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THERMOANALYTICAL INVESTIGATION OF THE SYNTHESIS OF PYRAZINE AND BIPYRAZINE VIA THE PYROLYSIS OF THE BIS(PYRAZINECARBOXYLATE)COPPER(II) COMPLEX

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Abstract

The pyrolysis of hydrated bis(pyrazinecarboxylate)copper(II) under an argon atmosphere proceeds via the loss of the water molecules at 84–95°C, ΔH=40.4 kJ (mol H_2O)$^{-1}$ followed by the thermal decomposition of the complex at 284–325°C, ΔH=97.0 kJ·mol^{-1}, yielding 0.72 mole of pyrazine, 0.28 mole of bipyrazine, and 2 mole of CO_2 per mole of complex.

Keywords: complexes, synthesis of pyrazine and bipyrazine

Introduction

This work deals with a thermoanalytical study of the bis(pyrazinecarboxylate)copper(II) complex, here denoted [Cu(pzCO_2)$_2$]. In the last decade, the chemistry of transition metal complexes containing bipyridine (bpy) and bipyrazine (bpz) ligands has been extensively investigated because of their remarkable photochemical and photophysical properties [1–4]. Most of the studies have been concentrated on the complexes with the bipyridine ligand, which is commercially available and relatively cheap. Bipyrazine is much more expensive, but can be conveniently prepared by the pyrolysis of the bis(pyrazinecarboxylate)copper(II) complex [5]. In spite of its great importance, to our knowledge, a quantitative study on the pyrolytic synthesis of bipyrazine has never been reported before.

Experimental

The [Cu(pzCO_2)$_2$(H_2O)$_2$] complex was prepared as follows: 25 g (0.2 mole) of pyrazinecarboxylic acid (Aldrich) and 8.0 g (0.2 mole) of NaOH were dis-

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solved in 100 ml of hot water, and 100 ml of an aqueous solution containing 25 g (0.1 mole) of $CuSO_4 \cdot 5H_2O$ were added dropwise. After 30 min, the blue precipitate was collected on a filter and dried in air. The complex can be purified by dissolving in hot water, and allowing the solution to stand at room temperature for several days in order to obtain well formed crystals. Analysis: Calcd for $C_{10}H_{12}N_4O_6Cu$: C, 34.5; H, 3.4; N, 16.1%. Found: C, 35.1; H, 3.2; N, 16.0%.

Recrystallization is not necessary for preparative purposes, but the complex should be dried at 120°C in order to prevent condensation of the hydration water molecules during the process. In this work, the pyrolysis of the complex was carried out in the hood, using a pyrex tube of 2.5 cm diameter and 1 m length, horizontally placed with one end connected to a bubbler trap filled with glass wool, and the other connected to a dry nitrogen line and a temperature probe, as described elsewhere [6]. The complex was placed inside the tube, and a very small flow of argon was passed for 20 min in order to ensure an inert atmosphere. The tube was locally heated using a tubular oven or a Bunsen burner, under a very slow flow of argon. Decomposition proceeds vigorously around 300°C yielding white clouds of sublimed pyrazine (*m.p.* 55°C, *b.p.* 115°C) and bipyrazine (*m.p.* 185°C). Crystallization of bipyrazine takes place all over the internal wall of the tube. Pyrazine can be collected in the bubbler trap immersed in an ice-water bath. After 20 min, the temperature was raised up to 400°C, and then the system was allowed to cool at room temperature. Bipyrazine was directly collected from the tube, and recrystallized from toluene or by sublimation. Analysis: Calcd for $C_8H_6N_4$: C, 60.7; H, 3.8; N, 35.4%. Found: C, 60.7; H, 3.8; N, 35.8%.

For analytical purposes, a 20 cm long tube was employed and the volatile products were captured in a series of bubbler traps containing water or barium hydroxide solution, respectively. The solutions were analysed by spectrophotometry for pyrazine and bipyrazine, and CO_2 was determined gravimetrically as $BaCO_3$. All the experiments were performed in duplicate.

Thermal analysis (TG and DSC) was carried out with a DuPont model 2000 equipment, under a nitrogen atmosphere, with a constant heating rate of 10 $deg \cdot min^{-1}$. In the DSC measurements an indium standard was used for calibration. Spectrophotometric measurements were carried out with a Hewlett-Packard, model 8452-A diode-array instrument, or a Guided-Wave model 260 fiber-optics spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer model 783 spectrophotometer, in KBr pellets, or using 10 cm pathlength NaCl cells in the case of gas samples.

