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A thermal and IR study of metal complexes of 2-amino-2-deoxy-D-glycero-L-gluco heptonic acid

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Abstract

Complexes of 2-amino-2-deoxy-D-glycero-L-gluco heptonic acid (GH) and Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) have been synthesised and characterised by elemental analysis and IR spectroscopy. The complexes have a general formula: $[M(G)_2(H_2O)_2]$ with variable water of hydration, except for the Cu(II) compound which is anhydrous $[Cu(G)_2]$. The thermal behaviour of these complexes has been studied by TG and DSC techniques. The thermal data indicate that for the Co(II), Ni(II), and Cu(II) complexes, the ligand is chelated via the carboxylate$^-$ and amino functional groups, whereas for the Mn(II) and Fe(II) complexes, the amino group remains protonated and does not bond to the metal.

Keywords: Amino acid complex; DSC; IR; TG

1. Introduction

Amino acids are of profound biological interest because they participate in many biochemical processes very essential to living systems. Metal ions are known to participate in many biochemical reactions and are widely distributed in living organisms [1]. The in vivo interaction of amino acids with transition metal ions are of immense biological importance [2,3]. Moreover, the metal–amino acid systems have been extensively used as models for studying metal–protein systems. For these reasons, the interactions of proteic α-amino acids with metal ions have been extensively studied [4]. However, there is less information about synthetic amino acids, such as those which come from sugars. The hydroxyl groups of the side chain present in the α-amino acid derived from sugars are important from a biological point of view because they are potential sites of interaction with protons, metal ions, or other charged biomolecules [5,6]. Intermolecular interactions involving amino acid side groups and other biological functional groups are vital for such biological events as protein structuring, specific and efficient catalysis by enzymes, and molecular recognition in hormone–receptor bonding [7].

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Table 1
Chemical analysis data: found % (calc. %)

Compound	Colour	C (%)	H (%)	N (%)	O (%)	M (%)
$[Mn(GH)_2(H_2O)_2]0.5H_2O$	Brown	30.66 (30.91)	6.07 (6.28)	5.11 (5.05)	48.14 (47.74)	10.02 (10.03)
$[Fe(GH)_2(H_2O)_2]1.8H_2O$	Brown	29.36 (29.51)	6.27 (5.98)	4.89 (4.82)	49.73 (49.69)	9.75 (10.01)
$[CoG_2(H_2O)_2]$	Red	30.95 (30.49)	5.94 (5.67)	5.16 (4.98)	47.11 (47.94)	10.85 (10.92)
$[NiG_2(H_2O)_2]$	Blue	30.96 (30.94)	5.94 (6.17)	5.16 (5.11)	47.13 (47.09)	10.81 (10.71)
$[CuG_2]$	Blue	32.85 (32.42)	5.51 (5.71)	5.47 (5.35)	43.76 (44.18)	12.41 (12.35)

In previous papers we have studied equilibria in aqueous solution between metal ions and some carbohydrate α-amino acids derivatives [8,9]. In this paper, we report the synthesis and the thermal behaviour of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes of galactose α-amino acid (2-amino-2-deoxy-D-glycero-L-gluco heptonic acid [GH: $C_7H_{15}NO_7$]).

2. Experimental

2.1. Reagents

2-Amino-2-deoxy-D-glycero-L-gluco heptonic acid (GH) was prepared according to the method of Galbis et al. [10] and recrystallised twice from doubly distilled water. All chemicals used were of analytical reagent grade or of equivalent quality.

2.2. Methods

C, H and N analyses were obtained using a Perkin-Elmer 240C microanalyser. TG/DTG and DSC data were obtained using a Mettler TA-3000 system with a Mettler TG-50 thermobalance and a Mettler DSC-20 differential scanning calorimeter, which was calibrated according to Mettler instructions. The atmospheres used for TG and DSC were air (flow, 100 ml min^{-1}) or nitrogen/air (flow, 100 ml min^{-1}; purity, 99.99% v/v). The heating rate was 10°C min^{-1} with sample masses around 13 mg for TG and 3 mg for DSC. The temperature ranges investigated were 35–900°C (TG) and 35–600°C (DSC).

Infrared (IR) spectra were obtained using KBr (4000–250 cm^{-1} range) pellets and a Perkin-Elmer 983G spectrophotometer.

2.3. Samples

The interactions of GH in aqueous media over a wide pH range with the metal ions Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), gave new compounds of composition: $[Mn(GH)_2(H_2O)_2]0.5H_2O$ (**I**), $[Fe(GH)_2(H_2O)_2]1.8H_2O$ (**II**), $[Co(G)_2(H_2O)_2]$ (**III**), $[Ni(G)_2(H_2O)_2]$ (**IV**) and $[Cu(G)_2]$ (**V**).

