Thermal stability and bonding in the silver complexes of ethylenediaminetetraacetic acid

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Abstract

The solid silver-EDTA complexes $AgH_3Y \cdot (3/4)H_2O$; Ag_2H_2Y; Ag_3HY and $Ag_4Y \cdot (1/2)H_2O$ (Y^{-4} is ethylenediaminetetraacetate anion) obtained by reaction of the Ag^+ ions with sodium salts of EDTA in different degrees of neutralization in aqueous media have been characterized by means of potentiometric titrations, IR spectrometry, elemental analysis and powder X-ray diffraction (XRD). Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to investigated the thermal stability of the complexes as well as the decomposition pathways. The thermoanalytical results associated with infrared data lead to the conclusion that the silver-carboxylate group bonding is primarily ionic. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The metal-ion complexes of ethylenediaminetetraacetic acid (EDTA) find widespread use in analysis [1,2], industry, foodstuffs, pharmacy and medicine. A number of these applications are in reviews and reports [3–5] available on the use of EDTA. Nevertheless, the number of chemical papers devoted to gaining an understanding of the nature of bonding [6] in, and the thermal stability of, EDTA-metal ion complexes is rather small.

In this context, limited information is available in the literature for solid state silver-EDTA complexes

[7–9]. They have been studied in few details, in part due to the weakness of the complexes formed by O-donor ligands and silver(I) cations [10].

For the present work silver-EDTA complexes were synthesized using different neutralization degrees of the ligand EDTA (H_4Y) generating complexes with the formulae: $AgH_3Y \cdot (3/4)H_2O$; Ag_2H_2Y; Ag_3HY and $Ag_4Y \cdot (1/2)H_2O$ (Y^{-4} is ethylenediaminetetraacetate anion). Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to investigated the thermal stability of the complexes as well as the decomposition pathways.

With the aim of evaluating the silver(I)-carboxylate group coordination bonding character and potential application of these compounds in photothermographic systems [11], thermoanalytical studies were

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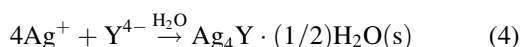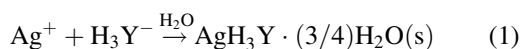[*] Corresponding author. Tel. +55+16-260-8209; fax: +55+16-260-8350.

associated with infrared and X-ray diffraction (XRD) data, respectively.

2. Experimental

The solutions were prepared using de-ionized water. The reagents were of analytical grade (PA) and used as received.

2.1. Preparation of the complexes

Silver nitrate were reacted with mono-, di-, tri- and tetra-sodium salts of EDTA (H_4Y) in 1:1, 2:1, 3:1 and 4:1 molar ratios, respectively, according to:

$$Ag^+ + H_3Y^- \xrightarrow{H_2O} AgH_3Y \cdot (3/4)H_2O(s) \quad (1)$$

$$2Ag^+ + H_2Y^{2-} \xrightarrow{H_2O} Ag_2H_2Y(s) \quad (2)$$

$$3Ag^+ + HY^{3-} \xrightarrow{H_2O} Ag_3HY(s) \quad (3)$$

$$4Ag^+ + Y^{4-} \xrightarrow{H_2O} Ag_4Y \cdot (1/2)H_2O(s) \quad (4)$$

The resulting solids were filtered off, washed with cold water and ethanol portions, dried in a vacuum oven at 50°C in dark flasks to avoid exposure to direct light.

2.2. Characterization of the complexes

In order to characterize the silver contents in each complex, at least three dried samples (ca. 0.2 g) were titrated pontentiometrically with standard 0.100 M NaCl using a silver wire as indicator electrode in presence of 2–3 ml of 10% nitric acid to avoid interference of the free ligand.

Elemental analysis for carbon, hydrogen and nitrogen were carried out in an EA-1108 CHNS-O Fisons Instrument.

The infrared spectra were obtained using KBr pellets (4000–200 cm^{-1}) in a MB-102 BOMEN Hartmann & Braun spectrometer equipped with Arid-Zone detector.

The complexes and thermal decomposition products were also characterized by powder XRD using CuKα radiation in a D5000 Siemens diffractometer at 2θ angle range of 20–75°.

