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THERMAL BEHAVIOUR OF [N(2-AMMONIUMETHYL) PIPERAZINIUM] PENTACHLOROCUPRATE(II) DIHYDRATE

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The thermal behaviour of single-crystals of the title compound has been investigated by means of thermal methods supported by optical microscopy. A complex change takes place on heating. After the loss of the two water molecules, leading to an amorphous phase, recrystallization takes place. This results in a solid (probably an anhydrous form) which reacts further, through partial liquefaction, to yield a red crystalline product whose structure has been characterized via X-ray powder spectra and electronic and IR spectroscopy.

Reactions involving solids, generally restricted to those occurring between or within solids, may involve two fundamental processes, determined by 1) a bond-breaking and bond-making operation, resulting in the production of nuclei of a new phase, and 2) transport of material to the reaction zone, causing the growth of these nuclei.

In this paper we investigate the thermal behaviour of the title compound, with the aim of dealing with a type of transformation in which the loss of a constitutent of the solid system (in this case water molecules) as the temperature is varied is accompanied by unforeseen changes leading to a modification of the coordination geometry of the chromophore. This phenomenon is visualized by a color change.

Experimental

The thermal curves were recorded by means of a Mettler TA 2000 thermal analyzer, employing sealed Al pans; a small hole was drilled in the sample pan for the escape of the water molecules produced in the reaction. A Reichert Zetopan optical microscope equipped with interference contrast and an Olympus OM 2 camera was also used. Infrared spectra were recorded in nujol mull and on KBr pellets as support with a Perkin–Elmer 180 spectrophotometer. Electronic spectra were recorded as mull transmission spectra, with a Shimadzu MPS 50L spectrophotometer. X-ray powder spectra were recorded with a Philips instrument.

Results and discussion

On elevation of the temperature, the title compound, containing discrete $CuCl_5^{3-}$ anions with a slightly distorted square-pyramidal coordination, $[N(2amet)pipzH_3]^{3+}$ ions and two water molecules of crystallization [1], shows a progressive loss of the crystallization water molecules; this is completed in the temperature range 373–383 K and is accompanied by a color change from yellow-green to red.

DTA determinations spanned the temperature range from room temperature to 573 K, but here reference will be made only to the evidence obtained up to 423 K. The thermal curves show a slow loss of the water molecules in the temperature interval from 303 to 353 K. Further heating leads to a rapid increase in the rate of dehydration, as evidenced by the formation of an endothermic peak; however, this is almost cut in two parts by a sudden exothermic event, as shown in Fig. 1.

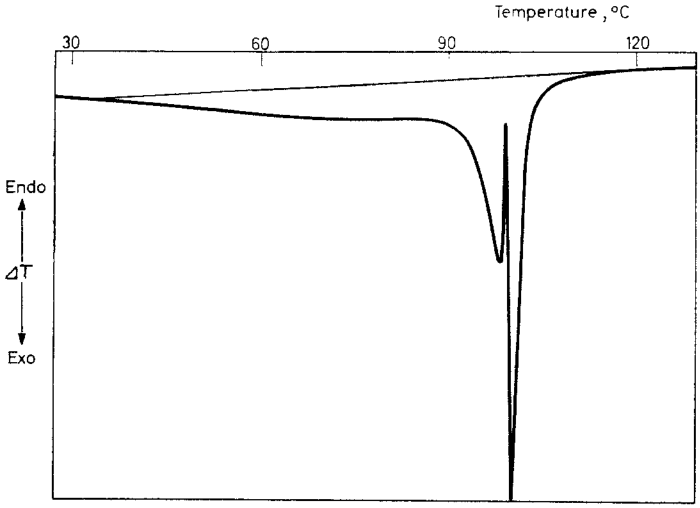

Fig. 1 Thermal curve recorded during the heating of the title compound. Such shape may change with the rate of heating

The heat of transformation is 187±16 J/g, corresponding to $\Delta H \cong 37.7$ kJ (mole H_2O)$^{-1}$. This value is rather low if compared with the heat per mole of water computed for the dehydration of crystal hydrates, $\Delta H \cong 56.5$ kJ (mole H_2O)$^{-1}$ [2]. The difference might be due to an exothermal crystallization peak, and/or to an unknown exothermal heat of transformation (vide infra).