Results and discussion

The thermoanalytical behaviour of the bis(pyrazinecarboxylate)copper(II) complex dihydrate is illustrated by the typical TG and DSC curves shown in

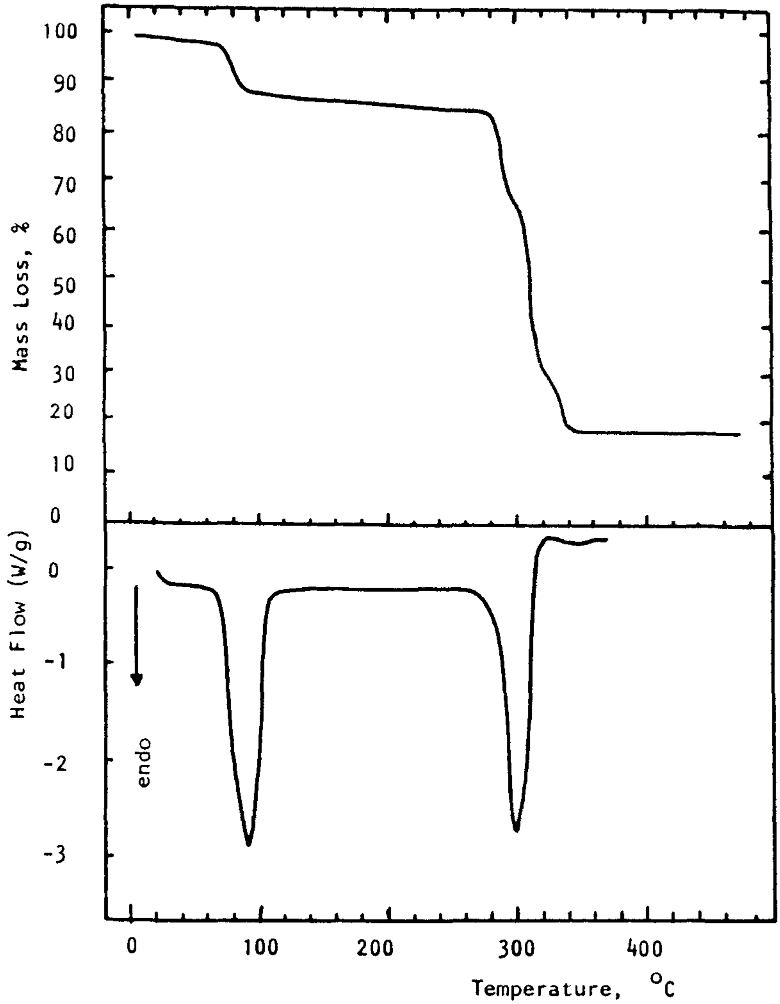

Fig. 1 TG and DSC curves for $[Cu(pzCO_2)(H_2O)_2]$, at a heating rate of 10 deg·min^{-1}, under nitrogen

Fig. 1. The loss of hydration water occurs in a single of endothermic step at 84–95°C, with ΔH=40.4 kJ (mol H_2O)$^{-1}$. The change in mass of 11.0±0.5% corresponds to the loss of 2 water molecules (theoretical = 10.36%), in agreement with microanalytical results. The activation energy estimated by means of Coats-Redfern method [7] for a first-order process was 240±20 kJ·mol^{-1}.

The thermal dehydration process leads to pronounced color changes, from light blue to dark marine blue. The electronic spectra of the complex in the solid state can be seen in Fig. 2. The starting complex exhibits a broad, composite, d-d band at 662 nm (15 100 cm^{-1}) and a shoulder around 1000 nm,

