Synthesis and Spectroscopic Characterization of *l*-aspartic Acid Complexes with Metals of the Lanthanides Family

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ABSTRACT

The complexes between *l*-aspartic acid and metals of lanthanide series (La^{3+}, Pr^{3+}, Eu^{3+}, Gd^{3+}) have been prepared and characterized using a variety of techniques including, infrared spectroscopy, ^{1}H NMR, ^{13}C NMR, elemental analysis and metal contents. The sought metal effect on the electronic environment of the chiral carbon and its neighbouring atoms was observed in case of Europium and Praseodymium. The ^{13}C downfield shift indicates a lower electron density at the carbon with consequent downfield shift observed on the α-H attached to it increasing its acidity.

Keywords: *l*-Aspartic acid, Lanthanides (III) complexes, IR, NMR.

1. INTRODUCTION

The coordination chemistry of lanthanides with amino acids has been widely investigated in the literature. The studies have been exclusively carried out at low pH values, typically under pH 4. This is understandable because lanthanides ions are so prone to hydrolysis, that hydroxides and/or oxides would be the final products at higher pH values [1]. In all reported structures of such complexes, the ligands coordinate to the metal centers through only the oxygen atoms of the carboxylate moiety. At high pH values, however, multiple binding of lanthanides ions by an amino acid (α -amino carboxylate, to be more exact) may be achieved with both the amino and the carboxylate groups participating in simultaneous coordination [2]. Such chelating effects may stabilize the metal complex by counteracting the undesirable hydrolysis and consequently high-nuclearity lanthanides clusters would form. Lanthanides clusters are expected to exhibit more promising magnetic properties as a consequence of the unique spectroscopic and electronic properties mainly associated with their 4f electronic configuration [2].

The different structural motifs of amino acids (phenylalanine, aspartic and glutamic acid) complexes have been described in Table 1. For example, the amino acids, alanine, phenylalanine, only have the carboxylate to coordinate the Ln ion. They differ in the alkyl group (–R) attached to the C in α position. Among the natural amino acids there are two

dicarboxylates, namely *l*-aspartic acid (asp) and *l*-glutamic acid (glu), these not only retain the nature of the amino acids but also possess bridging capability [3].

Table 1. Structural Data of Ln–aa Complexes.

Compound	Ln CN	Molecular structure	Bridges connecting Ln ions	Ref.
$[La_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	(4)
$[Pr_2(Glu)_2(ClO_4)(H_2O)_7](ClO_4)_3 \cdot 4H_2O$	9	Infinite 2D planes	Two bridges (I) through Cα, and two bridges (III) throughCγ	(5) and (6)
$[Sm(Asp)(H_2O)_4]Cl_2$	8	Infinite 2D planes	One bridge (I) through Cα, and one bridge (I) through Cβ	(7)
$[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	(8)
$[Gd_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	(9)
$[Ho(Asp)(H_2O)_5]Cl_2 \cdot H_2O$	8	Infinite 2D planes	One bridge (I) through Cβ, and one α-COO monodentate	(10)

There are three kinds of carboxylate bridges in these complexes, bridge I, bridge II and bridge III, see Figure 1. Thus it should be feasible to link discrete Ln_4O_4 cubane units into an extended network and this assumption has been confirmed by the reaction of $Dy(ClO_4)_3$ and aspartic acid to give a three-dimensional supercubane open frame work. The complex of the chemical formula $[Dy_4 (\mu_3\text{-}OH)_4 (asp)_3(H_2O)_8](ClO_4)_2 \cdot 10H_2O$ structure was explained by X-ray analysis [3]. The core component of this compound is a cationic cluster $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ (Figure 2) whose constituent lanthanides ions and triply bridging hydroxo groups occupy the alternate vertexes of a distorted cube [11].
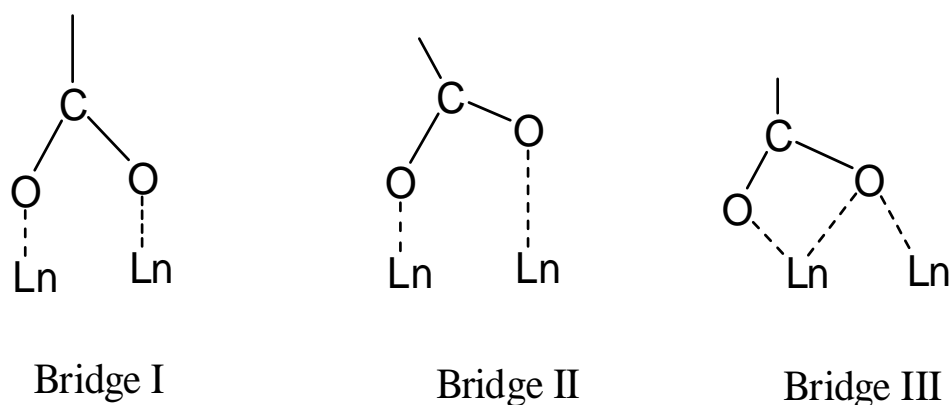

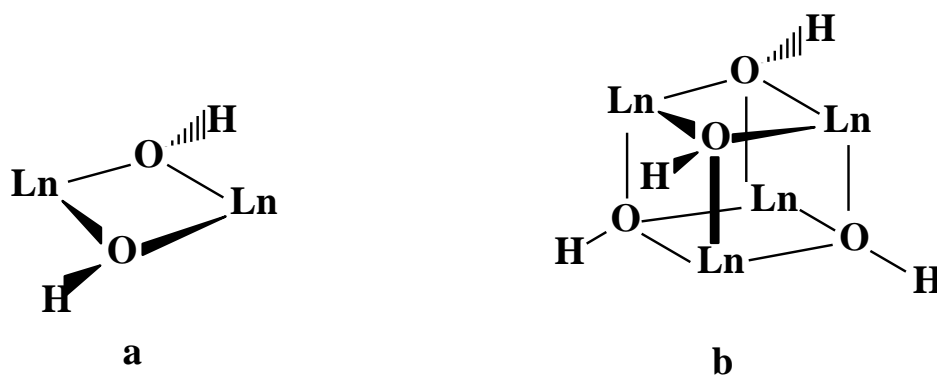**Figure 1.** Carboxylate Bridges Found in Ln-aa Structures.

Figure 2. Core components of Crystallographically Characterized Dinuclear (a) and Tetranuclear (b) Lanthanide-Hydroxo Species.

The predominantly ionic interaction is reflected in the variation of Ln_O distances. There is a close relation between the ionic radius of the central atom, and Ln_O distances. Regardless of the aa, a monotonous decrease in Ln_O distance is observed with a diminishing ionic radius. Due to the low stability of lanthanide complexes with amino acid and peptides, hydrolysis reactions are obvious competing processes. Of course, the extension of hydrolysis depends on the particular ion since the acidity of these f-transition metal ions increases with decreasing ionic radii. Thus, the smaller are the lanthanides, the more importance should be given to hydrolysis reactions. The interaction behaves in a purely electrostatic manner. This fact is reflected in the scarce participation of amino groups in coordination, and the dependence of K values with charge of ligand and lanthanide radius. In the solid state structure, carboxylate groups also play a very important role. Different spatial arrangements are found, but the presence of COO^- bridges is a common structural framework. In addition to the X-ray analysis which was discussed in the structures, also the complexes were characterized using a variety of techniques, including IR, ESI-MS, metal contents and microanalysis. The infrared spectra of these compounds have shown changes in the position and profiles of some bands, as compared to that of the free amino acids, suggesting the participation of the groups that produce these bands in the coordination bond with lanthanides. Major changes in all IR patterns, are related to the carboxylate bands [12]. In the case of *l*-phenylalanine for example, the bands at 1410 cm^{-1} and 1565 cm^{-1}, corresponding to the carboxylate symmetrical and asymmetrical stretchings, are shifted to higher wave numbers after complexation with Eu^{3+}, Tb^{3+}, thus indicating coordination through that group. A strong and broad absorption appears at $v= 3500-3600$ cm^{-1}, which is typical of molecules of high water content. A sharp peak around 3580 cm^{-1}, usually assigned to the stretching of μ_3-OH, was not observed in any of the these compounds. The peak is probably obscured by the broad water absorption. The presence of coordinated water molecules in all complexes is indicated by their characteristic rocking and wagging frequencies between 700 and 800 cm^{-1} and between 500 and 650 cm^{-1}, respectively. For complexes where ionic ClO_4^- serves as the counteranion, characteristic strong Cl-O stretching frequencies between 1090 and 1145 cm^{-1} are observed. In addition, a relatively strong peak at 903 cm^{-1} indicates the presence of a unidentate ClO_4^- in solid state complexes. Corresponding frequencies are absent from the IR spectrum of complexes, where the counteranions are chlorides [11]. The aim of this work is th synthesis of l-aspartic acid lanthanides complexes which have not been synthesized to see the effect of lanthanides metals on the spectroscopic of l-aspartic acids, which was confimed by infrared spectra shift and nuclear magnetic resonance shift.

2. EXPERIMENTAL

2. 1. Physical Measurements

IR spectra were recorded on perkin Elmer spectrum 100 instrument which an attenuated total reflection attachment, NMR data were recorded on a Bruker ANANCE III 400 MHz and 600 MHz, C, H, N, were determined by CHN elemental analysis instrument, the metal contents were determined by compleximetric titration with EDTA, using xylenol orange as indicator.

2. 2. Synthesis of Complexes

2. 2. 1. [La$_4$(OH)$_4$(*l*-Asp)$_5$(H$_2$O)$_8$](ClO$_4$)$_3$

An aqueous solution of lanthanum perchlorate was prepared by digesting (0.65 gm) La$_2$O$_3$ in concentrated perchloric acid (2 ml, 70 %), a suitable concentration of La(ClO$_4$)$_3$ (1.9 g, 4 mmol) was achieved by diluting the concentrated solution with 10 ml distilled water, *l*-aspartic acid (0.266 g, 2 mmol) was added as solid to the above aqueous solution of La(ClO$_4$)$_3$, one drop of an aqueous solution of HCl (1.0 M) was then added. The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5 M) was added dropwise to cause an incipient but permanent precipitate, pH = 5. The mixture was then filtered, and the filtrate was then reduced to about 5 ml. The hot solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about one week. The solid was collected by filteration, washed with cold diethyl ether, and dried under vacuum in a desiccator charged with silica gel. Yield = 0.056 g (1.6 %).

The presence of lanthanum metal was detected by xylenol orange indicator, [13]C (D$_2$O, 400 MHz, 25 °C): δ = 178.35, 174.66, 51.75, 36.49 ppm. *Anal*. Calc. for C$_{20}$H$_{50}$Cl$_3$La$_4$N$_5$O$_{44}$:C, 13.91; H, 2.92; N, 4.06; La, 32.82. Found: C, 13.60; H, 2.55; N, 4.02; La, 32.31. Main FT IR bands (KBr, cm^{-1}), v_{max} 3509, 3218, 1661, 1610, 1427, 1400, 1354, 1312, 1239, 1064, 934, 890, 851, 815, 785, 722, 660, 622, 578, 526, 475.