2.3. Thermal measurements

The TG curves were recorded using a TGA-951 thermogravimetric module (DuPont), coupled to a 9900 thermal analyser (DuPont) equipped with a HP model 7440A plotter. A sample of about 7 mg of each silver-EDTA complex was putted in an open platinum crucible and heated at a rate of 10°C min^{-1} under air or nitrogen (gas flow 100 ml min^{-1}) at atmospheric pressure.

In the DSC experiments, a DSC 910 apparatus (DuPont), coupled to a 9900 thermal analyser (DuPont) equipped with a HP model 7440A plotter was used. Samples of about 5 mg were putted in covered aluminum pans (perforated lid). These samples were heated at a rate of 10°C min^{-1} under air or nitrogen (gas flow 100 ml min^{-1}) at atmospheric pressure.

3. Results and discussion

3.1. Complexes characterization

The analytical data for the silver-EDTA complexes are listed in Table 1. These results agree with the general formulae $Ag_nH_{n-4}Y \cdot xH_2O$ (x=0 for n=2 and 3; x=1/2 for n=4 and x=3/4 for n=1).

XRD patterns of the silver-EDTA complexes suggest that the anhydrous complexes are isomorphous. The more characteristic lines obtained by powder diffraction method are shown in Table 2.

The bands for some characteristic groups in the infrared spectra of the silver-EDTA are listed in Table 3. The vibration frequencies of interest are the characteristic frequencies of the carboxyl group [12,13] and the C–N anti-symmetrical and symmetrical stretching [13]. The frequency of the band due COO group vibrations indicates the nature of its bond with metal (covalent or ionic) [14–16] and or if it is protonated [15].

The difference in frequency between the peak for the symmetrical vibration (v_sCOO^-) and the peak for the anti-symmetrical vibration (v_aCOO^-) of the group COO^- also indicates the degree of covalent bonding of EDTA chelates [17]. The frequency difference increases as the bonding becomes more covalent; chelates for which the difference (Δ) is 225 cm^{-1}

Table 1
Analysis of the silver-EDTA complexes

Compound	Found(Calc.) (%)			
	Ag	C	N	H
$AgH_3Y \cdot (3/4)H_2O$	26.4(26.1)	29.0(29.1)	6.15(6.79)	3.92(4.03)
Ag_2H_2Y	42.3(42.6)	24.3(23.7)	5.60(5.54)	2.99(2.79)
Ag_3HY	52.4(52.8)	19.5(19.6)	3.85(4.57)	2.12(2.14)
$Ag_4Y \cdot (1/2)H_2O$	59.2(59.2)	16.6(16.5)	3.95(3.84)	1.82(1.80)

or greater the bonding is concluded to be primarily covalent. If the difference is <225 cm^{-1}, the bonding is primarily ionic. The peaks for symmetrical and anti-symmetrical stretching vibrations of the group COO$^-$ and their Δ in silver-EDTA complexes are shown in Table 3.

The interpretation of silver-EDTA complexes infra-red data has shown the presence of unionized and uncoordinated COO group in whole complexes of the series except in $Ag_4Y \cdot (1/2)H_2O$. The peaks of the protonated COO group in frequencies below 1700 cm^{-1} suggest that an internal hydrogen bonding is formed [13,18].

The strongest and the most characteristic absorption band for the carboxyl group (COO$^-$) due to its anti-symmetrical vibration is present in the spectra of four silver-EDTA complexes. However, this band for $AgH_3Y \cdot (3/4)H_2O$ occurs at significantly higher frequency value (1634 cm^{-1}) than for other complexes of the series (near 1590 cm^{-1}). This event is related to

the fact of the ionized COO$^-$ groups in $AgH_3Y \cdot (3/4)H_2O$ are not coordinated to the silver(I) ion. The absorption band at 1634 cm^{-1} is assigned to the interaction between ionized and uncoordinated COO$^-$ groups and unionized COO group by internal hydrogen bonding [18]. The difference in frequency (225 cm^{-1}) between the peak for the symmetrical vibration (v_sCOO$^-$) and the peak for the anti-symmetrical vibration (v_aCOO$^-$) of the COO$^-$ group in $AgH_3Y \cdot (3/4)H_2O$ indicates the covalent character for this bonding which is related to the interaction between hydrogen and COO$^-$ group instead the interaction between silver and COO$^-$ group. The silver-carboxyl bonding character is demonstrated to be ionic for the other complexes of the series as it will be discussed below.