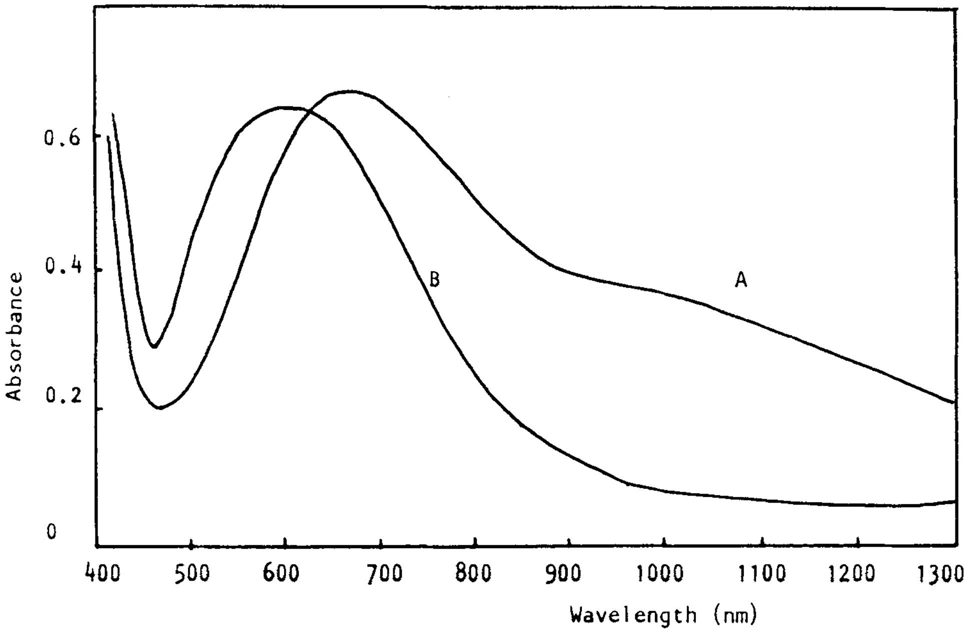

Fig. 2 Diffuse reflectance spectra of the $[Cu(pzCO_2)_2(H_2O)_2]$ complex (A) and of the dehydrated solid (B) after heating at 120°C

(10 000 cm^{-1}), while the dehydrated complex exhibits only a broad band at 600 nm, (16 600 cm^{-1}). The spectral changes are consistent with the coordination of the water molecules to the copper ion in the solid complex, as previously reported by Langfelderová *et al.* [8], for related complexes.

Figure 1 shows that the decomposition of the complex starts at 282°C, and is accompanied by three inflections in the thermogravimetric curves. The first two overlapping steps may be associated with the rapid release of CO_2, followed by the evolution of the volatile pyrazine and bipyrazine products. The corresponding change in enthalpy, ΔH=97.0 kJ·mol^{-1} is the sum of the reaction enthalpy and the vaporization enthalpies of the volatile products. The last step starts around 325°C and involves the decomposition of a residue containing 31% of the original mass, in a slightly endothermic process. The final product represents only 18% of the original mass, corresponding to the expected amount of the copper metal in the complex.

For analytical purposes, the pyrolysis of the $[Cu(pzCO_2)_2(H_2O)_2]$ complex was carried out in a tubular oven, as described in the experimental section. A typical electronic spectrum of the volatile products collected in the bubbler trap is shown in Fig. 3, in comparison with the spectra of the pyrazine and bipyrazine species. The spectrum of the mixture can be accurately fitted by the sum of the spectra of the two components, and thus the analytical determination

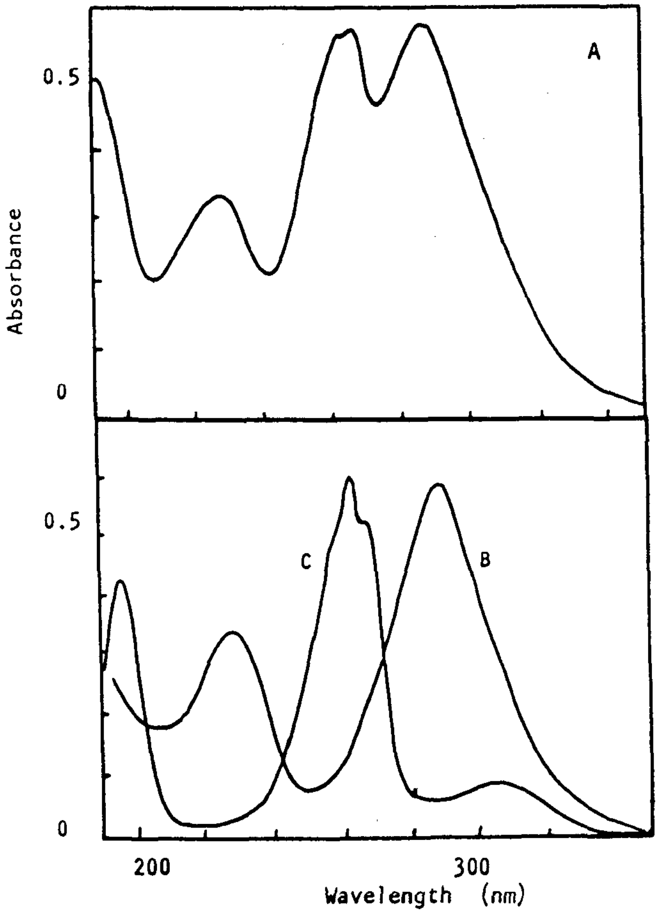

Fig. 3 Absorption spectra of the volatile products of the pyrolysis of $[Cu(pzCO_2)(H_2O)_2]$ at 330°C (A), and of pure samples of pyrazine (B) and bipyrazine (C), in aqueous solution, for comparison purposes

