E. Malinowska, D. Wojciechowska, M. Pietrzak, P. Selucky, *Eur. J. Org. Chem.* 2005, 2131.
- 20 M. Dakovic, Z. Popovic, G. Giester, M. Rajic'-Linaric, *Polyhedron* 2008, **27**, 210.
- 21 O. Z. Yesilel, H. Olmez, O. O. Yilan, H. Pasaoglu, O. Buyukgungor, *Z. Naturforsch. (B)* 2006, **61**, 1094.
- 22 B. Huang, L. Y. Xin, Q. Y. Du, *Huaxue Shijie* 2007, **48**, 132.
- 23 J. H. Xue, X. H. Hua, L. M. Yang, W. H. Li, Y. Z. Xu, G. Z. Zhao, G. H. Zhang, L. M. Liu, K. X. Liu, J. E. Chen, J. G. Wu, *J. Mol. Struct.* 2014, **1059**, 108.
- 24 B. R. Bao, Q. Cheng, W. G. Cao, Q. Xiang, Y. Li, Y. J. Zhao, *Nuclear Science and Techniques* 2005, **16**, 31.
- 25 G. M. Sheldrick, *Acta Crystallogr. A* 2008, **64**, 112.
- 26 Y. Hu, X. H. Wang, L. T. Guo, C. L. Zhang, H. B. Liu, X. C. Zhang, *Acta Phys. Sinica* 2005, **54**, 4124.
- 27 L. M. Yang, Y. Z. Xu, Y. L. Wang, S. W. Zhang, S. F. Weng, K. Zhao, J. G. Wu, *Carbohydr. Res.* 2005, **340**, 2773.
- 28 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.* 2004, **98**, 1284.
- 29 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.* 2007, **46**, 5508.

- 30 J. G. Wu, *Modern Fourier Transform Spectroscopic Techniques and Its Applications*, Science and Technology References Press, Beijing, 1994.
- 31 S. F. Weng, *Fourier Transform Infrared Spectrometer*, Chemical Industry Press: Beijing, 2005, pp. 270.
- 32 M. Bakiler, O. Bolukbasi, A. Yilmaz, *J. Mol. Struct.* 2007, **826**, 6.
- 33 L. Yu, X. H. Hua, Q. H. Pan, L. M. Yang, Y. Z. Xu, G. Z. Zhao, H. Wang, H. Y. Wang, J. G. Wu, K. X. Liu, J. E. Chen, *Carbohydr. Res.* 2011, **346**, 2278.
- 34 Y. Z. Xu, J. G. Wu, W. X. Sun, D. L. Tao, L. M. Yang, Z. F. Song, S. F. Weng, Z. H. Xu, R. D. Soloway, D. F. Xu, G. X. Xu, *Chem.-Eur. J.* 2002, **8**, 5323.
- 35 L. Q. Yang, J. G. Wu, Q. Zhou, J. Bian, Y. M. Yang, D. F. Xu, G. X. Xu, *Microchim. Acta* 1997, **14**, 251.
- 36 L. M. Yang, G. Z. Zhao, W. H. Li, Y. F. Liu, X. X. Shi, X. F. Jia, K. Zhao, X. Y. Lu, Y. Z. Xu, D. T. Xie, J. G. Wu, J. E. Chen, *Spectrochim. Acta A* 2009, **73**, 884.
- 37 R. J. Falconer, A. G. Markelz, *J. Infrared Millim. Terahertz Waves* 2012, **33**, 973.

Captions for Figures

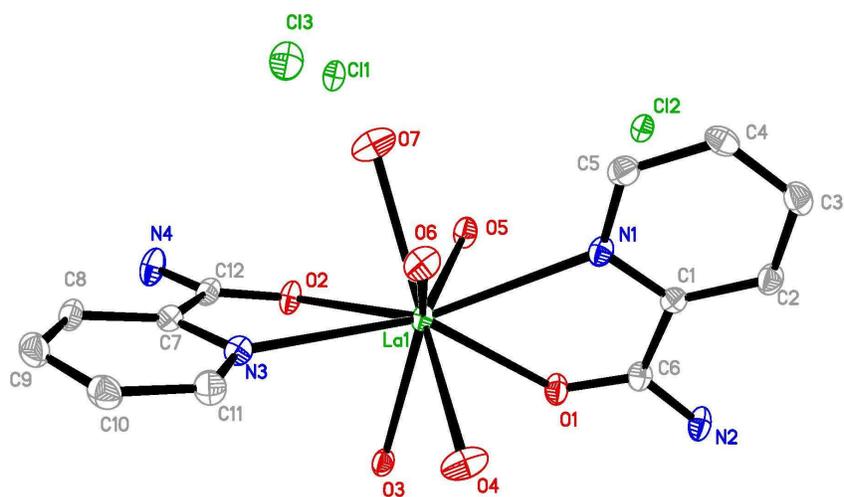
Fig. 1. The four kinds of crystal structures representing by La-pa (a), Er-pa (b), PrBr-pa (c) and NdN-pa (d)

