Thermochimica Acta, 207 (1992) 79–84
Elsevier Science Publishers B.V., Amsterdam

Conversion of a hydrogen bonded dinuclear copper(II) complex into a bridged carboxylate related complex by thermal treatment

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(Received 5 February 1992)

Abstract

The thermal behaviour of two dinuclear complexes of copper(II) ion with the 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil ligand was studied by thermogravimetric and differential scanning calorimetric techniques, IR spectroscopy and powder X-ray diffraction. From these studies, the transformation of the copper(II) dinuclear complexes to each other, either by thermal treatment, or by dissolution in the corresponding solvents, is discussed.

INTRODUCTION

Compounds containing a pyrimidine ring and an arylazo group are of interest, mainly because of their significant role in many biological systems and their potential antineoplastic activity [1–5]. Furthermore, using carboxyphenylazo pyrimidine derivatives as ligand, we have succeeded in isolating several polynuclear copper(II) complexes [6–9] with hydrogen bonding or bridging carboxylate groups in the syn–anti conformation. The magnetic behaviour of these polynuclear complexes adds a new point of interest to the study of pyrimidine molecules containing an arylazo group.

Most of the work concerning polynuclear metal complexes with this kind of ligand has been devoted to structural and spectroscopic studies; however, those reporting the thermal behaviour of this type of complex are scanty.

For this reason, in this paper we report the thermal behaviour of two dinuclear copper(II) complexes of 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil (hereafter denoted as LH_2) (see Scheme 1).

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EXPERIMENTAL

Apparatus

The microanalysis of carbon, hydrogen and nitrogen was carried out using a Perkin-Elmer model 240-C. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrophotometer using KBr and polyethylene pellets.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were recorded on a Mettler DSC-20 differential scanning calorimeter. TG diagrams were carried out in a dynamic atmosphere of pure air (100 ml min^{-1}), using samples varying in weight from 7.04 to 9.15 mg. DSC curves were obtained in a static air atmosphere with the samples varying in weight from 2.01 to 2.09 mg, at the same heating rate as for the TG plots.

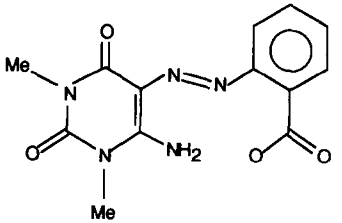
ESR spectra and magnetic susceptibility data were obtained as already described [7].

Preparation of the complexes

The ligand, and the complexes of formulae $[CuL]_2$ and $[CuLpy]_2 \cdot 0.5H_2O$ were prepared as already described [7].

RESULTS AND DISCUSSION

The solid-state infrared spectra of the complexes $[CuL]_2$ and $[CuLpy]_2 \cdot 0.5H_2O$ display features characteristic of the expected tridentate dideprotonated coordination mode of LH_2 [6,7]. Thus the ν(N=N) absorption, which appears at 1530 cm^{-1} in the free ligand, is shifted to lower frequencies, 1425 and 1410 cm^{-1}, respectively. The absorption attributable to ν(N–H) from the deprotonated amino group of L^{2-} appears in the 3212–3209 cm^{-1} range. Finally, the ν_{as}(COO) and ν_s(COO) bands present a large splitting, 250 cm^{-1}, which is consistent with a monodentate coordination mode of the carboxylate group [10–13].



Scheme 1. 6-Amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil.

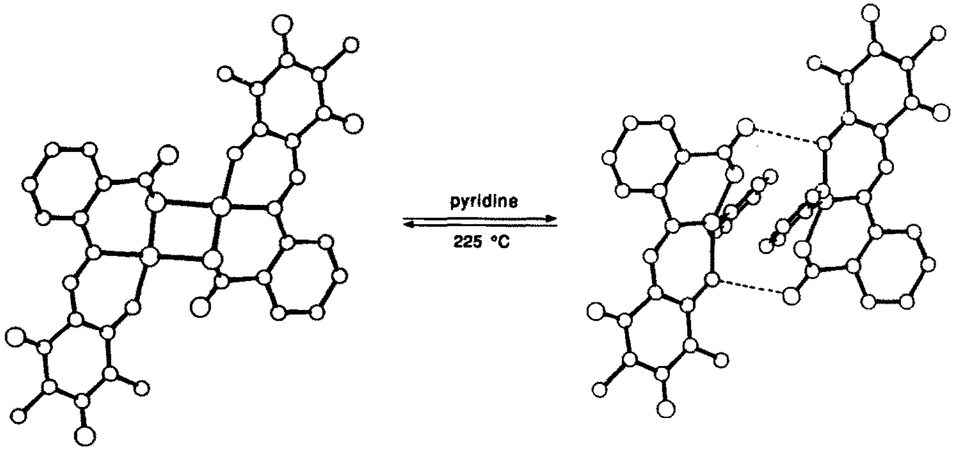


Fig. 1. Conversion scheme for the complexes $[CuL]_2$ and $[CuLpy]_2 \cdot 0.5H_2O$.

