

THERMAL DECOMPOSITION OF DIHYPOPHOSPHITO—(UREA)—COPPER(II)

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The physico-chemical properties of the newly synthesized complex $\text{Cu}(\text{H}_2\text{PO}_2)_2\text{CO}(\text{NH}_2)_2$ were investigated. The unit cell parameters and the mode of coordination of the urea molecule were determined. The thermal decomposition of the complex, which displays a topochemical character, was studied by thermogravimetric and mass-spectrometric methods. The end-products of the decomposition were detected. The activation energies of the process in the temperature ranges 323–330 K are 23.4 ± 1.4 and 20.64 ± 2.2 kcal/mol, respectively.

Studies on the properties and thermal decomposition of copper(II) hypophosphite and diamminecopper(II) hypophosphite dihydrate [1–4] have shown these copper complexes to be interesting subjects for solid-state chemistry. It has been found that the mechanism of thermal decomposition depends on the ligands introduced into the coordination sphere of the copper. This paper reports the results of an investigation on the physico-chemical properties and thermal decomposition of dihypophosphito-(urea)-copper(II) (DHUC), a new representative of the copper complexes of hypophosphorous acid.

Experimental

The complex was prepared from an aqueous solution containing a copper(II) salt, calcium hypophosphite and urea in 1:1:2 molar ratio. The solution was allowed to evaporate at room temperature for several days to form well-developed single-crystals of the product. The crystals are light-blue in colour, insoluble in ethyl alcohol, diethyl ether and other organic solvents, but well soluble in water.

Anal.: Calcd. for $\text{Cu}(\text{H}_2\text{PO}_2)_2\text{CO}(\text{NH}_2)_2$, wt. %: Cu, 25.05; H_2PO_2 , 51.28; N, 11.05; C, 4.73; H, 3.16. Found, wt. %: Cu, 25.00; H_2PO_2 , 47.61; N, 10.80; C, 4.87; H, 3.02.

X-ray structural studies were carried out with an RKOP camera installed in a cryostat at -10° , using copper radiation. X-ray diffraction investigations were

performed with a DRON-3 instrument using CuK_α radiation. IR spectra were recorded in vaseline oil or KBr pellets, with a UR-20 spectrometer.

Decomposition of the complex was studied in the temperature range 323–345 K and the pressure range 10^{-4} Pa. The weight loss during the process was determined by thermogravimetry. Evolved gas analysis was carried out with an MX-7303 spectrometer. A general mass-spectrum was recorded in the range 1–130. Condensed products were analysed by X-ray and chemical analysis. The fractional reaction α was determined from the weight loss (error $\pm 4\%$) and mass-spectrometric measurement of the mass 18 peak intensity (error $\pm 4\%$).

Results and discussion

The elemental analysis of the synthesized complex agreed with the molecular formula $\text{Cu}(\text{H}_2\text{PO}_2)_2\text{CO}(\text{NH}_2)_2$. Interplanar distances determined from the X-ray diffraction pattern are given in Table 1. The symmetry of the complex is triclinic, and there are 2 molecules in a cell with the dimensions:

$$a_0 = 7.01 \text{ \AA}; b_0 = 7.95 \text{ \AA}; c_0 = 7.63 \text{ \AA}; \alpha = 100^\circ; \beta = 120^\circ; \gamma = 80^\circ.$$

Table 1 Interplanar distances of DHUC

$d, \text{ \AA}$	I/I_0	$d, \text{ \AA}$	I/I_0
6.37	24	2.739	1
6.13	100	2.622	1
3.72	3	2.498	1
3.576	*	2.403	1
3.487	5	2.367	1
3.379	7	2.334	6
3.283	1	2.192	*
3.182	4	2.180	*
3.139	3	2.121	6
3.110	5	2.103	*
2.921	4	2.047	10
2.872	1	1.706	5

* Relative intensity lower 1%

The density derived from the X-ray data 2.35 g cm^{-3} , is in good agreement with that obtained by pycnometry, 2.31 g cm^{-3} . The IR spectrum of DHUC shows absorption bands corresponding to the frequencies of hypophosphite ion and urea vibrations. Table 2 gives the absorption bands of the DHUC spectrum in

