Thermal and spectroscopic study of the 3,4-(methylenedioxy) cinnamate compounds of transition metals in the solid state

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A B S T R A C T

In this study, the *trans*-3,4-(methylenedioxy)cinnamic acid was used as precursor for the synthesis of transition metal compounds, which were characterized by coupled TG-DTA/FT-IR system, elemental analysis, FT-IR spectroscopic study and titrimetric analysis with EDTA. The characterization by these techniques allowed to determine the hydration water content, number of ligand coordinated to the metal, thermal behavior and thermal stability, as well as monitor the main gaseous products released in each decomposition step. The elemental and titrimetric analyses were performed in order to support TG-DTA data. A theoretical FT-IR calculation was made using the Gauss View 5.0.2 W program and the vibration frequencies obtained were compared with the experimental ones showing as a result a difference of around $30 \, cm^{-1}$ between them. In these spectra were analyzed the main vibration modes as COO^- (carboxylate group), $-C=C-$ (aromatic ring, alkene), $-C-O-$ and $-CH_2$ (methylenedioxy group) and $-C-H$ (alkenes, aromatic).

1. Introduction

The cinnamates have been widely studied by different science areas for medicinal and commercial purposes. Furthermore, the cinnamic acid derivatives stand out by their natural occurrence in flowers, fruits and vegetables, consumed as dietary substances, as well as used as precursors in organic synthesis of others molecules or metallo-organic compounds [1–6].

Thus, the purpose of this study was synthesize and characterize the bivalent compounds of manganese, iron, cobalt, nickel, copper and zinc in the solid state, once studies involving thermal and spectroscopic characterization of the *trans*-3,4-(methylenedioxy) cinnamic acid as precursor, a derivative of the cinnamic acid, have not been found in the literature. In addition, carboxylate compounds are synthesized with a well-defined stoichiometry allowing the use of theoretical calculations to predict the structural arrangement [7–9], which are important parameters for future applications of the compounds in all types of systems.

The study carried out by TG-DTA aimed to determine the stoichiometric composition in relation to the number of ligands coordinated to the metal and the hydration water content, while the FT-IR analysis was based on the comparison between the theoretical and experimental spectra, in order to elucidate the structural arrangement through characteristic existing vibrations between these spectra [10]. Accordingly, calculations of the optimal molecular geometry and vibrational frequency of *trans*-3,4-(methylenedioxy)cinnamic acid and its metal compounds were made. Calculations based on the density functional theory (DFT) for organic compounds provide excellent vibrational frequencies when the frequencies calculated are scaled to compensate the approximate treatment of electron correlation for basis set deficiencies and anharmonicity [11].

2. Experimental

2.1. Compounds preparation from metal and ligand solutions

The *trans*-3,4-(methylenedioxy)cinnamic acid (HL) with 99% purity was obtained from Sigma.

For the solid state compounds, metal ions, water and ligand contents were determined from TG curves. The metal ions were

also determined by complexometric titration with standard EDTA solution [12,13] after igniting the compounds until formation of the respective oxides and their dissolution in hydrochloric acid solution.

Aqueous solution of the *trans*-3,4-(methylenedioxy)cinnamate salt (NaL) 0.1 mol L^{-1} was prepared from aqueous HL suspension by treatment with sodium hydroxide solution 0.1 mol L^{-1} and the pH was adjusted at around 7.5 using a pH-meter with a glass electrode, while the aqueous solutions of the bivalent metal ions were prepared by dissolving the respective chlorides (for Mn, Co, Ni and Zn) or sulfates (for Cu and Fe) with pH adjusted at around 5.0.

From the mixture of the freshly prepared solutions with slow addition and continuous stirring, the metal ions were completely precipitated from their original solution. Next, the precipitates obtained were washed with distilled water until elimination of chloride and sulfate ions, filtered through and dried on Whatman Nr. 42 filter paper and kept in desiccator over anhydrous calcium chloride.

2.2. Instrumental analysis

The attenuate total reflectance infrared spectra for the NaL, as well as for its metal-ion compounds were run on a Nicolet iS10 FT-IR spectrophotometer, using an ATR accessory with Ge window.

Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110CHNS-O Elemental Analyser from CE Instruments.

Simultaneous TG-DTA curves were obtained with the thermal analysis system model SDT 2960 from TA Instruments. The purge gas was air with a flow rate of 100 mL min^{-1}, heating rate of 20 °C min^{-1} ranging from 30 °C to 700 °C with sample mass of about 5.0 mg. Alumina crucibles were used for TG-DTA.

The measurements of the gaseous products were carried out using a Thermogravimetric Analyzer Mettler TG-DSC coupled to a FT-IR spectrophotometer Nicolet with gas cell and DTGS KBr detector. The furnace and the heated gas cell (250 °C) were coupled through a heated ($T = 225$ °C) 120 cm stainless steel line transfer 2 mm in diameter, and purged with dry air (50 mL min^{-1}). The FT-IR spectra were recorded with 32 scans per spectrum at a 4 cm^{-1} resolution.

