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COPPER(II) COMPLEXES OF *N*-ARYLGLYCINE DERIVATIVES

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ABSTRACT

The thermal properties of some Cu(II) complexes obtained in the reaction between copper(II) nitrate trihydrate and *N*-2-ethylphenylglycine (HEPG), *N,N*-4-ethylphenyl-(carboxymethyl)glycine (H_2EPCG) and *N,N*-3,4-dimethylphenyl(carboxymethyl)glycine (H_2DPCG) have been determined. Likewise, coordination modes of these glycine derivatives to the Cu(II) ion have been proposed.

INTRODUCTION

Although the interactions between glycine and its derivatives with metal ions have been studied in detail by a number of authors [1–8], relatively limited information is available on metal complexes of arylglycine derivatives. However, the interactions of Cu(II) with several arylglycinates in aqueous solution have been studied using ultraviolet spectroscopy [6,7,9] and thermal analysis [8,10,11].

The purpose of this paper is to compare and discuss the thermal properties as determined by thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) of some Cu(II) complexes obtained in the reaction of Cu(II) with *N*-2-ethylphenylglycine (HEPG), *N,N*-4-ethylphenyl(carboxymethyl)glycine (H_2EPCG) and *N,N*-3,4-dimethylphenyl(carboxymethyl)glycine (H_2DPCG). To establish the mode of coordination in the complexes investigated, spectral measurements have also been included.

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EXPERIMENTAL

N-2-Ethylphenylglycine and *N*,*N*-4-ethylphenyl(carboxymethyl)glycine were synthesized using a previously described method [12–14]. *N*,*N*-3,4-Dimethylphenyl(carboxymethyl)glycine was obtained as a disodium salt by condensation of 3,4-dimethylphenylamine with monochloroacetic acid in a basic medium (Na_2CO_3). When 5 N HCl is added to an aqueous solution of this salt until pH 2 is reached, the free acid is obtained. H_2DPCG was purified by recrystallization from hot ethanol.

The preparative methods of the three isolated Cu(II) complexes were similar: to 50 ml of an aqueous solution containing 8×10^{-3} mol of the corresponding acid, was added NaOH (0.1 M) until pH 6.5–7.0 was reached. Then, 4×10^{-3} mol of Cu(II) nitrate trihydrate was added. From the resultant solutions, a precipitate immediately appeared. The complexes were filtered, washed repeatedly with ethanol–water mixtures, and air dried. The elemental analyses of these complexes are (%)

Cu(EPG)$_2$ found: C, 57.04; H, 5.72; N, 6.73;

Cald. for $C_{20}H_{24}N_2O_4Cu$: C, 57.20; H, 5.76; N, 6.67.

Cu(DPCG)·2H_2O found: C, 42.96; H, 5.16; N, 4.26;

Cald. for $C_{12}H_{17}NO_6Cu$: C, 43.05; H, 5.12; N, 4.18.

Cu(EPCG)·H_2O found: C, 46.10; H, 4.74; N, 4.50;

Cald. for $C_{12}H_{15}NO_5Cu$: C, 45.50; H, 4.77; N, 4.42.

Analyses of C, H and N were performed at the Institute of Bio-organic Chemistry (CSIC) Barcelona. Copper was determined gravimetrically.

Infrared spectra in the 4000–200 cm^{-1} region were obtained on a Beckman spectrophotometer (model 4250), using KBr as dispersive medium. Ultraviolet–visible spectra were recorded on a Perkin-Elmer spectrophotometer (model Lambda 5). ^{1}H NMR spectra were carried out on a Hitachi/Perkin-Elmer FT-NMR R-600 spectrometer, using hexadeuterated dimethyl sulfoxide as solvent and TMS as internal standard.

Potentiometric titration curves were obtained on a Radiometer TTT-60 apparatus.