2. 2. 2. [La (*l*-Asp) (H$_2$O)$_4$]Cl$_2$

l-aspartic acid (0.133 g, 1 mmol) was added as solid to the aqueous solution of LaCl$_3$·7 H$_2$O, prepared by dissolving 0.743 g in 13 ml distilled water (2 mmol), The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5 M) was added dropwise to cause an incipient but permanent precipitate, pH = 5. The mixture was then filtered, and the hot clear filtrate solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about one week. The solid was collected by filteration, washed with cold diethyl ether/THF;1:1, and dried under vacuum in a desiccator charged with silica gel. Yield =0.20 g (48,42 %). The presence of lanthanum metal was detected by xylenol orange indicator, [13]C (D$_2$O, 400 MHz, 25 °C): δ=178.45, 174.65, 51.68, 36.46 ppm. *Anal*. Calc. for C$_4$H$_{14}$Cl$_2$LaNO$_8$:C, 11.61; H, 3.41; N, 3.38; La, 33.55. Found : C, 13.82; H, 3.43; N, 3.44; La, 30.98. Main FT IR bands (KBr, cm^{-1}), v_{max} 3316, 3207, 2192, 1600, 1576, 1551, 1489, 1420, 1359, 1270, 1236, 1143, 1120, 1099, 1077, 997, 975, 949, 924, 859, 800, 772, 755, 658, 599, 532.

2. 2. 3. [Pr$_4$(OH)$_4$(*l*-Asp)$_3$(H$_2$O)$_8$](ClO$_4$)$_5$·8H$_2$O

An aqueous solution of praseodymium perchlorate was prepared by digesting (0.41 gm) Pr$_6$O$_{11}$ in concentrated perchloric acid (1.5 ml, 70 %), a suitable concentration of Pr(ClO$_4$)$_3$ (1.2 g, 2 mmol) was achieved by diluting the concentrated solution with 8 ml distilled water,

l-aspartic acid (0.133 g, 1 mmol) was added as solid to the above aqueous solution of $Pr(ClO_4)_3$, one drop of an aqueous solution of HCl (1.0 M) was then added. The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5 M) was added dropwise to cause an incipient but permanent precipitate, pH = 6.

The mixture was then filtered, and the filtrate was then reduced to about 4 ml. The hot solution was tightly covered and allowed to evaporate gradually at room temperature. Faint-green precipitate appeared in about one month. The solid was collected by filteration, washed with cold diethyl ether/HF 1:1 v/v, and dried under vacuum in a desiccator charged with silica gel. Yield = 0.31 g (21.89%), m.p. = 231 °C. The presence of praseodymium metal was detected by xylenol orange indicator. *Anal*. Calc. for $C_{12}H_{51}Cl_5Pr_4N_3O_{52}$:C, 7.96; H, 2.84; N, 2.32; Pr, 31.13. Found: C, 6.52; H, 2.58; N, 1.60; Pr, 32.10. Main FT IR bands (KBr, cm^{-1}), v_{max} 3480, 3224, 2597, 2192, 2030, 1659, 1617, 1428, 1402, 1355, 1312, 1289, 1257, 1227, 1053, 935, 907, 850, 814, 792, 734, 681, 622, 586, 538, 502, 480.

2. 2. 4. [Eu$_4$(OH)$_4$(*l*-Asp)$_3$(H$_2$O)$_8$](ClO$_4$)$_5$·10H$_2$O

An aqueous solution of europium perchlorate was prepared by digesting (0.304 gm) Europium metal in concentrated perchloric acid (2 ml, 70 %), a suitable concentration of $Eu(ClO_4)_3$ (0.90 g, 2 mmol) was achieved by diluting the concentrated solution with 5 ml distilled water, *l*-aspartic acid (0.133 g, 1 mmol) was added as solid to the above aqueous solution of $Eu(ClO_4)_3$, one drop of an aqueous solution of HCl (1.0 M) was then added. The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5 M) was added dropwise to cause an incipient but permanent precipitate, pH = 6. The mixture was then filtered, and the filtrate was then reduced to about 4 ml. The hot solution was tightly covered and allowed to evaporate gradually at room temperature. Faint-pink precipitate appeared in about 27 days.

The solid was collected by filteration, washed with cold diethyl ether/THF 1:1 v/v, and dried under vacuum in a desiccator charged with silica gel. Yield = 0.32 g. (16.93 %) The presence of europium metal was detected by xylenol orange indicator, ^{13}C (D$_2$O, 400 MHz, 25 °C): δ = 174.41, 105.16, 101.66 ppm, *Anal*. Calc. for $C_{12}H_{55}Cl_5Eu_4N_3O_{54}$:C, 7.62; H, 2.93; N, 2.22; Eu, 32.51. Found: C, 7.74; H, 1.15; N, 1.85; Eu, 31.83. Main FT IR bands (KBr, cm^{-1}), v_{max} 3500, 3216, 2993, 2016, 1669, 1610, 1553, 1483, 1428, 1335, 1326, 1249, 1087, 954, 900, 887, 779, 759, 720, 678, 654, 616, 550, 529, 464, 452.

2. 2. 5. [Gd(*l*-Asp)(H$_2$O)$_4$](ClO$_4$)$_3$

An aqueous solution of gadolinium perchlorate was prepared by digesting (0.36 gm) Gd_2O_3 in concentrated perchloric acid (2 ml, 70 %), a suitable concentration of $Gd(ClO_4)_3$ (1.0 g, 2 mmol) was achieved by diluting the concentrated solution with 8 ml distilled water, *l*-aspartic acid (0.133 g, 1 mmol) was added as solid to the above aqueous solution of $Gd(ClO_4)_3$, one drop of an aqueous solution of HCl (1.0 M) was then added. The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5 M) was added drop by drop to cause an incipient but permanent precipitate, pH = 4. The mixture was then filtered, and the filtrate was then reduced to about 4 ml.

The hot solution was tightly covered and allowed to evaporate gradually at room temperature. Faint-green precipitate appeared in about one month. The solid was collected by filteration, washed with cold diethyl ether/HF 1:1 v/v, and dried under vacuum in a desiccator charged with silica gel. Yield =0.080 g, (12.12 %). The presence of gadolinium metal was detected by xylenol orange indicator. *Anal*. Calc. for $C_4H_{15}Cl_3GdNO_{20}$:C, 7.27; H, 2.29; N,

2.12; Gd, 23.80. Found: C, 7.93; H, 3.36; N, 2.28; Gd, 23.60. Main FT IR bands (KBr, cm-1), *v* $_{max}$ 3506, 3214, 1606, 1418, 1361, 1236, 1067, 934, 858, 715, 652, 623, 548, 421.

3. RESULTS AND DISCUSSION

All of the complexes are extremely soluble in water and readily soluble in common organic solvents, such as tetrahydrofuran, dichloromethane, acetone, and acetonitrile. The compounds were characterized using a variety of techniques, including IR, ^{13}C NMR, ^{1}H NMR, microanalysis (CHN) and metal content. The metal content was determined by complexometric titration with EDTA. The results of the elemental analysis confirm the formula of the most complexes, from compound (1) to compound (5), and also confirm a 1:1 metal to ligand stoichiometry for the complexes 1, 2 and 5, 4:3 metal to ligand ratio for compounds 3 and 4.

3. 1. Structure of the Complexes

According to the stoichiometry which was confirmed by elemental analysis the complex of aspartic acid [La(*l*-Asp)(H$_2$O)$_4$]Cl$_2$ similar to the complexes [Sm(Asp)(H$_2$O)$_4$]Cl$_2$ [7], [Ho(Asp)(H$_2$O)$_5$]Cl$_2$H$_2$O [10], they have 1:1 metal to ligand ratio, which contain infinite layers. The complex [Gd(*l*-Asp)(H$_2$O)$_4$](ClO$_4$)$_3$ also similar to the above complexes.

The complexes[Pr$_4$(OH)$_4$(*l*-Asp)$_3$(H$_2$O)$_8$](ClO$_4$)$_5$8H$_2$O and [Eu$_4$(OH)$_4$(*l*Asp)$_3$(H$_2$O)$_8$] (ClO$_4$)$_5$·10H$_2$O similar to the complex [Dy$_4$(μ_3-OH)$_4$(Asp)$_3$(H$_2$O)$_8$] (ClO$_4$)$_5$·10H$_2$O [3] in molecular formula, 4:3 metal to ligand ratio, which has cubane-like structure [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ with higher dimensionality, both COO$^-$ groups of the aa bridge Ln in the same cube, and also interlink [Ln$_4$(μ_3-OH)$_4$]$^{8+}$ cores.

The complex [La$_4$(OH)$_4$(*l*-Asp)$_5$(H$_2$O)$_8$](ClO$_4$)**$_3$** also has cubane-like structure.

3. 2. Characterization of the Complexes by Infrared Spectra

In the infrared spectra, all the complexes have a strong and broad absorption appears at $v = 3300$-3590 cm^{-1}, which is typical of molecules of high water content. A peak around 3505 cm^{-1}, previously reported and assigned to the stretching of a μ_3-OH [13], was not observed in any of all the compounds; the peak is probably obscured by the broad water absorption.

The presence of coordinated water molecules in all complexes is indicated by their characteristic rocking frequency at about 825 cm^{-1}.

Metal coordination results in appreciable shifts of the asymmetric stretching frequency of the carboxylate moiety of the amino acids ligand, from 1610 to about 1590 cm^{-1}. The symmetric carboxylate stretching frequency shifts from 1416 to 1422 cm^{-1}. Strong and characteristic Cl-O stretching frequencies between 1050-1170 cm^{-1} and 620-630 cm$^-$1 are observed for the ClO$_4$$^-$ counterions in all complexes.

### 3. 3. Characterization of Complexes by NMR Spectra

The ^{1}H NMR and ^{13}C NMR spectrum of the lanthanides complexes of *l*-aspartic acid undergo a shift to lower and higher field when it was compared with free *l*-aspartic acid. In complexes of *l*-aspartic with lanthanides, La^{3+}, Eu^{3+}, Pr^{3+} and Gd^{3+}. In compound [La$_4$(OH)$_4$(*l*-Asp)$_5$(H$_2$O)$_8$](ClO$_4$)$_3$ and [La(*l*-Asp)(H$_2$O)$_4$]Cl$_2$, the ^{1}H NMR resonance is shifted upfield, the alpha proton is shifted from 2.88 to 2.67 ppm, and beta proton is shifted from 3.95 to 3.82 ppm. In these compounds the shift is small because lanthanum metal is diamagnetic. In the

case of compounds $[Eu_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 10H_2O$ the up field resonance shift is much higher in the case of the europium metal, the band is broad according to lanthanides effects, from 2.88 to 2.20 ppm for α-proton , and from 3.95 to 3.49 ppm for β-proton. In compound $[Pr_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 8H_2O$, the shift is downfield, with broad band and the splitting is completely removed. In compound $[Gd\,(l\text{-}Asp)(H_2O)_4](ClO_4)_3$ the peaks of the amino acids in ^{1}H NMR is completely removed, according to the strong effect of gadolinium metal.

The characteristic shifts of ^{1}H NMR clearly show that *l*-aspartic acid is coordinated to the lanthanides ions via the carboxylic acid oxygen. The ^{13}C-NMR spectrum of aspartic complexes (Table 2) also confirms coordination via carboxylate group in aqueous solution, the C1 signal at 179.21 ppm in the free ligand is shifted to 178.45, 178.35 and 174.41 ppm in compounds 2, 1 and 4, and disappeared in the case of Pr^{3+} metal.

The C4 experience a small shift in the case of La^{3+}, but disappeared in the Pr^{3+} and Eu^{3+} compounds, probably due to the T_2 relaxation time increase following lanthanide coordination [14]. Also there is small shift in the C2 and C3 in La^{3+} complexes, about 0.3 ppm in C2 upfield and 1.3 ppm in C3 downfield, and shifting higher in complexes of Pr^{3+} and Eu^{3+} compounds, the spectrum of C2 and C3 is completely removed in Pr^{3+}, and shifted downfield in Eu^{3+}, about 53 ppm in the C2 and 65 ppm in C3.

