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Synthesis and characterization of Cu(II), Zn(II) and Sm(III) metal complexes with itaconic acid

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Resumen

Síntesis y caracterización de complejos metálicos de Cu(II), Zn(II) y Sm(II) con ácido itacónico. En este trabajo, se presentan los resultados de la síntesis en solución alcohólica y la caracterización de complejos metálicos de Cu (II), Zn (II) y Sm (III) con el ácido itacónico. Todos estos materiales se caracterizaron por espectroscopía FT-IR y de UV-visible, análisis termogravimétrico (TGA), análisis de volatilización térmica (TVA), conductimetría y difracción de polvo. Los análisis FT-IR y UV sugieren una coordinación monodentada para los complejos de zinc y cobre y los resultados termogravimétricos sugieren que existen dos moléculas de agua coordinadas en la estructura y cuya estequiometría sería $Zn(C_5H_4O_4)\cdot 2H_2O$ y $Cu(C_5H_4O_4)\cdot 2H_2O$, respectivamente, donde el ligando es el carboxilato de ácido ($C_5H_4O_4$). Para el complejo de samario se sugiere una estructura iónica con una estequiometría $Sm_2(C_5H_4O_4)_3\cdot 4H_2O$. El estudio de difracción de rayos-X indica que los complejos de Cu y Zn cristalizan en celdas monoclínicas con grupo espacial $P2_1/c$.

Palabras claves: ácido itacónico; itaconato; cristalización; complejos metálicos; complejos monodentados e iónicos

Abstract

In this work, the synthesis in alcoholic solution and characterization of Cu(II), Zn(II), and Sm(III) metal complexes with the itaconic acid are presented. All materials were characterized by the FT-IR and UV spectroscopy, thermogravimetric analysis (TGA), thermal volatilization analysis (TVA), conductimetry, and powder diffraction. FT-IR and UV-visible analyses suggest a monodentate coordination for the zinc and copper complexes and thermogravimetric results indicate the presence of two water molecules in the structure with a stoichiometry $Zn(C_5H_4O_4)\cdot 2H_2O$ and $Cu(C_5H_4O_4)\cdot 2H_2O$, respectively, where the ligand is the acid carboxylate ($C_5H_4O_4$). For the samarium complex an ionic structure with a $Sm_2(C_5H_4O_4)_3\cdot 4H_2O$ stoichiometry is suggested. The X-ray diffraction study indicates that the Cu and Zn complexes crystallize in monoclinic cells with space group $P2_1/c$.

Keywords: Itaconic acid; itaconate; crystallization; metal complexes; monodentade and ionic complexes

Introduction

Itaconic acid (IA) is a natural compound, which can be obtained from the fermentation of *Aspergillus itaconicus* and *Aspergillus terreus* fungi[1,2]. This dicarboxylic acid has two different acid groups that can be selectively esterified[3]. The acid and its esters, possibly due by their structural similarity with acrylates and methacrylates, have found interest in the preparation of high molecular weight polymers and various copolymers with other vinyl monomers since they were first polymerized by Cowie in the mid-70s[4-8]. This carboxylic acid has been used in the polymer industry in copolymerization reactions to improve properties such as adhesion, emulsion stability, and dye receptivity[9].

Moreover, itaconic acid has been employed in the synthesis of hydrogels (HG)[10,11], and more recently itaconic acid and the monomethoxy ethyl itaconate have been used in the synthesis of superabsorbent hydrogels (HG), finding that in some cases they are capable of absorbing up to 43,00% of their weight in water[12]. These materials are also capable to absorb metal ions from aqueous solutions[13]. It has been shown that the carboxylic groups of itaconic acid or its monoesters are responsible for the adsorption process of metallic ions and it is believed that this occurs through different mechanisms among which is the complexes formation[13].

