



Structural Analysis of Ti And Pb Citrate Using NMR and FT-Raman Signals and Quantum Mechanics Simulations

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Abstract Titanium citrate and lead and titanium citrate were prepared by polymeric precursor method in aqueous solution. This citrate was analyzed by ^1H , ^{13}C NMR and gHMBC–NMR (Hetero-nuclear multiple-bond correlation) to investigate the formation of the citrate complex and influence of the Pb^{2+} ion in this complex. These complexes were characterized by interaction between Ti^{4+} ion and citric acid carboxyls. Quantum mechanic simulations in level *ab initio* were used to study the electronic structure and natural charges (NBO) to both the complexes. Such techniques indicated the formation of an octahedral complex with an arrangement similar to Ti atom in the crystalline structure of the PbTiO_3 . A study using the technique FT-Raman made possible the confirmation of the interaction among the Ti^{4+} and Pb^{2+} ions with the citric acid carboxyls.

Keywords: Sol-Gel, NMR, FT-Raman, PbTiO_3 , Quantum mechanic simulation

1. Introduction

The new ceramic materials produced nowadays present unique physical or chemical characteristics, such as dielectric, optical, electromagnetic, catalytic and sensorial properties. Therefore, they are named “high performance ceramics” or “fine ceramics”. The development of these ceramic materials required new synthesis methods, via wet chemical processes (Sol-Gel methods), in substitution to the conventional methods by solid state reactions. Knowing that each material exhibits specific structural characteristics, in the microstructural as well as in the macroscopic level, the production of fine ceramics requires synthetic routes that achieve powders with controlled properties, in terms of composition, purity, mean particle size, and particle size distribution. [1, 2]

Thus, the research aiming at the improvement of the properties of the ceramic powders led to the development of new synthesis methods. These methods allow for the control at molecular level, ending up in a better stoichiometry and lower processing temperature, producing more reactive powders due to smaller particle sizes and higher specific surface areas. [3, 4]

Nowadays, researchers from all over the world in the electro ceramic area demonstrate enormous interest in the production of high performance ceramics, using the synthetic routes based on the process of polymeric precursor. [5, 6]

Titanium citrate was used by Kakihana et al. [7] in order to obtain barium or strontium titanate at low temperature. They observed, by means of carbon 13 Nuclear Magnetic Resonance (NMR), the formation of a heterometallic coordination compound, with composition $[\text{SrTi}(\text{C}_6\text{O}_7\text{H}_8)_3]$. Other titanium compounds have been shown to be able to form the same coordination compounds, such as for instance, PbTiO_3 and LiTiO_3 [8, 9].

Studies already undertaken show that heterometallic coordination compounds are stable and highly effective for the synthesis of ceramic powders. Therefore, the synthesis of PMN (magnesium and lead Niobate), PbTiO_3 and BaTiO_3 are related to the rigid control of the stoichiometry of the involved organic precursors. This technique is based mainly on the formation of soluble complex in solution, followed by elimination of solvent, resulting in a gel that keeps the random distribution of cations of the starting solution. In relation to the cations, when an appropriate proportion of organic precursors are used, a larger chemical homogeneity of the compound is promoted [10–12].

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The PbTiO_3 powders synthesized by the Polymeric Precursor Method, starting from titanium citrate and lead carbonate presented photoluminescent properties due to the fivefold and sixfold oxygen coordination configurations of the titanium. This combination was only possible due to sixfold coordinated titanium complexation by the citrate in solution [13].

Several synthesis methods based on modifications of the Polymeric Precursor Method have been proposed. They involve alterations in the stoichiometric proportions of citric acid: ethylene glycol or citric acid:metal. New synthetic routes for PbTiO_3 , using hydrogen peroxide, lead nitrate and metallic titanium treated with an ammonia solution for the precipitation and subsequent thermal treatment for obtaining of the crystalline PT (Lead Titanate) powder, free from undesired phases [14].

The NMR studies for carbon nuclei (^{13}C) and hydrogen nuclei (^1H) are used for the determination of compounds with different cations. Xiaohua Li et al. [15] performed experiments for the detection of signs of strontium nuclei (^{87}Sr), and Sambrano et al. [9] for detection of lithium nuclei (^7Li), making possible to detect with great efficiency the modifications of the electronic cloud of these atoms, when complexed with titanium citrate.

In this work the formation of the compounds was analyzed in the liquid phase, in such a way to obtain more controlled solid phase powder. The objective of this study was to understand the complexation of both titanium citrate and titanium and lead citrate in solution and to correlate the complexation influence on the formation of the PbTiO_3 solid phase.

2. Experimental

In order to prepare the titanium citrate (TiCit) and titanium and lead citrate (TiPbCit), a modified Polymeric Precursor route was used. Titanium isopropoxide (Aldrich) was used as Ti^{4+} cations source and the citric acid (CA) as the complexation agent. The modification introduced in the classical polymeric precursor method consists in the use of water as solvent for the reaction medium and of a reflux system. This procedure allows the reduction of the synthesis time of TiCit, as well as, the decrease of the external contamination, due to the closed system used in this synthesis.