The solutions were prepared in double-distilled carbon dioxide-free water. Solutions of different glycine derivatives were prepared by direct weighing from pure samples. Solutions of Cu(II) nitrate were prepared and standardised. A suitable volume of each solution was diluted to 2×10^{-4} M. In all cases, a solution of 0.4 M $NaNO_3$ was used to maintain the required ionic strength. A solution of carbonate-free sodium hydroxide 8.36×10^{-3} M was used as titrating agent.

Magnetic measurements were made at 20°C on a Bruker (model B-M4) magnetobalance, using Faraday's method.

The TG, DTG and DSC curves of the glycine derivatives and their Cu(II) complexes were obtained using a Mettler TA-3000 system equipped with a Mettler thermobalance (model TG-50) and differential scanning calorimeter (model DSC-20). The heating rate was 10°C min^{-1} and the sample weights varied between 1.30 and 10.19 mg. The furnace atmosphere consisted of pure air at a flow rate of 100 ml min^{-1}.

RESULTS AND DISCUSSION

Characterization and thermal behaviour of the free acids

In aqueous solution, these glycine derivatives act as weak acids. Their pK values, calculated (at 20°C and 0.1 M ionic strength in $NaNO_3$) by Bjerrum's method are: pK_1 = 4.83 (HEPG); pK_1 = 3.78 and pK_2 = 5.37 (H_2EPCG); and pK_1 = 4.95 and pK_2 = 5.87 (H_2DPCG).

The spectroscopic studies carried out on these glycine derivatives allowed the values collected in Table 1 to be obtained.

From the IR data of Table 1 it can be established that, in the solid phase, HEPG, H_2EPCG and H_2DPCG show dimeric structures with intermolecular hydrogen bonds between the COOH groups of two molecules of the glycine derivative.

In a recent paper [14] we reported on the thermal behaviour of H_2EPCG and its monosodium salt. The thermal behaviour of HEPG is very similar to H_2DPCG (Fig. 1). In both cases, the TG and DTG curves show a strong weight loss effect in the 120–250°C temperature range, followed by a new,

TABLE 1

Spectroscopic data for the glycine derivatives

	UV: λ(nm)	NMR: δ(ppm)	IR: ν(cm^{-1})
HEPG	283($\epsilon = 2\times10^3$), 237 ($\epsilon = 1\times10^4$)	1.15($-CH_3$)$_t$ 2.50($-CH_2$)$_q$ 3.80($-CH_2$) 6.30–7.10(CH)$_m$	3410 ν(N–H), 2680 ν(O–H), 2560 ν(O–H), 1715 ν(C=O)
H_2EPCG	299 ($\epsilon = 2\times10^3$), 246 ($\epsilon = 1.6\times10^4$)	1.15($-CH_3$)$_t$ 2.05($-CH_2$)$_q$ 4.30($-CH_2$) 6.55(–CH)$_d$ 7.10(–CH)$_d$	2600, 2520w ν(–OH), 1710 ν(C=O), 880 γ(OH) [14]
H_2DPCG	298($\epsilon = 3\times10^3$), 244 ($\epsilon = 1.6\times10^4$)	2.10($-CH_3$)$_s$ 2.15($-CH_3$)$_s$ 4.05($-CH_2$)$_s$ 6.35(C–H)$_d$ 6.90(C–H)$_d$	2610, 2520 ν(O–H), 1715 ν(C=O), 1650 ν(COO^-)