The $[CuLpy]_2 \cdot 0.5H_2O$ complex shows bands at 3475, 3060 and 765 cm^{-1} which are not observed in the anhydrous $[CuL]_2$ complex. The first of these is attributed to ν(O–H) from the water molecules, whereas the others are assigned to ν(C–H) and δ(C–H) absorptions from the pyridine ring, respectively. With regard to the region 600–200 cm^{-1}, both complexes show bands assigned to ν(M–N) and ν(M–O) absorptions [14], which are not observed in the ligand spectrum.

The powder EPR spectra of the complexes show triplet-state features and temperature dependence characteristic of antiferromagnetic exchange. Furthermore, the temperature dependence of the magnetic susceptibility supports the antiferromagnetic exchange in both complexes, with $2J$ values of -6.5 and -610 cm^{-1} for $[CuLpy]_2 \cdot 0.5H_2O$ and $[CuL]_2$, respectively. This fact can be explained (see Fig. 1) taking into account that for the former complex the exchange is supported by the hydrogen-bridging network [7]; while for the $[CuL]_2$ complex, the spectroscopic and magnetic data, as well as the thermal transformation (see below) can be appropriately interpreted [10–13,15,16] assuming a structure such as that proposed in Fig. 1. Furthermore, by using a computer program based on an MMX force field we have obtained the proposed structure which presents the lowest energy [17].

Thermogravimetric and DSC curves for $[CuL]_2$ and $[CuLpy]_2 \cdot 0.5H_2O$ are depicted in Fig. 2. The first step of the thermal decomposition of the $[CuLpy]_2 \cdot 0.5H_2O$ complex is the elimination of half a water molecule, which appears in the DSC curve as an endothermic effect between 110 and 125°C ($\Delta H = 15.43$ kJ mol^{-1}), this weight loss effect being in agreement with the experimental results obtained from the X-ray study of this compound [7]. Once dehydrated, the compound undergoes the elimination of

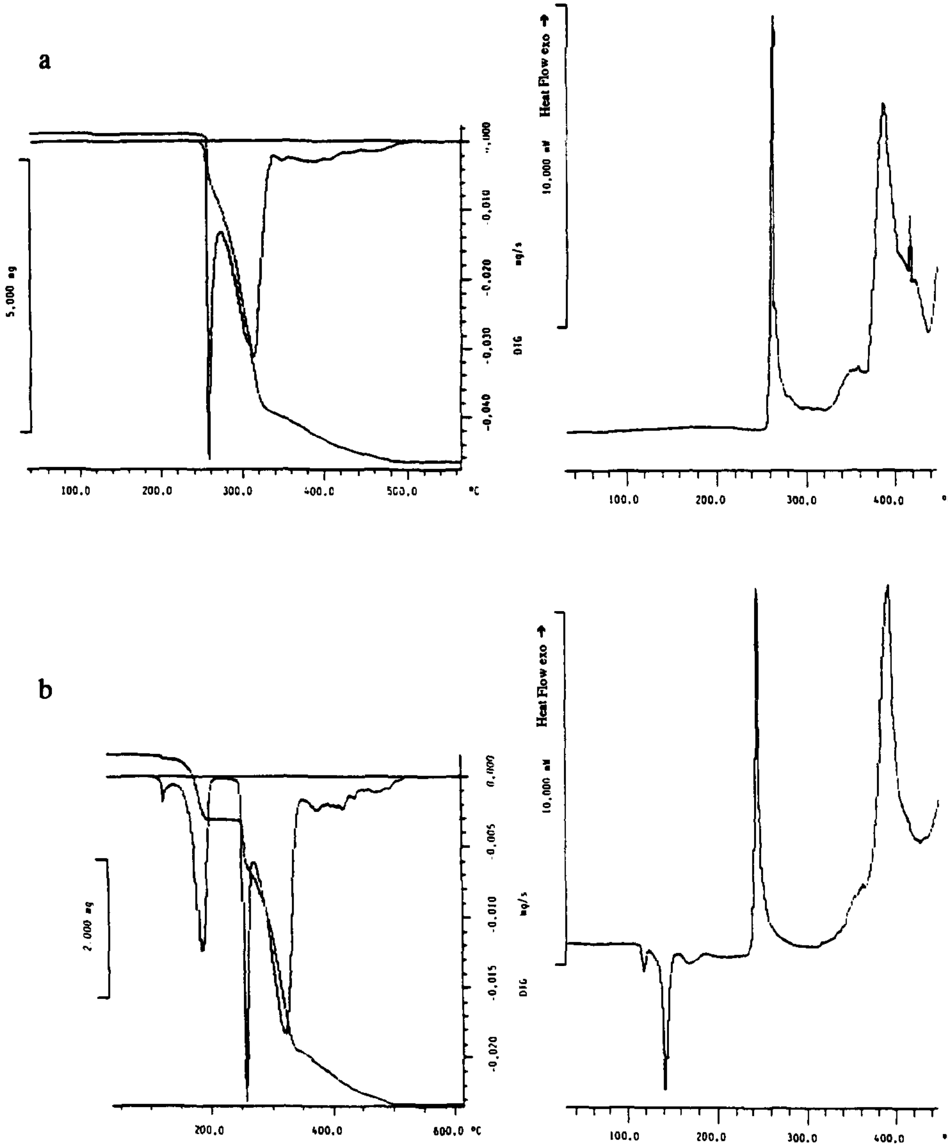


Fig. 2. TG and DSC curves of (a) $[CuL]_2$ and (b) $[CuLpy]_2 \cdot 0.5H_2O$.

the coordinated pyridine molecule. The expected endothermic behaviour for this process has been observed from the DSC curve at 141.1°C ($\Delta H = 51.95$ kJ mol^{-1}), which is in agreement with the values reported for a coordinated pyridine molecule [18].