Table 2. ^{13}C-NMR Data of *l*-Aspartic Acid and *l*-Aspartic acid Ln^{3+} Complexes δ (ppm).
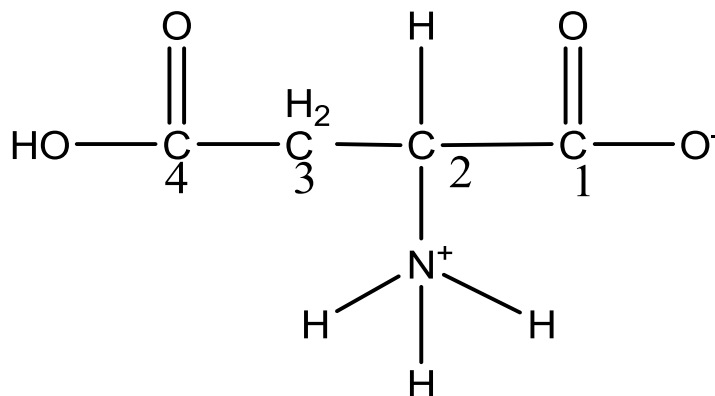
l-asp	Compound 2 LaCl₃	Compound 1 La(ClO₄)₃	Compound 3 Pr(ClO₄)₃	Compound 4 Eu(ClO₄)₃	Assignment
179.21	178.45	178.35	.....	174.41	C1
174.72	174.65	174.66	......	…..	C4
52.41	51.68	51.75	…..	105.16	C2
35.19	36.49	36.49	…..	101.66	C3