On the other hand, the use of itaconic acid as a ligand in the synthesis of metal complexes has also been reported in several

studies, in which were used different metal salts, in particular nitrates and carbonates. Among the first studies is that of Yasuda *et al.*[14] in which they found by acid-base titration that for Pb, Cu, Cd, Zn and Ni, the metal: itaconic molar ratio in the complexes was 1:1. Afterward, in 1987 Allan[9] synthesized itaconic acid complexes with Mn, Co, Ni, Cu and Zn, demonstrating by IR spectroscopy that the complexes, except for Cu, possessed water of crystallization and proposes that the metal: ligand: water molar ratio is 1: 1: 1. In 1994 El-Bellihi[15] studied complexes with Cu and Co, by elemental analysis, IR, TGA/DTA, and powder diffraction, obtaining that the empirical formula of these complexes was $M(C_5H_4O_4)_2.H_2O$. More recently Wibowo *et al*. (2018)[16] synthesized itaconic acid complexes with Zn, finding by X-ray diffraction, electron microscopy, IR spectroscopy, and thermogravimetric analysis, that the metal: ligand: water molar ratio is 1: 1: 2.

In particular, the interest in studying Cu and Zn complexes lies in the fact that these metals are involved in several biological processes and after iron they are the most abundant transition metals in the human body. There are a considerable number of metalloproteins and other enzymes that contain Cu and Zn[17]. Due to this they have also been used in the study of complex that presents antitumor and anticancer activity[18-20].

From the crystallographic point of view, transition metal (Zn, Cd)[16, 21], earth-alkaline (Ba, Ca)[22, 23], and lanthanide complexes (La, Gd, Tb, Dy)[24,25] with itaconic acid have been reported.

In these complexes, packing in the solid-state could originate diverse cohesive interactions that allow the formation of coordination polymers were water molecules would complete the geometry coordination around metals. In this sense, in recent years, significant attention had been paid in designing and development of coordination polymers which are undoubtedly very promising as multifunctional materials because they can have multiple applications in gas storage, heterogeneous catalysis, chemical sensors, energy conversion, drug delivery, among others[26].

To continue the study on the synthesis, characterization and applications of superabsorbent hydrogels, this work describes the synthesis of Cu (II), Zn (II) and Sm (III) metal complexes with itaconic acid, in alcoholic solution, and its characterization using FTIR, UV-visible spectroscopy, TGA, TVA, conductimetry, and powder X-ray diffraction techniques.

Experimental

Reagents

Itaconic acid (IA) (Aldrich 99%), copper acetate monohydrate [$Cu(CH_3COO)_2.H_2O$, Sigma-Aldrich 98%], zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$, Sigma-Aldrich 99.9%], samarium acetate hydrate [$Sm(CH_3COO)_3.H_2O$, Sigma Aldrich 99%). The solvents used in the synthesis were reactive grade methanol and ethanol and deionized 18 Ω water

Synthesis of the complexes

The synthesis was performed following a modification of the procedure described in the literature[27], where the metallic acetate is dissolved in 10 ml of methanol, and the itaconic acid in 10 ml of ethanol, with a ratio 1:2 molar (acetate: ligand). Mixing both solutions slowly and allowing them to react for 2 hours with gentle heating (~ 40 ºC). The final product is filtered under vacuum and washed several times with 10 ml portions of ethanol.

Characterization

The products were characterized by melting point measurements, solubility, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal volatilization analysis (TVA), conductimetry, and powder X-ray diffraction. For the Cu complex (II) a conductimetry study was carried out.

Infrared spectra were recorded on a Perkin Elmer 2000 FTIR instrument. The samples were prepared as KBr discs or films casting on KBr cells.

Thermogravimetric analyzes (TGA) were carried out using a Perkin-Elmer TGA-7 thermobalance and scans were performed at heating rates of 10 °C/min between 20 and 550°C under nitrogen flow. Thermal volatilization analysis was carried out in a vacuum line, heating the samples of about 100 mg from room temperature to 390°C for 30 min under a moderate initial vacuum. Volatile fractions were condensed at room temperature and analyzed by FTIR spectroscopy.

Conductimetric titrations were performed using a Benchtop conductivity Meter 860032 Sper Scientific. The measures were carried out by titring a solution 0.05 M itaconic acid with one of copper acetate of the same concentration. The conductance was measured for each addition of the saline solution. Each measure was made by triplicate. The molar ratio of the complex was determined by the inflection point in the conductance/titrant volume curve.

The electronic absorption spectra were performer using a Thermo Scientific Evolution 300 UV-Visible Spectrophotometer between 400-700 nm.