Fig. 2. The FTIR spectra of pa and its eight lanthanide complexes in the 3600–2800 and 1750–600 cm^{-1} region

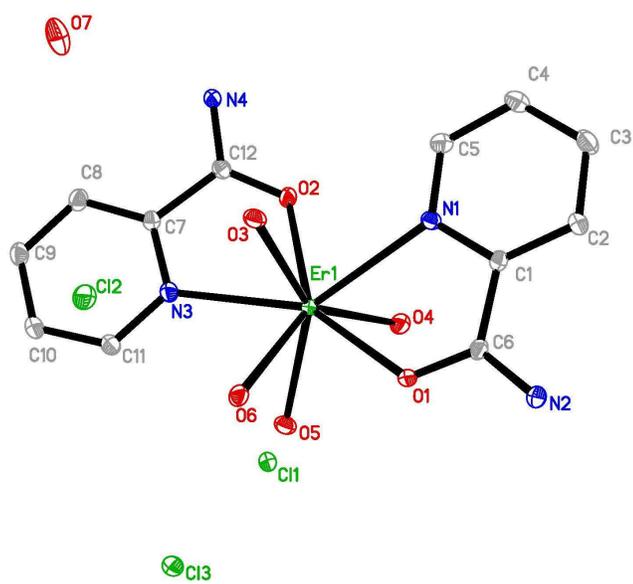
Fig. 3. The Raman spectra of pa and its eight lanthanide complexes in the 3700–2700 and 1700–100 cm^{-1} region (3700–100 cm^{-1} for PrBr-pa, Nd-pa and NdN-pa)

Fig. 4. The FIR spectra of pa and the lanthanide complexes in the 650–50 cm^{-1} region

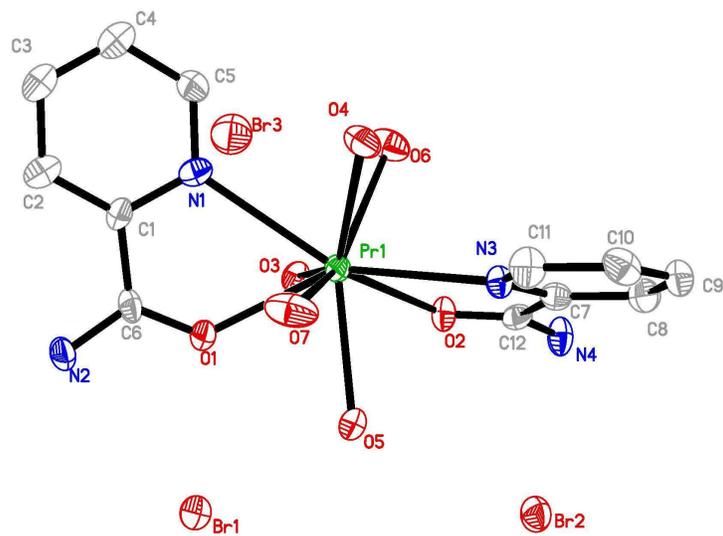
Fig. 5. The THz spectra of eight lanthanide-pa complexes