For the other complexes of the silver-EDTA complexes series the silver- carboxyl group bonding is primarily ionic. This statement is established by experimental evidences. The peak due to anti-symme-

Table 2
X-ray powder patterns of the complexes $Ag_nH_{n-4}Y \cdot xH_2O$

$AgH_3Y \cdot (3/4)H_2O$		Ag_2H_2Y		Ag_3HY		$Ag_4Y \cdot (1/2)H_2O$	
I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)
19	4.10	39	3.78	34	3.79	100	3.48
100	3.99	100	3.70	100	3.70	72	3.40
17	3.85	5	3.18	43	3.21	47	2.93
30	3.77	40	3.13	36	3.13	77	2.88
47	3.69	32	2.91	99	2.90	96	2.76
6	3.17	37	2.77	67	2.76	72	2.70
20	3.13	40	2.70	55	2.72	67	2.67
20.4	2.90	14	2.62	42	2.62	61	2.44
17	2.76	28	2.49	28.5	2.49	27	2.40
27	2.70	44	2.47	53	2.47	53	2.31
7	2.61	27.6	2.41	51	2.43	40	2.26
22	2.56	41	2.25	43	2.25	58	2.22
19	2.49	27.8	2.16	16	2.16	32	2.18

Table 3
Infrared data (4000–200 cm^{-1}) for the complexes Ag$_n$H$_{n-4}$Y·xH$_2$O and EDTA[*]

Compound	COOH group				Aminic group			Carboxylate group		
	$v_{C=O}$ (s)	δ_{OH} (m)	v_{C-O} (m)	CH$_2$COOH[a] (w)	δ_{Oh}[b] (m)	v_sC–N (m)	v_aC–N (w)	v_aCOO$^-$ (s)	v_sCOO$^-$ (m)	Δ
H$_4$Y	1712	1450	1316	1214	964	870	1135 and 1093	–	–	–
AgH$_3$Y·(3/4)H$_2$O	1679[c]	1438	1326	1212	958	871	1135 and 1091	1634	1409	225
Ag$_2$H$_2$Y	1631	–	1327	1213	960	862	1130 and 1089	1594	1402	192
Ag$_3$HY	1629[c]	–	1328	1207	955	845	1123 and 1088	1594	1404	190
Ag$_4$Y·(1/2)H$_2$O	–	–	1326	–	–	846	1124	1590	1406	184

[*] s: Strong; m: medium; w: weak; v: stretching; δ: deformation; s: symmetrical; a: anti-symmetrical.
[a] Absorption at 1250–1210 cm^{-1} is attributed tentatively to the –CH$_2$COOH group [13,16,19].
[b] Out of plane.
[c] Bands at 1679 and 1629 appears as a shoulder.

trical stretching vibration of COO$^-$ group for Ag$_2$H$_2$Y, Ag$_3$HY and Ag$_4$Y·(1/2)H$_2$O occur at the characteristic range (1615–1590 cm^{-1}) [14,15,19] for metal-carboxyl bonding with predominant ionic character. Besides the values of Δ for these three complexes are smaller than 225 cm^{-1} that also confirms the ionic character [17] of silver-carboxyl group bonding.

To investigate the presence of a silver–nitrogen coordinate bond, it has obtained data on C–N vibrations (Table 3). It has been noted that the symmetrical and anti-symmetrical C–N stretching bands shifts to longer wavelengths (smaller frequencies) with increasing degree of the neutralization of the ligand EDTA (H$_4$Y) for the Ag$_2$H$_2$Y, Ag$_3$HY and Ag$_4$Y·(1/2)H$_2$O; whereas there is no significant difference about C–N vibrations frequencies for AgH$_3$Y·(3/4)H$_2$O and the acid form of the ligand (H$_4$Y). These results suggest that the silver–nitrogen interaction will occur if only the nitrogen atoms of EDTA are not protonated and confirm that the silver ion is not coordinated in AgH$_3$Y·(3/4)H$_2$O complex. The shift of C–N anti-symmetrical stretching bands with the replacement of hydrogen–nitrogen interaction by silver–nitrogen one is analogous that occurs when the ionic radius of the metal coordinated to nitrogen atoms of EDTA increases [14,17,20–22].