The X-ray powder diffraction patterns for the itaconic complexes with Cu, Zn, and Sm were collected at room temperature in a Siemens D5005 diffractometer using CuKα radiation (λ = 1,5418 Å). A small quantity of each compound was ground mechanically in an agate mortar and pestle and mounted on a flat holder covered with a thin layer of grease. The samples were scanned from 5-50° 2θ, with a step size of 0.02° and counting time of 10s. Quartz was used as an external standard.

Results and discussion

The synthesis of the copper (II), zinc(II), and samarium (III) itaconic acid complexes were carried out as previously described. The copper complex was obtained with a yield greater than 80%, while that for Zn and Sm yields were about 65

and 35%, respectively. The three obtained products decompose before melting and, unlike the starting reagents, the complexes were insoluble in methanol and ethanol. The difference in solubilities about the starting materials, is indicative that a reaction took place. Another fact that shows the formation of the complexes is that the decomposition temperatures were different from that of the starting salts. Table 1 shows yields and some characteristics of the obtained complexes which are compared with those of the starting reagents.

Figure 1 shows the IR spectrum of the complex obtained from the reaction between itaconic acid and zinc acetate, which can be considered as representative of the three complexes synthesized in this work, since all the spectra were quite similar. The spectrum of the product is compared with that of the itaconic acid and the corresponding acetate.

There it can be seen several signals that indicate that itaconic acid reacted with Zn. The disappearance of the OH stretching signal of the carboxylic acid between 3400 and 2400cm^{-1} and displacement and splitting of the carbonyl signal from 1704 cm^{-1} at 1590 and 1389 cm^{-1}, characteristics of carboxylate groups, indicate that the carboxyls groups react with the metal ion. There is worth noting that de frequencies of these signals are different from those of Zn acetate, which are found in 1564 and 1443 cm^{-1}. Additionally, the double bond, C=C band that appears at 1629 cm^{-1} in the acid, due to the conjugation with the carboxyl group, is displaced at 1654 cm^{-1} in the product. All these observations are indicative of the formation of the complex, and further suggest that itaconic acid coordinates to the metal through the carboxylate groups. Furthermore, the O-H stretch band (3600 and 2600 cm^{-1}), suggests that the complexes contain a certain amount of water, as confirmed by the TGA studies that will be described later.

On the other hand, it is a known fact that carboxylates can coordinate to metal ions in different ways and how they do so is related to the value of the difference between the frequencies of the asymmetric (ν_{As}) and symmetric (ν_S) bands of the carboxylate groups, as was proposed by Deacon and Phillips[28]. They found that when the values of $\Delta\nu_{As-S} \leq 100$ cm^{-1}, the acetates act as bidentate chelates or bidentate-bridges; if values are $\Delta\nu_{As-S} \geq 200$ cm^{-1} they act as monodentate ligands and when values are between 100 cm^{-1} and 200 cm^{-1} they form ionic compounds.

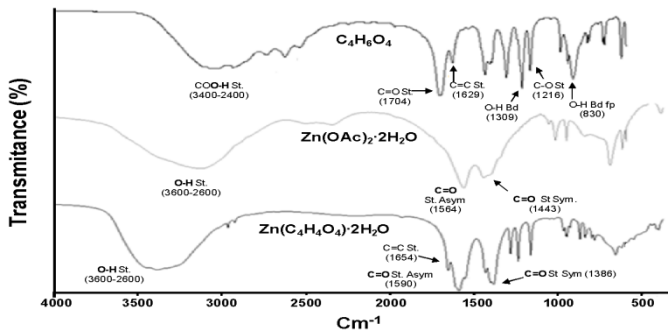


Fig. 1: FTIR spectra of itaconic acid ($C_5H_6O_4$), zinc acetate $Zn(Ac)_2{\cdot}2H_2O$, and the reaction product.

In table 2 are shown the frequencies values in the zone 1300 to 1750 cm^{-1} of the complexes, as well as for the salts and IA. There it can be seen that the values of $\Delta\nu_{As-S}$ for Zn and Cu complexes are 204±6 y 197±6 respectively, these values are in the border of a monodentate coordination and an ionic interaction. In order to clarify the type of interaction for these complexes, the UV-Visible spectra of the copper complex were compared with the copper acetate. In the case of the acetate, the spectrum showed a maximum at 774 nm while for the complex the maximum appears at 686 nm. The electron pairs of the carboxylate groups ligands in ionic compounds, do not alter the crystalline field and no change would have been seen in the spectrum if the copper complex ($Cu(C_5H_4O_4)$) would be ionic. Therefore this hypsochromic shifting of the maximum from 744 to 686 nm confirms that coordination between each carboxylate group in IA and the metallic ion must be monodentate; thus, IA acts as a bidentate ligand.