Once pyridine and water molecules are thermally eliminated, the TG and DSC diagrams of the complexes are identical, as are the IR spectra and powder X-ray diffractograms (see Fig. 3). Therefore, when the complex

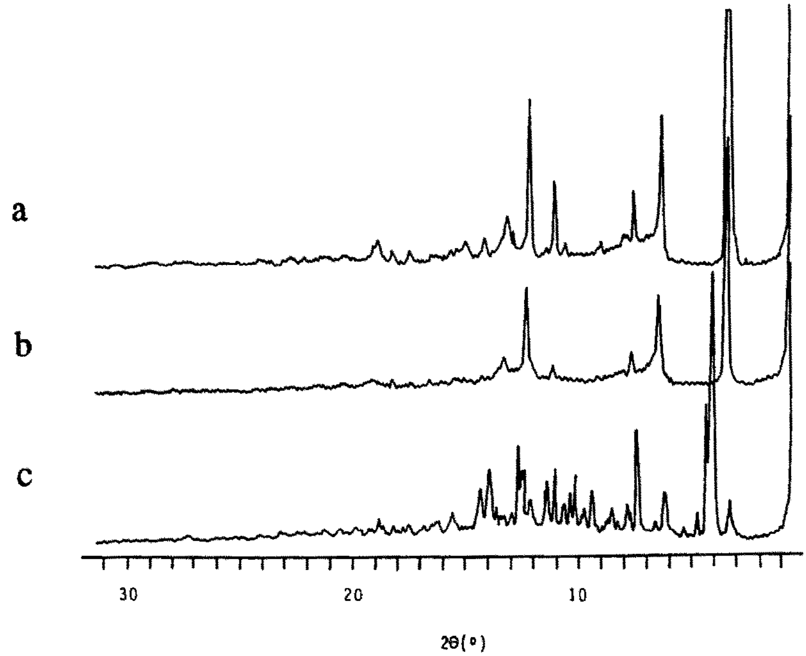


Fig. 3. Powder X-ray diffractograms of (curve a) $[CuL]_2$, (curve b) $[CuLpy]_2 \cdot 0.5H_2O$ heated at 225°C, (curve c) $[CuLpy]_2 \cdot 0.5H_2O$.

$[CuLpy]_2 \cdot 0.5H_2O$ is heated at temperatures immediately above those corresponding to the elimination of pyridine and water molecules, a molecular rearrangement occurs and the complex $[CuL]_2$ is obtained.

Pyrolytic processes of these compounds occur in two different steps. The first one, which overlaps with the combustion of organic matter, appears in the TG curves as weight losses of approximately 10%, a value which is in accordance with that calculated for a decarboxylation process (9.72%). This is supported by DSC curves in which this process appears as a strong sharp exothermic effect at about 264°C, which is in agreement with those reported for coordinated carboxylate groups [19–22].

After the decarboxylation process, the exothermic decomposition takes place to give CuO as a final product. This last step is very similar to that reported previously for the $Cu(DZ)_2py$ complex [18], which is not surprising taking into account that the decarboxylation of the ligand 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil might lead to 6-amino-1,3-dimethyl-5-phenylazouracil (namely DZH).

Keeping all these aspects in mind, we can conclude that the thermal transformation of $[CuLpy]_2 \cdot 0.5H_2O$ into $[CuL]_2$ and the synthesis of $[CuLpy]_2 \cdot 0.5H_2O$ from $[CuL]_2$ involve drastic rearrangements in the structures of the complexes. Thus, the synthesis of $[CuL]_2$ by thermal treatment is particularly favoured in this case by the disposition of the $[CuLpy]_2 \cdot$

$0.5H_2O$ molecules in the crystal packing, as schematized in Fig. 1. Once pyridine molecules are eliminated both monomeric units approach each other, giving rise to a new bond between the coordinated oxygen atom and the copper ion of the neighbour unit. In contrast, the dinuclear structure of $[CuL]_2$ is destroyed by addition of pyridine. Subsequently, the monomeric units crystallize in pairs to form dinuclear entities via hydrogen bonding, formed between the coordinated N–H group and the uncoordinated oxygen atom belonging to the second unit (see Fig. 1).

ACKNOWLEDGEMENT

J.M.D.-V. and J.M.M.-S. are grateful to the Spanish Ministerio de Educación y Ciencia for an FPI grant.

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