Nuclear magnetic resonance (NMR) determinations demand the use of a low apparent viscosity of the liquid that imposes diluted solutions. Thus, it was prepared a TiCit solution with the concentration of 0.0750 moles of titanium per liter of solution. A ^{13}C NMR spectrum of this solution was obtained and analyzed. Lead carbonate was added to the titanium citrate aqueous solution ($\text{Pb}:\text{Ti} = 1:1$) stirred at 70°C for 20 min and a NMR spectrum of this solution was obtained and analyzed. The flow sheet of the synthesis process and analysis is shown in Figure 1.

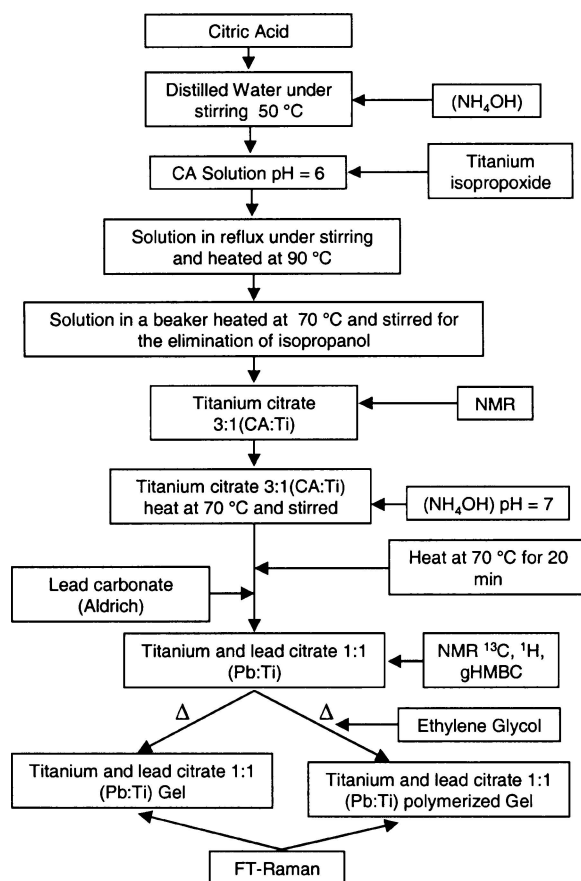


Figure 1. Flow sheet for the preparation of the of titanium and lead citrate (TiPbCit).

The BRUKER equipment model DRX400, 9.4 Tesla, operating at 400,13 MHz for ^1H and 100,13 for ^{13}C frequency was used for obtaining ^1H and ^{13}C spectra, respectively. A $\text{D}_2\text{O}/\text{TSPA-d}_4$ —“Trimethylsilyl propionic-2,2,3,3-d₄ acid, sodium salt” solution was used like external reference to adjust the field homogeneity and as reference for ^1H and ^{13}C NMR spectra. The temperature was maintained constant at 303K during all the experiments.

Besides the ^{13}C NMR, the gHMBC—“Heteronuclear multiple-bond correlation” technique was also used in this work for characterization of metal citrates synthesized by the polymeric precursor method. This technique consists of long distance bidimensional coupling experiments, by means of the ^1H - ^{13}C gHMBC inverse detection.

This experiment correlates the chemical shifts of hydrogen 1 and carbon 13 to more than one bond. Together with the gHSQC—“Hetero single-quantum coherence” experiment this technique is very useful to establish the bonds of several existing carbons in a molecule, mainly the carbons that are not bonded to hydrogen atoms. The bonds in which one can observe a correlation between a hydrogen and a carbon 13 is limited to 2, 3 and up to 4 [16, 17].

Moreover, the NMR - gHMBC technique allows for a better visualization of the titanium and lead citrate complexation sites. This technique turns easier the identification

of the citric acid carbon atoms that are being affected by the complexation with the titanium and lead atoms.

The Raman scattering spectra were collected in a Fourier Transform Spectrograph (Bruker FT-Raman RFS100/S), using a backscattered geometry and a laser operating in the infrared wavelength region (1064 nm) with 150 mW of nominal power [18]. The FT-Raman technique was used to avoid the possibility of fluorescence of the material, which are usually four orders of magnitude more intense than the Raman scattering. The citrate (100 mL) solution was placed in a beaker over a hot plate, and heated (70°C) until it's gelling, and then placed on a metallic sample holder for the performance of the experiments.

Quantum mechanical calculations were carried out, aiming at advising the procedures of synthesis and experimental analysis. It was adopted an experimental-theoretical interactive methodology for the understanding of the complexation mechanisms of the two analyzed models. It should be pointed out that the theoretical calculations are of fundamental importance for the interpretation of the NMR spectra. A first-principles molecular calculation was used to simulate the variation of the electronic structure of the CA and when the complexation mechanisms of the two analyzed models (TiCit and TiPbCit). The restricted Hartree-Fock (RHF) formalism has been considered to optimize the geometry of the considered systems. For this simulation it was built a cluster, whose geometry was optimized. The 6-31G base function was selected for carbon, hydrogen, oxygen and titanium and the LanL2DZ base function was chosen for the lead, using the Gaussian 98 program [19].

The most stable conformations for the molecules of citric acid (CA), titanium citrate (TiCit) and titanium and lead citrate (TiPbCit) were considered for the construction of the complexation models. Charge natural are charges based in the natural bond orbital (NBO) [20–22], it were used to comparing the CA, TiCit and TiPbCit molecules with their respective variations and correlations with the experimental values of ^{13}C NMR, as well as, the long distance carbon-hydrogen NMR-gHMBC correlations. This correlation between charge natural and ^{13}C NMR data are described like the displacement of these charges that cause a variation in the chemical shift of the ^{13}C data, so the variation of the charge natural calculated maybe be followed for a displacement in the chemical shift. In these calculations the interactions with solvent weren't considered.