Table 1. Yield, color, solubility, decomposition temperatures of the complexes obtained.

Compound[(a)]	Yield (%)[(a)]	Color	Solubility	Melting or decomposition temperature (ºC)
Itaconic acid		white	ethanol, methanol	165
$Cu(CH_3COO)_2.H_2O$	-	blue	ethanol	116
$Zn(CH_3COO)_2.2H_2O$	-	white	ethanol, methanol, water	237 (d)
$Sm(CH_3COO)_3.H_2O$	-	beige	water	300 (d)
$Cu(C_5H_4O_4)\cdot2(H_2O)$	85,00	green-blue	hot THF	>240 (d)
$Zn(C_5H_4O_4)\cdot2(H_2O)_2$	65,22	white	DMSO	>390 (d)
$Sm_2(C_5H_4O_4)_3\cdot4(H_2O)$	35,05	white	water	>330 (d)

[(a)] Compositions and yields calculated based on the results obtained in the thermogravimetric study: (d) = decomposes. THF = tetrahydrofuran. DMSO = dimethyl sulfoxide.

Table 2. Frequency values in the 1300 to 1750 cm^{-1} region for complexes, acetates and IA.

Compound	$\nu C{=}O_{AS}$ (cm^{-1})	$\nu C{=}O_S$ (cm^{-1})	$\Delta\nu_{AS-S}$ (cm^{-1})	$\nu C{=}C$ (cm^{-1})
$Cu(C_5H_4O_4)\cdot2H_2O$	1615	1418	197	1654
$Zn(C_5H_4O_4)\cdot2H_2O$	1590	1386	204	1652
$Sm_2(C_5H_4O_4)\cdot4H_2O$	1546	1433	113	1643
$Cu(OAc)_2.H_2O$	1600*	1435-1426[28]	165	-
$Zn(Oac)_2.2H_2O$	1564	1443	121	-
$Sm(OAc)_3.H_2O$	1544	1455	89	-
IA	1700	-	-	1629

Since both, acetate and the Zn complex are colorless, it was not possible to obtain their UV-vis spectra, but given the similarities between the Cu and Zn complexes and the $\Delta\nu_{As-S}$ value obtained for Zn complex, it can be assumed that this complex is also monodentate.

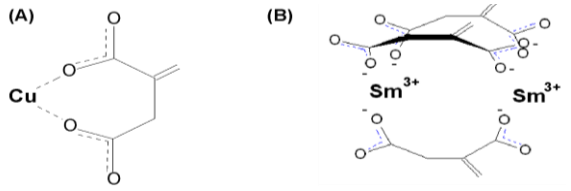


Fig. 2: Hypothetical representation of the ($C_5H_4O_4$)/metal junction. (a) Cu($C_5H_4O_4$) (monodentate) (b) $Sm_2(C_5H_4O_4)_3$ (ionic). Here water molecules are not shown, only the metal-($C_5H_4O_4$) interaction.

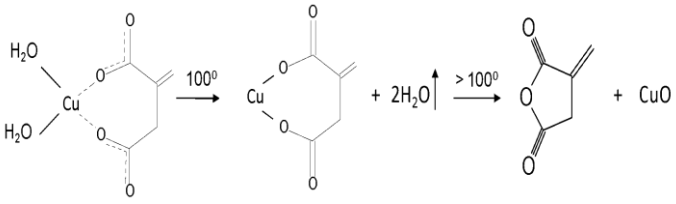
As for both complexes the interaction between the carboxylate groups and the metal center is of a monodentate type, it means that both carboxylate groups must participate in the coordination as shown in Figure 2a. This would suppose a neutral species and the itaconic-metal relationship would be 1: 1.

In the case of the Sm complex, the $\Delta\nu_{AS-S}$ value is 113 ± 6, which strongly suggests that this complex is ionic. Besides this metal ion produces a different type of coordination from the other metals, the samarium is trivalent and the ligand-metal ratio could be 3:2 See figure 2b.

