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Characterization of two dinuclear complexes of the gadolinium ion by IR and Raman

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Abstract

In this work, we studied by IR and Raman spectroscopy studies, the structure of dinuclear complexes of the gadolinium ion (Gd^{3+}) with the oxalic and the glycolic acid; comparing the two spectra : the free acid and its complex in the similar experimental conditions. Both complexes were formed in an aqueous solution according to the acidity of (5.50 < pH < 7.50) and at a molar ratio ***q=[Gd^{3+}][ligand]=2/2***. The spectroscopies results clearly show that the vibration band of the carbonyl function C=O (1760 ± 40cm^{-1}) of the two acids completely disappeared after the formation of the complex Gd(III)-acids, most the absorption band of the hydroxyl OH (3500 ± 100cm^{-1}) of the acid function O=C–OH of the two acids were not observed after the complex acids by the Gd^{3+} ion indicating that this function was deprotonated before participating in the godolinic complex formation. Thus, we observed that the peak of the OH (ν>3650cm^{-1}) in α position of the glycolic acid was reduced in the case of Gd-glycolate. These results show that all the oxygen atoms of the acids studied are related to the gadolinium ion and verified that by the appearance of new peaks characteristic of the vibration Gd–O link (197 ± 10cm^{-1}) and (490 ± 80cm^{-1}) on the spectra of the complex Gd–acids. The absence of doubling peaks spectra of the complexes (new peaks) show that the structures are symmetrical. Gadolinium ions have been inserted in mononuclear tetradentate site (Gd-Oxalate : –COOGdOOC–) and mononuclear tridentate site (Gd-Glycolate : –C–OHGdOOC–).

Keywords: lanthanides ions, Gadolinium complexes, oxalic acid, glycolic acid, indirect photometry, stability constant

1. Introduction

The gadolinium ion exists in human serum, it can form certain complexes with certain proteins [1]. The studies by Antelli P. L. [2] revealed a great interaction of the gadolinium ion with albumin from the human blood. Another study shows that the ternary complex "Albumin–Gd–DTPA" can be metabolized in vivo to form another ternary complex "Lysine–Gd–DTPA" [3]. Moreover, the gadolinium ion is poorly absorbed by the digestive tract in its ionic form. Thus, the Gd(III) ion is found in the center of a medical revolution of the first importance [4,5,6]. Since the approval of the first contrast agent based on Gd(III) in 1988, $[Gd(DTPA).H_2O]^{2-}$, 30 tons of gadolinium have been administered to patients around the world. However, gadolinium ion is highly toxic in its hydrated form$[Gd(H_2O)_8]^{3+}$. Its complexation with an organic ligand reduces its toxicity and this complexation should be administered in the form of a complex thermodynamically very stable and inert chemically and kinetic [7]. The solution consists of enclosing the cations of the gadolinium ion in the linear or cyclic ligands to form complex non–toxic, inert and stable in the body [8]. The most widely used ligands are polyaminocarboxylates and their derivatives. In this sense, we studied two structures of gadolinium colorless complexes with the oxalic acid and the glycolic acid. The two complexes have been studied in details by Riri M.et al. [9] and the results obtained by indirect photometry showed that the two complexes are dinuclear and have the same composition (***2, 2, 2***). The two complexes were formed from two ions Gd^{3+}, two ligands (acid) and two protons H^+. The stability constants of these complexes are $\log K'_{222} = 26.99 \pm 0.05$ (Gd–Oxalate) and $\log K'_{222} = 22.97 \pm 0.05$ (Gd–Glycolate) [9]. The general reaction of the formation of these two gadolinic complexes is as follows:

$$2Gd^{3+} + 2L^{n-} + 2H^{+} \longleftrightarrow (2,2,2)^{8-2n} + 2H_2O$$

- We noted (2, 2, 2) to simplify the writing of the colorless complex formed.

- *2*, *2* and *2* are the stoichiometric coefficients related to the (Gd^{3+}) ion, acid studied in its basic form and the number of protons H^+ involved in the reaction.
- L^{n-} represents the ligands (oxalate: n=2 and glycolate: n=1).

