Preparation and thermal study of the potassium, magnesium, calcium and barium compounds with an L-alanine derivative containing an ester function

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(Received 10 February 1992)

Abstract

The compounds K(Rala) $\cdot$ H$_2$O and M(Rala)$_2$ $\cdot$ nH$_2$O (M = Mg, n = 4; M = Ca and Ba, n = 2; Rala$^-$ = C$_{11}$H$_{16}$NO$_4^-$), obtained by condensation reaction between ethyl-α-ketocyclo-pentylcarboxylate (C$_8$H$_{12}$O$_3$) and the L-alanine in the presence of the metallic salt, have been prepared and studied. The compounds are characterized by elemental analysis, by IR, UV and mass spectroscopy, NMR and thermal analysis (TG, DTA and DSC).

INTRODUCTION

Magnesium and calcium have important biological functions when bound to proteins, aminoacids and ionophores [1, 2]. In biological systems, calcium is coordinated by oxygen atoms, usually to carboxylate groups, and magnesium tends to be bound by nitrogen donors.

In our laboratory we have studied the potassium glycine Schiff base obtained by reaction between the ethyl-α-ketocyclopentylcarboxylate (a β-ketoester), and glycine in the presence of potassium hydroxide, together with the copper complex of the same Schiff base [3]. Amino acid Schiff bases of pyridoxal have biological importance in vitamin B$_6$ trans-aminations and enzymatic decarboxylations [1, 4].

The present work reports on the synthesis, characterization and thermal study of the alkaline earth compounds obtained from the L-alanine Schiff base of the same β-ketoester, which are mainly in the tautomeric enamine–imine form. The ester function provides new possibilities of interaction with metallic cations.

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EXPERIMENTAL

Equipment and reagents

L-Alanine, ethyl-α-ketocyclopentylcarboxylate and metallic salts were obtained from Lancaster. All chemicals were of analytical grade.

Elemental analysis of C, N, H was performed in a Perkin-Elmer 2400CHN elemental analyzer. The metal contents were gravimetrically determined as carbonates and complexometrically with EDTA. The percentages obtained correspond closely to those of the proposed formulae (Table 1).

The Fourier transform infrared (FTIR) spectra of the compounds and the 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. The NMR spectra were recorded in a Brucker WP 200SY apparatus using D_2O as the solvent and dioxane as the reference standard.

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, 10 and $20°C\ min^{-1}$. 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 the same conditions as the TG studies. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC-4 apparatus with a heating rate of $5°C\ min^{-1}$ and flowing argon atmosphere ($45\ cm^3\ min^{-1}$). The sample masses for the thermal studies were 5–10 mg.

Mass spectra of the compounds were performed in a Kratos MS-25 apparatus by the electronic bombardment technique.

TABLE 1

Conductivities and elemental analysis (%) of the compounds

Compound [a]	C		H		N		M		Λ [b] $(\Omega^{-1}\ cm^2\ mol^{-1})$
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
K(Rala) · H_2O	46.1	46.6	6.2	6.3	4.8	4.9	13.8	13.8	103
Mg(Rala)$_2$ · 4H$_2$O	48.1	48.3	7.3	6.9	5.1	4.9	4.4	4.5	74 [c]
Ca(Rala)$_2$ · 2H$_2$O	50.0	49.3	6.8	6.4	5.3	4.8	7.6	7.6	187
Ba(Rala)$_2$ · 2H$_2$O	42.2	43.9	5.7	5.4	4.4	4.1	21.9	22.0	211

[a] Rala = $C_{11}H_{16}NO_4^-$. [b] $c = 10^{-3}$ M, H_2O. [c] In DMF.

Preparation of the potassium Schiff base compound $[K(Rala) \cdot H_2O]$

The ketoester (ethyl-α-ketocyclopentylcarboxylate) was dissolved in an aqueous solution of potassium hydroxide (0.2 mol and 20 cm^3 of H_2O). Reaction was completed when the oily drops of the ketoester were no longer observed. To this solution was added dropwise a solution of L-alanine (0.2 mol and 20 cm^3 of H_2O). The resulting solution was placed in a desiccator over calcium chloride until crystalline filamentous needles of the desired compound were obtained. The yield was 50–60%. The reactions are shown in the following scheme