3.2. Thermoanalytical results

All the mass losses and temperature intervals for the thermal events observed for the compounds investigated in the present work are summarized in Table 4, while the TG curves under nitrogen and air are presented in Figs. 1 and 2, respectively. The DSC curves under nitrogen and air are presented in Figs. 3 and 4, respectively.

The thermal decomposition of the acid H$_4$Y under nitrogen occurred between 237–451°C, generating a carbonaceous residue, which burns slowly up to 958°C. These observations are in agreement with the previous findings of Wendlandt [23], under air. The DSC curve showed a strong endothermic process
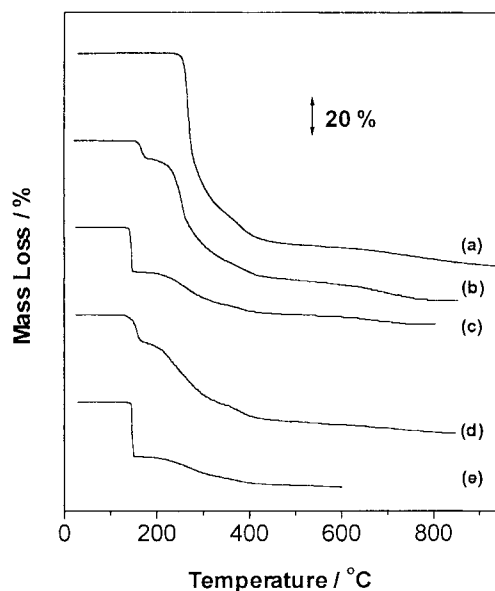

Fig. 1. TG curves of H$_4$Y (a); AgH$_3$Y·(3/4)H$_2$O (b); Ag$_2$H$_2$Y (c); Ag$_3$HY (d) and Ag$_4$Y·(1/2)H$_2$O (e), under *nitrogen* atmosphere (10°C min^{-1}; Pt crucible; N$_2$ flow 100 ml min^{-1}).

Table 4

Mass loss and temperature range relating to the thermal decomposition processes of silver-EDTA complexes and EDTA

Process	TG data temperature interval (°C)	Mass loss or residue (%)		DSC peaks[a] (°C)
		TG	Calc.	
Air atmosphere				
$AgH_3Y \cdot (3/4)H_2O \rightarrow Ag^{od} + xCO_2 \uparrow^e + (3/4)H_2O \uparrow + L^f$	146–191	8.6[b]	–	168.3(ex)
$Ag^{od} + L^f \rightarrow Ag^{od}$	191–797	26.0[c]	26.1	243.1(en); 470.5(ex); 521.7(ex)
$Ag_2H_2Y \rightarrow 2Ag^{od} + xCO_2 \uparrow^e + L^f$	123–186	13.2[b]	–	142.5(ex); 160.3(ex)
$2Ag^{od} + L^f \rightarrow 2Ag^{od}$	186–599	44.0[c]	42.6	253.2(ex); 444.9(ex): 453.2(ex); 475.8(ex)
$Ag_3HY \rightarrow 3Ag^{od} + xCO_2 \uparrow^e + L^f$	124–157	19.4[b]	–	150.1(ex)
$3Ag^{od} + L^f \rightarrow 3Ag^{od}$	172–797	52.5[c]	52.8	240.9(en); 432.5(ex); 464.7(ex); 492.1(ex); 506.3(ex)
$Ag_4Y \cdot (1/2)H_2O \rightarrow 4Ag^{od} + xCO_2 \uparrow^e + (1/2)H_2O \uparrow + L^f$	112–143	24.4[b]	–	141.9(ex)
$4Ag^{od} + L^f \rightarrow 4Ag^{od}$	144–523	59.0[c]	59.2	490.1(ex); 505.6(ex)
Nitrogen atmosphere				
$H_4Y \rightarrow L^f + gases$	237–343	72.7[b]	–	
$L^f \rightarrow C^g$	343–958	25.5[b]	–	255.9(en)
$AgH_3Y \cdot (3/4)H_2O \rightarrow Ag^{od} + xCO_2 \uparrow^e + (3/4)H_2O \uparrow + L^f$	144–191	8.5[b]	–	167.5(ex)
$Ag^{od} + L^f \rightarrow Ag^{od}$	191–796	26.1[c]	26.1	242.8(en)
$Ag_2H_2Y \rightarrow 2Ag^{od} + xCO_2 \uparrow^e + L^f$	123–183	12.9[b]	–	142.5(ex); 161.5(ex)
$2Ag^{od} + L^f \rightarrow 2Ag^{od} + C^g$	183–796	46.2[c]	–	224.6(en); 247.2(en)
$Ag_3HY \rightarrow 3Ag^{od} + xCO_2 \uparrow^e + L^f$	133–191	21.3[b]	–	143.7(ex)
$3Ag^{od} + L^f \rightarrow 3Ag^{od} + C^g$	191–797	55.6[c]	–	
$Ag_4Y \cdot (1/2)H_2O \rightarrow 4Ag^{od} + XcO_2 \uparrow^e + (1/2)H_2O \uparrow + L^f$	136–159	25.1[b]	–	141.9(ex)
$4Ag^{od} + L^f \rightarrow 4Ag^{od} + C^g$	181–596	61.1[cc]	–	