The optical microscopy experiments show that in the range 303–363 K the formation of an amorphous phase takes place and progressively leads to the darkening of the crystal observed in transparence between crossed polarizers (Fig. 2a, b, c, d). In this range the behaviour of the observed crystals is quite similar to the one recorded during the thermal monomerization of single-crystals of 9-cyanoanthracene photodimer [3, 4]. In that case too the reaction appeared to take place mainly on particular planes

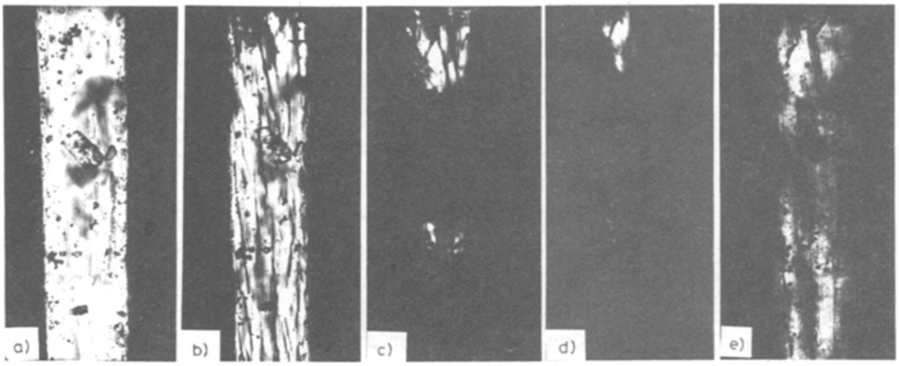

Fig. 2 Sequence of micrographs of a single crystal examined in transparence between crossed polarizers: a) 292 K, b) 341.6 K, c) 351 K, d) 360.8 K, e) 370.6 K

and along preferred directions, and to evolve alternating periods of regular growth to sudden darkenings of relatively large areas. A striking example is shown in Fig. 3a, b, c, where a sequence of micrographs of the simultaneous reactions of two crystals differing in orientation (as shown by the different extinction directions) is reported. To a first approximation, we assume that in the present case the same kind of interpretation as given earlier [4] may apply. The identification of the crystallographic planes and directions, however, is left to further studies.

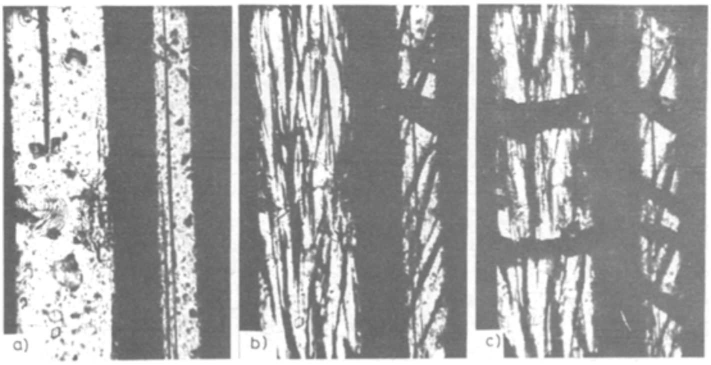

Fig. 3 Sequence of micrographs of a couple of differently oriented single crystals: a) 296 K, b) 337 K, c) 350 K. See text

After more or less complete darkening, the crystals again become clear (Fig. 2e), indicating that recrystallization has occurred. This happens at about the same temperatures as those recorded in thermal experiments, corresponding to the sudden exothermal events interrupting the endotherms at about 373 K. Exothermal behaviour of this kind has previously been observed during the monomerization of the photodimer of 9-cyano-10-acetoxyanthracene [3].

The regained transparence of the crystal does not last for long. In fact, at these temperatures the transformation of the yellow-green starting material to the dark-red product takes place rather quickly, helped by the observed formation of a liquid phase [5]. If black and white films are used, the formation of liquid phases and the dark red colour of the product may, on the developed film, simulate the formation of another amorphous phase because of low both the amount and actinism of the light transmitted by the observed material. However, the product of the complex transformation is crystalline, as shown by the presence of the extinction phenomenon.

The physical properties, infrared, electronic (Fig. 4) and powder X-ray spectra (Fig. 5) of the thermally-obtained red compound indicate that it is the same compound as that separated from concentrated hydrogen chloride in the presence of a metal/cation molar ratio of 1/1, with formula $Cu_5Cl_{22}[N(2amet)pipzH_3]_4$. This compound contains four independent copper(II) atoms in the cell, having four different types of geometry [6].