Table 2 IR data of DHUC and urea

Urea, cm^{-1}	Assign. [7]	DHUC, cm^{-1}	Hypophosphite ion, calcd., cm^{-1} [5]	Assign. [5]
		462m	484	δOPO
		535m		
		552m		
560	δNCN			
580	$\delta\text{CO}, \delta\text{NCO}$	608w		
790	δNH_2	799sh		
1008	νCN	818s	810	$\delta\text{HPH}, \delta\text{OPO}$
1055		1050s	1050	$\nu_s\text{PO}$
		1085s	1090	$\omega\text{HPH}, \omega\text{OPH}$
1158	δNH_2	1136vs	1166	δHPH
		1180sh	1199	$\nu_{as}\text{PO}$
1469	νCN	1485s		
		1540w		
1610	$\delta\text{NH}_2, \nu\text{CO}$	1585s		
1630	δNH_2	1638s		
1685	νCO	1660s		
		2410s	2308	$\nu_{as}\text{PH}$
		2429m	2356	$\nu_s\text{PH}$
		3160w		
		3210m		
3265		3245m		
3346	$\nu_s\text{NH}$	3328s		
3450	$\nu_{as}\text{NH}$	3398s		

comparison with those calculated for hypophosphite with equalized P–O bonds [5]. The values corresponding to the hypophosphite ion in DHUC are in good agreement with those calculated for the purely ionic salt of hypophosphorous acid. At the same time, in the region $400\text{--}700\text{ cm}^{-1}$ there are additional bands at 535, 552 and 608 cm^{-1} , which correspond either to the Cu–O vibrations in the chain structure model of hypophosphites [5] or to the vibrations along the metal-urea coordination bond. To determine the mode of urea coordination, the absorption bands of urea and the complex were compared [6]. The shifts of the bands due to coordination can be traced directly. A comparison of the $\nu_{\text{C-N}}$ and $\nu_{\text{C=O}}$ stretching frequencies of DHUC and urea and a consideration of the modes of urea coordination by metals [6–9] suggest that the urea is coordinated by the oxygen atom. However, decreases in the ν_{NH} stretching frequencies point to the possibility of urea attachment via a nitrogen atom as well.

The decomposition of DHUC begins with a marked rate at about 320 K, and proceeds topochemically through the formation and growth of nuclei of the

product in the crystal bulk. In the temperature range 323–330 K, the decomposition proceeds with a relatively small rate, and the crystals melt and darken. Masses 2, 17, 18 and 44 are found in the mass-spectrum of decomposing DHUC. The condensed products include copper, phosphorus, ammonium ions, phosphite ions, phosphate ions and a small amount of urea, which does not usually decompose under these conditions [10]. The decomposition of the complex at 331–345 K proceeds quite violently, with a sharp darkening of the crystal, and is accompanied by a substantial exothermic effect. The mass spectrum reveals masses of 2, 17, 18, 34 and 44. The condensed products include copper(I) phosphide, ammonium ions, phosphite ions and phosphate ions. Urea is not detected at all. At higher temperatures, the decomposition has an explosive character; the products of the process and the peculiarities of the reaction were not studied. On the basis of the results obtained, together with data on the decomposition of hypophosphite compounds of copper [2–4], the following scheme of DHUC decomposition can be suggested:

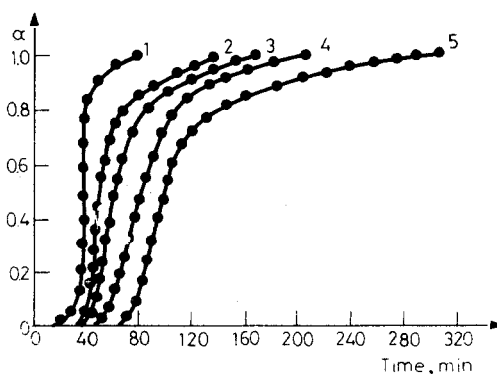
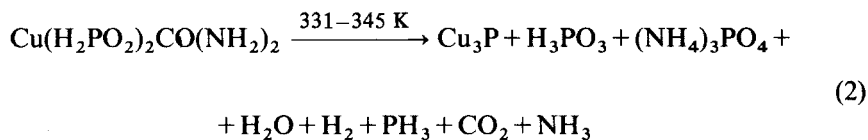
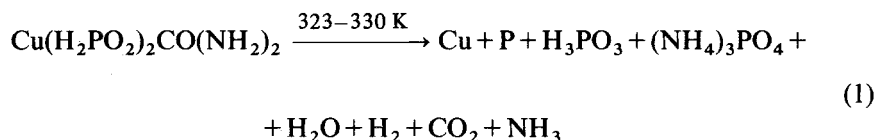