The characteristics of the reaction products and the results obtained by IR spectroscopy clearly indicate that itaconic acid reacted with the metal through the carboxylate groups. IR spectra also suggest the presence of water in the compound. However, these results do not indicate the structure or stoichiometry of the complexes, as well as how many IA molecules there are per metal atom and whether the water is part of the complex or it is just moisture in the sample.

In order to try to estimate the stoichiometry of the complexes, a TGA study was carried out, which in addition to determine the stability of the compounds, allows to establish the degradation process of the material and compute the metal-ligand ratio for all the compounds.

In figure 3, the thermograms obtained for the Zn/($C_5H_4O_4$) and Cu/($C_5H_4O_4$) complexes, in which the metal is divalent, are shown.



Scheme 1: Degradation process of the Cooper complex in TGA

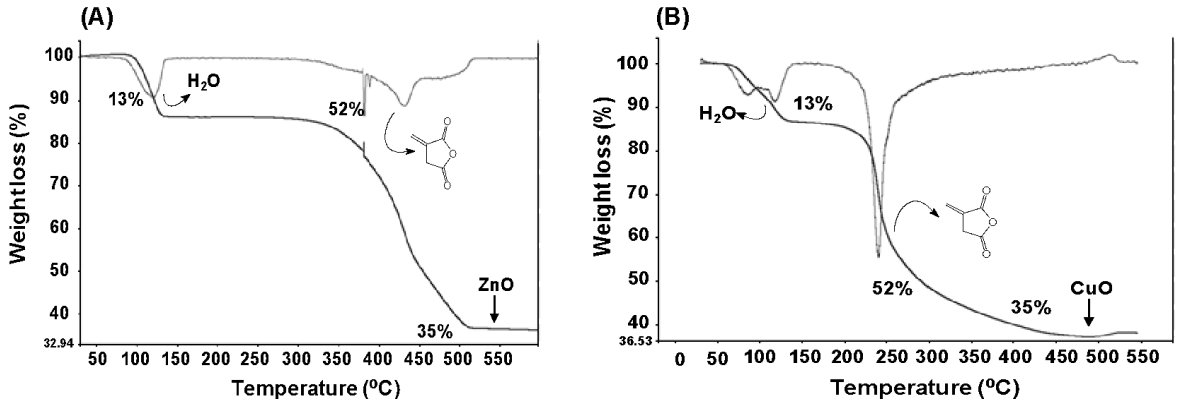


Fig. 3: TGA and DTGA thermograms of the Zn/($C_5H_4O_4$) (A) and Cu/($C_5H_4O_4$) (B) complexes.

Table 3. Compositions measured by TGA and calculated values for the Zn, Cu, and Sm complexes.

Components	Complex molar composition calculated (%)	Sample composition measured by TGA (%)[a]	Complex molar composition obtained by TGA (%)
	$Zn(C_5H_4O_4)\cdot 2(H_2O)$		
Zn	28.5	35[b]	28.1
Ligand	55.8	52[c]	59.2
$2H_2O$	15.7	13[d]	13
	$Cu(C_5H_4O_4)\cdot 2(H_2O)$		
Cu	28.0	36[b]	28.8
Ligand	56.3	51[c]	58.3
$2\cdot H_2O$	15.7	13[d]	13.0
	$Sm_2(C_5H_4O_4)_3\cdot 4(H_2O)$		
2·Sm	39.7	Nd	-
3·Ligand	50.8	Nd	-
$4\cdot H_2O$	9.5	10[d]	10

[a] Measured by TGA using equation of **Scheme 1**; [b] Residue al mass ZnO or CuO; [c] Weight loss in the second step as itaconic anhydride; [d] Weight loss in the first step (H_2O).

The curve shows that the material loses weight in two clearly differentiated stages; the first one occurs approximately between 80 and 138ºC and that corresponds to 13% of the mass of both samples. It is well known that water is released at temperatures close to 100ºC and when it is coordinated it can be released at slightly higher temperatures[28]. The fact that water releases ends close to 140º for the Zn complex and 150º for the Cu complex, allows us to suppose that the water present would be coordinated with the metal.