The lanthanides metals generally act as a lewis acid and have the amino acids carbonyl oxygen which is coordinated to the metal acts as a lewis base.
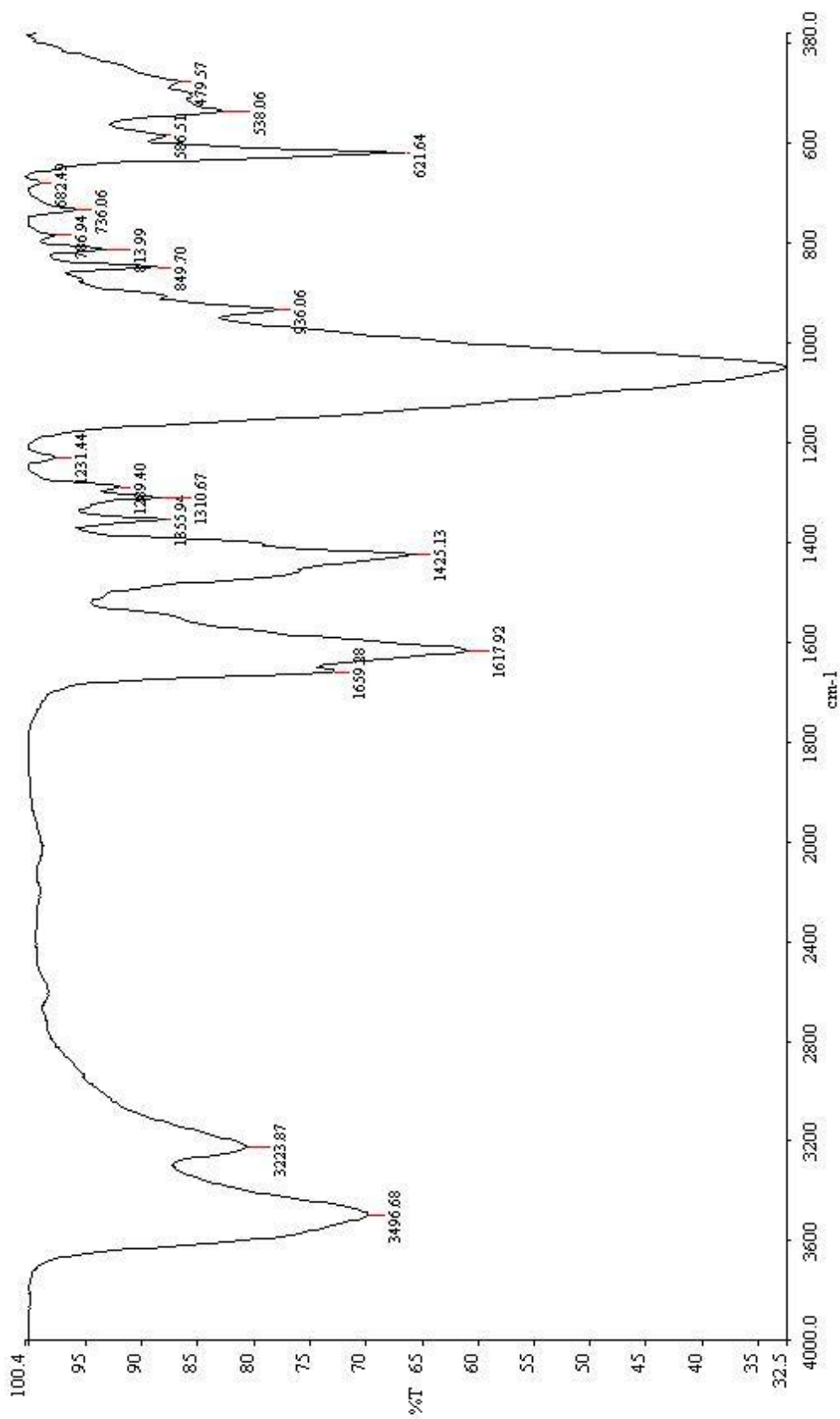
This is ideal situation for the lanthanides shift effect. It has been observed with Europium, Praseodymium and Gadolinium more than with lanthanum because of its lacks the required f-orbitals. The effect is transmitted to the α–carbon and its proton.
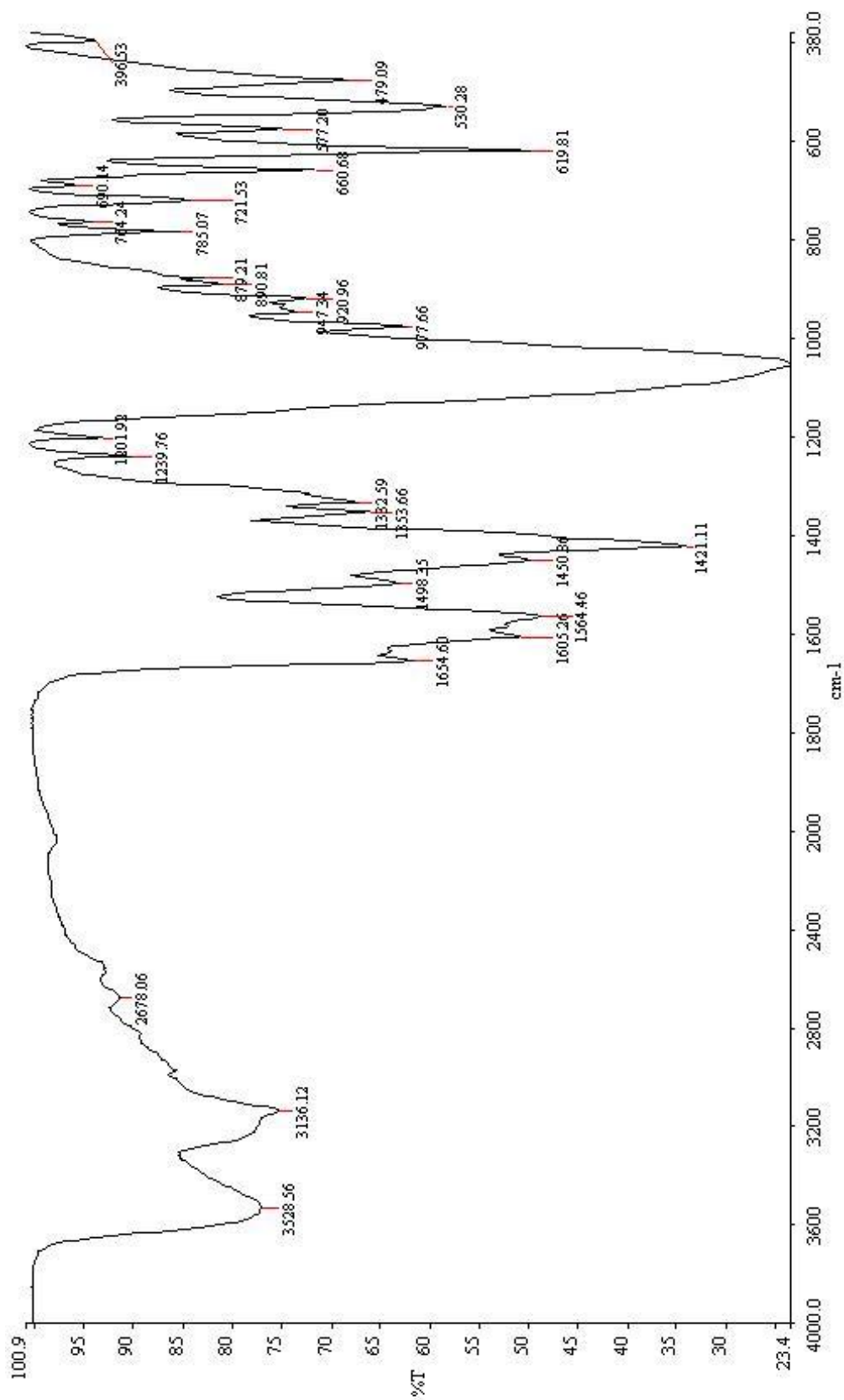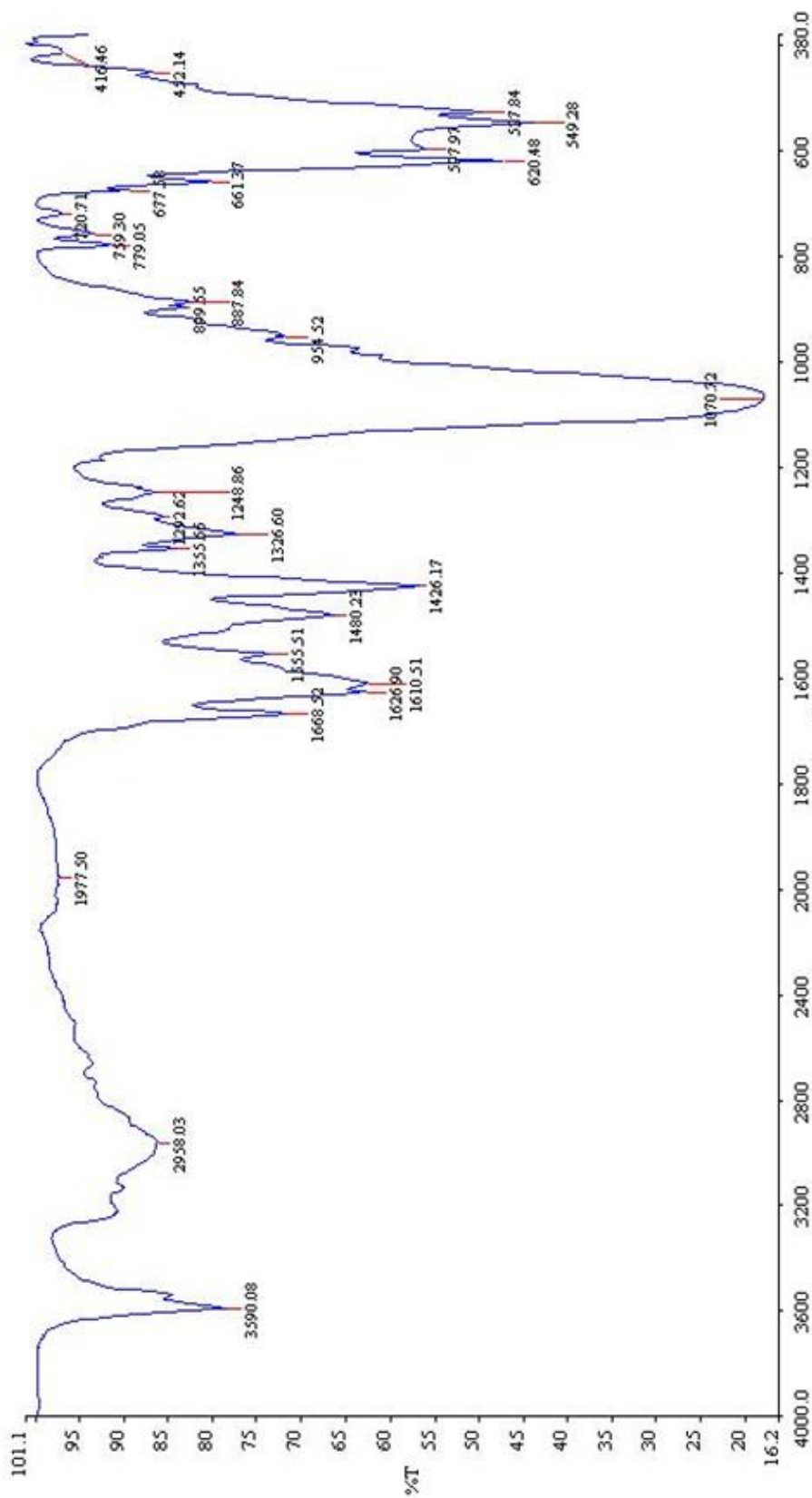
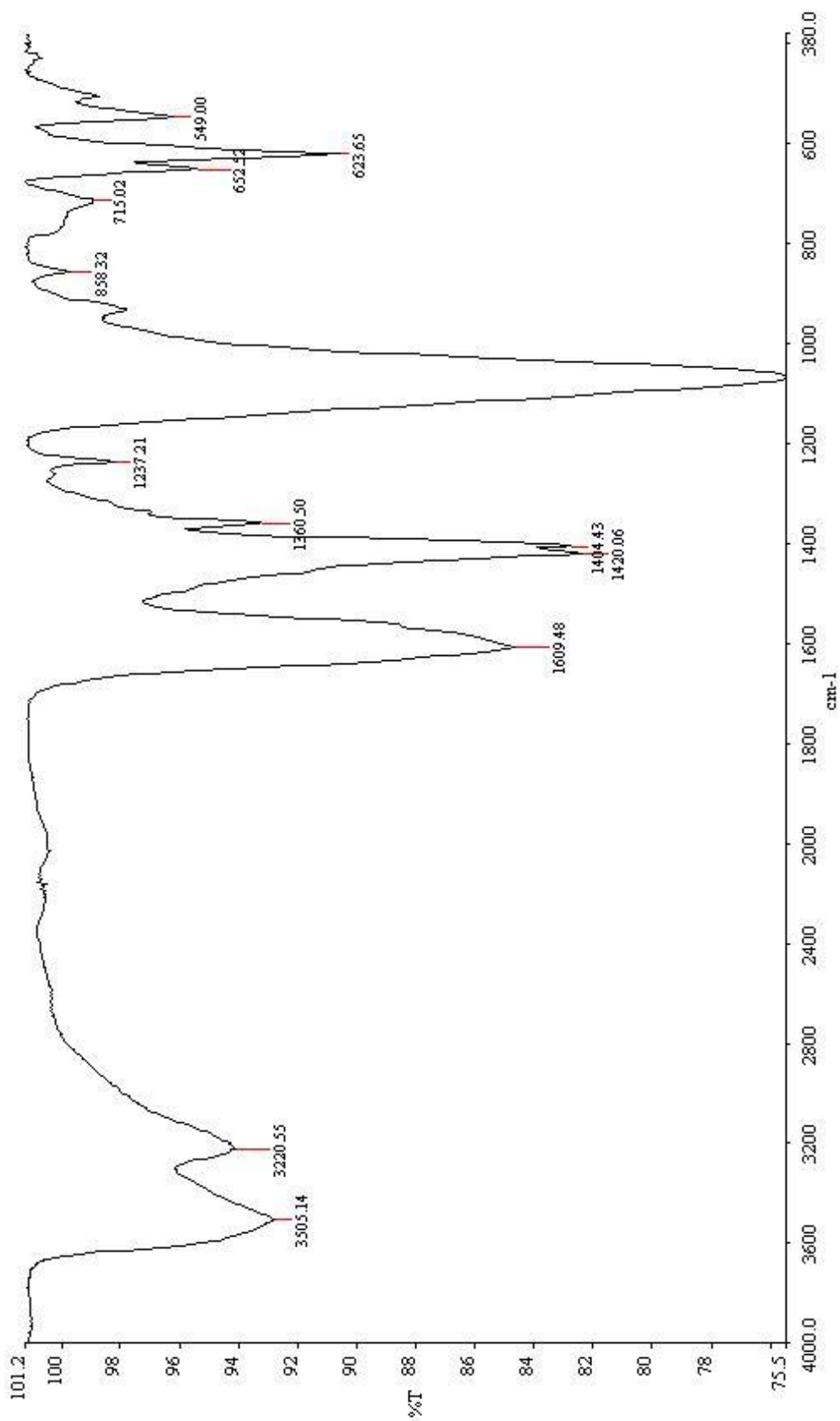**Spectrum (1).** Infrared Spectrum of the $[La_4(OH)_4(l\text{-}Asp)_5(H_2O)_8](ClO_4)_3$
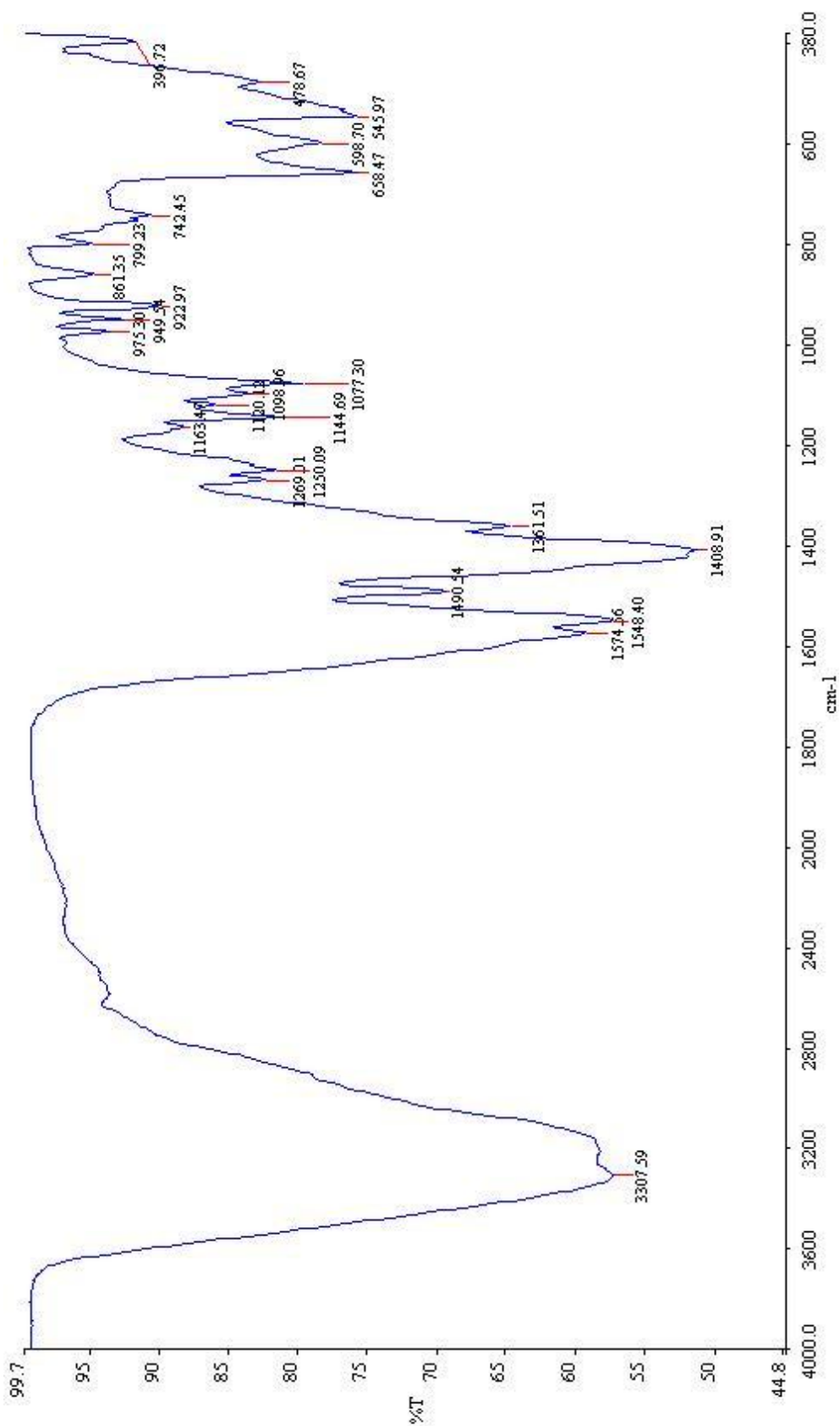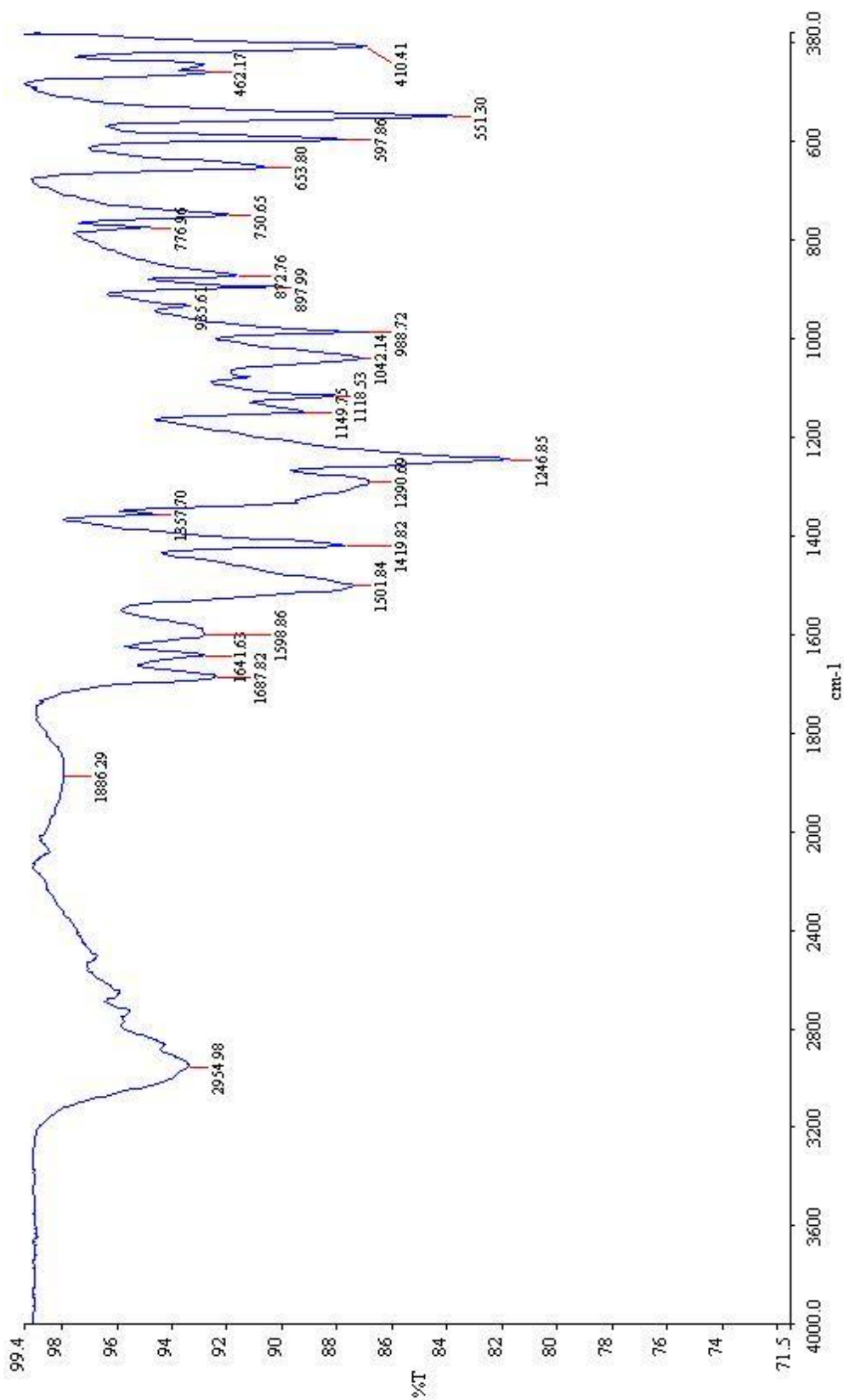
Spectrum (2). Infrared Spectrum of the [La$(l$-Asp$)$ $(H_2O)_4]Cl_2$