is greatly facilitated. For this reason, a direct spectrophotometric analysis was preferred in this work. Most of the analyses were carried out at the maximum wavelengths for pyrazine (262 nm) and bipyrazine (290 nm), using the equations:

$$A_{262}=\varepsilon_{pz,262}\cdot b\cdot c_{pz}+\varepsilon_{bpz,262}\cdot b\cdot c_{bpz}$$

and

$$A_{290}=\varepsilon_{pz,290}\cdot b\cdot c_{pz}+\varepsilon_{bpz,290}\cdot b\cdot c_{bpz}$$

where A is the measured absorbance, $b=1$ cm, c_{pz} and c_{bpz} are the concentrations of pyrazine and bipyrazine, respectively, and $\varepsilon_{pz,262}=6.07\times10^3$, $\varepsilon_{bpz,262}=5.70\times10^3$, $\varepsilon_{pz,290}=6.7\times10^2$ and $\varepsilon_{bpz,290}=1.90\times10^4$ M^{-1} cm^{-1}.

A number of experiments were performed, by varying the mass of the complex, heating time, and argon flow rate. The results were practically equivalent within an experimental error of 10%.

A black residue is formed in the pyrolysis, representing 30±3% of the original mass. This residue contains the species responsible for the inflection above 325°C in the thermogravimetric curve. Elemental analysis of this residue yielded C=23.6; N=13.3 and H=1.5%, which is consistent with the composition $CuC_2NH_{1.6}$. The diffuse reflectance spectrum in the visible region exhibited no characteristic absorption band in the 400–1700 nm range. The infrared spectrum exhibited a very broad band at 1600–1400 cm^{-1}, three weak bands at 1150, 1010, 850 cm^{-1} and a broad band at 600–450 cm^{-1}, suggesting a species containing C–C=N or C=C–N bonds. The residue was insoluble in all the solvents employed, e.g., acetonitrile, N,N'-dimethylformamide, dimethylsulfoxide, chloroform, dichloromethane, toluene, benzene, diethyl ether, *n*-hexane, water and acetic acid, suggesting a complex polymeric structure. When this residue is heated above 340°C, there is a 42% loss in mass, with no significant increase in the yield of pyrazine or bipyrazine. The final mass corresponds to 18% of the mass of the starting complex, in agreement with the thermogravimetric results which indicated the formation of metallic copper.

Based on the analysis of the thermal decomposition products, the following reaction can be proposed for the pyrolysis of the $[Cu(pzCO_2)(H_2)_2]$ complex:

$$[Cu(pzCO_2)(H_2O)_2] \rightarrow$$
$$(0.72\pm0.05)pz+(0.28\pm0.02)bpz+(2.0\pm0.2)CO_2+CuC_2NH_{1.6}+(2.0\pm0.1)H_2O$$

or

$$C_{10}H_{10}N_4O_6Cu \rightarrow$$
$$0.72C_4N_2H_4+0.28C_8N_4H_6+2.0CO_2+CuC_2NH_{1.6}+2H_2O$$

The mass balance for the various elements yields C=9.1±0.6; H=10.6±0.5; N=3.6±0.2; O=6.0±0.5, and Cu=1.0.

In order to confirm the proposed stoichiometry, several volumetric determinations were carried out by heating the complex under an argon atmosphere, and collecting the released gas in an inverted graduated cylinder filled with water. The measured volumes were proportional to the mass of the complex, corresponding to 2.2±0.2 mole of gas for each mole of $[Cu(pzCO_2)_2(H_2O)_2]$. The infrared spectrum of this gas exhibited only the absorption peaks characteristic of CO_2 at 2350 cm^{-1}.

As in the pyrolysis of copper(II) complexes of carboxylic acids reported in the literature [9] the thermal decarboxylation of the pyrazinecarboxylate ligand should be induced by the copper(II) ions, via an internal redox process, leading to the formation of pyrazine radicals and CO_2. The pyrazine radicals can dimerize, yielding bipyrazine, or abstract a hydrogen atom from the reaction mixture, forming pyrazine. The reasonable yields of bipyrazine and pyrazine, with high purity, make the pyrolitic process very convenient for preparative purposes.

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Zusammenfassung — Die Pyrolyse von hydratiertem Bis-(pyrazincarboxylat)kupfer(II) in einer Argonatmosphäre verläuft über den Verlust der Wassermoleküle bei 84–95°C, $\Delta H=40.4$ kJ/mol H_2, gefolgt von einer thermischen Zersetzung des Komplexes bei 284–325°C, $\Delta H=97.0$ kJ/mol, wobei man je 1 mol Komplex 0.72 mol Pyrazin, 0.28 mol Bipyrazin und 2 mol CO_2 erhält.