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PREPARATION AND THERMAL STUDY OF THE MAGNESIUM, CALCIUM AND BARIUM COMPOUNDS WITH A GLYCINE SCHIFF BASE CONTAINING AN ESTER FUNCTION

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ABSTRACT

The compounds $M[Rgly]_2 \cdot nH_2O$ (M = Mg and Ca, $n = 4$; M = Ba, $n = 2$; $Rgly^- = C_{10}H_{14}NO_4^-$), obtained by the condensation reaction between ethyl-α-ketocyclopentylcarboxylate and glycine in the presence of the metallic salt, were prepared and studied. The compounds were characterized by IR and UV spectroscopy, differential thermal analysis and thermogravimetric analysis.

INTRODUCTION

Amino-acid Schiff base metal compounds have biological importance in vitamin B_6 transaminations and enzymatic decarboxylations [1,2]. Magnesium and calcium have important biological functions when they bind to proteins, aminoacids and ionophores [1,3].

In our laboratory we have studied the potassium glycine Schiff base obtained by reaction between ethyl-α-ketocyclopentylcarboxylate (a β-keto-ester) and glycine in the presence of potassium hydroxide, together with the copper complex of the same Schiff base [4].

The present work reports on the synthesis, characterization and thermal study of the alkaline earth compounds obtained from this Schiff base.

EXPERIMENTAL

Equipment and reagents

The ethyl-α-ketocyclopentylcarboxylate and metallic salts were obtained from Lancaster. Glycine was obtained from Doesder. All chemicals were of analytical grade.

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The Fourier transform infrared (FTIR) spectra of the compounds and the successive decomposition residues at increasing temperatures were recorded using a Perkin–Elmer M1700 apparatus provided with a data station, using KBr pellets. The UV spectra were recorded on a Varian–Techtron apparatus, Model 635.

Thermogravimetric (TG) curves were obtained in flowing air and argon ($45\ cm^3\ min^{-1}$) using a Perkin–Elmer Model 3600 instrument coupled to a data station; the heating rate was $5\,°C\ min^{-1}$.

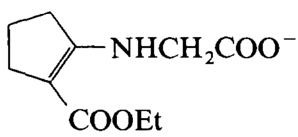
Differential thermal analysis (DTA) was performed using a Perkin–Elmer 3600 instrument, using alumina to dilute the samples, with a heating rate of $5\,°C\ min^{-1}$ in flowing air and argon ($45\ cm^3\ min^{-1}$).

Preparation of the compounds

Barium compound ($Ba[C_{10}H_{14}NO_4]_2 \cdot 2H_2O$)

The β-ketoester (0.2 mol) was dissolved in a barium hydroxide aqueous solution (0.2 mol and 20 cm^3 of water). Reaction was complete when the oily drops of ketoester were no longer observed. To this solution was added drop-wise a solution of glycine (0.1 mol) in water (50 cm^3). The resulting solution was placed in a desiccator over calcium chloride until crystalline needles of the desired compound were obtained. The yield was 50–60%. The reactions are shown in the following scheme:

$$2C_8H_{12}O_3 + 2NH_3^+CH_2COO^- + Ba(OH)_2 \longrightarrow Ba[C_{10}H_{14}NO_4]_2 \cdot 2H_2O$$

where $C_{10}H_{14}NO_4^-$ = 

= $Rgly^-$

Magnesium and calcium compounds ($M[C_{10}H_{14}NO_4]_2 \cdot 4H_2O$, M = Mg, Ca)

The preparation procedure is similar in both compounds. They were obtained by reaction between the metallic nitrate and the potassium glycine Schiff-base ($K[C_{10}H_{14}NO_4] \cdot H_2O$) whose preparation is described in ref. 4. A solution of the metallic nitrate (0.1 mol and 20 cm^3 of water) was added to a solution of the potassium Schiff-base (0.2 mol and 50 cm^3 of water). A precipitate was immediately obtained (yield, 40%). The reaction is

$$2K[C_{10}H_{14}NO_4] + M(NO_3)_2 + 4H_2O \rightarrow M[C_{10}H_{14}NO_4]_2 \cdot 4H_2O + 2KNO_3$$

All the solutions used in the preparations must be CO_2 free. Elemental analysis of C, N and H were performed at the Laboratory of Instrumental Techniques (University of Granada, Spain). The metal contents were gravimetrically determined as carbonates. The percentages obtained correspond closely to those of the proposed formulae (Table 1).