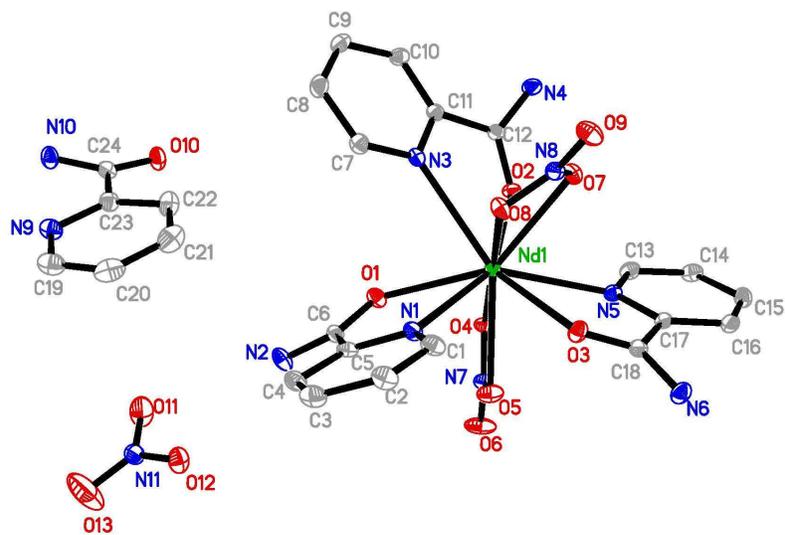
(a)



(b)



(c)



(d)

Fig. 1. The four kinds of crystal structures representing by La-pa (a), Er-pa (b), PrBr-pa (c) and NdN-pa (d)