The second stage begins above 200 and ends near 500°C. For zinc-complex, this stage takes place at least two processes, as evidenced by the change in the rate of degradation around 450ºC and which is more evident in the DTGA curve. In the case of the cooper-complex, it appears to occur in one step. This stage, which represents a weight loss of 52 and 51%, respectively, corresponds to the release of the ligand. It can be released as itaconic anhydride, as may be expected in this temperature range[15,29].

At this point, it is worth mentioning that in the IR spectrum (not shown) of the small amount of condensation product released when the Cu complex is heated to around 250 ºC in the TVA, the main IA bands appear, confirming that the ligand is effectively released at this time.

When heating reaches temperatures close to 500ºC, a residue with a mass equivalent to 35-37% of the initial weight is obtained. This residue corresponds mainly to metal oxide, in this case ZnO or CuO. The formation of metallic oxides is in agreement with previously reported results[1,9,30,31]. The entire degradation process that occurs in the TGA experiment is shown in Scheme 1.

At this point is important to remark two aspects related to the degradation process: It is well known that when polyitaconates are heated at temperatures near 100°C, they form anhydrides and release their side chains as alcohol[3,32]. This fact suggests that the complexes may begin to decompose at temperatures close to 100 °C, in a similar way to form the itaconic anhydride which can undergo further heating, in other decomposition products that subsequently volatilizes at a higher temperature. The little amount itaconic acid observed in the degradation process when the sample was heating over 250°C in TVA, could be a secondary product resulting from the hydrolysis of the anhydride and the released water during the heating of the complex at this temperature. In the TVA, the heating was not progressive as in TGA. It was done fast and, probably, water release from the complex at the same time the anhydride was formed.

Knowing the degradation products and their proportion, it is possible to calculate the corresponding components of the complex assuming an empirical formula of $M_n(C_5H_4O_4)_m \cdot Z(H_2O)$.

The percentage composition obtained by TGA for the Zn and Cu complexes is shown in table 3, and the measured values are close similar to the empirical formula of $M(C_5H_4O_4)\cdot 2H_2O$.

To corroborate the $(C_5H_4O_4)$/Cu molar ratio in the copper complex, conductometric evaluation was carried out in the complex formation reaction. For this, methanolic solutions of itaconic acid and copper acetate of equimolar concentrations of approximately 0.05 M were prepared. Methanol was used as a solvent since the copper complex is insoluble in this solvent and its contribution to conductance must be negligible. The average behavior of the conductance *vs*. the volume of copper salt added to the IA solution is represented in figure 4. The two curves intersect around 5 mL, which is the volume used of the IA solution. This fact corroborates that the $(C_5H_4O_4)$/Cu ratio is 1:1 as suggested by IR spectroscopy and indicated by the TGA.

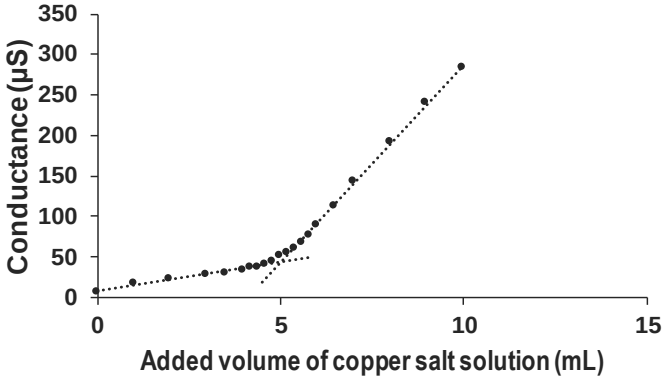


Fig. 4: Variation of conductance *vs*. added volume of the copper (II) solution.

The TGA of the Sm complex (figure 5), as for the two previous complexes, shows two processes of mass loss, the first one that occurs around 100ºC, is associated with the water release of the complex, and that corresponds to 10% of the total mass of the sample. The second one, which surely involves the loss of the ligand, begins at 250º and continues over 600ºC out of the range of work of the instrument. This fact prevent us to determine experimentally how much mass is lost at this stage and therefore determine its composition.

However, from the IR results it can be assumed that the samarium complex is ionic and as for the others two complexes, the metal does not change its valence after it is formed.