The two acids studied in this work present two types of probable chelating sites to form the two organometallic complexes because of the availability of free electron pair of oxygen. Indeed, the only chelation site of the oxalic acid is two carboxylic functions COOH, and the glycolic acid present two different chelating sites : the carboxylic function COOH and the OH group in α position.
We used the IR and Raman spectroscopic to identify the different chelation sites to form two colorless gadolinic complexes. Finally, these two techniques help us to propose the probable structures of the two complexes studied in this work.

2. Materials and methods

2.1. Chemicals

Oxalic acid, Glycolic acid, Chrome Azurol S (H_4Ch), Gd(III) nitrate and other chemicals were commercial products (Aldrich, Prolabo,….) of the purest available and analytical grade, used as received.

2.2. IR spectroscopy

The samples were prepared by weighing the appropriate amount of the oxalic and the glycolic acids (ligands) and $Gd(NO_3)_3.6H_2O$ adding H_2O, mixing and finally adjusting the pH with concentrated HCl or NaOH. The concentration of the analyzed samples is 10^{-3} M. The analyses of the samples were performed using an infrared spectrometer, Fourier transform (FT–IR), Perkin Elmer BX, equipped with a DTGS detector, a splitter and a cesium iodide window. In this configuration, the analysis was performed in the middle infrared region 6000 to 250 cm^{-1} using small samples whose size is less than $1mm^3$. Liquid samples are placed between two very pure plates salt (KBr). These plates are transparent, the spectra relative to the free ligand (oxalate and glycolate ions) and the complex have been plotted for frequencies from 4400 to 400 cm^{-1}.

2.3. Raman spectroscopy

Complexes at a concentration of 5.10^{-2} M, are precipitated quickly at room temperature. The precipitate was filtered and dried in a drying oven and the complex formed is insoluble in water, methanol and ethanol. The Raman spectra of the ligands (oxalic and glycolic acid) and there new gadolinium complexes was performed using an Fourier transformation Raman spectrometer (FT–Raman) VERTEX 70 with a range of measurement (4000 to 50 cm^{-1}), laser source NdYag (1.064µm), a nominal power of 500 MW, detecting Ge with high sensitivity and a resolution of 4 cm^{-1} (64 scan). The spectra relative to the free acids and Gd(III)–carboxylate complexes have been plotted for frequencies from (3600 to 150 cm^{-1}).

3. Results and discussion

3.1. IR spectroscopic study

The IR spectroscopic studies can identify different donors groups of acids studied, that are involved in chelation sites for the formation of the complex detected in solution by interaction ligand–gadolinium ion. To analyze and compare the IR spectra registered, we have prepared for each of the two studied acids two separate solutions with identical concentrations and at the same pH (free acid and its complex). In figure 1, we have shown an example of IR spectra of the oxalic acid registered from a solution of the free form (free oxalic acid) as well as from a solution of the complex form (Gd–Oxalate) in addition to a solution of gadolinium ions (Gd^{3+}). Table 1 summarizes the experimental frequencies obtained from experimental and theoretical spectra [10, 11, 12] of OH, C=O, COO^- and –CC=O functions.
According to the results obtained by the analysis of the different spectra plots, we see a significant reduction in the relative frequencies of all functions vibration : O–H, C=O and COO^- after the formation of the two complexes (Gd–Acid). For both acids studied, there are important reduction percentage (>50%) (we based on the spectra of the free acid and the spectra of its complex by calculating the ratio : height of the band of the free acid / height of the same band after the complexation, to know the diminution of the band). In view to the vibration frequencies of all the functions of the molecule ligand for both acids studied, it is clear that the percentage of the reduction is significant (> 50%), which certainly indicates a high stability of the complexes formed in the solution, as well as the participation of the chelating sites of all the oxygen atoms of each carboxylic function COOH and the oxygen of the OH in α position of the glycolic acid. Indeed,