Spectrum (3). Infrared Spectrum of the $[Pr_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 8H_2O$

Spectrum (4). Infrared Spectrum of the $[Eu_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 10H_2O$

Spectrum (5). Infrared Spectrum of the [Gd (*l*-Asp)(H$_2$O)$_4$](ClO$_4$)$_3$

Spectrum (6). Infrared Spectrum of *l*-Aspartic acid
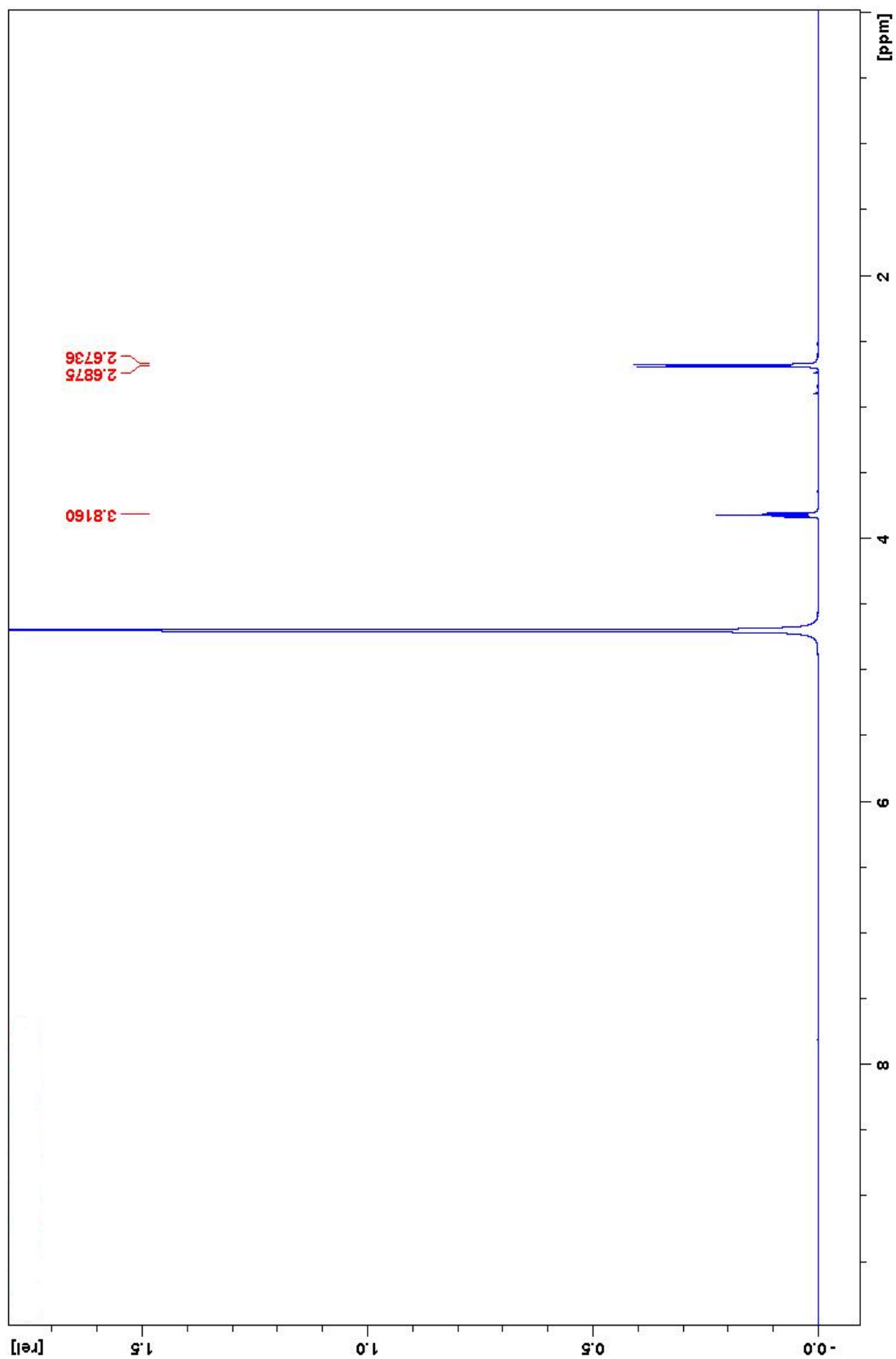
Spectrum (7). ^{1}H NMR Spectrum of [La (l-Asp) (H$_2$O)$_4$]Cl$_2$
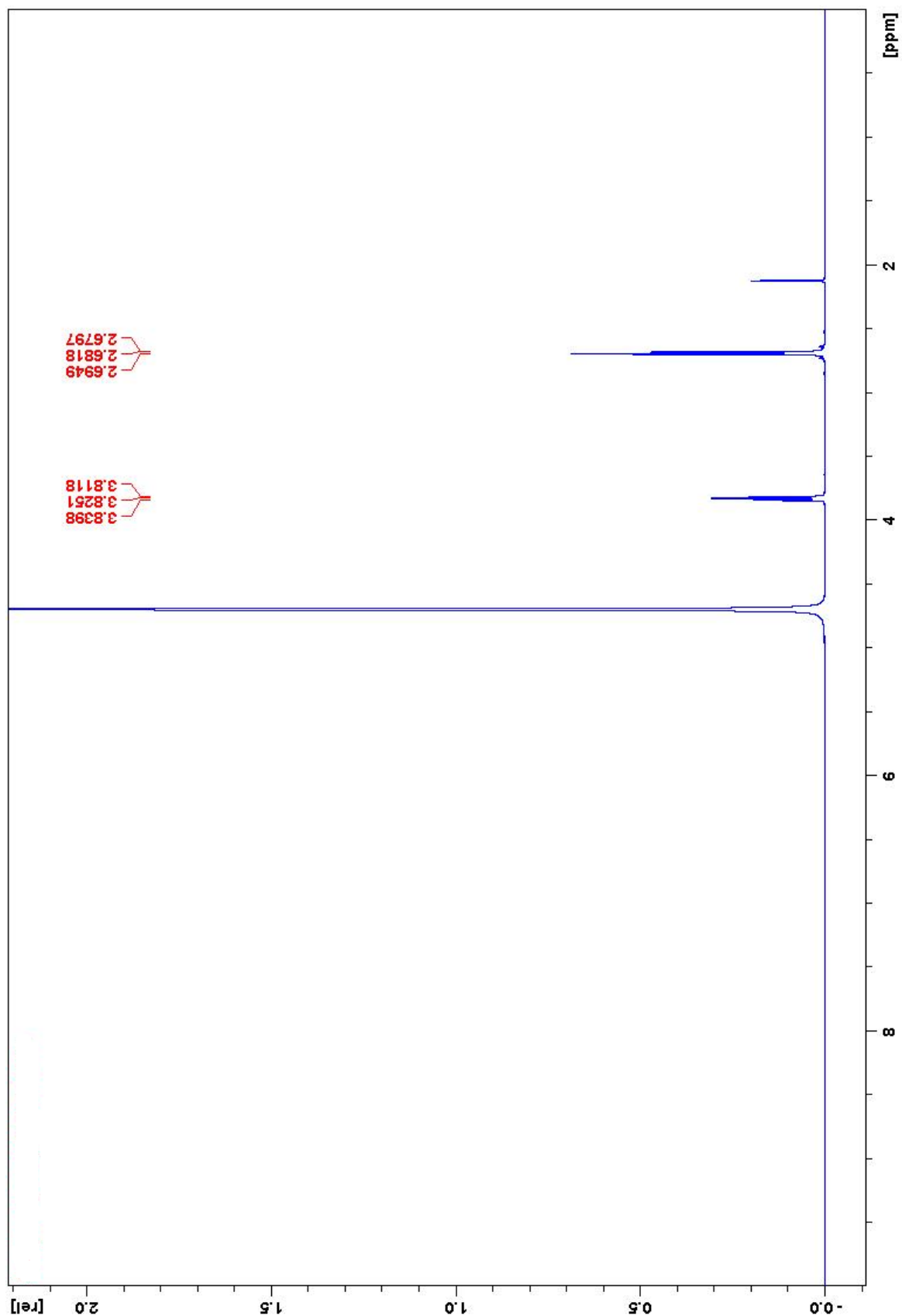
Spectrum (8). ^{1}H NMR Spectrum of $[La_4(OH)_4(l\text{-}Asp)_5(H_2O)_8](ClO_4)_3$
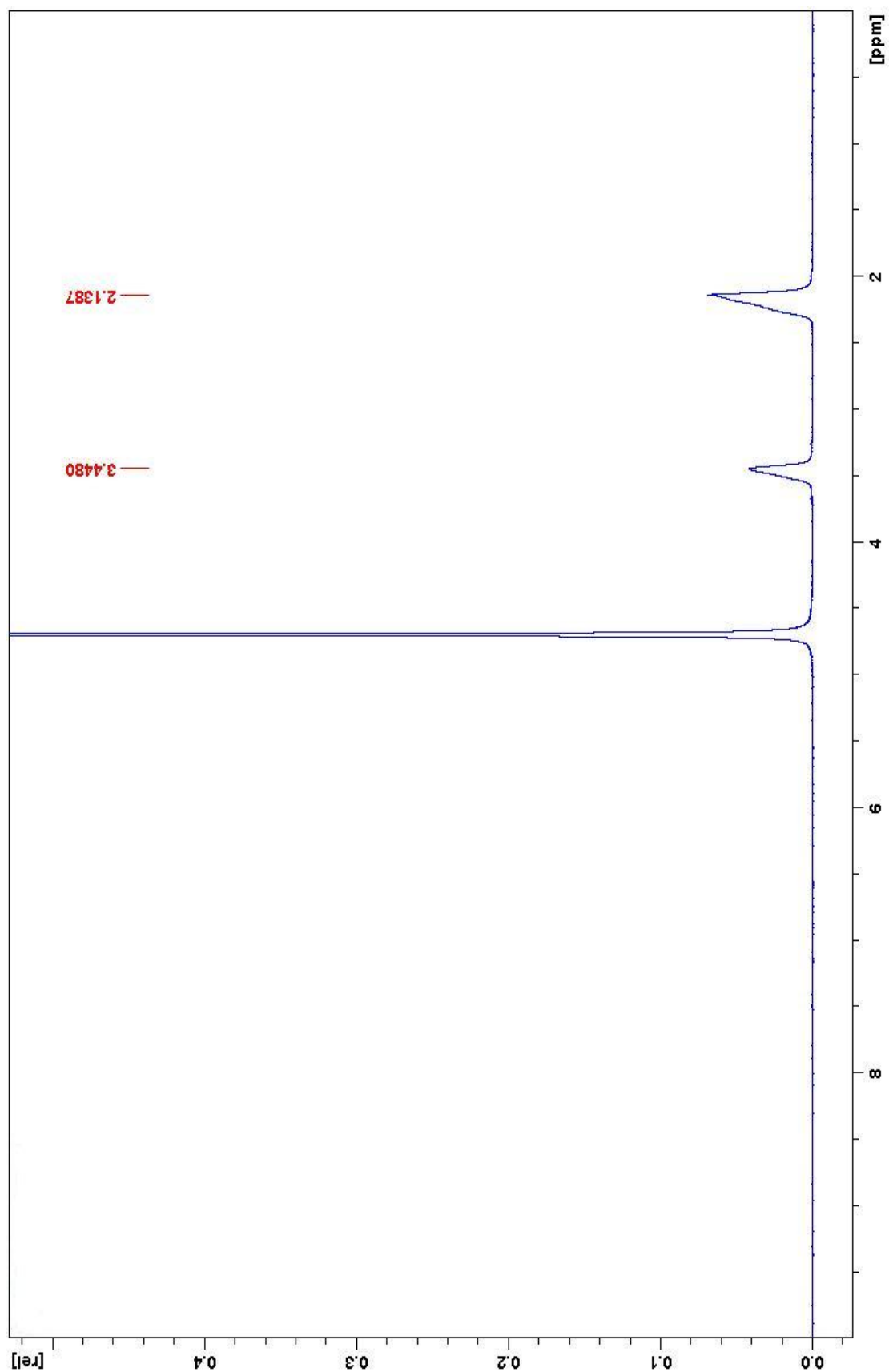
Spectrum (9). ^{1}H NMR Spectrum of $[Eu_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 10H_2O$