3. Results and Discussion

Initially, the natural charges of the carbon atoms of the CA molecule were calculated, based on geometry depicted in Figure 2. This procedure is fundamental for the construction of the starting model of the compounds TiCit and TiPbCit (Figures 3 and 4) because the relation between charge and the chemical shift. The comparison of the results of natural charge, for the citric acid (Table 1 and Figure 2), shows that

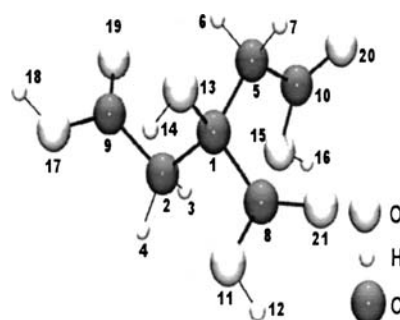


Figure 2. Theoretical Model for the citric acid (CA) molecule, with the numbering of the atoms.

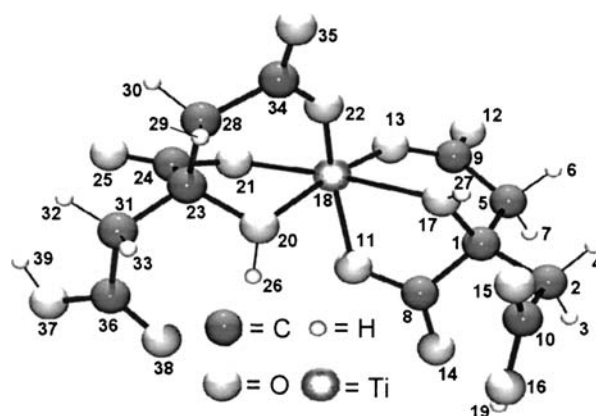


Figure 3. Theoretical Model for the titanium citrate complex, with the numbering of the atoms existing in the molecule.

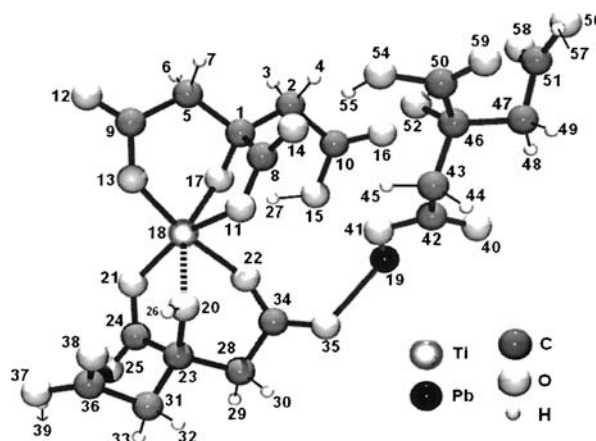


Figure 4. (Model II) Theoretical model for the molecule of titanium and lead citrate, with the numbering of the atoms.

symmetry exists between the carbons C2–C5 and C9–C10, and that the carbon atoms C1 and C8 are not symmetrical.

The complexation form between the titanium ion and two CA molecules was analyzed in the Table 1 and Figure 3. In the model calculated for TiCit (Figure 3), the following symmetry was observed among carbon atoms C1–C23, the central carboxyls C5–C28, the

Table 1. Values of natural charge and chemical shift for the citric acid, for the titanium citrate and for the titanium and lead citrate

Carbon Number	Acid Citric (CA)		Titanium Citrate (TiCit)			Titanium and Lead Citrate (TiPbCit)		
	Natural charge	¹³ C NMR shift (ppm)	Natural charge	¹³ C NMR shift complexed (ppm)	¹³ C NMR shift Not complexed (ppm)	Natural charge	¹³ C NMR shift complexed (ppm)	¹³ C NMR shift Not complexed (ppm)
C1	0.24	76.2	0.22	91.2	76.3	0.18	83.8	78.1
C23			0.22	91.2	76.3	0.20	86.1	78.1
C46						0.21	89.3	78.1
C2	-0.57	46.1	-0.57	46.3	46.3	-0.59	47.8	48.5
C31			-0.57	46.3	46.3	-0.59	45.6	48.5
C47						-0.60	45.6	48.5
C5	-0.57	46.1	-0.59	45.7	46.3	-0.58	47.8	48.5
C28			-0.59	45.7	46.3	-0.57	47.8	48.5
C43						-0.56	49.0	48.5
C8	0.97	179.6	0.96	188.7	179.8	0.94	189.0	184.5
C24			0.96	188.7	179.8	0.91	177.8	184.5
C50						0.92	—	184.5
C9	0.99	176.3	0.98	176.7	176.4	0.93	181.9	181.4
C34			0.98	176.7	176.4	1.02	191.7	181.4
C42						0.97	189.6	181.4
C10	0.99	176.3	0.94	176.4	176.4	0.93	188.6	181.4
C36			0.94	176.4	176.4	0.93	182.0	181.4
C51						0.93	—	181.4

carbons of the side carboxyls C8–C24 and C9–C34. It is important to point out that from the complexation of the titanium ion with the CA molecules, the system acquires the conformation of an irregular octahedron, similar to the octahedron formed in the crystalline PbTiO₃ unit.