preliminary studies of IR combined with the results obtained by indirect photometry [9] indicate undoubtedly that the chelation sites present in the molecules of these dinuclear complexes studied for the two acids are formed by an atom of metal (gadolinium) related to four oxygen atoms of two COO functions belonging to two different oxalates and gadolinium metal atom linked to three oxygen atoms of the COO and OH in α position belonging to two different glycolate. Therefore, these two complexes detected are cyclic formed from two molecules of ligand related by tridentate and tetradentate mononuclear and lateral chelation sites. The bibliographical studies [13-17] indicate that the gadolinium ion may be involved in the formation of cycles of 4 or 5 members, by the interaction with donor groups of certain ligands such as the oxygens of the carboxyl function (COOH), or the hydroxyl group (OH), or the nitrogen of the amine function in α position (α–NH_2). For both acids studied, we can say that these two gadolinic complexes have two different structures consisting of two lateral mononuclear sites : two tridentate site (Gd–glycolate) and two tetradentate site (Gd–oxalate) which bind two molecules of ligand. Some studies [10, 18,19] show that due to the predominance of electrostatic character of the metal–Oxygen in the molecule of the complex formed (transition metals or lanthanides), the relative frequencies of vibration bands of the bond (M–O) are characterized by weak intensities. These vibrations can be coupled to other modes of vibration are observed in a wide range of frequency (150-780cm^{-1}) and can be attributed to the frequency : $\upsilon_{M\text{-}O}$ (M–O carboxylic acid), $\upsilon_{M\text{-}O}$ (M–O carbonyl) and sometimes represent $\upsilon_{M\text{-}O}$ of M–hydroxyl). The vibration bands for the Gd–O link of the two complexes may be not detected in the IR spectra obtained due to the low concentration of samples. The Raman spectroscopy studies give a spectrum with clear vibrations with this link Gd–O and give more information about those vibrations.

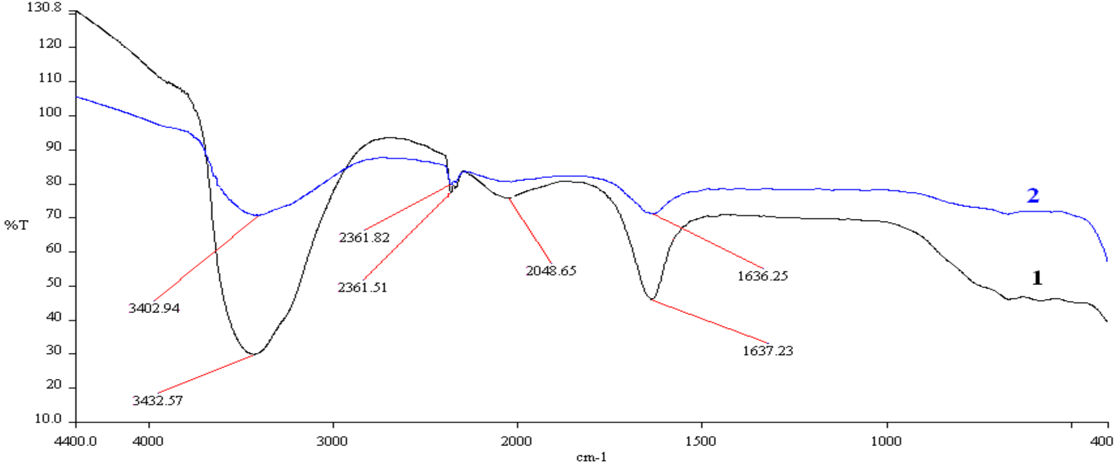

Figure 1 : IR Spectra of oxalic acid, (1) free acid, (2) complex (Gd(III-Oxalate), q=[Gd^{3+}]/[oxalate]=2/2.

We have shown in Table 1, the experimental vibration of the main functions OH, COO, CO and CCO obtained by IR and bibliographic reference cited for these vibrations bands.

Table 1: IR frequencies of the main functions of the two carboxylic acids studied.

