

## **SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF *N*-2,3-DIMETHYLPHENYLGLYCINATE, *N*-2,4-DIMETHYLPHENYLGLYCINATE AND *N*-2-ETHYLPHENYLGLYCINATE COMPLEXES OF Zn(II)**

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(Received 3 January 1984)

### **ABSTRACT**

Three complexes containing bidentate *N*-2,3-dimethylphenylglycine, (2,3-HDPG), *N*-2,4-dimethylphenylglycine, (2,4-HDPG) and *N*-2-ethylphenylglycine, (2-HEPG) acids have been prepared and characterized. These compounds have the general formula  $Zn(2,3-DPG)_2 \cdot 2 H_2O$ ,  $Zn(2,4-DPG)_2$  and  $Zn(2-EPG)_2 \cdot 2 H_2O$ , respectively. The structure of the complexes as inferred from their chemistries have been found to be compatible with the infrared spectral data. The thermal behaviour of these complexes has been studied from their TG, DTG and DSC diagrams obtained in a dynamic atmosphere of pure air. Heats of dehydration have been calculated from DSC curves.

### **INTRODUCTION**

*N*-2,3-Dimethylphenylglycine, *N*-2,4-dimethylphenylglycine and *N*-2-ethylphenylglycine are excellent complexing agents for Cu(II) [1–2]. The addition of copper(II) sulphate to an aqueous solution of sodium *N*-arylglycinates produces an intense green colour giving two distinct types of complex, dependent on the nature of the aryl residue. The essential difference between the two structures is that in one, the aromatic nitrogen atom and one of the carboxyl oxygen atoms act as donors, in the other, both oxygen atoms act as donors and the nitrogen atom is a non-donor [1].

As part of our programme to investigate the interaction of a variety of glycine derivatives with metal ions, the present communication reports the coordination mode and thermal behaviour aspects of several Zn(II) complexes.

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## EXPERIMENTAL

*N*-2,3-Dimethylphenylglycine, *N*-2,4-dimethylphenylglycine and *N*-2-ethylphenylglycine were synthesized using previously described methods [3,4]. Zinc nitrate was used as inorganic salt.

Analyses of C, H and N were performed on a Carlo Erba microanalyser (model 1106). Zinc was determined by atomic absorption.

Infrared spectra in the region 4000–200  $\text{cm}^{-1}$  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).

Thermogravimetric studies on the isolated complexes and free glycine derivatives, were carried out in a dynamic atmosphere of pure air (100 ml  $\text{min}^{-1}$ ) on a Mettler TG 50 thermobalance with a heating rate of 10°C  $\text{min}^{-1}$ . The DSC curves were recorded on a Mettler differential scanning calorimeter (model DSC-20) at a heating rate of 5°C  $\text{min}^{-1}$  in the temperature range 35–550°C.

*Preparation of the complexes*

The preparation methods of the three complexes was similar: to 50 ml of an aqueous solution containing  $6 \times 10^{-3}$  mol of the corresponding acid, was added NaOH (0.1 M) until pH 6.5–7.5 was reached. Then,  $3 \times 10^{-3}$  mol Zn(II) nitrate tetrahydrate was added. From the resultant solutions, a white precipitate immediately occurred. The complexes were filtered, washed repeatedly with ethanol–water mixtures, and air dried. The complexes prepared, along with their elemental analyses, are presented in Table 1.

## RESULTS AND DISCUSSION

The IR spectra of bis(2,3-dimethylphenylglycinate)Zn(II) dihydrate, bis(2,4-dimethylphenylglycinate)Zn(II) and bis(2-ethylphenylglycinate)Zn(II)

TABLE 1

Elemental analysis and colours of compounds (calculated values in parentheses)

	Colour	C(%)	H(%)	N(%)
<i>N</i> -2,3-HDPG	white	66.90 (67.02)	7.42 (7.31)	7.79 (7.82)
Zn(2,3-DPG) <sub>2</sub> · 2 H <sub>2</sub> O	white	52.04 (52.47)	6.23 (6.16)	5.78 (6.12)
<i>N</i> -2,4-HDPG	white	66.98 (67.02)	7.52 (7.31)	7.85 (7.82)
Zn(2,4-DPG) <sub>2</sub>	white	56.81 (56.95)	5.80 (5.74)	6.27 (6.64)
<i>N</i> -2-HEPG	white	66.92 (67.02)	7.41 (7.31)	7.93 (7.82)
Zn(2-EPG) <sub>2</sub> · 2 H <sub>2</sub> O	white	52.83 (52.47)	6.10 (6.16)	6.25 (6.12)

dihydrate, show, as more significant bands those indicated in Table 2. These bands are of diagnostic value in the study of the structures of these and similar compounds [5,6].