[a] ex: Exothermic process; en: endothermic process.

[b] Relative to mass loss.

[c] Relative to residue.

[d] Characterized by XRD.

[e] Characterized by test with $Ba(OH)_2/x$ as estimated on Table 5.

[f] Partially decomposed ligand.

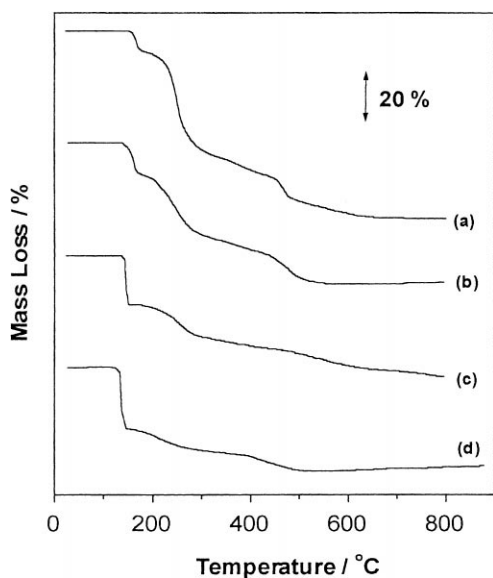[g] Carbon residue; –: not calculated (mixture).

Fig. 2. TG curves of $AgH_3Y \cdot (3/4)H_2O$ (a); Ag_2H_2Y (b); Ag_3HY (c) and $Ag_4Y \cdot (1/2)H_2O$ (d), under *air* ($10°C \ min^{-1}$; Pt crucible; air flow 100 ml min^{-1}).

with a peak at $255.9°C$ ($\Delta H = 173.8 \ kJ \ mol^{-1}$), correspondent to the main decomposition.

The four complexes decomposed in a very similar way, except by the amount of the mass lost in the first
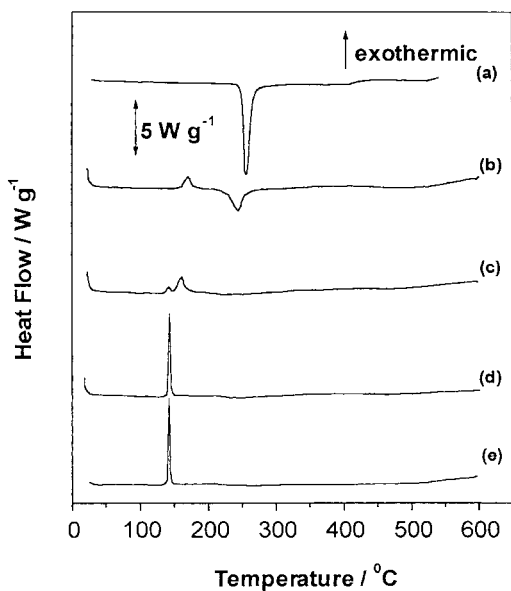