The complexes of GH were prepared as follows: a hot solution (20 ml) at pH 7.5 containing 0.5 g of ligand was mixed (slowly with stirring), in a molar ratio of 1 : 2 (M : L), with a solution of the corresponding metallic nitrate. The solutions were allowed to stand at room temperature and the complexes precipitated almost immediately. They were filtered off, washed consecutively with water, ethanol and diethylether, and air dried. Chemical analysis data are recorder in Table 1.

3. Results and discussion

In general, the shapes of TG and DSC curves show that the thermal behaviour of the Mn(II) and Fe(II) complexes is very similar to that of the free amino acid [11], which suggests that there is a weak metal–ligand interaction in both complexes. In all cases, on heating the complexes, two processes occur: dehydration and pyrolitic decomposition.

3.1. Dehydration processes

The TG and DSC profiles over the temperature range 30–250°C indicate loss of water of moisture, hydration and coordination. The humidity content is lost in the range 30–50°C.

The TG data are recorded in Table 2. The percentages are referred to the initial sample mass free

Table 2
TG data analysis

Complex	Process	Temperature (°C)	Mass loss[a] (%)	Residue compound	Residue %
$[Mn(GH)_2(H_2O)_2]0.5H_2O$	Dehydration				
	$0.5H_2O$	58–95	1.64 (1.64)		
	$2H_2O$	100–168	6.20 (6.57)		
	Pyrolysis	200–260	38.9		
	Combustion of residue	600		MnO	13.01 (12.94)
$[Fe(GH)_2(H_2O)_2]1.8H_2O$	Dehydration				
	$1.8H_2O$	80–180	5.66 (5.66)		
	$2H_2O$	180–210	6.01 (6.29)		
	Pyrolysis	210–280	41.2		
	Combustion of residue	600		FeO	12.52 (12.55)
$[CoG_2(H_2O)_2]$	Dehydration				
	$2H_2O$	160–	(6.63)		
	Pyrolysis	160–340	39.0		
	Combustion of residue	440		Co_2O_3	14.99 (15.26)
$[NiG_2(H_2O)_2]$	Dehydration				
	$2H_2O$	125–190	6.92 (6.63)		
	Pyrolysis	190–310	39.0		
	Combustion of residue	380		NiO	13.55 (13.76)
$[CuG_2]$	Pyrolysis	180–270	73.2		
	Combustion of residue	420		CuO	15.50 (15.54)

[a] Calculated values are given in parentheses.

of moisture ($T = 50°C$). The complexes of Mn(II) and Fe(II) have first decomposition stage in the range 58–98°C and 80–180°C, respectively. This first dehydration process probably is due to the loss of hydration water, which may be bound to the sugar chain of the ligand by hydrogen bonds. The relatively high value of the temperature-range for the Fe(II) complex indicates a strong water–ligand interaction. Moreover, the low value of the dehydration enthalpy found (11.1 kJ/mol H_2O for compound **II**) suggests that there is a structural change associated with this dehydration process, that makes it less endothermic.

In the Mn(II) complex, the coordination-water loss starts near to 100°C, whereas for the Fe(II), Co(II), and Ni(II) complexes, this water loss takes place at temperatures higher than 150°C, which suggests the existence of stronger water–metal ion interactions in the latter cases. For the Co(II) complex, this process overlaps with the pyrolitic degradation. The results show that Cu(II) complex is anhydrous.

3.2. Pyrolitic process

Once dehydrated, the compounds decompose, without fusion, in the 180–800°C temperature range (Table 2). This behaviour is similar to that found in other α-amino acids complexes [8,9]. There is a very large mass-loss, which takes place in the temperature range 180–315°C, except for the Co(II) complex. For this compound, the mass-loss starts at 145°C. This first pyrolitic process probably is due to the intramolecular dehydration of the sugar chain of the amino acid. The DSC curves show that this degration is slightly endothermic, being the corresponding dehydration enthalpies values between 4.1 kJ/mol H_2O (compound **III**) and 13.7 kJ/mol H_2O (compound **I**). The mass-loss corresponds to 12 molecules of water for the complexes. The chemical analysis of the residue resulting of this decomposition is in agreement with this assigment.

When increasing the temperature, the DSC curves showed that the decomposition of the residue continues in an exothermic process. The final residues

Table 3
Infrared assignments (cm^{-1})

Compound	$\nu(NH_3^+)$	$\nu_a(COO)$	$\nu_s(COO)$	$\Delta\nu$
$[Mn(GH)_2(H_2O)_2]0.5H_2O$	1621	1614 1578	1401	177[a]
$[Fe(GH)_2(H_2O)_2]1.8H_2O$	1622	1613 1578	1401	176[a]
$[CoG_2(H_2O)_2]$		1624	1398	226
$[NiG_2(H_2O)_2]$		1608	1412	196
$[CuG_2]$		1611	1396	239

[a] ν_a = average value.

obtained for the complexes, in air atmosphere, were characterised by IR spectroscopy and are summarised in Table 2. In all cases, the calculated and found residues values are in good agreement.

