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Synthesis of the first example of a dinuclear syn–anti carboxylate-bridged copper(II) complex from a related hydrogen-bonded dinuclear copper(II) complex by thermal treatment

J.M. Moreno [a,*], R. Cuesta [a], J.M. Dominguez-Vera [a] and D. Galisteo [b]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada (Spain)*

[b] *Departamento de Química Orgánica, Escuela Superior de ETS, Universidad de Valladolid, 47011 Valladolid (Spain)*

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Abstract

The synthesis of the first example of a dinuclear syn–anti carboxylate-bridged copper(II) complex from a related hydrogen-bonded dinuclear copper(II) complex with the ligand 1,3-dimethyl-5-[(2-carboxyphenyl)azo]barbituric acid by thermal treatment is discussed. This method is particularly useful because direct synthesis of the dinuclear syn–anti carboxylate-bridged copper(II) complex is difficult. Both complexes have been studied by thermogravimetric and differential scanning calorimetric techniques, and from spectroscopic and X-ray diffraction measurements.

INTRODUCTION

The use of carboxyphenylazopyrimidine derivatives as ligands has provided our group with a versatile route in the synthesis of polynuclear copper(II) complexes. Within these copper complexes, the metal ions have shown a remarkable trend to (4 + 1) coordination mode. Because the carboxyphenylazo derivative usually coordinates in a double-deprotonated tridenate fashion and assuming that the remaining equatorial position is occupied by a secondary monodentate ligand such as water, pyridine, etc., two possibilities can be considered with regard to the axial position. In the first, the axial position is occupied by a monodentate ligand, either identical or not to that in the equatorial position, while in the second case the axial position is occupied by an oxygen atom belonging either to the pyrimidine ring or to the carboxylate group, in this case in a syn–anti configuration. The former case leads to mononuclear or hydrogen-bonded complexes

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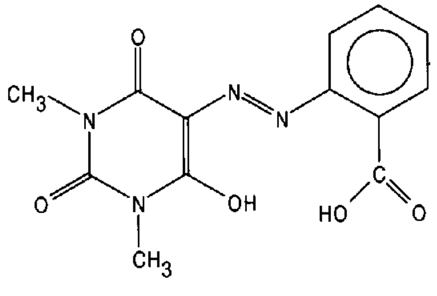
[*] Corresponding author.



H_2L

Scheme 1.

while the latter leads to polynuclear copper(II) complexes by a tetradentate coordination mode of the ligand; several examples of both possibilities have been obtained by our group [1–3].

Recently, we have reported the synthesis of a dinuclear copper(II) complex from a related hydrogen-bonded dinuclear copper(II) complex by thermal treatment [4]. This method is a useful way to obtain polynuclear metal complexes from related mononuclear or hydrogen-bonded complexes, particularly when the direct synthesis is unfavoured.

In this paper, we report on the conversion by thermal treatment of the hydrogen-bonded $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ into the first example of a dinuclear syn–anti carboxylate-bridged complex of formula $[Cu(L)(pzH)]_2$, where H_2L is 1,3-dimethyl-5-[(2-carboxyphenyl)azo]barbituric acid (see Scheme 1) and pzH is pyrazole.

EXPERIMENTAL

Apparatus

The microanalyses of carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer model 240-C. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrometer using KBr and polyethylene pellets. EPR spectra and magnetic susceptibility data were obtained as already described [1].

Thermogravimetric (TG) curves were recorded on a Setaram TAG S16 thermobalance in a dynamic atmosphere of Ar/O_2 (4:1) (100 ml min $^{-1}$) and with a scan rate of 5°C min^{-1}, using samples varying in weight from 6.01 to 6.32 mg. Differential scanning calorimetry (DSC) curves were recorded on a Setaram DSC 11 differential calorimeter in a He/O_2 (4:1) atmosphere with the samples varying in weight from 2.01 to 2.05 mg, at the same heating rate as for the TG plots.

Preparation of the complexes

The ligand H_2L was prepared as already described [5].