6.0136 ——

6.4987 ——
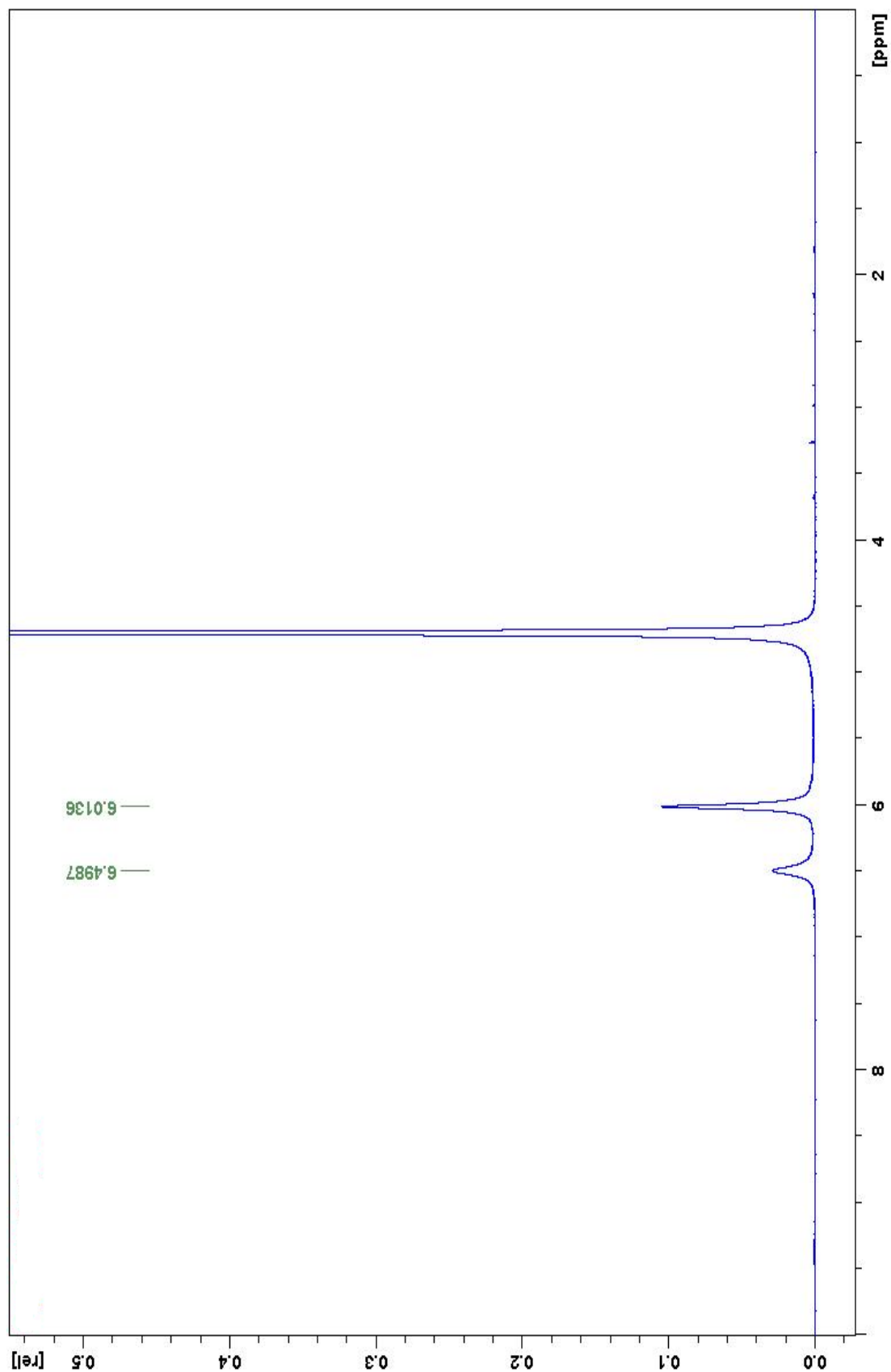
Spectrum (10). ^{1}H NMR Spectrum of $[Pr_4(OH)_4(l\text{-Asp})_3(H_2O)_8](ClO_4)_5 \cdot 8H_2O$
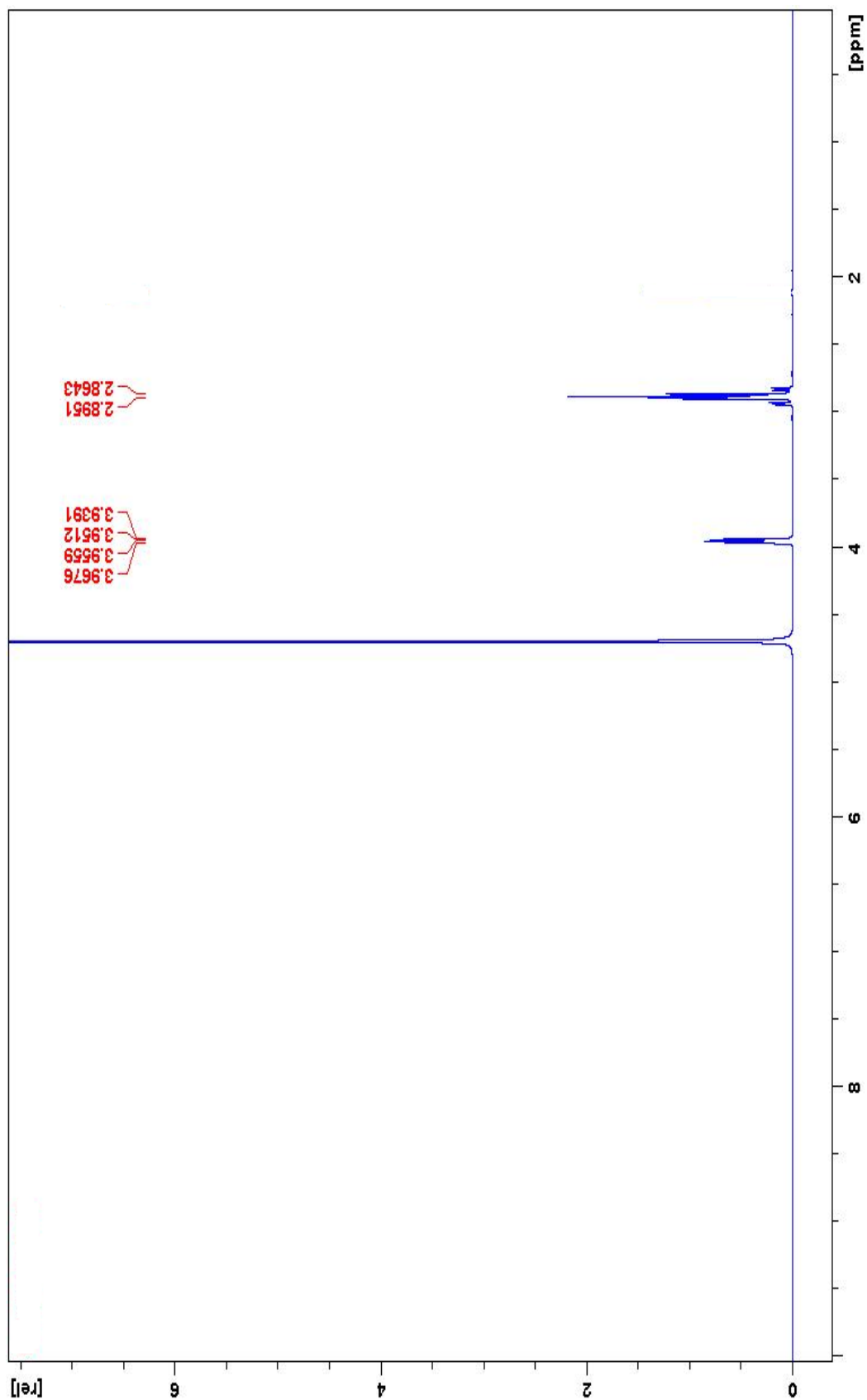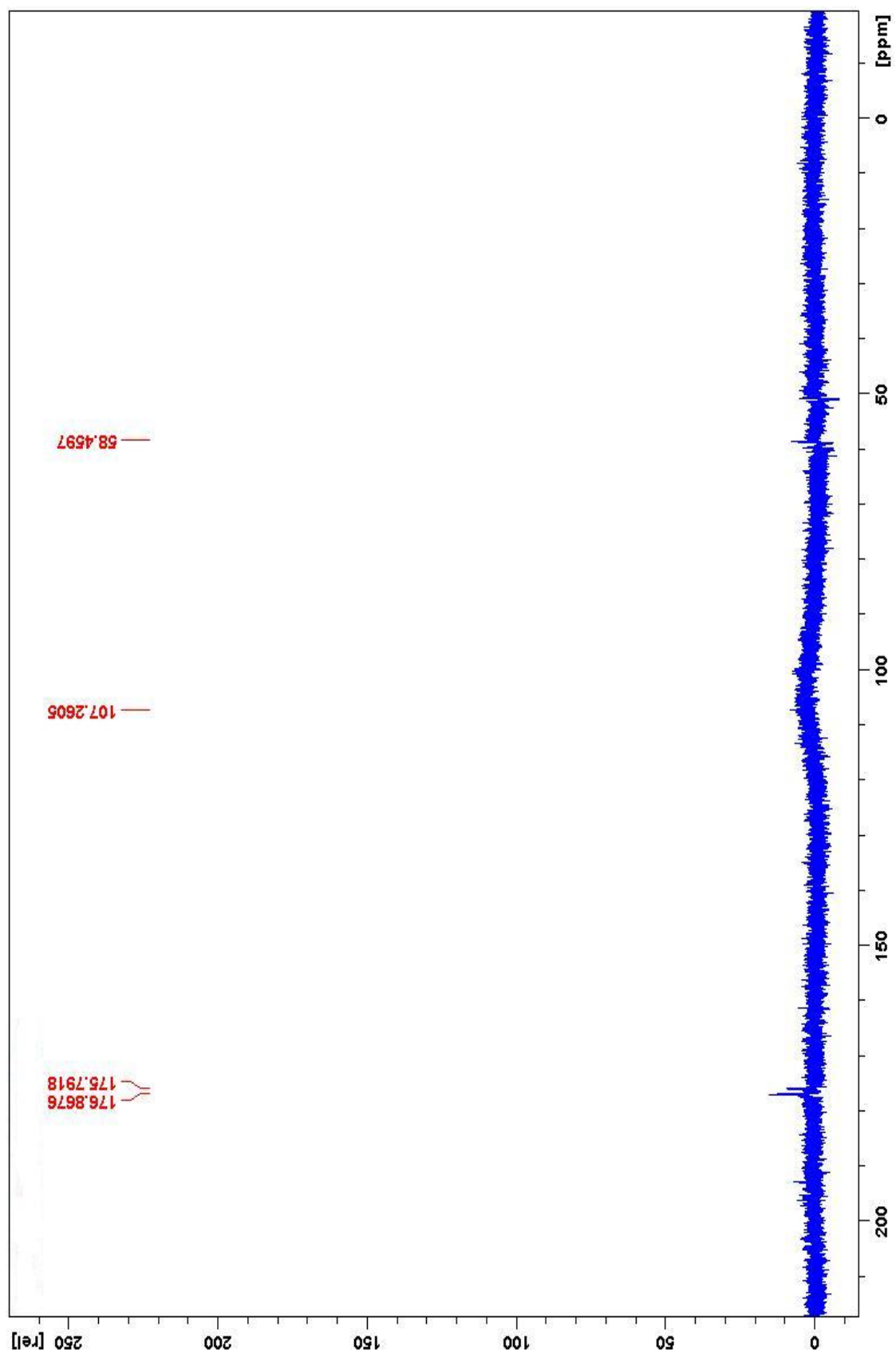
Spectrum (11). ^{1}H NMR Spectrum of the *l*-aspartic acid