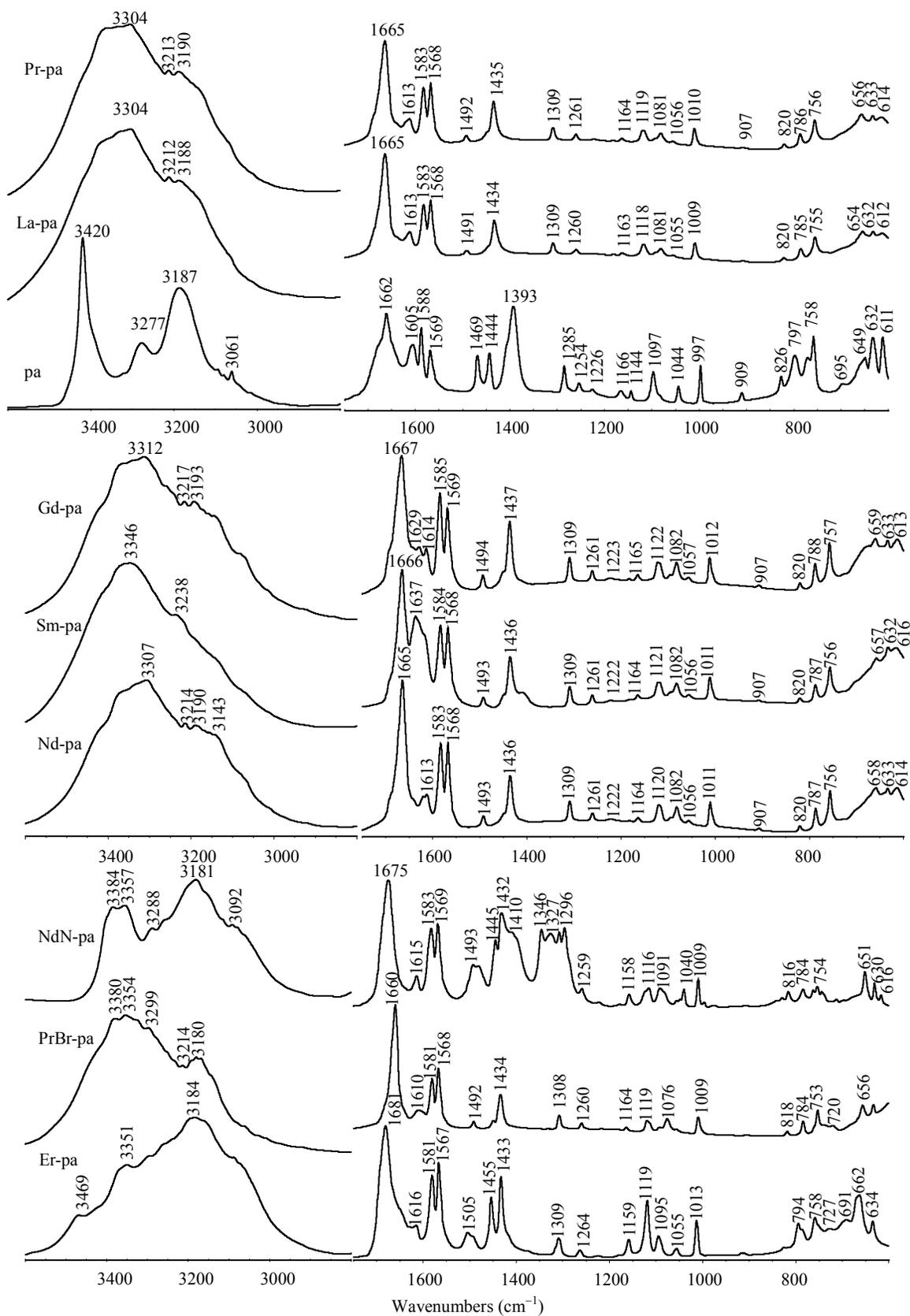
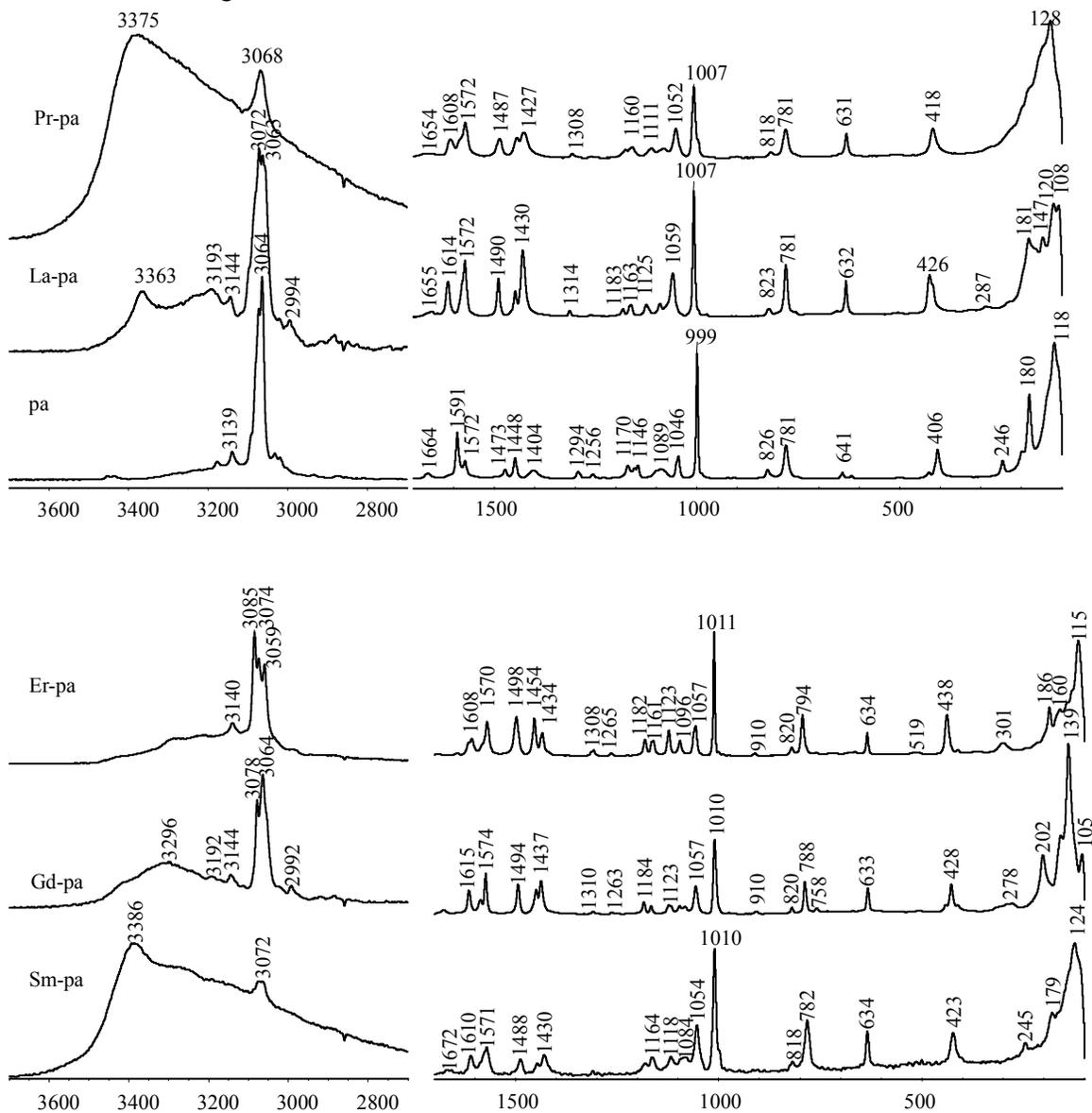