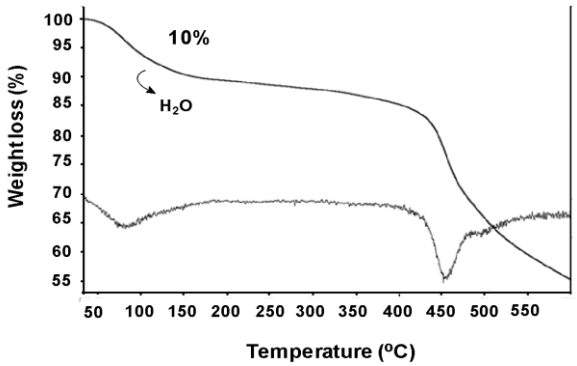


Fig. 5: TGA and DTGA thermograms of the Sm/IA complex.

These facts strongly suggest that the molar composition of the complex may be $Sm_2(C_5H_4O_4)_3$ as shown in figure 2. Moreover, if the purified complex has a water contents of about 10%, ninety percent corresponds to the $Sm_2(C_5H_4O_4)_3$, indicating the complex must contain 4 water molecules. This structure shows some resemblance to the stoichiometry of the samarium complexes with amino acids previously reported by Contreras *et al.*[33].

The X-ray diffractograms of Cu and Zn itaconate complexes are shown in figure 6. For samarium complex an amorphous pattern was obtained.

The powder patterns of the reagents used in the synthesis were calculated from their crystal structures searched in the Cambridge Structural Database (CSD, version 5.41, March 2020)[34], for itaconic acid (ITACON), copper acetate MEQKEZ) and zinc acetate (ZNAQAC05). Figure 7 shows the comparison of powder patterns between the reagents and the formed complexes where it is evident the formation of new compounds.

For the Cu and Zn itaconate complexes, the powder patterns were completely indexed using the program Dicvol04[34], which gave a unique solution in monoclinic cells. The systematic absences determined the space group to be $P2_1/c$. This result confirms a previous study reported for the Zn complex[16].

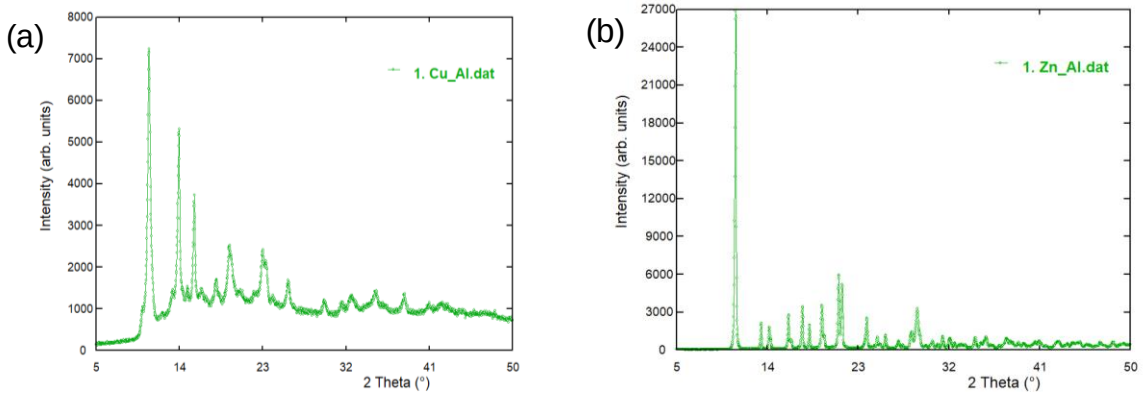


Fig. 6: X-ray diffractograms of (a) Cu and (b) Zn itaconates.