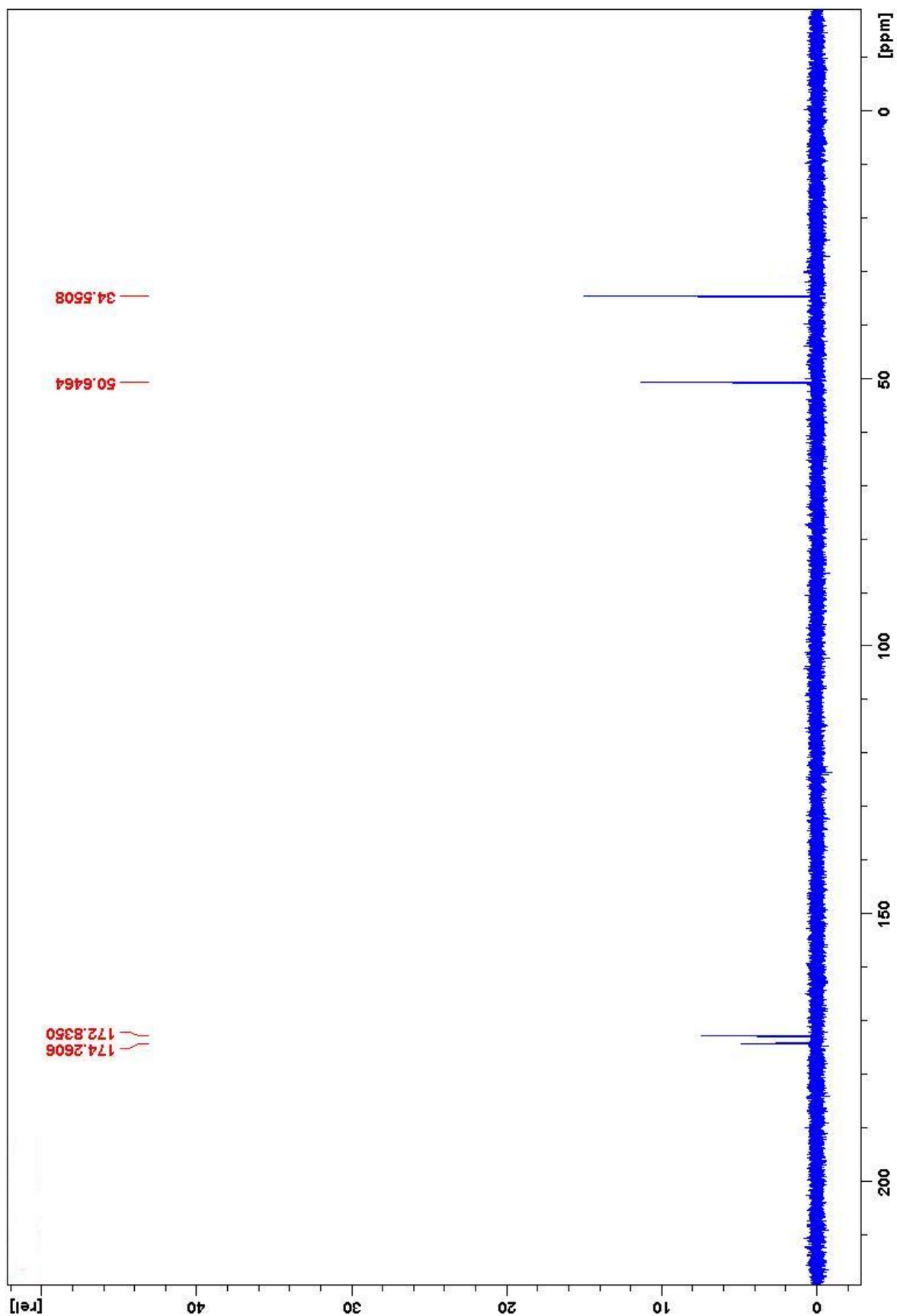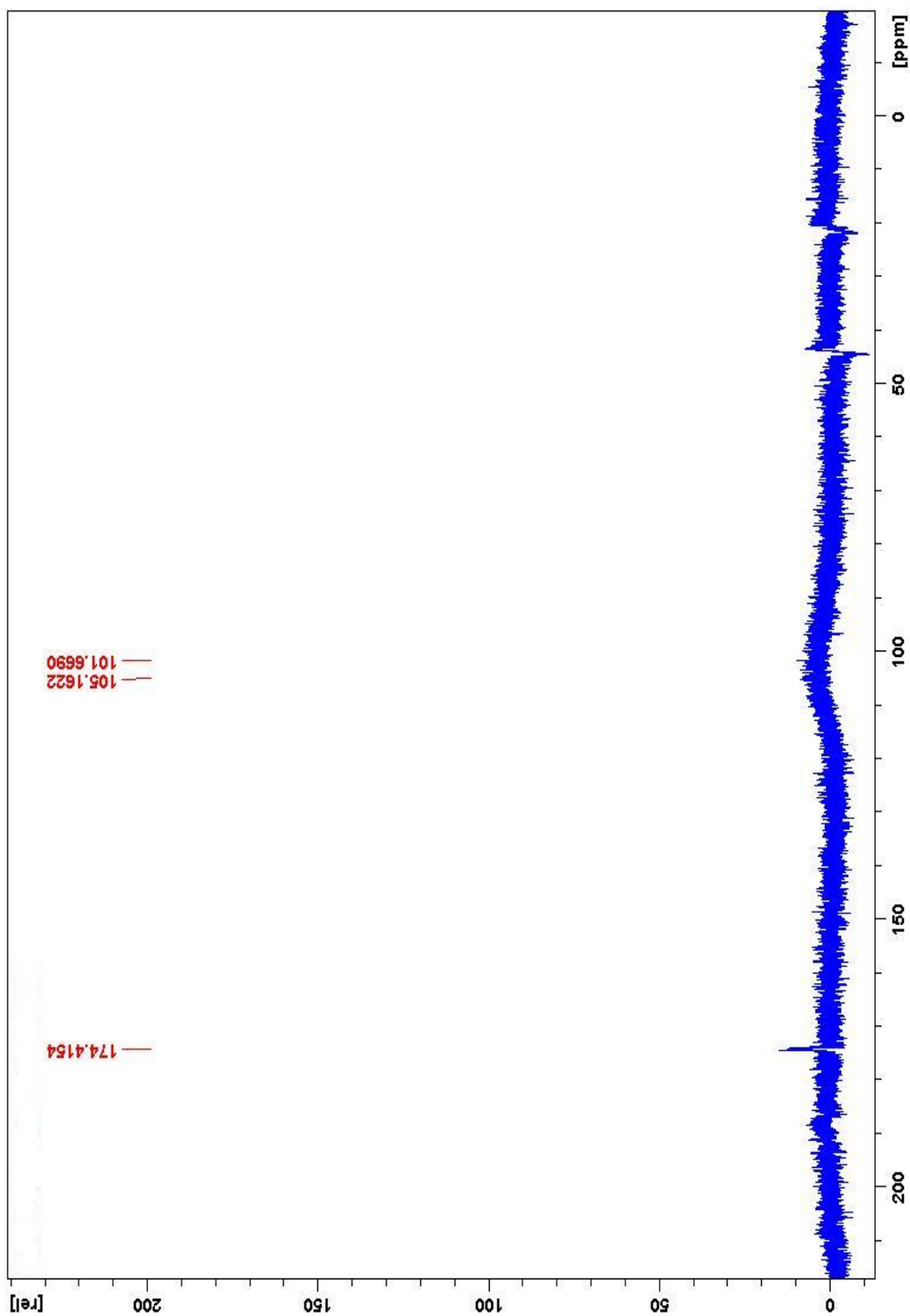
Spectrum (12). ^{13}C NMR Spectrum of *l*-aspartic acid
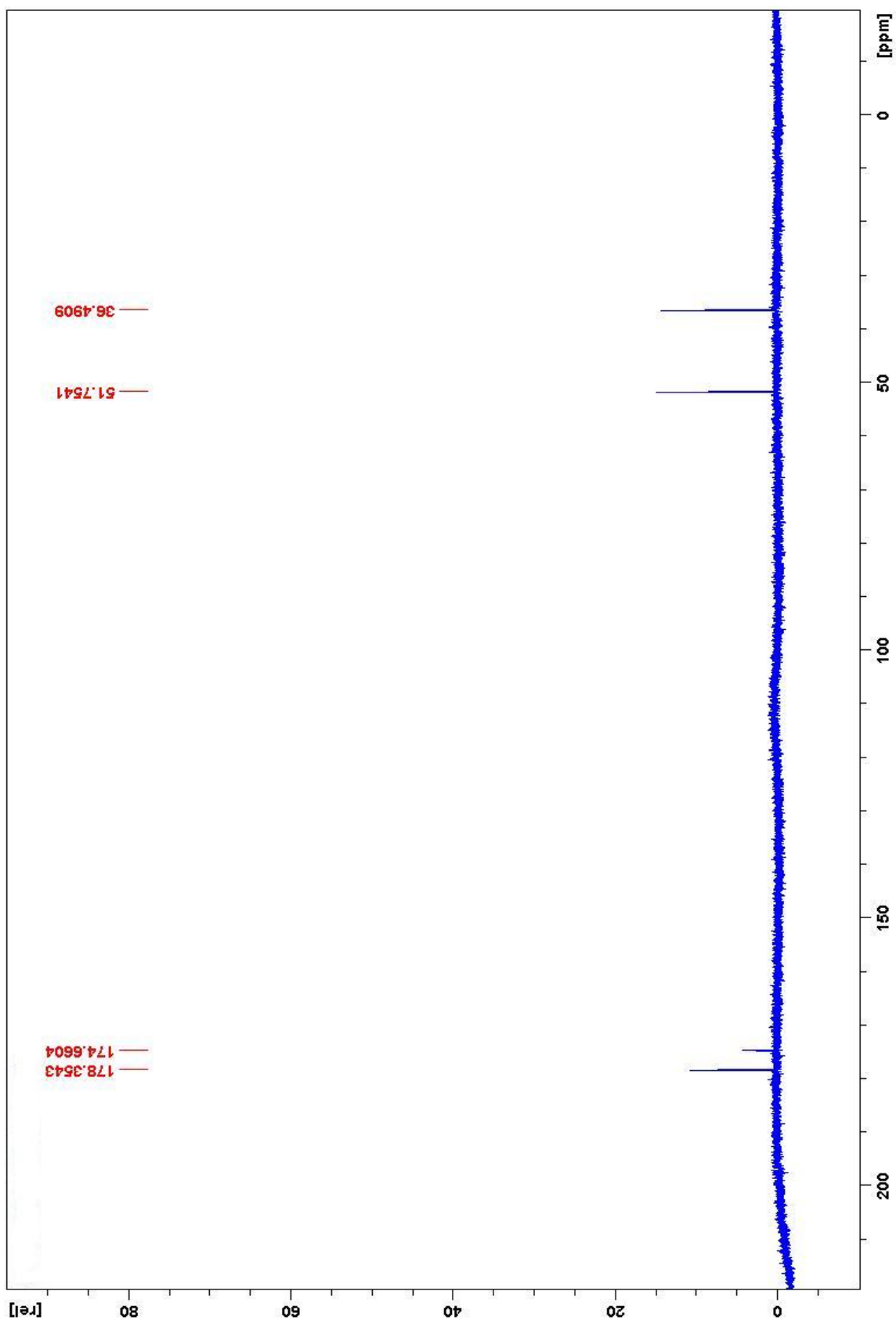
Spectrum (13). ^{13}C NMR Spectrum of $[La_4(OH)_4(l\text{-}Asp)_5(H_2O)_8](ClO_4)_3$
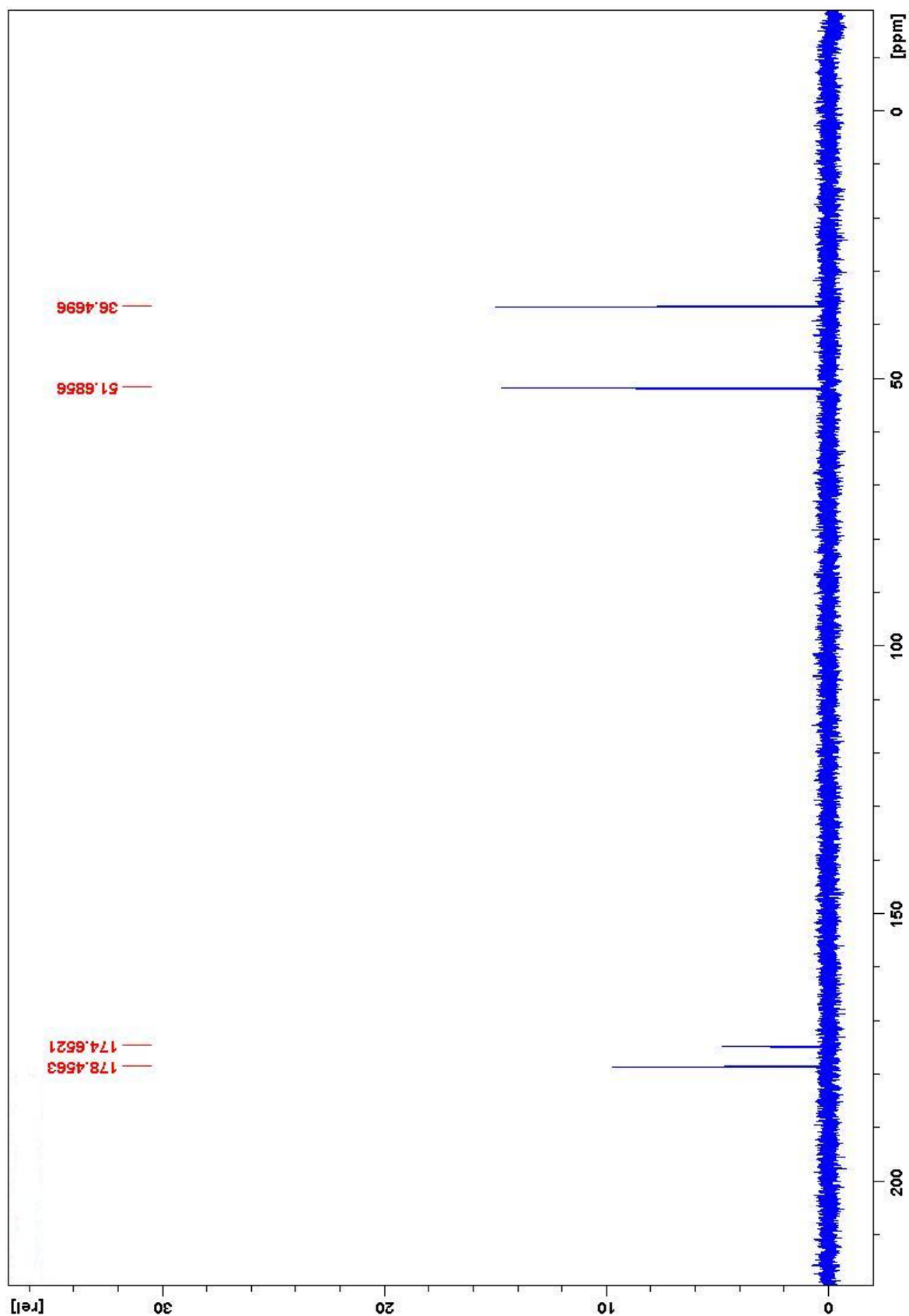
Spectrum (14). ^{13}C NMR Spectrum of [La(l-Asp) ($H_2O)_4$]Cl_2