2.3. Computational strategy

In this study, the quantum chemical approach taken to determine the molecular structures was Becke's three parameter hybrid theory [14] and the Lee–Yang–Par (LYP) correlation functional [15], using 6-311++g(d) as basis sets for calculations [16,17]. The molecular calculations performed in this study were made using the Gaussian 09 routine [18]. The theoretical infrared spectrum was calculated using a harmonic field [19] based on C_1 symmetry (electronic state ^1A). Frequency values (not scaled), relative intensities, assignments and description of the vibrational modes are presented. The geometric optimization was computed using Berny's optimized algorithm [20] and the calculations of vibrational frequencies were also implemented to determine an optimized geometry constitutes minimum or saddle points. The principal infrared active fundamental modes assignments and descriptions were made by the Gauss View 5.0.2 W graphics routine [21].

3. Results and discussion

3.1. Compounds

From synthesized compounds, a thermal study was performed by classical and instrumental techniques to establish the stoichiometry. The analytical and thermoanalytical (TG) results of the synthesized compounds are summarized in Table 1, which are in agreement with the general formula: $Mn(L)_2 \cdot 2H_2O$, $Fe(L)_2 \cdot 1H_2O$, $Co(L)_2 \cdot 2H_2O$, $Ni(L)_2 \cdot 2H_2O$, $Cu(L)_2 \cdot 1H_2O$ and $Zn(L)_2 \cdot 2H_2O$, where L = 3,4-(methylenedioxy)cinnamate. Additionally, the gaseous products of each compound released from their thermal decomposition were monitored on-line by TG-DTA/FT-IR system.

3.2. TG-DTA/FT-IR analysis

The TG-DTA analysis of the compounds is shown in Fig. 1(a–f). The TG-DTA curves of these compounds show mass losses in three, four or up to five consecutive and/or overlapping steps and thermal events corresponding to these losses. Furthermore, the thermal decomposition of the anhydrous compounds studied, in general, has presented itself heavily dependent on the nature of the transition metal ions. However, the first mass loss step and corresponding thermal events of the hydrated compounds in the TG-DTA curves are similar, except for the iron and nickel compounds, which loose water slowly in one and two steps, respectively. As a result, the endothermic events observed in the corresponding DTA curves of these compounds are weak, probably due to slow hydration water loss. After the hydration water loss of the compounds, they have thermal stability up to about the following temperatures 169 °C (Fe), 248 °C (Cu), 260 °C (Mn, Co and Zn) and 289 °C (Ni). Accordingly, from now onward the discussion will be centered on the anhydrous form.

The decomposition of the anhydrous manganese compound, Fig. 1(a), occurs in two steps respectively. The first one, up to 360 °C and with mass loss of 21.52% (TG), is associated with the weak exotherm event (DTA) in the 255–347 °C temperature range. Regarding the gaseous products monitored on-line in this step by the TG-DTA/FT-IR system, they are due to the organic ligand fragmentation which releases carbon dioxide as main gaseous product followed by carbon monoxide, safrole ($C_{10}H_{10}O_2$) and formaldehyde as secondary products. In the second step, the thermal decomposition occurs with mass loss of 54.33% (TG) correlated to an intense exothermic peak at 424 °C in the DTA curve due to the oxidation of the organic matter with release of carbon

Table 1
Analytical and thermoanalytical (TG) data of the $M(L)_2 \cdot nH_2O$ compounds; M = metal; L = 3,4-(methylenedioxy)cinnamate.

Compounds	Oxide (%)			Ligand lost (%)		Water (%)		C (%)		H (%)		Residue
	Calcd.	EDTA	TG	Calcd.	TG	Calcd.	TG	Calcd.	E A	Calcd.	E A	
$Mn(L)_2 \cdot 2H_2O$	16.11	15.90	16.36	76.28	75.85	7.61	7.79	50.75	50.01	4.27	3.90	Mn_3O_4
$Fe(L)_2 \cdot 1H_2O$	17.50	16.90	17.13	78.55	79.02	3.95	3.85	52.65	51.80	3.98	4.10	Fe_2O_3
$Co(L)_2 \cdot 2H_2O$	16.81	16.50	15.38	75.64	76.79	7.55	7.83	50.35	50.08	4.23	4.00	Co_3O_4
$Ni(L)_2 \cdot 2H_2O$	15.66	15.20	15.70	76.79	76.91	7.55	7.39	50.35	49.80	4.23	4.02	NiO
$Cu(L)_2 \cdot 1H_2O$	17.14	16.80	16.57	78.96	79.43	3.90	4.00	51.78	51.00	3.92	4.00	CuO
$Zn(L)_2 \cdot 2H_2O$	16.83	16.50	15.90	75.73	76.40	7.44	7.70	49.65	50.01	4.17	4.03	ZnO

Calcd.: calculated; C: carbon; H: hydrogen; TG: thermogravimetry; EA: elemental analysis; and EDTA: ethylenediaminetetraacetic acid.