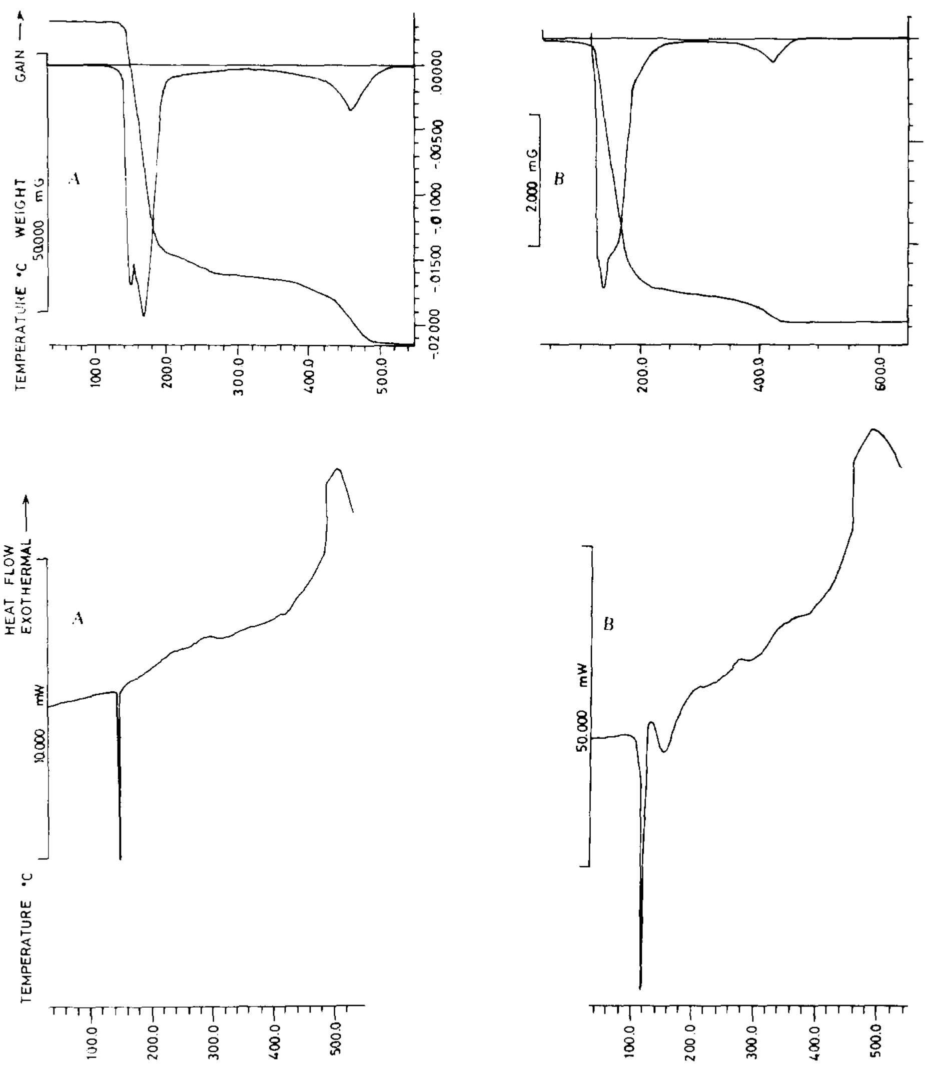

Fig. 1. TG and DSC curves for (A) H_2EPCG and (B) H_2DPCG.

weak weight loss effect at about 450°C. At 500°C the total elimination of the samples occurs.

The DSC curves of HEPG and H_2DPCG display endothermic effects at 146 and 118°C, respectively. These effects correspond to fusion. Values of fusion enthalpies calculated from the areas of these effects were 32.9 and 14.8 kJ mol^{-1}. Likewise, the DSC curve of H_2DPCG, shows a new endothermic effect at 122°C that could be assigned to the release of water between two glycine derivative molecules. This behaviour permits a decomposition mechanism to be proposed for H_2DPCG analogous to that suggested by Khramov et al. [15] and González-Vilchez et al. [16] for the thermal decomposition of iminodiacetic acid and its disodium salt. At 200°C, the pyrolytic decomposition of both glycine derivatives starts, showing pronounced, non-resolved exothermic effects at 520 (HEPG) and 500°C (H_2DPCG).