Fig. 1 Isothermal decomposition (fractional mass loss) curves of decomposition of $\text{Cu}(\text{H}_2\text{PO}_2)_2 \cdot \text{CO}(\text{NH}_2)_2$ (process 1). Pressure 1 Pa. Temperature, K: 1 – 330, 2 – 329, 3 – 327, 4 – 325, 5 – 323

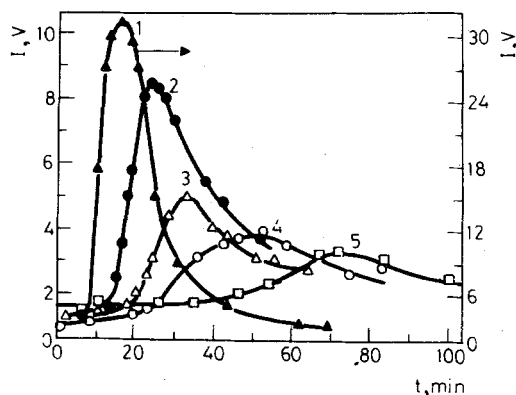


Fig. 2 Isothermal decomposition (rate of H_2O evolution) curves of decomposition of $\text{Cu}(\text{H}_2\text{PO}_2)_2 \cdot \text{CO}(\text{NH}_2)_2$ (process 2). Pressure 10^{-4} Pa. Temperature, K: 1 – 345, 2 – 342, 3 – 338, 4 – 335, 5 – 331.

Intensity $1 \text{ V} \cdot \text{min}$ corresponds to $2.2 \cdot 10^{15}$ H_2O molecules/min

The dissociation of the complex is assumed to be the elementary act of the process. Further reaction proceeds by two routes: the independent redox reaction of copper hypophosphite decay and the hydrolysis of urea in the acidic medium of the thermal decomposition products. At 331–345 K, interaction becomes possible between the copper and phosphorus formed initially in reaction (1), giving copper(I) phosphide. The interaction is accompanied by an appreciable exothermic effect [4], bringing about the complete hydrolysis of the urea to carbon dioxide and ammonia, which in turn forms salts with oxyacids of phosphorus.

The kinetic curves of the decomposition are given in Figs 1 and 2 for processes (1) and (2), respectively. According to the thermogravimetric and mass-spectrometric data the values of the activation energies are 23.7 ± 1.4 and 2064 ± 2.2 kcal/mol, respectively.

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Zusammenfassung — Physikalisch-chemische Eigenschaften der neu dargestellten Komplexverbindung $\text{Cu}(\text{H}_2\text{PO}_2)_2 \cdot \text{CO}(\text{NH}_2)_2$ wurden untersucht. Die Parameter der Elementarzelle und die Koordination des Harnstoffmoleküls wurden bestimmt. Die thermische Zersetzung der Komplexverbindung erfolgt topochemisch, sie wurde mittels Thermogravimetrie und Massenspektrometrie verfolgt und ihre Endprodukte nachgewiesen. Die Aktivierungsenergien der Zersetzung betragen im Temperaturintervall 323–330 K, $23,4 \pm 1,4 \text{ kcal mol}^{-1}$ und im Temperaturintervall 331–345 K, $20,64 \pm 2,2 \text{ kcal mol}^{-1}$.

Резюме — Исследованы физико-химические свойства нового синтезированного комплекса $\text{Cu}(\text{H}_2\text{PO}_2)_2 \cdot \text{CO}(\text{NH}_2)_2$. Определены параметры кристаллической решетки и координация молекул мочевины. Термическое разложения комплекса, носящее топохимический характер, было изучено термогравиметрическим и масс-спектрометрическим методом. Определены конечные продукты разложения. Энергии активации составляли $23,4 \pm 1,4$ и $20,6 \pm 2,2$ ккал · мол⁻¹ при температурах, соответственно, 323–330 и 331–345 К.