

THERMAL BEHAVIOUR OF Cu(II)-UREA COMPLEX

B. C. Stojceva Radovanovic and P. I. Premovic

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CIRILA I METODIJA 2, 18000 NIŠ,
YUGOSLAVIA

The urea complex of copper was synthesized and its structure was established by Fourier transform infrared (FTIR), electron spin resonance (ESR) and atomic absorption spectroscopy and elemental analysis to be $\text{Cu}(\text{urea})_4\text{Cl}_2$. The thermal behaviour of this complex has been studied by thermogravimetry and differential thermal analysis and FTIR and ESR. Thermal analysis shows that the decomposition of the complex occurs in four stages of weight loss of different intermediates followed by three endothermal effects. The complex is thermally stable up to 428 K. The ESR and FTIR behaviour of the Cu(II)-urea complex during thermolysis was studied between 428 and 633 K. The experimental results suggest that in this temperature range the complex decomposition occurred forming thermodynamically stable regions of Cu(II) which are ferromagnetically coupled.

Keywords: Cu(II)-urea complex, thermal behaviour, structure

Introduction

Metal complexes with ligand systems containing oxygen and nitrogen donor atoms are a very important class of coordination compounds [1-4]. It is known that the urea complex of copper plays an important role [5, 6]. In order to explain the mechanism of action of the complex in various physicochemical processes it is necessary to have a complete knowledge of the molecular structure and the thermal behaviour of the complex.

The present paper describes the preparation of a copper(II)-urea complex and the confirmation of its structure by Fourier transform infrared (FTIR), electron spin resonance (ESR) and atomic absorption (AA) spectroscopy and elemental analysis. The mechanism of thermal decomposition of this complex has been studied by thermogravimetry (TG) and differential thermal analysis (DTA) and FTIR and ESR spectroscopy.

Experimental

The analysis of carbon, hydrogen and nitrogen was carried out with a Carlo Erba 1106 microanalyzer.

Copper was determined using a Perkin-Elmer 1100 AA spectrometer.

The infrared spectra were recorded with a Perkin-Elmer 1600 FTIR spectrophotometer using the potassium bromide pellet (1 mg/150 mg KBr) technique.

The electron spin resonance spectra were recorded in the solid state on a Brüker 200 D ESR spectrometer in the X-band. The nominal frequency was 9.56 GHz.

The thermogravimetric curve was recorded on a Du Pont 951 TG analyzer in a dynamic atmosphere of air and a heating rate of 10 deg·min⁻¹.

Differential thermal analysis was carried out with a 407 Netzsch Derivatograph in a dynamic atmosphere of air, under the following conditions: heating rate 10 deg·min⁻¹, sensitivity of the DTA 1/10 and employing Al₂O₃ as a reference substance.

Preparation of the complex

The complex was prepared from ethanolic solutions of copper chloride and urea in 1:2 molar ratio. The solution was allowed to reflux during 3.6·10³ s. The resulting green solid was filtered, washed with ethanol and dried. Yield 59%, m.p. 428 K. The complex is soluble in water.

Analysis results for Cu(C₄H₁₆N₈O₄)Cl₂:

Found: C: 12.54%; H: 4.07%; N: 29.64%; Cu: 16.97%;

Calc.: C: 12.75%; H: 4.25%; N: 29.75%, Cu: 16.88%;

Results and discussion

The elemental analysis and atomic absorption data of the copper(II)-urea complex indicate that its composition may be Cu(urea)₄Cl₂.

The complex in polycrystalline form shows anisotropic ESR spectrum ($g_{\parallel} \approx 2.23 > g_{\perp}$) characteristic of square-planar geometry [7].

The most important infrared absorption frequencies of both urea and the complex along with their assignments are presented in Table 1. The bands at 3450 and 3380 cm⁻¹ in the spectrum of urea assigned to the H-N stretching vibrations are observed at almost the same frequencies in the spectrum of the complex. This indicates that nitrogen-to copper bands are not present [8]. However, the intense absorption bands at 1680 and 1610 cm⁻¹ corresponding to the C=O

stretching and the N–H bending vibrations are shifted to lower frequencies ($\Delta\nu=40\text{ cm}^{-1}$) in the spectrum of the complex indicating coordination through oxygen [9]. The participation of oxygen atom in coordination is further evidenced by the presence of the non-ligand band in the spectrum of the complex at 450 cm^{-1} due to Cu–O stretching vibration.

