The synthesis and thermal behavior of di[µ-hydroxo-diaquo (squarato) of métals trivalents (Fe, Al and Ga)

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ABSTRACT:

A new series of mixed metals and squarates of formula $[M(C_4O_4)(OH)(H_2O)_2]_22H_2O$ with (M=Al,Ga) has been synthesized, wen we report a work on the preparation of mixtures, the goal was to prepare a porous hybrid phase. But we obtained the phase prepared previously by J. T. Wobleski and D. B. Brown, thus of new phase belonging to the same family (Di[μ -hydroxo-diaquo squarato of de trivalents metals). So we have also obtain this phase as well as with metal gallium (Ga) and aluminum (Al).

The thermal decomposition of the precursors has been studied in vacuum between 100 and 600 °C, by powder thermodiffractometry for a compound of this family (M = Al) followed by a comparison between the temperature connect to thermal degradation of three compounds of this family. It is shown that crystalline intermediate phases are formed during the degradation.

KEYWORDS: ORGANIC-INORGANIC HYBRID MATERIALS, THERMODIFFRACTOMETRY

RESUME:

Une nouvelle série de squarate métaux de formule $[M(C_4O_4)(OH)(H_2O)_2]_22H_2O$ avec (M = AI, Ga) a été synthétisée, comme nous rapportons un travail sur la préparation de mélanges, le but était de préparer une phase poreuse hybride. Mais nous avons obtenu la phase préalablement préparé par J. T. Wobleski et D. B. Brown, donc de nouvelle phase appartenant à la même famille $(Di[\mu-hydroxo-diaquo squarato de métaux trivalents)$. Nous avons également obtenir cette phase avec le gallium (Ga) et l'aluminium (AI).

La décomposition thermique de précurseurs a été étudié dans le vide entre 100 et 600 °C, par de la thermodiffractometry pour un composé de cette famille (M = Al), suivie d'une comparaison entre la température de la dégradation thermique de trois composés de cette famille. On montre que des phases cristallines intermédiaires sont formés lors de la dégradation.

MOTS CLES : MATERIAUX HYBRIDE ORGANIQUE INORGANIQUE, THERMODIFRACTOMETRIE.

1. Introduction

Metal-organic framworks represent a new class of porous crystaline materials for which it is possible to design organic linkers and inorganic joints [1]. The literature has been enriched by many oxoanion-based compounds possessing interesting structural features. The hydroxo squarates of trivalent metal trihydrates of the general formula $M(C_4O_4)(OH)(H_2O)_3$, with M = (Fe, Cr and Al), have been synthesized for the first time by Niu and West (1963) [2].

The $[Fe(C_4O_4)(OH)(H_2O)_2]_22H_2O$ has been prepared by (J. T. Wrobleski and D. B. Brown 1978) [3], the Registration of X-ray diffraction by the powder indicates that it is identical to that reported by West and Niu within the limits of experimental error.

In 1980, Jhon and P. Chesick [4] note that it was time to study the structure of these compounds. They prepared the [Cr (C₄O₄)(OH)(H₂O)₃] and thus described the electronics and structural properties. The present work was undertaken to extend the scope of this comparative study to include aluminum (III) squarate which contains carbon-oxygen-cation linkages, the present work extends these studies by reporting thermal observations.

2. Experimental Section

2.1. Material:

All chemicals were used as received. $(H_2C_4O_4)$ is named squaric acid, the other reagents were $M(NO_3)_39H_2O$, with (M = Fe, Al), and Ga(NO₃)₃H₂O, and (C₂H₈N₂).

2.2. Synthesis of $[M(C_4O_4)(OH)(H_2O)_2]_2H_2O$ with M = Fe, Al and Ga:

The synthesis of compounds described here was carried out by dissolving the metal nitrate considered (Al, Fe, Ga) (5.10-4 mol) and amines (2.5.10-3 mole) in each one in 20 ml of distilled water. To the mixture (metal, amine) is added 0.11 g of squaric acid. The compounds were obtained as precipitates. The powder was recovered by filtration and dried in air.

2.3. Collection of X-ray Powder Data for [M(C₄O₄)(OH)(H₂O)₂]₂2H₂O M = Fe, Al, Ga.

High-quality powder data were obtained with a Siemens D500 diffractometer using monochromatic Cu K α_1 radiation ($\lambda = 1.5406$ A°) selected with an incident beam curved-crystal germanium monochromator, with the parafocusing Bragg-Brentano geometry whose characteristics have been reported elsewhere [5]. The powder was mounted in a side-loaded sample holder [6]. The pattern was scanned at room temperature, over the angular range 10- 46° (2 θ), with a step length of 0.04° (2 θ) and a counting time of 60 s step⁻¹. The stability of the X-ray source was checked by recording again the diffraction lines at low angles.

2.4. Thermal analyses:

The thermal decomposition of $[Al(C_4O_4)(OH)(H_2O)_2]_22H_2O$ was studied by temperaturedependent X-ray diffraction (TDXD), comprising a curved-position-sensitive detector from INEL (CPS120) and a monitored high-temperature attachment from Rigaku. The detector was used in a semi-focusing arrangement by reflection (CuKa1 radiation) as described elsewhere [7]. In this set up the sample is stationary and an angle of 18° between the incident beam and the surface of the sample was selected.

3. Results and Discussion

3.1. Identification of the products

Figure 1 display the superpotion of the two diffraction patterns which clearly shows the isotype of our products to those of J.T.Wrobleski and D.B.Brown [3] so they are isostructural, and Figure 2 display the isotype of the three compounds.