When the ¹³C NMR spectra (Figures 5a and 5b) are compared with the CA theoretical data, (Table 1, Figure 2 and Figure 3), it can be verified in the Ti spectrum the splitting of the peaks related to the methylene carbons at the region between 40–60 ppm, related to the central carbons at 70–95 ppm and related to the side and central carboxyls at 170–194 ppm. Moreover, it is verified that the carbons C1–C23 and C8–C24 undergo a lack of protection, thus indicating a reducing of electronic densities of these carbons due to the influence of titanium ion. Also a slight lack of protection is verified for the carbons C9 and C34, what can be explained as a function of a decrease in the electronic density, due to an inductive effect. Therefore, the chemical shifts of the carbons C5 and C28 suffer a contrary effect, that is a protection, due to the anisotropic protection effect provoked by the titanium electronic density. The carbons C2–C31 and C10–C36 do not undergo any change in the chemical shift, indicating that they are not affected by the complexation.

Comparing the natural charges calculated for the carbon atoms in TiCit and TiPbCit (Table 1), it is observed that after the complexation with the lead ion a exist strong alteration in the carbon charge values occur.

Upon the attributions of the chemical shifts in the ¹³C NMR spectrum for the compound TiPbCit, Figure 5c, the charges were considered as a parameter for the comparison with the chemical shift relating to each carbon of the system (Table 1). The charge values calculated for the compound TiPbCit will need be compatible qualitatively with the ¹³C NMR values of chemical shift determined experimentally.

The inductive effect provoked by the lead ion in the carbons C24, C31 and C47 should generate a lack of protection effect. However, an opposite effect is observed, due to the anisotropic effect caused by the electronic density of the metal.

For the Carbon C34, a lack of protection effect is observed, which is enhanced by the fact that it suffers an inductive effect of the electronic density decrease provoked by the Ti and Pb ions, thus contributing to render it the most unprotected carbon of the molecule in the NMR spectrum.

The carbon C10 undergoes a remarkable lack of protection due to the fact that is directly bound to the tricyclic ring {3,2,1}, formed by the atoms C1, C5, C9, O13, Ti18, O11, C8, O17. For the other carbons can be that the inductive effect is predominant and responsible for the calculated charge.

For the methylene region, it was performed an average of the charge values found and the chemical shift was attributed in agreement with these values.

Figure 6 demonstrates the NMR-gHMBC spectrum for TiPbCit, at the (Ti:Pb = 1:1) metal molar ratio. The ¹H