3.3. IR spectra

In the 1700–1300 cm^{-1} region of the IR spectra are present the bands of the amino acid shifted by the coordination with the metal ions. The most significant IR data for the complexes are summarised in Table 3. The corresponding assignments have been made from literature data concerning the free ligand [11] and metal complexes of other amino acid derivatives [12–14].

IR spectroscopy is one of the most frequently used techniques for determination of the number and nature of functional groups involved in the coordination of multidentate amino acids in the solid state [11]. The $\Delta\nu^-_{COO}$ ($\Delta\nu^-_{COO} = \nu_a - \nu_s$) is a measurement of the strength of the COO–M bond. The higher the $\Delta\nu^-_{COO}$ value, the stronger the bond. Ni(II), Co(II), and Cu(II) complexes have a much higher $\Delta\nu^-_{COO}$ value than the free ligand. This means that the COO–M bond must be quite strong in the three cases, especially in the Co(II) and Cu(II) derivatives. The low value of $\Delta\nu^-_{COO}$ in the Mn(II) and Fe(II) complexes suggests that the carboxylate group interacts weakly with the metal ions. Conversely, the $\delta(NH_3{}^+)$ band, which is characteristic of the zwitterion, disappears in the Co(II), Ni(II), and Cu(II) complexes. This fact indicates that the $-NH_2$ group must be involved in the coordination in these cases. These results suggest that, in the three latter compounds, the amino acid must be strongly chelated to the metal ion by the $-COO^-$ and $-NH_2$ groups, forming a stable five-member ring, while, in the Mn(II) and Fe(II) complexes, the ligand is bonded only with the $-COO^-$ group. Monodentate interaction through the weaker ligand–field carboxylate O donor has been identified in a variety of crystal structures of complexes prepared at low pH [15]. These results agree with the thermal behaviour of these compounds.

From the aforementioned results it can be concluded that all the complexes obtained have two coordination-water molecules, except Cu(II) which is anhydrous. In Co(II), Ni(II) and Cu(II) complexes, the amino acid acts as chelate, linking the metal ion via carboxylate and amino functional groups. For Mn(II) and Fe(II) complexes, the amino group remains protonated and does not bond to the metal ion.

References

[1] F. Zhang, A. Odani, H. Masuda, O. Yamauchi, Inorg. Chem. 35 (1996) 7148.
[2] S. Yano, Coord. Chem. Rev. 92 (1988) 113.
[3] D.M. Whitfield, S. Stojkovski, B. Sarkar, Coord. Chem. Rev. 122 (1993) 171.
[4] R. Andreoci, G. Battistuzzi, L. Benedetti, G. Grandi, Inorg. Chim. Acta. 46 (1980) 215.
[5] H. Kozlowski, P. Decock, I. Olivier, G. Micera, A. Pusino, L.D. Pettit, Carbohyd. Res. 197 (1990) 109.
[6] M. Jezowska-Bojczuk, H. Kozlowski, P. Decock, M. Cerny, T. Trnka, Carbohyd. Res. 216 (1991) 453.
[7] T. Sugimori, H. Masuda, O. Yamauchi, Bull. Chem. Soc. Jpn. 67 (1994) 131.
[8] C. Valenzuela-Calahorro, M.A. Díaz-Díez, E. Sabio-Rey, F.J. García-Barros, E. Román-Galán, Polyhedron 11 (1992) 563.
[9] M.A. Díaz-Díez, F.J. García-Barros, E. Sabio-Rey, C. Valenzuela-Calahorro, J. Inorg. Biochem. 53 (1994) 109.
[10] J. Galbis, J.C. Palacios, E. Román, Carbohyd. Res. 114 (1983) 158.
[11] E. Sabio Rey, Ph.D. Thesis, Universidad Nacional de Educación a Distancia (UNED), Madrid, 1990.
[12] G.W.C. Hung, Thermochim. Acta 23 (1978) 233.
[13] M. Tomassetti, E. Cardarelli, R. Curini, G. D'Ascenzo, Thermochim. Acta 113 (1987) 243.
[14] M.J.F. Jackovitz, E.J.A. Durkin, J.L. Walter, Spectrochim. Acta A 23(1) (1967) 67.
[15] T. Kiss, in: K. Burger (Ed.), Biocoordination Chemistry: Coordination Equilibria in Biologically active Systems, ch. III, Ellis Horwood, London, 1990.