Fig. 3. DSC curves of H_4Y (a); $AgH_3Y \cdot (3/4)H_2O$ (b); Ag_2H_2Y (c); Ag_3HY (d) and $Ag_4Y \cdot (1/2)H_2O$ (e), under *nitrogen* atmosphere ($10°C \ min^{-1}$; covered Al crucible; N_2 flow 100 ml min^{-1}).
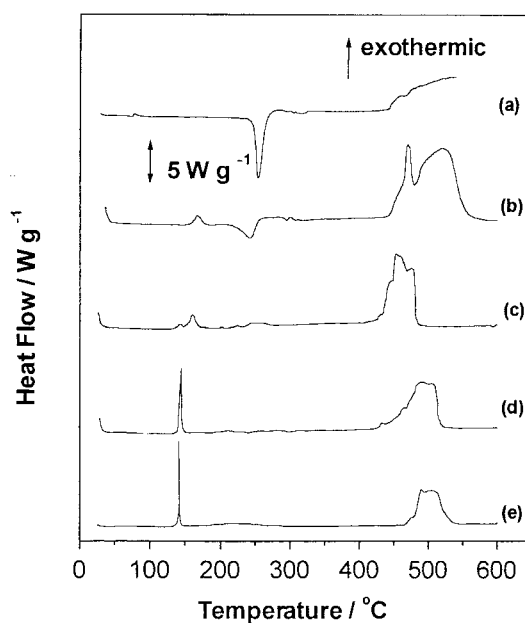
Fig. 4. DSC curves of H_4Y (a); $AgH_3Y \cdot (3/4)H_2O$ (b); Ag_2H_2Y (c); Ag_3HY (d) and $Ag_4Y \cdot (1/2)H_2O$ (e), under *air* ($10°C \ min^{-1}$; covered Al crucible; air flow 100 ml min^{-1}).

step, under both atmospheres. XRD patterns of the product of this reaction showed the presence of metallic silver and an amorphous material. Experiments carried out of the thermobalance reveled a volume expansion during this process with gas evolution at such temperatures and that the carbonaceous residue is brownish-black.

When that gas is bubbled in a solution containing $Ba(OH)_2$, a white precipitate is formed, confirming that it is CO_2 [24]. The decarboxylation reaction with CO_2 evolution for some EDTA complexes has been described [25–29]. The mixture of the residue of the first decomposition step of $AgH_3Y \cdot (3/4)H_2O$ and Ag_3HY with water resulted in two phases. One is a black solid and the other a yellowish solution in both cases. Titration of the liquid phase with standard NaOH showed two jumps at pH 4 and 8, suggesting the presence of at least two different sources of H^+, probably from carboxylic and aminic groups [30].

Correlation between the titration data and the amount of CO_2 calculated from the mass loss in each case (Table 5), shows that the decarboxylation reaction is dependent of the amount of silver and if

Table 5
Molar amount of CO_2 evolved per mol of each complex estimated by the first mass losses from TG curves

Compound	Amount of CO_2 (mol)	
	Air	Nitrogen
$AgH_3Y \cdot (3/4)H_2O$	0.5[a]	0.5[a]
Ag_2H_2Y	1.5	1.5
Ag_3HY	2.7	3.0
$Ag_4Y \cdot (1/2)H_2O$	3.8[a]	4.0[a]

[a] Estimated by considering simultaneous water loss.

the proton is bonded to the carboxylic group in the complex.

The shape of the DSC curves in the temperature lower than 200°C (correspondent to the first TG step) showed that the decomposition process is different for the complexes. In the DSC curve of the $AgH_3Y \cdot (3/4)H_2O$, only one exothermic peak is observed around 168°C. For Ag_2H_2Y, two exothermic processes appeared at 142 and 161°C, while Ag_3HY and $Ag_4Y \cdot (1/2)H_2O$ curves showed only one sharp exothermic peak around 145°C.