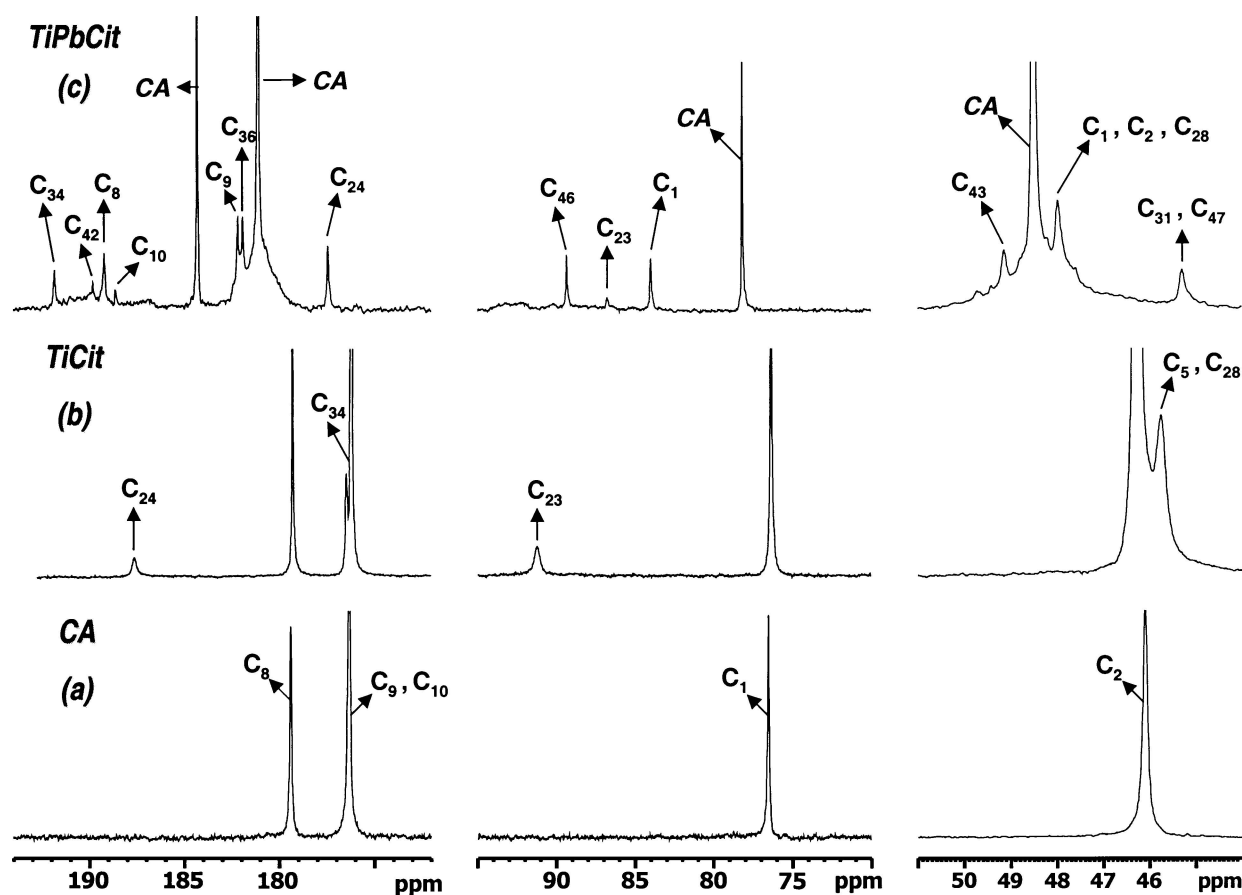


Figure 5. (a) ^{13}C NMR spectrum for the pure citric acid, (b) ^{13}C NMR spectrum for the titanium citrate and (c) ^{13}C NMR spectrum for the titanium and lead citrate, with the indication of the carbons related to each chemical shift.

NMR spectrum, represented in the upper segment of the NMR -gHMBC spectrum can be divided in three different regions. The region 1, with a chemical shift in the range between 2.20–2.50 ppm, refers to the chemical shift of the methylene hydrogens of the free CA, usually represented by two doublets. The region 2, with chemical shift in the range between 2.50–2.75 ppm, is attributed to the methylene hydrogens of the CA molecules, probably complexed to the titanium ion. Finally, the region 3, with chemical shift in the range from 2.75 to 3.30 ppm, is related to the complexation of the lead ion to the titanium citrate.

It can be clearly observed that the methylene hydrogens of the side carboxyls of the citric acids complexed to the lead ion suffer a larger lack of protection than the methylene hydrogens complexed to the titanium atom. This can be explained considering that the bond between the lead ion and the titanium citrate occurs in a directional way and it is partially covalent, exerting therefore an effect to reduce the electronic density, which is larger than the one of the titanium ion, and affecting, preferentially, the carboxyls of the carbons C34 and C42.

The ^{13}C NMR spectrum represented on the left side of the gHMBC spectrum, Figure 6, is also distributed in three different regions. Region A, in the range between 40–60 ppm, is related to the chemical shifts of the methylene carbon

atoms of the complexed and noncomplexed citric acids. The region B, in the range between 60–100 ppm, is relative to the chemical shifts of the central carbon atoms of the complexed and non-complexed molecules of citric acid. Finally, the region C in the range between 160–200 ppm, can be attributed to the carbon atoms, as from the side carboxyls, as from the central carboxyls of the complexed and non complexed citric acid molecules.

Figure 7 is an amplification of the chemical shift regions related to the methylene carbon atoms and the central carbon atoms of the citric acid molecules.

Taking into account the charge results calculated for the carbon atoms, Table 1, the peak at 45.6 ppm can be attributed to the carbons C31 and C47, refers to the non-complexed side carboxyl of the citric acid molecule bound to the lead atom.

Therefore, the complexation region 1 is coherent with that result, because the methylene hydrogens are linked to the methylene carbons of the free carboxyls in the CA molecule, bonded to the titanium ion. It is also observed, in the ^1H spectrum in the range between 2.6–2.7 ppm, a deformation in the doublet relative to the interaction between the methylene hydrogens and the titanium ion, and also a slight coupling in the region 2 to the ^{13}C NMR peak at 45.6 ppm. This effect can be ascribed to the coupling

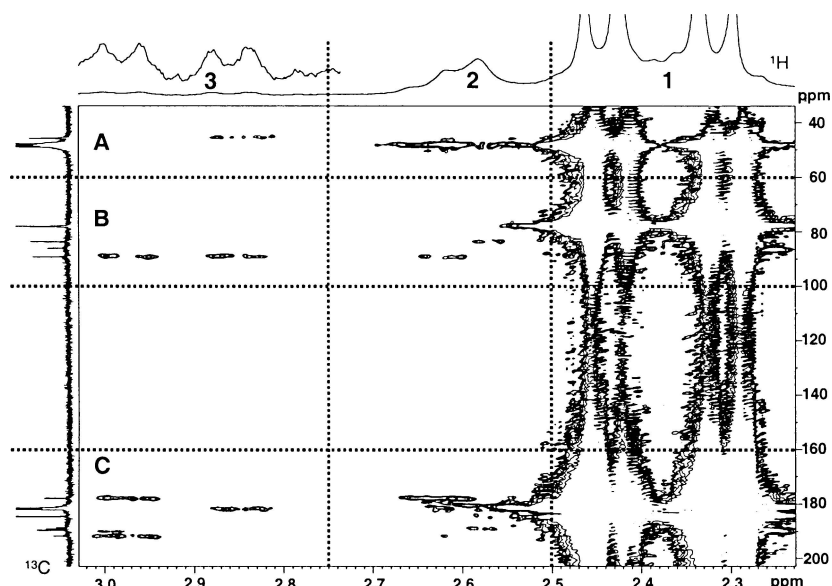


Figure 6. NMR - gHMBC spectrum for TiPbCit, with description of the complexation regions for hydrogen (^1H) and carbon (^{13}C).