Characterization and thermal behaviour of the isolated complexes

In aqueous medium HEPG, H_2EPCG and H_2DPCG react with Cu(II) ions to give green complexes. The metal : ligand ratios of these complexes (1 : 1 for H_2EPCG and H_2DPCG and 1 : 2 for HEPG complexes) have been calculated using spectrophotometric and potentiometric methods [17,18].

The stability constants of the complexes have been calculated by application of Bjerrum's method [18] to the potentiometric titration curves of aqueous solutions containing Cu(II) and glycine derivatives in 1 : 1 and 1 : 2 ratios. Only values for the stability constants of complexes of H_2EPCG and H_2DPCG have been obtained. These values were: $K_1 = 8.5.10^4$ (Cu–H_2EPCG); and $K_1 = 6.5.10^3$ and $K_2 = 1.9.10^4$ (Cu–H_2DPCG).

The ultraviolet–visible spectra of the complexes show bands at 266, 278, 371 and 755 nm (Cu–HEPG); 307, 380 and 725 nm (Cu–H_2EPCG) and 308, 385 and 725 nm (Cu–H_2DPCG). In the pH range 3.5–11.5 the spectra of the complexes show a hypochromic effect on the bands centred at 371, 380 and 385 nm, which practically disappear for pH values higher than 9.0. In the same pH range the bands centred at 278 and 308 nm undergo hyperchromic and hypsochromic effects while the band at 307 nm of the Cu(II) complex of H_2EPG shows hyperchromic and bathochromic effects. Likewise, the three complexes show, in the visible region, only one band whose position suggests an octahedral geometry for these complexes [19]. From the positions of these bands, the following values of Δo have been calculated: 13250, 13800 and 13800 cm^{-1}, respectively. On the other hand, from aqueous solutions containing Cu(II) and the corresponding glycine derivative, and in accordance with the above preparative methods, the complexes $Cu(EPG)_2$, $Cu(EPCG) \cdot H_2O$ and $Cu(DPCG) \cdot 2H_2O$ were isolated. The magnetic measurements realized on these complexes, made it possible to obtain the following values for the magnetic moment of the Cu(II) ion: 1.85, 1.90 and 1.88 BM, respectively.

The IR spectra of $Cu(EPG)_2$, $Cu(EPCG) \cdot H_2O$ and $Cu(DPCG) \cdot 2H_2O$ show as more significant bands those indicated in Table 2. The assignments have been made according to the literature values for these compounds [20–23].

At 3210 cm^{-1}, the IR spectrum of $Cu(EPG)_2$ shows one band that can be assigned to an N–H stretching vibration. This band is considerably shifted towards a lower wavenumber in relation to its position in the IR spectrum of the free glycine derivative (see Table 1). This observation is compatible with the assumption that the nitrogen atom is directly linked to the metal ion [24].

TABLE 2

IR absorption bands of copper(II) isolated complexes (cm^{-1})

$Cu(EPG)_2$	$Cu(EPCG)\cdot H_2O$	$Cu(DPCG)\cdot 2H_2O$	Assignment
–	3300 m	3370 s	ν(O–H)
3210 m	–	–	ν(N–H)
3060 w			
3040 w	2970 m	2970 w	
2960 m	2930 w	2950 w	ν(C–H)
2880 w	2860 w	2920 w	
1625 vs	1665 s	1605 vs	$\nu_{as}(COO^-)$
1495 s	1520 s	1505 s	ν(C=C)
–	1395 s	1395 s	$\nu_s(COO^-)$

The bands in the 3400–3300 cm^{-1} region can be assigned to ν(O–H) of water. On the other hand, the three compounds show one absorption band around 1600 cm^{-1} due to the stretching vibration carboxylate groups linked to metal ions. The position of these bands are in accordance with those of the oxygen–metal bonds, which, in these compounds, must be essentially electrostatic [25].