3.1. Structure

The chemical formula was derived from the comparison of the diffractograms of products to those of the ICDD-PDF2 database by intermédière of DIFFRACPlus program with the (software EVA) they were identical to the card-indexes N° 00-031-1739 (figure 1). The structure was described by Jhon and P.Chesick [4].

(d) $[Fe(C_4O_4)(OH)(H_2O)_2]_22H_2O$

3.2. Thermal Behavior of [Al(C₄O₄)(OH)(H₂O)₂]₂2H₂O

In the thermal study of the compounds of this family with trivalent metals (Fe , V) it was mentioned that in the curve of weight loss there are two inflections .

In the case of M = Fe, the first transformation as shown in Table 1 occurs in the temperature range 160 ° C, corresponds to a weight loss of 17.3 % and the second at 290 ° C corresponds to a weight loss of 64.8 %. Wrobleski and Brown suggest that hydrogen bond between the squarate and water are sufficiently strong, that makes lose water that is in the crystal lattice at the first decomposition, while the water coordinated to the metal part in the second stage. The X -ray diffraction of the final residue after cooling shows the presence of iron oxide.

The thermal behavior of the iron compound differs completely from that in which the metal is vanadium. In the case of M = V, the first change relates to loss of 2 mol of water per dimer at 80 ° C, and the second to a loss of 6 mol per diamer at 150 ° C and the final residue is vanadium oxide at high temperature.

In this paragraph is exposed the comparing thermal of decomposition $[Al(C_4O_4)(OH)(H_2O)_2]_2$, $2H_2O$ with the preceding , using a different technique than that reported in the literature, it is the X-ray on thermodifractometrie powder and which consists, in this case , to record every 45 min a diagram of X-ray diffraction on the sample which undergoes an increase in temperature from the ambient to 600 ° C.

Figure 3 shows the successive powder patterns obtained during the thermal decomposition of $[Al(C_4O_4)(OH)(H_2O)_2]_22H_2O$ obtained under dynamic air. The TDXD plot shows the decomposition scheme of the precursor into the final product Al_2O_3 , it appears two transformations in the temperature range.



Figure 3: TDXD plot for [Al(C₄O₄)(OH)(H₂O)₂]₂, 2H₂O performed at a heating rate of 13° Ch-1 (counting time for each pattern 2700 s)from 18 °C to 600 °C.

It is shown that the first transformation occurs in the temperature range 95 -105 ° C. By comparison, it is accompanied by a mass loss corresponding to dehydration resulting from the water residing in the crystal lattice. It is noted that the transformation start temperature of the product is close to that of dehydration of $[V(C_4O_4)(OH)(H_2O)_3]$ (S. M. Condren H. O. Mcdonald 1973), and it is fully lower than which has been observed for $[Fe(C_4O_4)(OH)(H_2O)_2]_22H_2O$. (J. T. Wrobleski D. B. Brown 1978). This transformation does not affect the position of the rays, this reflect the isomorphism of the compounds $M(C_4O_4)(OH)(H_2O)_3$ with $[M(C_4O_4)(OH)(H_2O)_2]_22H_2O$, and the compound retains its shape in at least one direction in space.

As the first step corresponds to dehydration with only a slight loss of water molecules, this suggests that the hydrogen bonding is strong between the squarate and water so that water of Crystal network is lost before the water with is coordinate to metal.

The second transformation with is observed at 210 $^{\circ}$ C shows the disappearance of water from the crystal lattice, which is accompanied by destruction of the molecular achitecture. This phenomenon seems to be related to the structure of the compound and the mass loss therefore causes a significant structural rearrangement in the compound. At high temperature, the diffraction X-ray is a mixture which shows an aluminum carbonate and aluminum oxide. This is verified by the identification of the last diagram of the rays at 600 $^{\circ}$ C, using EVA software.

thermogravimetric Study				Study thermodiffractométrique	
V(C ₄ O ₄)(OH) 3(H ₂ O)		$[Fe(C_4O_4)(OH)(H_2O)_2]_22H_2O$		[A1(C ₄ O ₄)(OH)(H ₂ O) ₂] ₂ 2H ₂ O	
T (°C)	Transfomation	T (°C)	Transfomation	T (°C)	Transfomation
	repported		repported		repported
80	Loss of 2 mol of	160	Loss of 4.6 mol of	100	Diminition peak
	water/mol de		water/mol de		intensity
	dimère		dimère		
150	Loss of 6 mol of	290	Loss of 6 mol of	210	Disappearance of the
	water/mol de		water/mol de		main peaks
	dimère		dimère		characterizing the
					original material
Beyond	At high	Beyond	After cooling:	Beyond	At high temperature:
150 °C	temperature:	290°C	residue comprising	290°C	aluminum oxide Al 2
	vanadium oxide		Fe2O3 oxide		O 3 + aluminum
	V2O3				carbonate

Table 1: Summary of changes in compound under the effect of the increase in temperature

6. Conclusion

In this work, we have associated the di $[\mu$ -hydroxo diaquo (squarato) to trivalent metals and completed a family of compounds. The X-ray diffraction on the powder depending on the temperature (thermodiffractométrie) plays an important role in understanding the degradation precursor until oxides or amorphous phases appears. It has been shown that a crystal phase is formed during the degradation of the material by temperature rising effect, and finally the squaric acid is decomposed completely and appears the aluminum oxide and its carbonate.

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