Function	expérimental Spectra	Ref. [10,11,12]
	ν(cm^{-1})	
–OH	3620 – 3500	3650 – 3100
–C=O	1740 – 1690	1800 – 1700
$–COO^{-}$	1000 – 400	700 – 590
–C–C=O		550 – 465

3.2. Raman spectroscopic study

Raman spectroscopic studies were necessary to complete our study and refine the proposed structures for these two organometallic complexes of gadolinium ion. And to confirm the results obtained by IR spectroscopy and have more spectroscopic data on these two gadolinic complexes, we have conducted complete Raman spectroscopic studies by drawing two separate spectra, one for the free acid and another for the complex Gd-acid (the same acid in the same operating conditions). We have shown in figure 2 an example of the Raman spectrum of the oxalic acid and its complex. The frequency of the vibration bands on the main functions (OH, COOH, C=O) of free and complex ligand were identified in the experimantal spectra. The experimental results drawn from the spectra of the oxalic acid and its complex are shown in Table 2.

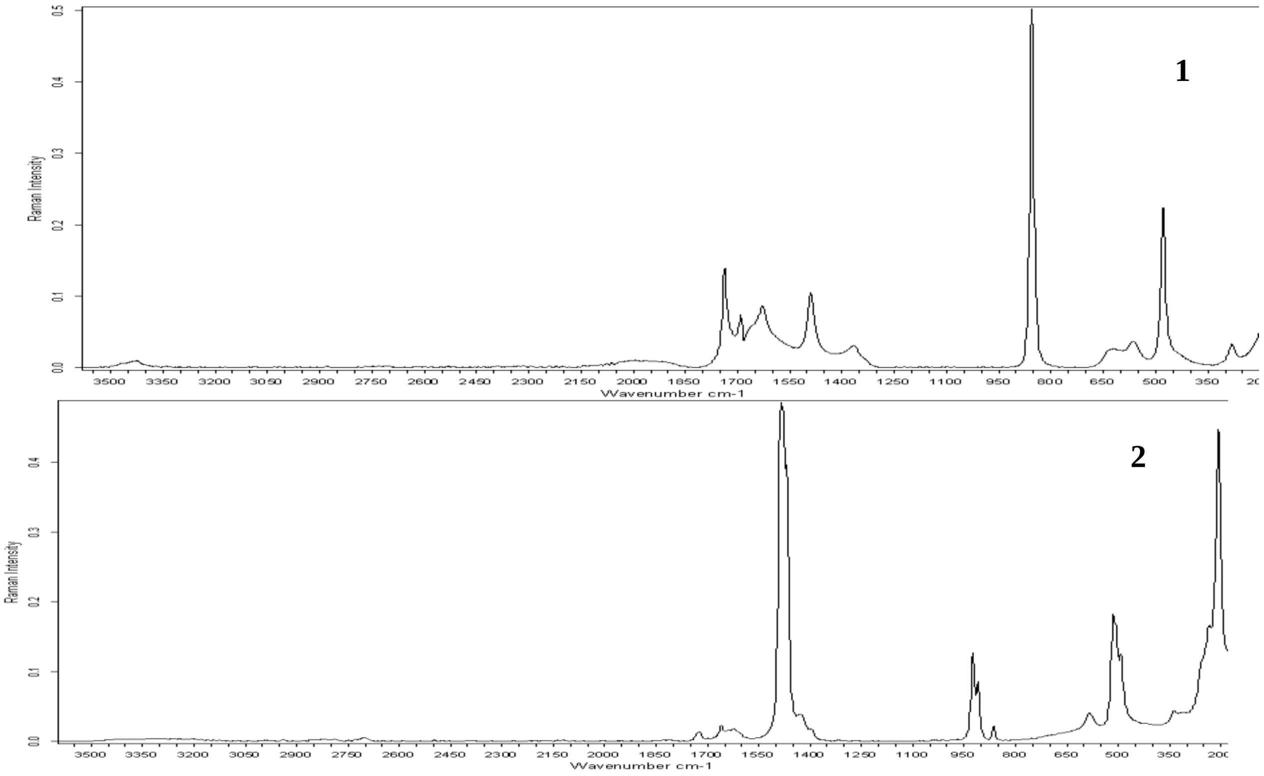

Figure 2: Raman spectra for the free oxalic acid and its complex, (1) free oxalic acid, (2) complex Gd-Oxalate. Recording interval spectra [3600–200]cm^{-1}, q=[Gd^{3+}]/[oxalate]=2/2.

The experimental results obtained by Raman of functions vibration of the free acid and the vibration after the formation of the complex and the necessary interpretations for each band are shown in Table 2.