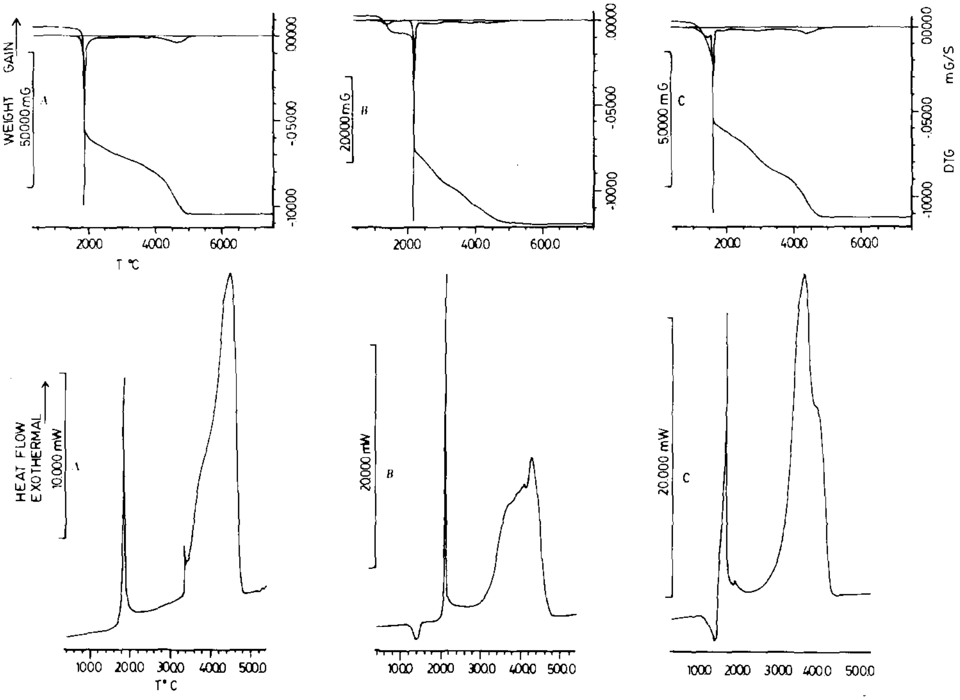

Fig. 2. TG and DSC curves for copper(II) complexes of (A) HEPG, (B) H_2EPCG and (C) H_2DPCG.

From the above results it is suggested that the coordination of the anion EPG to Cu(II) occurs in bidentate form through the nitrogen and oxygen atoms of amine and carboxylate groups. This coordination mode has also been found in other metal complexes of amino acid derivatives [26,27]. For Cu(EPCG)·H_2O and Cu(DPCG)·$2H_2O$ the coordination of the glycine derivative to Cu(II) ion could occur in bidentate or tridentate form, using only the oxygen atoms of carboxylate groups or these atoms plus the nitrogen atom of the amine group.

The TG and DSC diagrams for these Cu(II) compounds are given in Fig. 2.

Under the experimental conditions used in the present work, the dehydration of Cu(EPCG)·H_2O and Cu(DPCG)·$2H_2O$ takes place in one step. The observed weight losses for these processes (5.9 and 11.6%, respectively) are in good agreement with theoretical values (5.69 and 10.76%). The expected endothermic behaviour for the dehydration processes associated with these compounds has been observed in their DSC curves (endothermic effects at 136.9 and 143.1°C, respectively).

The values of dehydration enthalpy for these two compounds are: 73.7 and 43.7 kJ mol^{-1}, respectively. These values are analogous to those obtained in the dehydration processes of other glycinate compounds [22, 23]. Once dehydrated, the anhydrous compounds decomposed immediately, showing rapid and strong decompositions at 180°C ($Cu(EPG)_2$), 210°C Cu(EPCG), and 170°C Cu(DPCG), followed by a slow decomposition from these temperatures to 500°C; at this temperature the residual weights are 18.4, 23.9 and 24.7%, respectively, of the original weight, which corresponds closely to the theoretical values expected for CuO (18.94, 25.11 and 23.76%, respectively). The nature of the residue has been verified by X-ray diffraction and IR spectroscopy.

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