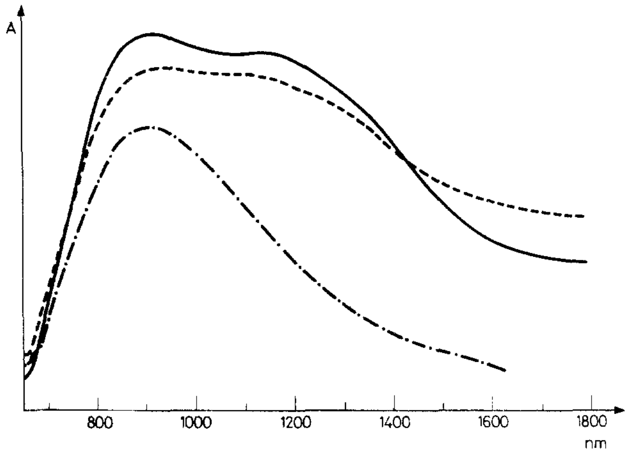

Fig. 4 Comparison among the electronic spectra of the yellow-green $CuCl_5(LH_3) \cdot 2\ H_2O$ complex (—.—.—), red "crystallized" $Cu_5Cl_{22}(LH_3)_4$ (— — —) and red "thermally" obtained $Cu_5Cl_{22}(LH_3)_4 \cdot L(HCl)_3$ (———) complexes

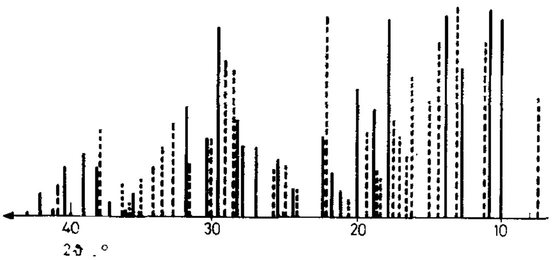

Fig. 5 Comparison the X-ray powder spectra of the yellow-green $CuCl_5(LH_3) \cdot 2\ H_2O$ complex (———) and of the red compounds (— — —)

The overall thermal process may therefore be schematized as follows:

$$5\,CuCl_5[LH_3]\cdot 2\,H_2O \xrightarrow[-\,10\,H_2O]{303-358\ K} 5\,CuCl_3[LH_3] \xrightarrow{368-373\ K}$$

$$\longrightarrow Cu_5Cl_{22}[LH_3]_4[L(HCl)_3]$$

Disregarding the chemical aspects of the present problem, the analogous behaviour of the studied compound and of the 9-cyanoanthracene photodimer appears to be further supporting evidence what was deduced from studies on the dehydration/rehydration reactions of crystal hydrates [7, 8]. The mechanisms of the reactive transformations of crystalline solids are not so much dependent on the chemical compositions and structures of the solids themselves as on the presence and properties of interphasal zones, such as the external surfaces of the crystals and probably also some internal surfaces of defect origin.

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Zusammenfassung – Das thermische Verhalten von Einkristallen der Titelverbindung wurden mittels thermischer Methoden und optischer Mikroskopie untersucht. Beim Erhitzen verläuft ein komplexer Prozeß. Nach dem zu einer amorphen Phase führenden Verlust von zwei Wassermolekülen findet eine Rekristallisation statt. Dabei wird eine feste Substanz, wahrscheinlich in wasserfreier Form, erhalten, die über partielle Verflüssigung unter Bildung eines roten kristallinen Produktes weiterreagiert, dessen Struktur durch Röntgenpulverspektren sowie Elektronen- und Infrarotspektroskopie charakterisiert wurde.

Резюме – Термическое поведение монокристаллов ряда соединений исследовано термическими методами, дополненных оптической микроскопией. При нагревании этих кристаллов протекают сложные превращения. Потеря двух молекул воды приводит к образованию аморфной фазы с последующей ее кристаллизацией. Это может быть следствием того, что твердая, вероятно, безводная форма реагирует дальше с частичным разжижением, образуя красный кристаллический продукт, структура которого была установлена с помощью рентгеновских спектров, электронных спектров поглощения и ИК спектроскопии.