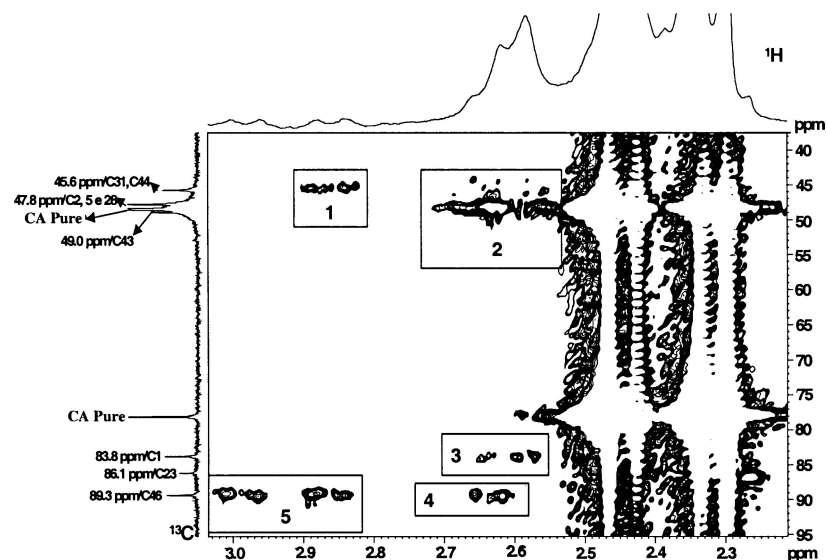


Figure 7. ^{13}C and ^1H NMR - gHMBC spectra for TiPbCit, with the values of chemical shift and numbering of the carbon atoms, for the regions of the methylenes and central carbons of the pure CA and complexed CA molecules.

between the methylene hydrogens of the CA molecule and the carbon atom C31 belonging to the initial titanium citrate molecule, with the consequent smaller chemical shift when compared to the carbon atom C47.

The ^{13}C NMR shift at 47.8 ppm is attributed to the carbons C2, C5 and C28 that coincide with the complexation region 2. This is in agreement with the ^1H NMR shift for the methylene hydrogens bonded to the titanium ion. This shift is of minor importance for the hydrogens, as it is a mesomeric effect caused by the metals. The peaks at 83.8 and 86.1 ppm belong to the central carbons of the CA molecules, bonded to the titanium and lead ions, and they are coupled to the methylene hydrogens of the network former titanium

citrate, regions 3 and 5, respectively. The peak at 89.3 ppm belongs to the carbon C46 linked to the lead ion and suffers a large lack of protection, as it suffers an inductive effect from the lead ion.

An enlargement of the chemical shift regions regarding the carbon atoms of the side and the central carboxyls of the citric acid molecules is shown in Figure 8. This correlation allows visualizing with a higher accuracy the regions of the complexation of CA molecules with the metals from the system.

It is observed that the ^{13}C NMR spectrum shift at 177.8 ppm couples, as with the ^1H NMR peak for the citrate complexed to the titanium, at the 2.50–2.60 ppm range, as

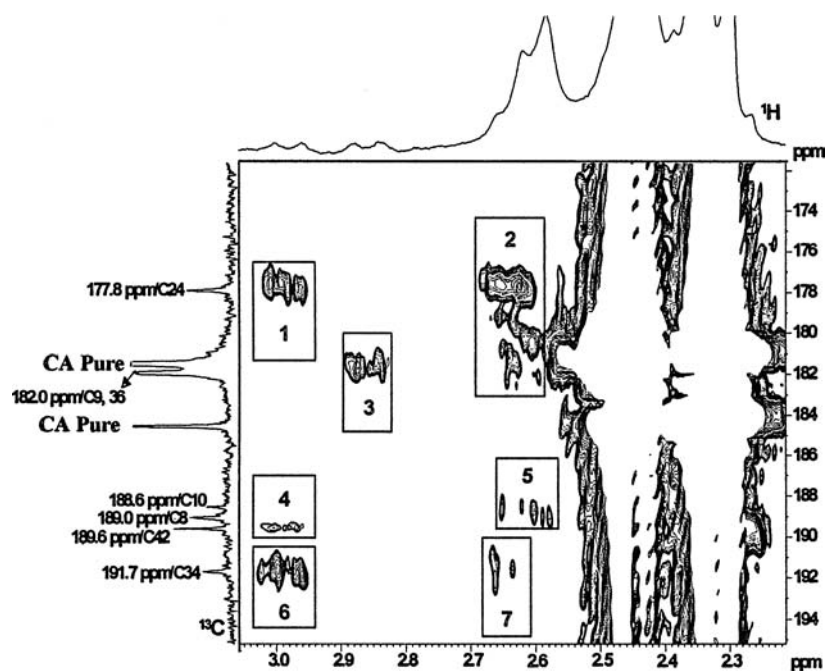


Figure 8. ^{13}C and ^1H NMR – gHMBC spectra for TiPbCit, with the values of chemical shift and numbering of the carbon atoms, for the regions of the coupling of the side and central carboxyls of the pure CA and complexed CA molecules.

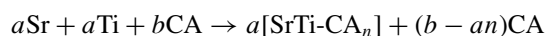
with the peak at the shift range between 2.90–3.30 ppm. This fact proves that the model is coherent with the results, because the carbon C24 is linked, to the titanium ion as, well as to the lead ion, and influenced by both.