Fig. 2. The FTIR spectra of *pa* and its eight lanthanide complexes in the 3600–2800 and

1750– 600 cm^{-1} region

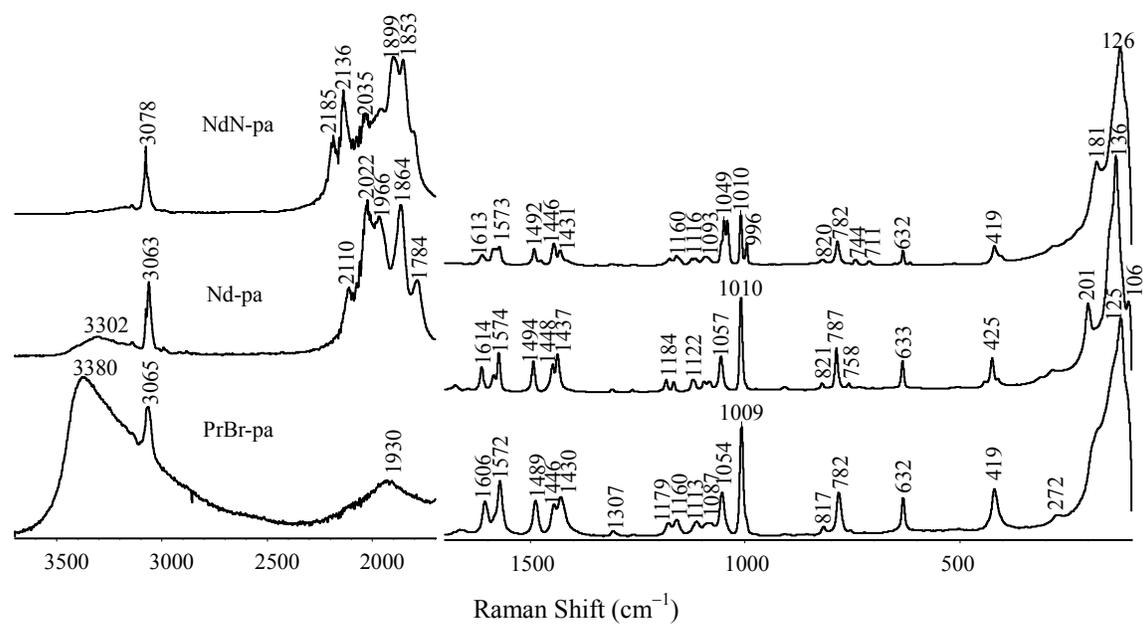


Fig. 3. The Raman spectra of pa and its eight lanthanide complexes in the 3700–2700 and 1700–100 cm^{-1} region (3700–100 cm^{-1} for PrBr-pa, Nd-pa and NdN-pa)