Spectrum (15). ^{13}CNMR Spectrum of $[Pr_4(OH)_4(l\text{-}Asp)_3(H_2O)_8](ClO_4)_5 \cdot 8H_2O$

Spectrum (16). ^{13}C NMR Spectrum of [Eu$_4$(OH)$_4$(*l*-Asp)$_3$(H$_2$O)$_8$](ClO$_4$)$_5$·10H$_2$O

4. CONCLUSION

The complexes of aspartic acid [La(l-Asp)(H_2O)$_4$]Cl$_2$, [La$_4$(OH)$_4$(l-Asp)$_5$(H_2O)$_8$](ClO$_4$)$_3$ and [Gd(l-Asp)(H_2O)$_4$](ClO$_4$)$_3$ have 1:1 metal to ligand ratio, which contain infinite layers. The complexes [Pr$_4$(OH)$_4$(l-Asp)$_3$(H_2O)$_8$](ClO$_4$)$_5$·8H_2O and [Eu$_4$(OH)$_4$(l-Asp)$_3$(H_2O)$_8$](ClO$_4$)$_5$ Have 4:3 metals to ligand ratio.Metal coordination results in appreciable shifts of the asymmetric stretching frequency of the carboxylate moiety of the aspartic acid ligand, from 1610 to about 1590 cm^{-1}.

The symmetric carboxylate stretching frequency shifts from 1416 to 1422 cm^{-1}. The shift in ^{1}H NMR resonance in the case of lanthanum metal is upfield and small because lanthanum is diamagnetic, but in the case of Europium the upfield resonance shift is much higher. In the case of Praseodymium the shift is downfield, with broad band and the splitting is completely removed. In compound [Gd (l-Asp)(H_2O)$_4$](ClO$_4$)$_3$ the peaks of the amino acids in ^{1}H NMR is completely removed, according to the strong effect of gadolinium metal. The characteristic shifts of ^{1}H NMR and C-13 NMR clearly show that l-aspartic acid is coordinated to the lanthanides ions via the carboxylic acid oxygen.

SUPPLEMENTARY INFORMATIONS

The supplementary informations (Infrared spectra, NMR Spectra for l-aspartic acid and complexes) are available as free of charge on request.

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REFERENCES

[1] Legendzewicz J., Huskowska E., Argay G. Y., Waskowska, A., *J. Less-Common Met*. 146 (1989) 33.

[2] Benelli C., Caneschi A., Gatteschi D., Paradi N. A. L., *Magnetic Molecular Materials* 198 (1991) 233.

[3] Ma B. Q., Zhang D. S., Gao S., Jin T. Z., Yan C. H., Xu G. X., *Angew. Chem. Int. Ed.* 39 (2000) 3644.

[4] Ma A., Li L., Lin Y., Xi S., *Jiegou Huaxue* 14 (1995) 5.

[5] Li X., Pan K., *Jiegou Huaxue* 4 (1985) 75.

[6] Csoregh I., Kierkegaard P., Legendziewicz J., Huskowska E., *Acta Chem. Scand. Sect. A* 41 (1987) 453.

[7] Torres J., Kremer C., Kremer E., Pardo H., Suescun L., Mombrú A., Domínguez S., Mederos, A., Herbst-Irmer, R., Arrieta, J. M., *J. Chem. Soc., Dalton Trans.* (2002) 4035.

[8]   Zheng H. D., Pan K. Z., *Jiegou Huaxue* 11 (1992) 393.

[9]   Wang J., Hu N., Yang K., Zhang H., Niu C., *Acta Cryst. Sect. C* 59 (2003) 52.

[10] Csöregh I., Kierkegaard P., Legendziewicz J., Huskowska E., *Acta Chem. Scand.* 43 (1989) 636.

[11] Wang R., Liu H., Carducci M. D., Jin T., Zheng C., Zheng Z., *Inorg.Chem.* 40 (2001) 2743-2750.

[12] Celia R. C., Ana M. G. M., Segio R. D. E. L., *J. Braz. Chem. Soc*. 8(6), (1997) 597-602.

[13] Wang R, Selby H. D., Liu H., Michael D. C., Jin T., Zheng Z., Anthis J. W., Staples R. J., *Inorg. Chem.* 41 (2002) 278-286.

[14] Becker E.D., *High resolution NMR-Theory and Chemical Applications*, Academic Press, New York, 1980.