The peaks at 181.9 and 182.0 ppm are ascribed to the carbons C9 and C36, respectively. The atom C9 belongs to the CA molecule bonded to the titanium atom (region 2). The atom C36 belongs to the CA molecule bonded to the titanium and lead ions (region 3). The peaks at 188.6 and 189.0 ppm correlate with the carbons C10 and C8, respectively, and they are coupled to the CA molecule only linked to the titanium ion (region 5). The peak at 189.6 ppm is attributed to the carbon C42, that belongs to the CA molecule that is only linked to the lead ion (region 4). Finally, the peak at 191.7 ppm is ascribed to the carbon C34, which is the carbon atom that most suffers the effect of electronic density decrease, because it is bonded to both, titanium and lead ions. It can be observed once again that the theoretical results fit very well with the experimental results.

Experiments involving the technique of Raman spectroscopy have been used in many works, as a manner of monitoring the reaction stages. Recent works using this technique were undertaken for the study of the PbTiO_3 phase change with increasing calcination temperature [15].

Analyzing the Raman spectra of Figure 9, some evidences of heterometallic compound formation of the type PbTi-CA_3 can be noticed, which is very similar to the that proposed for BaTiO_3 [12]. The present work demonstrates that the Ba^{2+} and Ti^{4+} ions are complexed by the citric acid in solution, forming a stable stoichiometric heterometallic compound ($\text{Ba}:\text{Ti} = 1:1$), which is the same used for the ti-

tanium and lead citrate ($\text{Pb}:\text{Ti} = 1:1$). The complexation can be schematically represented by the following reaction. (The reaction charges were omitted to simplify the example).



Evidences for the formation of heterometallic compound of the type $\text{Pb}:\text{Ti}:\text{CA} = 1:1:3$ (i.e. PbTi-CA_3) can be observed in Figure 9. This figure shows the spectra of pure citric acid (a), citric acid with ethylene glycol (polymerized) (b), pure titanium citrate (c), titanium citrate with ethylene glycol (polymerized) (d), titanium and lead citrate (e) and titanium and lead citrate polymerized (f). An important observation is that the Raman spectra are interpreted in terms of a simple overlap of the individual spectra, from the pure citric acid (a), up to the $\text{Pb}:\text{Ti}:\text{CA}:\text{EG}$ spectrum (f).

The simultaneous presence of the lead and titanium cations, in a solution of citric acid and ethylene glycol, can cause considerable changes in the chemical shift $\nu(\text{C}=\text{O})$, for the Raman spectrum in the region close to 1750 cm^{-1} .

Comparing the spectra of pure citric acid and citric acid with ethylene glycol in the region between $1600\text{--}1800\text{ cm}^{-1}$ it can be noticed that upon the addition of ethylene glycol, three different peaks cease to exist in that region, related to the free carboxyls of the citric acid, and only one large peak exists. This effect is observed in all the compositions analyzed in the present work, what shows that the addition of ethylene glycol before the cations, as earlier proposed by Pechini (1967), directly affects the possible metal complexation sites. This is harmful for the formation of the

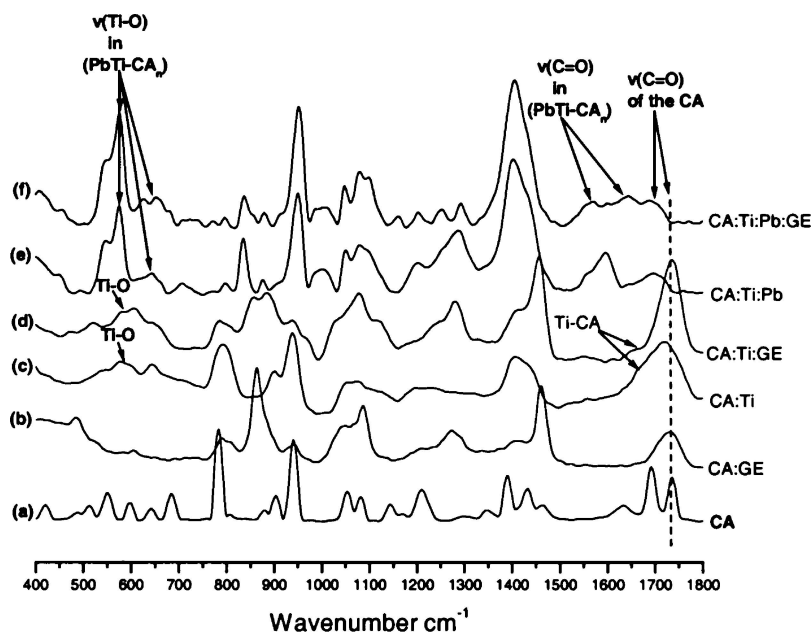


Figure 9. FT-Raman spectra. (a) Pure citric acid, (b) Citric acid with ethylene glycol, (c) Citric acid with titanium, (d) Citric acid, titanium and ethylene glycol, (e) Citric acid, titanium and lead and (f) Citric acid, titanium, lead and ethylene glycol.

complexes, because ethylene glycol is directly competing for the complexation sites.

In the spectrum of Figure 9c, it is observed that with the addition of titanium to the pure citric acid, occurs a modification (enlargement) of the peak close to 1750 cm^{-1} . This fact happens due to complexation of the carboxyls with the titanium ion, what confirms the previous discussion on the competition for the complexation sites. Later, with the addition of ethylene glycol to the titanium citrate, the resulting spectrum, Figure 9d, was obtained. The polymerization effect facilitates the visualization of the shoulder relative to the complexation of titanium with the carboxyl in the region close to 1750 cm^{-1} . So, for titanium citrate, with or without polymerization, there is a peak in the region 600 cm^{-1} attributed to the Ti–O bonds.