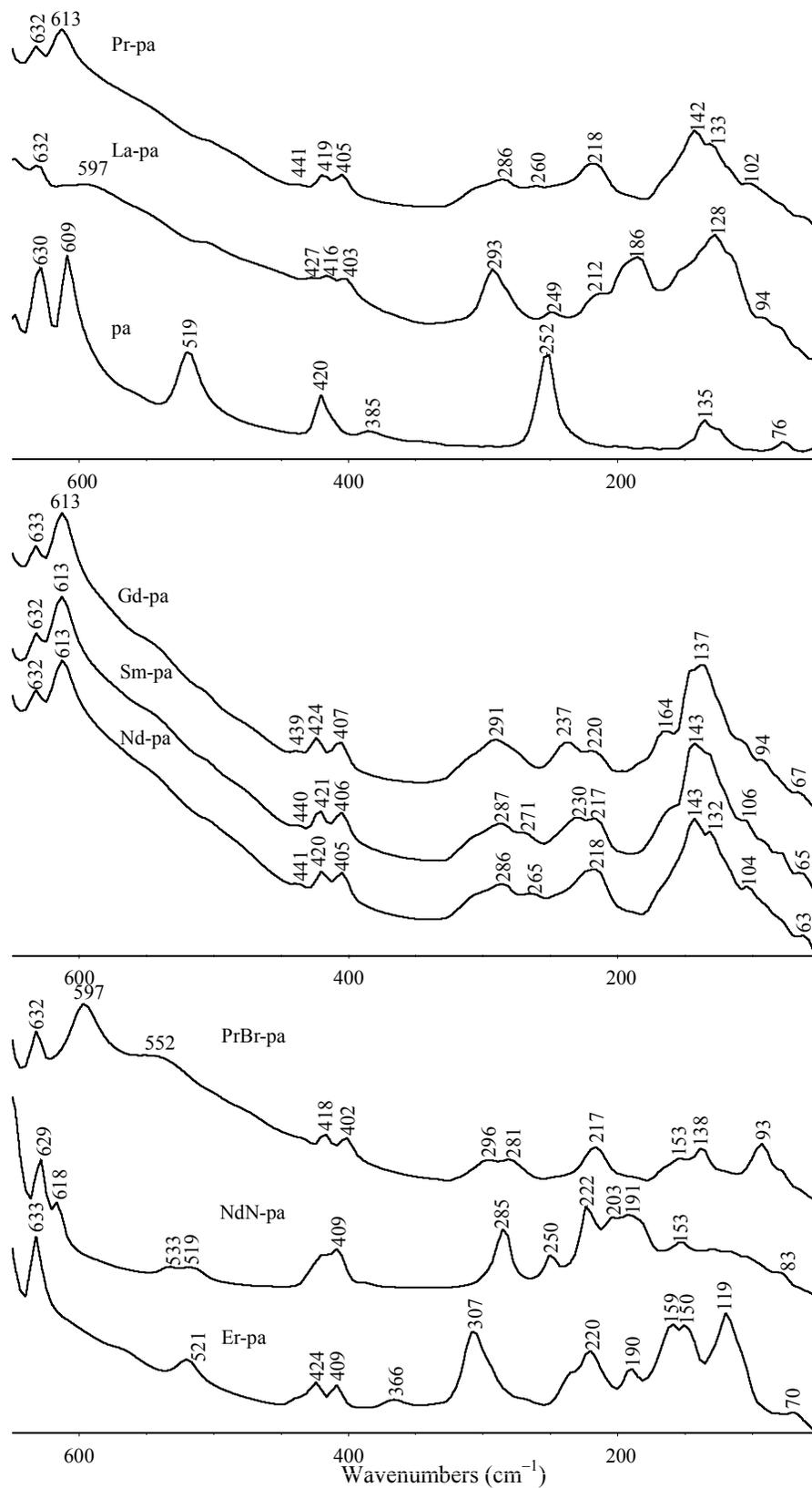


Fig. 4. The FIR spectra of *pa* and the lanthanide complexes in the 650–50 cm^{-1} region