In the  $3200\text{ cm}^{-1}$  region the three complexes show a band that can be assigned to an N–H stretching vibration. This band is considerably shifted toward a lower wavenumber in relation to its position in the IR spectra of the free glycine derivatives. This observation is compatible with the assumption that the nitrogen atom is linked directly to metal ion [7].

In the  $1720\text{--}1700\text{ cm}^{-1}$  region the spectra of 2,3-HDPG, 2,4-HDPG and 2-HEPG show a strong band assigned to the resonance carbonyl stretching vibration. Likewise, the spectra of the Zn(II) isolated glycine derivative complexes show only one band at about  $1600\text{ cm}^{-1}$  that can be assigned to  $\nu(\text{C}=\text{O})$ . The absorption in the  $1600\text{ cm}^{-1}$  region indicates that the resonance in the carboxylate ion is preserved in the complexes and therefore oxygen-to-metal bonds in these complexes must be essentially electrostatic [5,6,8].

From the above results it is suggested that the coordination of the glycinato derivatives to Zn(II) ions occurs in bidentate form through nitrogen and oxygen atoms of amine and carboxylate groups, such as has been indicated in the structure below. This coordination mode has been also found in other metal complexes of aminoacid derivatives [9–11].

In the ultraviolet–visible region the spectra of these complexes show three bands, with maxima at the values of wavelength indicated in Table 2. These bands are not appreciably shifted in relation to their positions in the spectra of the free glycine derivatives.

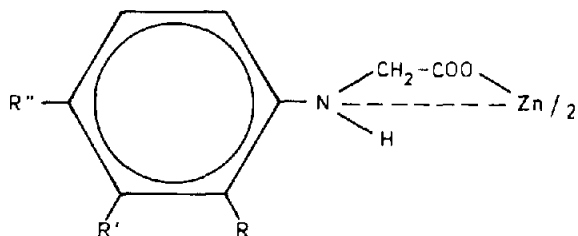
The thermal behaviour of *N*-2,3-dimethylphenylglycine, *N*-2,4-dimethylphenylglycine and *N*-2-ethylphenylglycine has been inferred from their TG, DTG and DSC curves. None of these glycine derivatives show crystallisation water.

Melting temperatures of 2,3-HDPG ( $159.1^\circ\text{C}$ ) 2,4-HDPG ( $127.6^\circ\text{C}$ ) and

TABLE 2  
Infrared and ultraviolet spectral data

	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	absorption maxima (nm)		
<i>N</i> -2,3-HDPG	2800–2500 <sup>a</sup>	3420	3000–2900 <sup>a</sup>	1710	1585	204	240	286
Zn( <i>N</i> -2,3-DPG) <sub>2</sub> · 2 H <sub>2</sub> O	3460 3420	3285	3050–2800 <sup>a</sup>	1585	1490	204	240	285
<i>N</i> -2,4-HDPG	2800 2500 <sup>a</sup>	3410	3000–2900 <sup>a</sup>	1715	1510	202	238	291
Zn( <i>N</i> -2,4-DPG) <sub>2</sub>	—	3255	3050–2800 <sup>a</sup>	1610	1505	202	239	291
<i>N</i> -2-HEPG	2800–2500 <sup>a</sup>	3425	3000–2850 <sup>a</sup>	1715	1605	202	240	283
Zn( <i>N</i> -2-EPG) <sub>2</sub> · 2 H <sub>2</sub> O	3600 3430	3240	3050–2800 <sup>a</sup>	1630	1500	202	240	286

<sup>a</sup> Several bands.