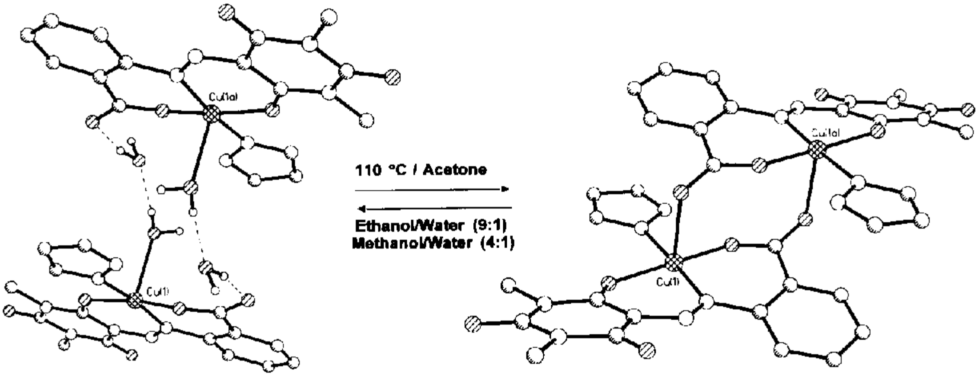
$[Cu(L)(pzH)(H_2O)] \cdot H_2O$ was prepared by adding 0.2 g (3 mmol) of pyrazole to a stirred solution of $[Cu(L)(H_2O)]_n$ [6] (1.15 g, 3 mmol) in methanol/water (50 cm^3, 4:1) at room temperature. After 10 min, a dark green homogeneous solution resulted, from which, by slow evaporation in the refrigerator for two days, dark green crystals of $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ were obtained. These were filtered off, washed with methanol and air-dried: yield, 85%. (Found: C, 40.8; H, 4.0; N, 17.5; Cu, 13.4. $C_{16}H_{18}N_6O_7Cu$ requires C, 40.9; H, 3.8; N, 17.9; Cu, 13.5%.)

$[Cu(L)(pzH)]_2$ was obtained by heating the compound $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ at 110°C in a thermobalance using a flow of air and a scan rate of 5°C min^{-1}. The resulting green microcrystalline powder was recrystallized in dry acetone. After two days, black crystals were obtained by slow evaporation at 4°C: yield, 80%. (Found: C, 44.4; H, 3.2; N, 19.2; Cu, 14.7. $C_{32}H_{28}N_{12}O_{10}Cu_2$ requires C, 44.3; H, 3.2; N, 19.4; Cu, 14.6%.)

RESULTS AND DISCUSSION

It must be pointed out that several attempts to obtain the $[Cu(L)(pzH)]_2$ complex by direct synthesis were unsuccessful.

As can be observed from the crystal structures of both compounds shown in Fig. 1, the ligand presents two different coordination modes, namely tridentate and tetradentate. This is clearly shown in the solid-state infrared spectra of the complexes. The infrared spectrum of $[Cu(L)(pzH)(H_2O)] \cdot$



$\{[Cu(L)(pzH)(H_2O)] \cdot H_2O\}_2$ $[Cu(L)(pzH)]_2$

Fig. 1. Interconversion scheme of the complexes $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ and $[Cu(L)(pzH)]_2$.

H_2O displays features characteristic of the expected tridentate dideprotonated coordination mode. Thus, the existence of water and pyrazole can be inferred from the ν_a(O–H), ν_s(O–H) and ν(N–H) bands at 3548, 3453 and 3283 cm^{-1}, respectively. Formation of relative strong hydrogen bonding is consistent with the broad bands in the range 3600–2900 cm^{-1} due to ν(N–H) and ν(O–H). The coordination through the azo group is indicated by the displacement of approx. 130 cm^{-1} to lower frequencies of the ν(N=N) absorption, which appears at 1524 cm^{-1} in the free ligand. The monodentate coordination mode of the carboxylate group is consistent with the large splitting exhibited by the $\nu_a(CO_2)$ and $\nu_s(CO_2)$ bands, at 1580 and 1401 cm^{-1}, which amounts to approx. 180 cm^{-1} [7–10].

However, the infrared spectrum of the $[Cu(L)(pzH)]_2$ complex, in keeping with its anhydrous structure, does not exhibit any absorption attributable to ν(O–H). The ν(N–H) band belonging to the pyrazole appears at 3359 cm^{-1}. As in the former complex, the ν(N=N) absorption of the azo group is shifted to lower frequencies by approx. 185 cm^{-1}. As mentioned above, the ligand is able to coordinate in a tetradentate fashion, bridging two copper atoms, either by an exocyclic oxygen atom of the pyrimidine ring or by the carboxylate group. In the present case, the ν(C=O) absorptions appear at the same frequencies as in the free ligand, suggesting that the fourth coordination site belongs to the carboxylate group. Finally, it should be pointed out that even though the carboxylate group coordinates in a bridging syn–anti bidentate fashion, a large splitting of 235 cm^{-1} corresponding to the $\nu_a(CO_2)$ and $\nu_s(CO_2)$ bands is observed. This splitting might be due to a strong intramolecular hydrogen bond formed between the N–H, belonging to the pyrazole ring, and the anti-coordinated oxygen atom of the carboxylate group.

The powder EPR spectra of the complexes are suggestive of magnetically coupled copper(II) ions, exhibiting triplet-state features. Interestingly, in DMSO solution the EPR spectra of both complexes show a similar pattern which has been explained by the presence of a similar monomer–dimer equilibrium [11]. Although both complexes exhibit a very weak magnetic interaction, which can be explained on the basis of their crystal structures, the nature of the interactions is very different. Thus, the former complex has an antiferromagnetic interaction, as is usual when the pathway interaction involves a hydrogen bonding network [12–14], while the latter is ferromagnetic, as can be expected in view of the syn–anti coordination mode of the carboxylate group [15, 16].