When lead ions are added to the titanium citrate, a great modification is observed in the peak in the region close to 1730 cm^{-1} , with the subsequent existence of two peaks, one at 1696 cm^{-1} and other at 1596 cm^{-1} , showing the Pb^{2+} ion linked directly to the titanium complex and affecting the carboxyls of the complex. This effect can also be observed in the region close to 550 cm^{-1} , where occurs an enlargement and a much more visible separation of the peaks. In the spectrum, Figure 9(f), takes place the polymerization of the titanium and lead citrate, what defines better the peaks in the regions close to 550 cm^{-1} and in the interval between $1500\text{--}1800\text{ cm}^{-1}$. The entrance of the lead atom leads to a modification in the orientation of the metal plans in relation to the oxygens of the molecule of titanium and lead citrate, reinforcing the theory of lead as a network orientator.

Figure 10 compares the Raman spectrum of the pure citric acid [23], Fig. 10(a), with a spectrum of the titanium and

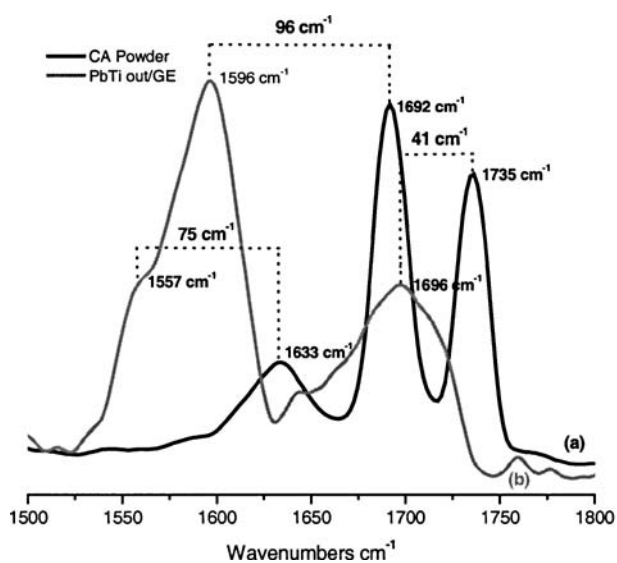


Figure 10. FT-Raman spectra for the citric acid and the Ti and Pb citrate, with an enlargement the carboxyl region.

lead citrate, Fig. 10(b), for a frequency in the region between $1500\text{--}1800\text{ cm}^{-1}$ [24]. There are two strong and sharpened peaks at 1750 cm^{-1} and 1692 cm^{-1} in the anhydrous citric acid, Fig. 10(a). It is also observed a less intense peak at 1633 cm^{-1} , that can be ascribed to the central carbon of the molecule, linked to a hydroxyl and a carboxyl, or even related to the stretching of the group --COO^- , relatively well intense in the Raman spectra [12].

Those peaks at 1735 cm^{-1} and 1692 cm^{-1} are attributed, respectively, to the stretching $\nu(\text{C=O})$ of the central carboxyl, and stretching $\nu(\text{C=O})$ of the lateral carboxyls.

These peaks are used as guidelines to determine if the carboxyl-COOH of the citric acid is or is not coordinated with the metal.

A shift is observed in the signal, Figure 10(b), from 1735 cm^{-1} to 1696 cm^{-1} . This can be ascribed to the bond of the central -COOH group possibly to the titanium ion. Also a displacement from 1692 to 1596 cm^{-1} is observed, which is possibly related to the bond of one of the side carboxyls with a Ti^{4+} ion or yet to a Pb^{2+} ion.

Finally, a peak displacement is observed from 1633 cm^{-1} to 1557 cm^{-1} , what can be referred to decrease of the electronic density in the central carboxyl. In the spectrum (b) we can visualize a very intense displacement in the region related to the complexed carboxyls. This can be attributed to the electronic density of the cation complexed in the system, which, in this case, is the lead atom with a high electronic density.

4. Conclusions

The correlation between the experimental and theoretical results allowed the proposal of a model for titanium and lead citrate complex.

The theoretical results show that the titanium citrate, when the lead ion is added, suffers considerable changes, in the values of natural charge for the atoms of carbon and hydrogen in relation to the values of pure titanium citrate. These changes can be explained by the directional and covalent bond between the lead atom and the titanium citrate, what causes an electron withdrawing effect much larger than the one due to the titanium atom. These results were of fundamental importance to the determination of the complexation model of the titanium and lead citrate, because they coincide pretty well with the chemical shifts of the ^{13}C NMR, ^1H and gHMBC spectra.

The FT-Raman experiments were used as a further technique to confirm the formation of a complex, involving atoms of titanium and lead. Upon the addition of lead atoms to the pure titanium citrate, variations were observed in the bands related to the Ti-O bonds. This permitted to deduce that the titanium and lead atoms belong to the same citrate complex.

These studies demonstrated that the obtained citrates present, in its liquid phase, octahedral plans formed by oxygen and the metal, which closely resemble the octahedral plans of the crystalline PbTiO_3 unit cell. This allows to propose that the titanium and lead citrate possesses a topological characteristic which is formed at the moment of the complexation in the liquid phase, and that such characteristic will be of fundamental importance for the final properties of the solid.

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