The DSC data when related to the calculations in Table 5 data, suggest that the decarboxylation process occurs in two different ways. In the Ag_3HY and $Ag_4Y \cdot (1/2)H_2O$ complexes, CO_2 is released in a 1:1 molar ratio in relation to the silver, in a similar model of the Kolbe reaction [31]:

$$R-COO^- \rightarrow R^\bullet + CO_2 \uparrow + e^- \qquad (5)$$
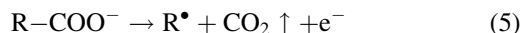
In the $AgH_3Y \cdot (3/4)H_2O$, the decaboxylation occurs via a 1/2 CO_2: 1 Ag molar ratio process. The difference is probably due to the presence of a protonated carboxylic group, as confirmed by the IR data.

The Ag_2H_2Y presented both kinds of reaction, since it have both ionized and protonated groups. These reactions are represented by the two exothermic DSC peaks and the overlapped TG process evidenced by the DTG curve.

The absence of endothermic peaks lower than 200°C suggests that the loss of the hydration water molecules, present according to the elemental analysis data in some complexes, occurs simultaneously with the decaboxylation step in a similar way as it has been described for few EDTA complexes [25,27,32], or the energy involved in the dehydration is masked by strong decaboxylation exothermic peaks.

Finally the organic matter is decomposed in subsequent steps characteristic for each complex and atmosphere, resulting in metallic silver as main residue in both atmospheres, according to the XRD data.

According to the data in Table 4, the TG residues under nitrogen are frequently higher than the calculated for metallic silver, which is explained by the presence of small amounts of carbon. This is not observed under air atmosphere, since the carbon is burned as demonstrated by the DSC exothermic peaks in the 400–600°C range (Figs. 3 and 4). This oxidation of the carbonaceous material resulting from the decomposition processes under air generating broad exothermic peaks at this range temperature has been related for some EDTA complexes [25,33,34].

The presence of metallic silver as residue immediately after the first step of the decomposition independently of the atmosphere used, shows that the oxidation–reduction processes occurs between the complexes constituents, without participation of the
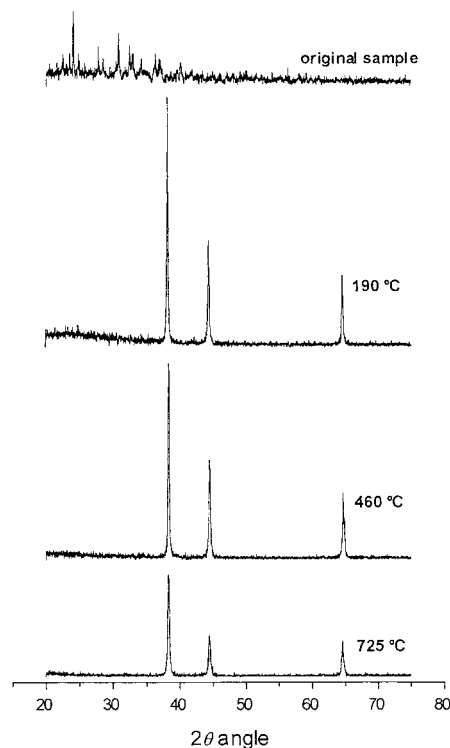

Fig. 5. XRD patterns of Ag_3HY and the products of thermal reactions at different temperatures under nitrogen (2θ angles for Ag^o: 38; 44 and 64.5° [35]).

external gases. In Fig. 5, an example of the decomposition of Ag_3HY is demonstrated by using XRD patterns [35] of the products of reaction at different temperatures showing clearly the presence of Ag^o since the first step.

4. Conclusion

The IR data showed that the $Ag^+–COO^-$ group bonding presents a predominantly ionic character in the complexes studied.

The decaboxylation process is dependent of the degree of protonation of the carboxyl group in the ligand as showed by the DSC curve.

The presence of metallic silver at the end of the first decomposition step independently of the atmosphere pointed out the potentialities of the use of the these compounds as imaging material in photothermographic systems. The reduction of silver occurring even without the presence of other reductive agent is an advantage in such applications.

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