$R'' = H$	$R' = R = CH_3$	2,3-HDPG
$R' = H$	$R'' = R = CH_3$	2,4-HDPG
$R'' = R' = H$	$R = CH_2-CH_3$	2-HEPG

2-HEPG (142.1°C) have been obtained from DSC curves. The values of the corresponding fusion enthalpies are  $7.9 \text{ kJ mol}^{-1}$ ,  $6.7 \text{ kJ mol}^{-1}$  and  $24.7 \text{ kJ mol}^{-1}$ , respectively. Once the glycine derivative is melted, a strong decomposition process takes place, which, in all cases, ends at about 550°C with the total combustion of the sample.

The TG and DSC plots of Zn(II) glycinate derivative complexes are given in Fig. 1. Thermogravimetric results indicate that the decomposition of these complexes occurs in two steps: (i) dehydration; and (ii) decomposition to zinc oxide.

Under the experimental conditions used in this work, dehydration occurs in one step for  $Zn(2-EPG)_2 \cdot 2 H_2O$  whereas for  $Zn(2,3-DPG)_2 \cdot 2 H_2O$  the dehydration process takes place in two steps.

$Zn(2-EPG)_2 \cdot 2 H_2O$  becomes completely dehydrated in the temperature

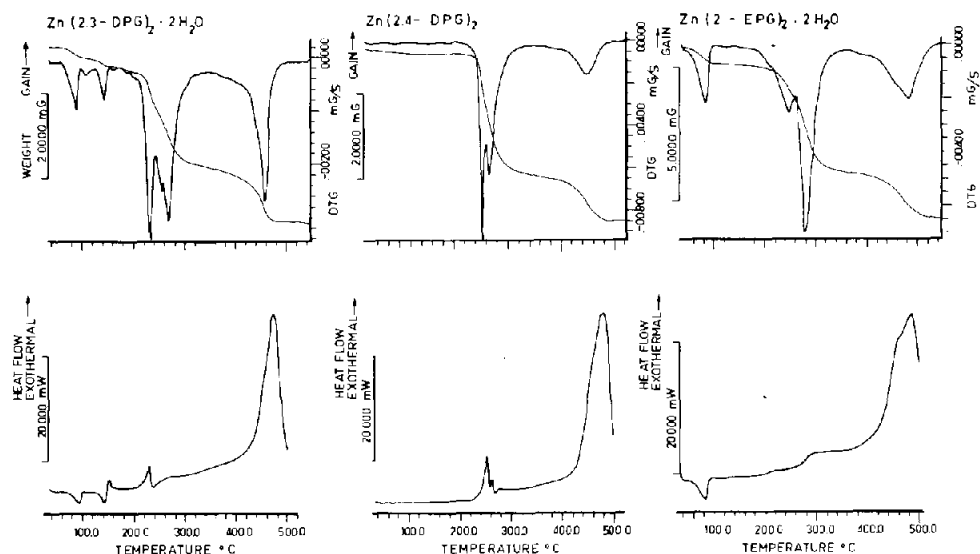


Fig. 1. Thermogravimetric and DSC curves for Zn(II) complexes.

range 50–110°C. The observed weight-loss was 7.33% and corresponds to two molecules of water. The theoretical value calculated from this dehydration (7.87%) is in good agreement with the experimental value. The expected endothermic behaviour for this process has been observed from the DSC curve (endothermic effect centered at 94.2°C). The dehydration enthalpy calculated was 57.3 kJ mol<sup>-1</sup>.

The thermogravimetric curve of Zn(2,3-DPG)<sub>2</sub> · 2 H<sub>2</sub>O shows that dehydration of this complex occurs in two steps. In each of these one molecule of water is eliminated. The observed weight-losses for both steps were 4.47 and 4.07% (theoretical value 3.93%). In the DSC curve, the dehydration process is responsible for the two endothermic effects at 94.2 and 143.7°C. From the area of these effects, dehydration enthalpies were calculated (61.1 and 62.7 kJ mol<sup>-1</sup>, respectively).

Anhydrous Zn(II) glycinato derivative complexes are thermally stable to 220°C. The TG curves show a fast decomposition in the temperature range 220–300°C, followed by a slow decomposition from 300 to 500°C; at this temperature the residual weights are 16.9% (2,3-DPG complex), 18.8% (2,4-DPG complex) and 17.1% (2-EPG complex) of the original weight which correspond closely to the theoretical values expected for ZnO (17.77% for 2,3-DPG and 2-EPG complexes, and 19.29% for the 2,4-DPG complex).

The nature of the residue has been verified by X-ray diffraction and IR spectroscopy.

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