Thermogravimetric and DSC curves for $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ are depicted in Fig. 2. The first step in the thermal decomposition of the $[Cu(L)(pzH)(H_2O)] \cdot H_2O$ complex is the elimination of both coordinated and hydration water molecules, which appears in the DSC curve as an endothermic effect between 75 and 115°C ($\Delta H = 22.51$ kJ mol^{-1}), the weight loss value obtained from the TG curve (7.9%) being in agreement

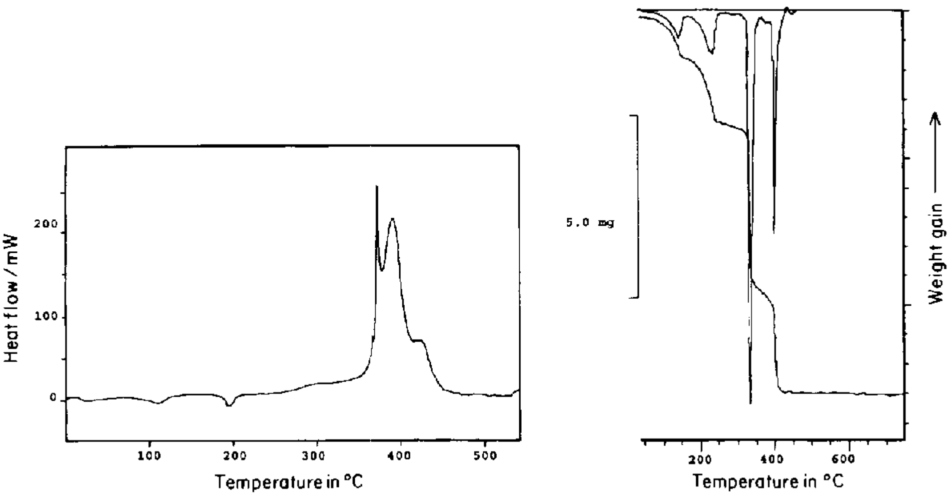


Fig. 2. TG and DSC curves of [Cu(L)(pzH)(H_2O)] · H_2O. Above 110°C, the [Cu(L)(pzH)]$_2$ complex is obtained.

with the experimental results obtained from the X-ray study of this compound (7.67%). The fact that both water molecules are removed at the same temperature can be explained from the number of hydrogen bonds present in the structure [11]. Once the water molecules are thermally eliminated, the TG and DSC diagrams of both complexes are identical, as are their IR spectra. Thus, heating the [Cu(L)(pzH)(H_2O)] · H_2O complex in a temperature range immediately above that corresponding to the elimination of both water molecules, and before elimination of the coordinated pzH occurs, involves a molecular rearrangement in the solid state to give the [Cu(L)(pzH)]$_2$ complex. As can be observed from Fig. 1, both monomeric units of the former complex are appropriately disposed in the crystal packing to approach each other, once the dehydration processes have been completed, forming a new bond between the non-coordinated oxygen atom of the carboxylate group and the copper(II) ion of a neighbour unit related by an inversion centre. It should be noted that even at very low heating rates, the crystallinity of the starting complex was lost, as a consequence of the diffusion of water molecules toward the surface of the crystals.

Next, the curves reveal that the [Cu(L)(pzH)]$_2$ complex undergoes elimination of the pyrazole group. This appears as an endothermic effect in the DSC curve at 206°C ($\Delta H = 23.65$ kJ mol^{-1}), while in the TG diagram the observed weight loss (15.5%) fits with that calculated theoretically (15.69%).

The pyrolytic processes of [Cu(L)] occur in two different steps. Pyrolysis processes of the closely related ligand H_2L^1 in the [Cu(L^1)] complex, where H_2L^1 is 6-amino-1,3-dimethyl-5-[(2′-carboxyphenyl)azo]uracil, occur in two steps [4], the first step corresponding to a decarboxylation process. In the present compound, however, this first step appears in the TG curve as a weight loss of approximately 35%, a value which would be in accordance with that calculated for the combustion of the carboxyphenyl moiety (32.8%). This appears in the DSC diagram as a strong sharp exothermic effect centred at 336°C. Both the TG and DSC curves show that this intermediate is unstable, as has been reported for related compounds [17], and continues to decompose up to 449°C to give CuO as the final residue of the pyrolytic decomposition.

In conclusion, the thermal treatment has proved to be an effective method of polynuclear copper(II) complex synthesis. Moreover, the importance of this method is enhanced when there are difficulties in direct synthesis, as occurs in the present case. Nevertheless, the application of this method is limited by two main factors. First, a linear temperature range, in which the starting compound will be stable, is needed in order to stop the thermal process. Second, an appropriate disposition of the monomeric units of the starting complex in the crystal packing seems to be the crucial factor, because molecular rearrangements in the solid state are limited by the symmetry of the crystal packing.

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