Identification of the experimental vibration bands observed :

We identified all the vibration bands obtained for the free oxalic acid ($C_2H_2O_4.2H_2O$), its complex (Gd(III)-Oxalate), the free glycolic acid ($C_2H_4CO_3$) and the Gd(III)-Glycolate. Indeed, these two ligands present vibration bands of different links: C–C, O–H, C–C–O, C=O, COO$^-$, C–C–OH and O–H in α position of the glycolic acid. In figure 2, the absorption band at 3440cm^{-1} free oxalic acid (3550 cm^{-1} glycolic acid) of low intensity corresponds to the vibration of the O–H of the carboxylic function [10,17-19]. This band is completely absent in the spectrum of the complex form of the two acids, which indicates the participation of this function after deprotonated in the chelation site for the formation of these two dinuclear gadolinic complexes. This result confirms the results obtained by IR. Thus, we find that the intense peak of OH in α position of the free glycolic acid (very intense peak) is reduced (weak intensity) with the Gd–glycolate complex. We explained this decrease by: the OH group is related to Gd^{3+} by the free electron pair of oxygen in α position without deprotonation [17,18,20]. The vibration relative to the carbonyl function C=O is observed at 1738cm^{-1} (oxalic acid) and 1708cm^{-1} (glycolic acid) for both free ligands [10,17,21] with a mean intensity. This band was totally disappeared in the spectra of the complexes which indicates that the complexation equilibrium is displaced in the direction of the formation of a stable complexes, and the oxygen atom of the carbonyl function C=O also participates in the chelating site of the two gadolinic complexes. Two weak bands located at the frequencies 1659cm^{-1} (Gd–Oxalate) and 1635cm^{-1} (Gd–Glycolate) on the complexes spectra represent the vibration of the H_2O molecules [10]. The frequency at 1490cm^{-1} (free oxalic acid) and 1480cm^{-1} (free glycolic acid) due to the vibration in the plane of C–OH [12,17,18,22] has completely disappeared after the complexation. A very intense and thin peak observed on the two complexes spectra at 1486cm^{-1} corresponds to the symmetrical vibration of NO_2 [17,18,19]. The spectra of the complexes Gd (III)-oxalate and Gd (III)-glycolate present two bands observed in frequency 925cm^{-1}, which represents the vibration of the NO_3^- group [17,19]. The vibrations of C–C bond are generally observed in several wavenumbers [19,23].

Table 2: Identification of frequency bands related to the vibration of the Raman spectra of the free and complex forms of the oxalic acid.

Free oxalic acid	Gd–Oxalate	Corresponding bands
3440 vw	………	υ(OH)
1738 s	………	υ(C=O)
…….	1659 vwbr	υ(H_2O)
1628 wbr	………	υ(H_2O)
1490 m	………	δ(C-OH) + υ(C-O)
……	1486 vs	υ(NO_2)
……	925 m	υ(NO_3^-)
855 vs	863 vw	δ(C-C) + υ(C-O)
630 wbr	……..	υ(O-C=O)
560 wbr	585 wbr	υ_{as}(C-O) + δ_s(C-C-OH)
478 m	514 m	δ(C-C-O) + δ(C-C)
…..…	492 m	υ(Gd-O)
…….	340 w	υ(Gd-O)(NO_3)
…….	207 s	υ(Gd-O)

Frequency domain [3600–200]cm^{-1}, ***q***=[Gd^{3+}] / [Oxalate]=***2/2***, C=5.10^{-2} M.

Notation :

ν: stretching; ν_{as}: asymmetric stretching; ν_s: symmetric stretching; δ: in-plane bending; γ:out-of-plane bending; ω: wagging; τ: twisting; ρ: rocking; t : torsional**,** vs: very strog; s: strong; w: weak; vw: very weak; m: medium; br: broad.