$$C_8H_{12}O_3 + NH_3^+CH(CH_3)COO^- + K(OH) \longrightarrow K(C_{11}H_{16}NO_4) \cdot H_2O + H_2O$$
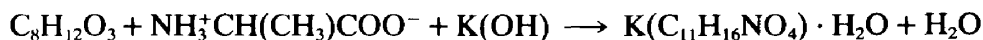
where $Rala^- = C_{11}H_{16}NO_4^-$
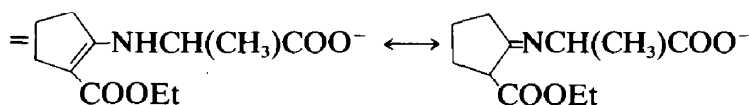
Preparation of alkaline earth Schiff base compounds,
$M(Rala)_2 \cdot nH_2O$ ($M = Mg$, n = 4; $M = Ca$ and Ba, n = 2)

The Schiff base compounds were obtained by reaction between the metallic nitrate and the potassium compound, K(Rala) $\cdot$ H$_2$O. A solution of the metallic nitrate (0.1 mol and 20 cm^3 of H_2O) was added to a solution of the potassium Schiff base (0.2 mol and 50 cm^3 of H_2O). A precipitate was immediately obtained and washed with several amounts of water. The reaction is

$$2K(Rala) + M(NO_3)_2 + nH_2O \rightarrow M(Rala)_2 \cdot nH_2O + 2KNO_3$$
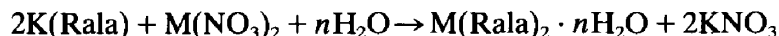
All the solutions used in the preparations must be CO_2 free.

Mass spectrometry and NMR spectra

The molecular ion was not observed in all compounds studied by mass spectrometry, but the ligand (RalaH, m/z 227) and other ligand fragments have been detected.

The ^1H NMR spectra of the potassium and alkaline-earth compounds are consistent with the proposed structure. For K(Rala) $\cdot$ H$_2$O the δ_H (ppm) values are: 1.15(3H, t, $-CH_2Me$), 1.24(3H, d, $-CHMe$), 1.64(2H, m, $-CH_2CH_2CH_2-$), 2.42(4H, m, $-CH_2CH_2CH_2-$), 3.80(1H, q, $-CHCOO$), and 4.04(2H, q, $-CH_2Me$). For Mg(Rala)$_2$ $\cdot$ 4H$_2$O the δ_H (ppm) values are: 1.29(3H, t, $-CH_2Me$), 1.40(3H, d, $-CHMe$), 1.80(2H, m, $-CH_2CH_2CH_2-$), 2.48(4H, m, $-CH_2CH_2CH_2-$), 3.95(1H, q, $-CHCOO$), and 4.18(2H, q, $-CH_2Me$). For Ca(Rala)$_2$ $\cdot$ 2H$_2$O the δ_H (ppm) values are: 1.31(3H, t, $-CH_2Me$), 1.38(3H, d, $-CHMe$), 1.80(2H, m, $-CH_2CH_2CH_2-$), 2.46(4H, m, $-CH_2CH_2CH_2-$), 3.95(1H, q, $-CHCOO$),

and 4.18(2H, q, $-CH_2Me$). For Ba(Rala)$_2 \cdot$ 2H$_2$O the δ_H (ppm) values are: 1.28(3H, t, $-CH_2Me$), 1.37(3H, d, $-CHMe$), 1.79(2H, m, $-CH_2CH_2CH_2-$), 2.49(4H, m, $-CH_2CH_2CH_2-$), 3.96(1H, q, $-CHCOO$), and 4.16(2H, q, $-CH_2Me$).

RESULTS AND DISCUSSION

Infrared and electronic spectra

The IR spectra are similar in all compounds obtained and the most important frequency bands are shown in Table 2. The OH stretching vibrations of molecules of water of crystallization appear as a wide or split band in the 3500–3300 cm^{-1} region. The NH stretching vibration appears in the 3300–3370 cm^{-1} zone, in the same region as that of the analogous potassium compound. The broad band at 2113 cm^{-1} characteristic of the zwitterionic form of the amino acid, is not present in all Schiff bases studied.