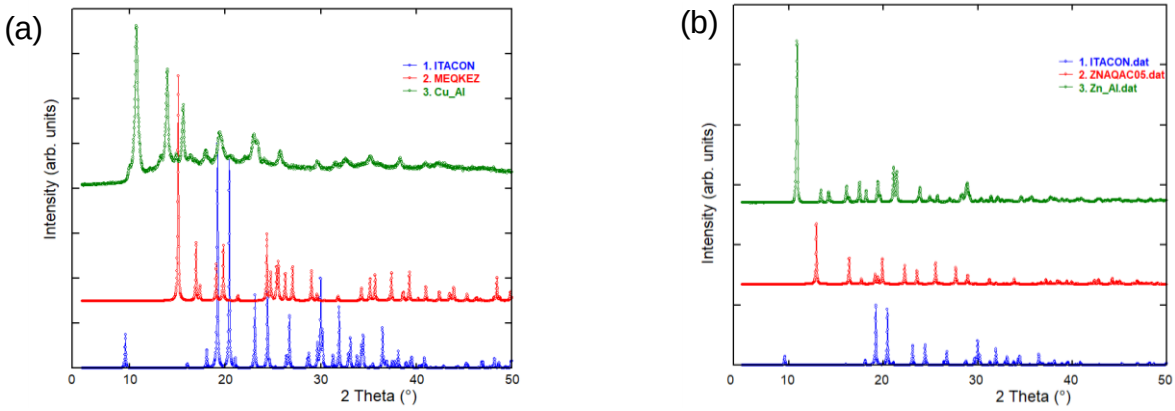


Fig. 7: (a) X-ray powder diffraction patterns for itaconic acid, Cu acetate and Cu itaconate complex. (b) X-ray powder diffraction patterns for itaconic, Zn acetate, and Zn itaconate complex.

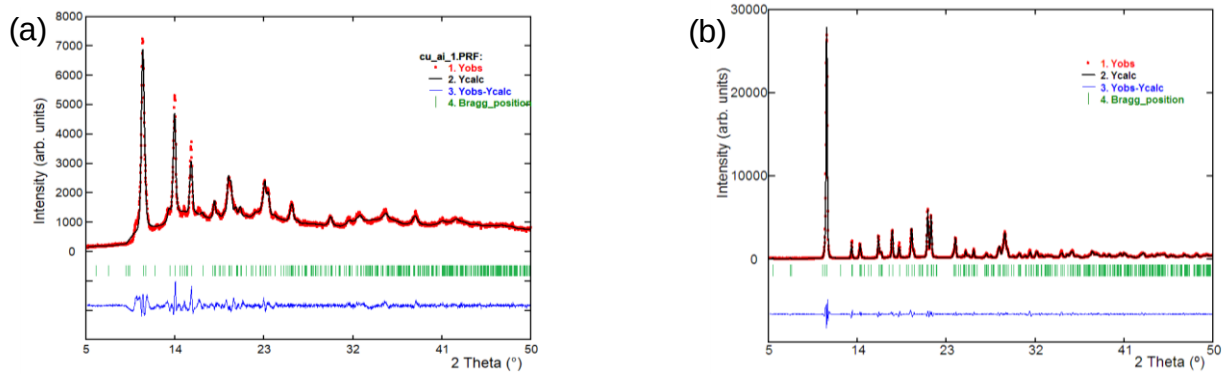


Fig. 8: Le bail refinement for (a) Cu and (b) Zn itaconates.

With the purpose of confirming the unit cell parameters, a Le Bail refinement[36] of the whole diffraction pattern without structural was carried out using the Fullprof program[36]. Figure 8 shows a very good fit between the observed and calculated patterns in both cases. Unit cell parameters for Cu itaconate: *a*= 13.121(3) Å, *b*= 14.747(3) Å, *c*=10.556(4) Å, β = 111.48(2)°, V= 1900.6(1) $Å^3$. Unit cell for Zn itaconate: a= 17.319(1) Å, b= 7.2015(5) Å, c= 13.1540(8) Å, β= 110.981(4)°, V= 1531.7(1) $Å^3$.At present, more work is caring out in our laboratories to obtain more information about the crystal structure of the complexes, especially of the samarium.

Conclusions

The method of synthesis allows obtaining complex in good yields. The combined studies of IR and TGA strongly suggest that the divalent metals, Zn and Cu form covalent monodentate complexes with a molar radio M: ($C_5H_4O_4$) 1:1 and two water molecules: $M(C_5H_4O_4)\cdot 2H_2O$, while for Sm an ionic complex with a Sm:($C_5H_4O_4$) molar radio 2:3 and with 4 molecules of water is proposed. The X-ray diffraction study indicates that the Cu and Zn complexes crystallize in monoclinic cells with space group $P2_1/c$, whereas Sm complex has been obtained as an amorphous material.

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