Table 1 FTIR spectral data of urea and Cu(II)–urea complex at room temperature and heated at different temperatures [frequency (cm^{-1})]

Assignment of band	Urea	Cu(II)–urea complex				
		293 K	433 K	513 K	573 K	653 K
$\nu(\text{NH})$	3450(s)	3450(s)	3320(s)	3320(m)	3315(m)	
	3380(s)	3370(s)	3240(s)	3240(m)	3020(m)	3020(w)
$\nu(\text{CO})+\delta(\text{NH})$	1680(s)	1640(s)	1640(s)	1630(m)	1620(m)	
	1610(m)	1570(m)				
$\nu(\text{CN})+\delta(\text{NH})$	1450(m)	1470(m)	1475(m)	1465(w)	1460(w)	1460(w)
$\phi(\text{NH})+\tau(\text{NH})$	1150(s)	1145(s)	1410(s)	1400(m)	1390(m)	1390(w)
$+\phi(\text{CN})$	780(w)	760(w)	1150(s)	1150(m)	1150(m)	1150(w)
$\nu(\text{Cu}-\text{O})$		450(m)	450(m)	450(m)	450(m)	

s: strong; m: medium; w: weak

In order to study the physicochemical changes during thermal treatment, the variations in the FTIR spectra of the complex at various temperatures were studied. For recording the effect of temperature the complex was kept at 433, 513, 573 and 653 K for $4.5 \cdot 10^2$ s. It is seen (Table 1) that the intensities of functional infrared bands 3450 and 3370 cm^{-1} (νNH); 1640 and 1570 cm^{-1} ($\nu\text{CO} + \delta\text{NH}$); 1470 cm^{-1} ($\nu\text{CN} + \delta\text{NH}$); 1145 , 1150 and 760 cm^{-1} ($\phi\text{NH} + \tau\text{NH} + \phi\text{CN}$) are decreased and they disappeared during heating. The complex heated at 653 K does not retain the characteristic infrared features of the original complex.

The variations in the ESR spectra of the thermolysed complex also suggest that in the same temperature range the copper(II)-urea complex undergoes distinct structural changes forming thermodynamically stable regions of Cu(II) which are ferromagnetically coupled [10].

Figure 1 illustrates TG-DTG-DTA curves obtained for the complex with a dynamic heating program.

Thermal analysis shows that the complex is thermally stable up to 428 K. Its thermal decomposition occurs in four stages of weight loss of different intermediates followed by three endothermic effects, the first of which is due to melting (Experimental). From the TG, DTG and DTA curves it is clear that the first decomposition stage from 428 to 523 K corresponds to the loss of cyanic acid

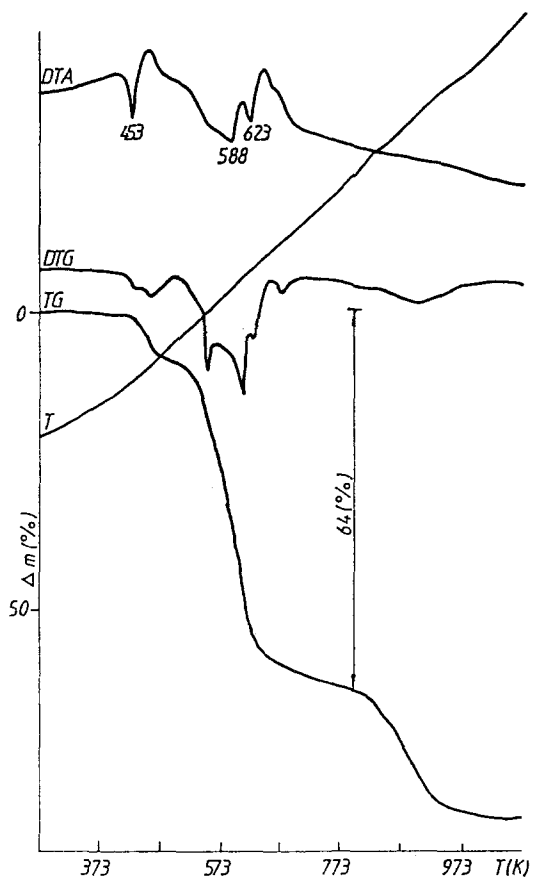
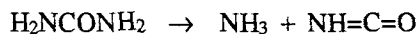