TABLE 1

Elemental analysis of the compounds (calc and [obs.])

Compound [a]	%C	%H	%N	%M	$\%H_2O$ [b]
$Mg(Rgly)_2 \cdot 4H_2O$	46.13	6.92	5.38	4.67	13.84
	[44.5]	[6.4]	[5.2]	[4.6]	[12.7]
$Ca(Rgly)_2 \cdot 4H_2O$	44.77	6.71	5.22	7.46	13.40
	[42.7]	[6.5]	[5.2]	[7.7]	[12.3]
$Ba(Rgly)_2 \cdot 2H_2O$	40.18	5.35	4.68	22.98	6.03
	[39.5]	[4.9]	[4.7]	[23.1]	[6.0]

[a] $Rgly = C_{10}H_{14}NO_4^-$.
[b] Calculated from TG curves.

RESULTS AND DISCUSSION

Infrared and electronic spectra

The IR spectra are similar in all the investigated compounds. The most important frequency bands are shown in Table 2. The OH stretching vibrations of the crystallization water molecules appear as a wide or split band in the 3500–3300 cm^{-1} region. The NH stretching vibration appears in

TABLE 2

Infrared spectra of the Schiff-base compounds

Compound	ν(OH)	ν(NH)	ν(CH)	ν(COO) ν(ester)	ρ(NH)	Other
$K(Rgly) \cdot H_2O$	3480s [a]	3350s	2940m	1650s	775m	1400s
	3320s		2920m	1590s		1285s
						1120s
						1050s
						675b
$Mg(Rgly)_2 \cdot 4H_2O$	3490s	3344s	2956s	1653s	775m	1414s
	3406s			1608s		1271s
						1112s
						1053s
$Ca(Rgly)_2 \cdot 4H_2O$	3485s	3376s	2956s	1654s	775m	1421s
				1584s		1277s
						1106s
						1043s
$Ba(Rgly)_2 \cdot 2H_2O$	3460s	3340s	2960s	1660s	780m	1420s
				1580s		1280s
						1120s
						1050m
						690b

[a] s = strong, m = medium, b = broad.

the 3300–3370 cm^{-1} zone, in the same region as the analogous potassium compound.

Two bands appear in the 1650–1580 cm^{-1} zone. The larger wavenumber band is assigned to the ester group and is at a similar frequency to that of the potassium Schiff-base compound; this indicates that there is no significant metal–ester interaction. The second band, attributable to the ionized carboxylate, is situated in the 1600–1580 cm^{-1} zone, and is an asymmetric carboxylate vibration ($\nu_{asym}COO^-$). The symmetric carboxylate band, $\nu_{sym}COO^-$, appears at 1414, 1421 and 1480 cm^{-1} for Mg, Ca and Ba compounds, respectively. This band is at a frequency similar to that found for the other amino-acid Schiff-base compounds [5–8].

The UV spectra are similar in all the compounds investigated and are similar to the potassium Schiff-base spectrum [4]. The spectrum consist of two bands placed at 300 nm (log $\epsilon = 2.8$) and 190 nm (log $\epsilon = 2.7$). The former band is related to the ester group [9] and shows no variation with respect to the same band in the potassium compound; this corroborates the absence of metal–ester interaction. The other band, at 190 nm, has a shoulder at 200 nm caused by electronic transitions in the amino and carboxylate groups [10,11].