Table 1. Crystal Data and Structure Refinement for eight lanthanide-pa complexes

	La-pa	Pr-pa	Nd-pa	Sm-pa	Gd-pa	Er-pa	PrBr-pa	NdN-pa
CCDC No.	918184	918186	918185	918187	918190	918191	918192	841635
chemical formula	LaCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	PrCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	NdCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	SmCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	GdCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	ErCl ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	PrBr ₃ ·(C ₆ H ₆ N ₂ O) ₂ ·5H ₂ O	Nd(C ₆ H ₆ N ₂ O) ₃ (NO ₃) ₂
Formula weight	579.60	581.60	584.93	591.04	597.94	607.95	714.98	818.78
<i>T</i> , K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	Triclinic	monoclinic	Triclinic
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$				
<i>a</i> , Å	28.898(6)	28.794(6)	28.770(6)	28.712(6)	28.616(6)	8.6514(17)	29.485(6)	10.180(2)
<i>b</i> , Å	7.7600(16)	7.7507(16)	7.7390(15)	7.7286(15)	7.7264(15)	9.1529(18)	7.8780(16)	11.926(2)
<i>c</i> , Å	19.778(4)	19.683(4)	19.629(4)	19.559(4)	19.526(4)	14.048(3)	20.344(4)	13.693(3)
α , deg	90	90	90	90	90	96.25(3)	90	105.79(3)
β , deg	104.39(3)	104.34(3)	104.26(3)	104.11(3)	104.04(3)	99.78(3)	103.39(3)	97.96(3)
γ , deg	90	90	90	90	90	105.83(3)	90	95.69(3)
<i>V</i> , Å ³	4296.1(15)	4255.8(15)	4235.8(15)	4209.1(14)	4188.1(14)	1040.4(4)	4597.1(16)	1567.9(5)
<i>Z</i>	8	8	8	8	8	2	8	2
<i>D</i> _{calcd} , g cm ⁻³	1.792	1.815	1.834	1.865	1.897	1.941	2.066	1.734
μ (Mo <i>K</i> α), mm ⁻¹	2.401	2.705	2.869	3.211	3.589	4.458	7.371	1.739
<i>F</i> (000)	2288	2304	2312	2328	2344	594	2736	818
Crystal size (mm ³)	0.21×0.18 × 0.16	0.22× 0.18 ×0.14	0.16 × 0.13 × 0.10	0.23 × 0.21 ×0.05	0.40 × 0.35 × 0.21	0.14 × 0.10 × 0.06	0.17 × 0.14 × 0.06	0.23 × 0.21 × 0.17
θ range for data collection (°)	1.45 to 27.48	2.27 to 27.47	2.28 to 27.47	1.46 to 27.47	1.47 to 27.49	2.34 to 27.48	1.42 to 27.54	1.57 to 27.48
Limiting indices	-37≤ <i>h</i> ≤35, -10 ≤ <i>k</i> ≤9, -25≤ <i>l</i> ≤25	-36≤ <i>h</i> ≤31, -10 ≤ <i>k</i> ≤10, -25≤ <i>l</i> ≤ 25	-37≤ <i>h</i> ≤26, -9≤ <i>k</i> ≤10, -25≤ <i>l</i> ≤ 25	-37≤ <i>h</i> ≤31, -9 ≤ <i>k</i> ≤10, -18≤ <i>l</i> ≤25	-36≤ <i>h</i> ≤36,-1 0 ≤ <i>k</i> ≤9, -25 ≤ <i>l</i> ≤20	-11≤ <i>h</i> ≤11,-1 1 ≤ <i>k</i> ≤11, -18 ≤ <i>l</i> ≤18	-38≤ <i>h</i> ≤31,-8 ≤ <i>k</i> ≤10, -18 ≤ <i>l</i> ≤26	-13≤ <i>h</i> ≤13,-1 5 ≤ <i>k</i> ≤15, -17 ≤ <i>l</i> ≤17
Reflections collected / unique	15489/4909	14466 /4841	14524 / 4833	10409/4779	15503/4784	13460/4760	11646/5249	13994/7310
<i>R</i> _{int}	0.0571	0.0521	0.0353	0.0515	0.0463	0.0366	0.0598	0.0335

Completeness to θ_{\max}	99.6 %	99.3 %	99.7 %	99.2 %	99.8%	99.8 %	98.8 %	99.1 %
Data / restraints / parameters	4909 / 0 / 248	4841 / 0 / 244	4833 / 14 / 332	4779 / 17 / 286	4784 / 0 / 244	4760 / 12 / 300	5249 / 16 / 244	7130 / 6 / 442
GOF on F^2	1.242	1.105	1.135	1.180	1.238	1.201	1.221	1.203
R1 [$I > 2\sigma(I)$]	0.0538	0.0419	0.0262	0.0747	0.0357	0.0246	0.0646	0.0376
wR2 [$I > 2\sigma(I)$]	0.1180	0.0831	0.0598	0.1905	0.1016	0.0679	0.1694	0.1048
R1 (all data)	0.0628	0.0497	0.0276	0.0827	0.0396	0.0254	0.0820	0.0415
wR2 (all data)	0.1223	0.0870	0.0607	0.2012	0.1163	0.0684	0.1984	0.1214
Largest diff. peak and hole ($e \cdot \text{\AA}^{-3}$)	0.816 and -0.867	0.766 and -0.631	0.865 and -0.385	3.550 and -1.829	1.163 and -1.372	1.000 and -0.554	1.060 and -1.048	1.377 and -1.171

Table of Contents

Four kinds of structures varied with different rare earth ions and anions have been observed for lanthanide-picolinamide complexes.