Two bands appear in the 1650–1580 cm^{-1} zone. The larger wavenumber band is assigned to the ester group and is situated at a frequency similar to that of the potassium Schiff base; this indicates no significant metal–ester

TABLE 2

IR spectra of the compounds

Compound	v(OH)	v(NH)	v(CH)	v(ester)	v(COO)	Other
L-Alanine		3083s	2988m	1593s	1593s	2113w,b
					1413m	1621s
						1363s
						1307s
						773m
K(Rala) $\cdot$ H$_2$O	3426s	3339m	2988m	1647s	1596w	1573s
			2967m		1402s	1284s
			2866m			776m
						680m,b
Mg(Rala)$_2 \cdot$ 4H$_2$O	3437m,b	3316sh	2977m	1651s	1618s	1577s
			2866m		1422m	1385s
						1274s
						777m
						669m,b
Ca(Rala)$_2 \cdot$ 2H$_2$O	3447m,b	3350sh	2977m	1651sh	1574s,b	1385s
			2868m		1425m	1271s
						776m
						670m
Ba(Rala)$_2 \cdot$ 2H$_2$O	3447s,b	3301sh	2981w	1646s	1610s	1567s
			2960w		1407m	1385s
			2847w			1270s

TABLE 3

Thermal study of the compounds

Compound	Atmo-sphere	DTA[a] peaks (°C)	TG plateau			DSC peak		E_a (kcal mol⁻¹)
			Temp. (°C)	Obs./calc. mass loss (%)	Cpd.	(°C)	(kcal mol⁻¹)	
$K(Rala) \cdot H_2O$	Air	91en, 160en, 194en, 278ex, 348ex, 635ex	120 650	5.2/6.3 75.6/75.6	$K(Rala)$ K_2CO_3			78[b] 87[c]
	N_2	85en, 155en, 193en, 275en				85	4.0	
$Mg(Rala)_2 \cdot 4H_2O$	Air	95en, 242ex, 358ex, 450ex	103 600	3.6/3.3 82/84.6	$Mg(Rala)_2 \cdot 3H_2O$ $MgCO_3 + C$			105[b] 91[c]
	N_2					87	42.4	
$Ca(Rala)_2 \cdot 2H_2O$	Air	71en, 251ex, 440ex	90 140 600	4.3/3.4 8.0/6.8 71/77	$Ca(Rala)_2 \cdot H_2O$ $Ca(Rala)_2$ $CaCO_3 + C$			
	N_2							
$Ba(Rala)_2 \cdot 2H_2O$	Air	40en, 247ex, 306ex, 379ex	50 520	8/5.8 57/68.5	$Ba(Rala)_2$ $BaCO_3 + C$	77	9.3	

[a] Key: en, endothermic; ex, exothermic. [b] Calculated from method of ref. 13. [c] Calculated from method of ref. 14.

interaction. The second band, attributable to the ionized carboxylate, is situated in the 1600–1580 cm^{-1} zone, and it is an asymmetric carboxylate vibration ($v_{asym}COO^-$). The symmetric carboxylate band, $v_{sym}COO^-$, appears at 1414, 1421 and 1480 cm^{-1} for magnesium, calcium and barium compounds, respectively. This band is situated at a frequency similar to that of the same band of other aminoacid Schiff base compounds [5–8].

The UV spectra are similar in all compounds obtained and similar to the potassium glycine Schiff base spectrum [3]. The spectrum consists of two bands placed at 300 nm (lg $\varepsilon = 2.8$) and 190 nm. The former band is related to the ester group [9–11] and it shows no variation with respect to the same band of the potassium compound, which corroborates no metal–ester binding.

Thermogravimetric study

Thermogravimetric study of all compounds obtained is carried out in air and argon atmosphere with a heating rate of 5°C min^{-1}. The TG curves obtained in air atmosphere are similar in all compounds and show a mass loss at 80–110°C until a plateau is reached. This mass loss is consistent with the water loss from hydrated compounds (Table 3). The activation energy E_a of the water loss process was calculated using the Horowitz and Metzger method and the results are consistent with first order kinetics for the dehydration process [12, 13]. In Table 3 E_a values calculated by an alternative method [14] are also given.

At most high temperatures the mass loss is progressive until a defined plateau is reached (about 500°C). This plateau is consistent 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 500°C zone and a mixture of carbon and metallic carbonate is obtained as final residue.

In DTA curves performed in air and argon atmosphere an endothermic peak appears in the 80–110°C region. This peak corresponds to the dehydration process (Table 3). An exothermic peak in DTA performed in air atmosphere appears at 440–520°C and it 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 [3], is caused by the release of CO_2 and ethylcarboxylate loss. However, in the alkaline earth compounds studied here no peak is observed in this zone and the ethylcarboxylate group remains united to the molecule. In argon atmosphere DTA curves also show an exothermic effect (about 350–450°C) that corresponds to the progressive organic matter carbonization (Table 3).

ACKNOWLEDGEMENTS

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