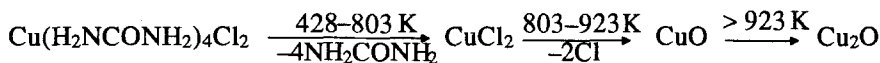
Fig. 1 TG-DTG-DTA curves of the complex

(11.42% experimental loss; 11.48% theoretical loss). The most probable thermal decomposition of urea from the complex may be represented as:



The continued loss, decomposition stages II and III up to 803 K corresponds to the complete decomposition of the four urea molecules (64.19% experimental loss; 64.17% theoretical loss) followed by endothermic effects at 588 and 623 K, respectively. As the temperature is raised to 923 K the complete loss of chlorine and conversion to copper(I)oxide occur (83.08% experimental loss; 83.03 theoretical loss) [11].

Based on the results of thermal analysis supported by the FTIR and ESR spectral data the mechanism of the thermal decomposition of the complex is proposed as:



References

- 1 R. B. Penland, S. Mizushima, C. Curran and I. V. Quagliano, *J. Am. Chem. Soc.*, **79** (1957) 1575.
- 2 M. Kishita, M. Inoue and M. Kubo, *Inorg. Chem.*, **3** (1964) 237.
- 3 I. Bullock, *J. Inorg. Nucl. Chem.*, **29** (1967) 257.
- 4 M. Vicens, M. Prats, J. J. Fiol and A. Terron, *Inorg. Chim. Acta*, **158** (1989) 59.
- 5 E. V. Miller, *Chemistry of Plants*, Reinhold, New York 1957.
- 6 P. R. Geissler and S. Rosenblatt, U.S. Pat. 3523018 (1970).
- 7 D. W. Smith, *Inorg. Chem.*, **5** (1966) 2236.
- 8 A. Zamaguchi, R. B. Penland, S. Mizushima and T. J. Jane, *J. Am. Chem. Soc.*, **80** (1958) 527.
- 9 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1962.
- 10 H. J. Emeleus and A. G. Sharpe, *Advances in Inorganic Chemistry and Radiochemistry*, Academic Press, New York 1970.
- 11 P. C. Srivastava, B. N. Singh, S. K. Ghosh and N. C. Ganguly, *J. Thermal Anal.*, **31** (1986) 1153.

Zusammenfassung — Der Harnstoffkomplex von Kupfer wurde hergestellt, seine Zusammensetzung ergab sich anhand von FTIR-, ESR- und Atomabsorptionsspektroskopie-Untersuchungen sowie Elementaranalyse mit der Formel $\text{Cu}(\text{Harnstoff})_4\text{Cl}_2$.

Mittels TG, DTA, FTIR und ESR wurde auch das thermische Verhalten dieser Komplexe untersucht. Die Thermoanalyse zeigte, daß der Zersetzungsprozeß über verschiedene Zwischenprodukte in vier Stufen mit Massenverlust verläuft, gefolgt von insgesamt drei endothermen Effekten. Bis 428 K ist der Komplex thermisch stabil. Das ESR- und FTIR-Verhalten des Cu(II)-harnstoffkomplexes bei der Thermolyse wurde im Temperaturbereich 428-633 K untersucht. Die experimentellen Ergebnisse lassen darauf schließen, daß bei der Zersetzung des Komplexes in diesem Temperaturbereich thermodynamisch stabile Regionen von ferromagnetisch gekoppeltem Cu(II) gebildet werden.