Two important new bands observed at 492cm^{-1} and 207cm^{-1} (Gd(III)-Oxalate) / 527cm^{-1} and 187cm^{-1} (Gd (III)-glycolate) with mean intensities, correspond to the formation of Gd–O bond (oxygens of the carboxyl function of the two acids), and a new peak was observed at 760 cm^{-1} (Gd (III)-glycolate) which corresponds to the vibration of the Gd–OH bond in α position of the glycolic acid [18,19]. In addition, there is a third new band observed at 340cm^{-1} (Gd(III)-Oxalate) / 333cm^{-1} (Gd(III)-glycolate) due to the vibration of Gd–O–NO_2 bond [14,17,18,20]. The absence of doubling peaks in the spectra of the two systems Gd–acids shows that the two structures of the complexes formed are symmetric. These results confirm and complement those obtained by the previous studies of the IR spectroscopy.

4. Proposed structures

All the experimental results obtained allowed us to propose a structure which is very close to the real structure for this dinuclear organometallic complexes formed in solution at pH range 5.50–7.50 by the interaction of trivalent gadolinium ion with two organic acids: oxalic and glycolic. Indeed, these experimental results as well as the work on the tungstic and aluminum complex with these two acids [24, 25] clearly show that these organometallic complexes and for this family of dinuclear gadolinic complexes, the donors oxygens of the carboxylate functions as well as the oxygen atom of the OH in α position of each ligands are involved in the formation of different chelation sites. For this dinuclear complexes of gadolinium ion identified have a single composition (2, 2, 2) [9,17], there is formation of two identical mononuclear tridentate sites (Gd-glycolate) and two identical mononuclear tetradentate sites (Gd-oxalate), the gadolinium ion is ready inserted in the center of each of the two sites, which are independent and not bound by any metallic bridge Gd–Gd or Gd–Oxygen. Therefore, from these results, we propose in figures 3 and 4, the two most probable structures for the two dinuclear gadolinic complexes formed by the oxalic acid and the glycolic acid in a dilute solution.

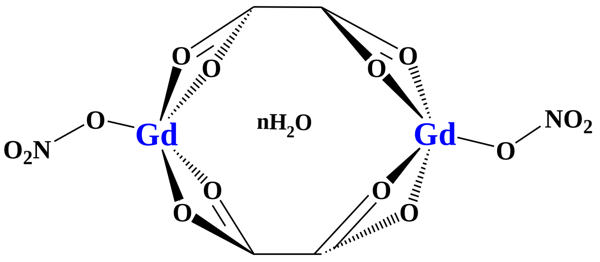

Figure 3 : Probable structure of the complex $Gd_2Oxalate_2.2NO_3.nH_2O$.

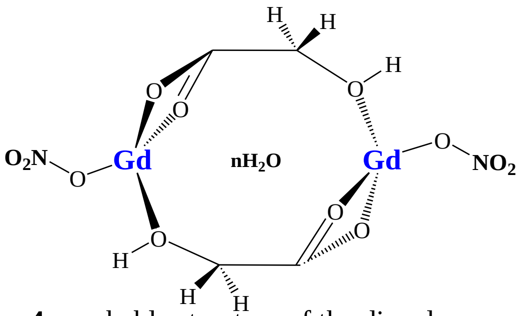

Figure 4 : probable structure of the dinuclear gadolinic complex of glycolic acid $Gd_2Glycolate_2.2NO_3.nH_2O$

Conclusion

In this work, we used two spectroscopic techniques such as IR spectroscopy and Raman to identify different chelation sites and propose structures of the two colorless organometallic complexes formed in solution by the interaction of the Gd(III) ion with the oxalic and the glycolic acid. The results obtained by IR and Raman spectroscopic studies performed on two ligands and their gadolinic complexes showed that the two oxygens of the ionized function (COO^-) and the oxygen of the OH group in α position (glycolic acid) participate in the chelation sites. The nature of the chelation sites has been elucidated and analyses indicate the presence of two sites mononuclear tridentate for complex Gd-glycolate and two sites mononuclear tetradentate for complex Gd-oxalate. However, the bibliographical studies [23-26] show that the two tungstic complexes of the oxalic and glycolic acid are mononuclear complexes of the same type with a single mononuclear tetradentate site where only the oxygen of the acid function HO–CO and the oxygen of OH group in α position of the glycolic acid are involved in the formation of the chelating site. All of these studies allowed us to propose the probable structures for these two gadolinic complexes.

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