Thermogravimetric study

A thermogravimetric study of all the compounds obtained was carried out in air and argon atmosphere with a heating rate of 5 °C min^{-1}. The TG curves obtained in air atmosphere, similar in all the compounds, show a weight loss at 80–110 °C until a plateau is reached. This weight loss is consistent with loss of water from hydrated compounds (Table 1 and Fig. 1). The activation energy (E_a) of the water loss process was calculated by the Horowitz and Metzger method and the results are consistent with first-order kinetics for the dehydration process [12,13].

At high temperatures, the weight loss is progressive until a clear plateau is reached ($\approx$ 500 °C). This plateau is in agreement with the metallic carbonate calculated from the proposed formulae. The carbonate was identified by IR spectroscopy. In argon atmosphere, no defined plateau is reached in the $\approx$ 500 °C zone, and a mixture of C and metallic carbonate is obtained as the final residue.

In the DTA curves measured in air and argon atmosphere, an endothermic peak appears in the 80–110 °C region. This peak corresponds to dehydration (Table 3 and Fig. 1). An exothermic peak in the DTA curve recorded in air atmosphere appears at 440–520 °C: this corresponds to the combustion of organic matter; the released CO_2 is bubbled through a barium hydroxide solution trap.

The peak detected at 173 °C in the copper(II) glycine Schiff-base complex obtained previously by us [4], is caused by the release of CO_2 and the loss of

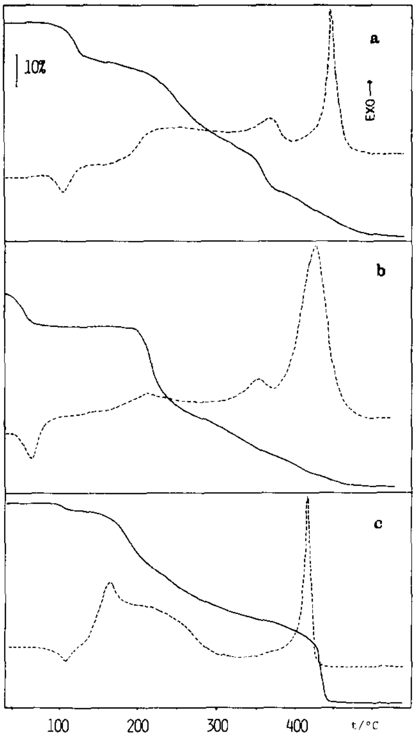


Fig. 1. Thermal analysis of the compounds in air atmosphere: a, $Mg(Rgly)_2 \cdot 4H_2O$; b, $Ca(Rgly)_2 \cdot 4H_2O$; c, $Ba(Rgly)_2 \cdot 2H_2O$. The TG weight losses are represented by a solid line (———), and the DTA curves by a dashed line (— — —).

the ethylcarboxylate group. However, in the alkaline earth compounds studied here, no peak is observed in this zone and the ethylcarboxylate group remains attached to the molecule. In argon atmosphere, the DTA curves also show an exothermic effect ($\approx$ 350–450 °C) that corresponds to the progressive carbonization of organic matter (Table 3).

TABLE 3

Differential thermal analysis of the Schiff-base compounds

Compound	Atmosphere	Rate (°C min^{-1})	Peak (°C) [a]	E_a (kJ mol^{-1}) [b]
$Mg(Rgly)_2 \cdot 4H_2O$	Air	5	95end, 365exo, 451exo.	104
	Ar	5	94end, 358exo.	
$Ca(Rgly)_2 \cdot 4H_2O$	Air	5	80end, 360exo, 452exo.	106
	Ar	5	67end, 350exo.	
$Ba(Rgly)_2 \cdot 2H_2O$	Air	5	110end, 160exo, 444exo.	109
	Ar	5	103end, 440exo.	

[a] end = endothermic, exo = exothermic.

[b] Calculated with the method of ref. 12.

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