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THERMAL DECOMPOSITION AND KINETIC STUDIES ON A BINUCLEAR COPPER(II)—UREA COMPLEX*

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A binuclear copper(II)—urea complex was synthesized and its structure was established from elemental analyses, IR, UV and visible spectroscopy and magnetic susceptibility measurements to be $[OC(NH_2)_2Cu(OH)_2]_2$. The kinetics of the thermal decomposition of the complex were studied by recording thermogravimetric measurements in streams of nitrogen and oxygen. TG analysis showed three main steps of decomposition, leading to Cu_2O formation in the final stage.

Metal coordination compounds containing urea have been studied intensively both structurally and spectroscopically [1–4]. So far, however, the number of thermochemical investigations on urea complexes is rather limited [5]. No thermal analytical studies of copper(II), a metal which is known to coordinate to urea, have been reported so far. It is known that, apart from the coordination bond between the copper ion and urea, the complex also plays an important role in catalysing the enzymatic activities in plants, as well as urease inhibitor properties.

Experimental

Preparation of the complex

The complex was prepared from an aqueous solution of copper sulphate and urea in 1 : 1 molar ratio, at pH 3.2. The solution was allowed to evaporate under heating for about an hour; the resultant solid complex was filtered off and washed with ethanol and anhydrous ether to apparent dryness. The complex was stored in a vacuum desiccator over calcium sulphate until used. The complex was muddy-green in colour and gave the following elemental analysis.

Anal. calcd. for $[OC(NH_2)_2Cu(OH)_2]$; C, 7.69%, H, 3.85%, N. 17.83% and Cu, 40.12%; Found C, 7.72%, H, 3.70%, N, 17.91% and Cu, 40.40%.

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Apparatus

The IR spectra were recorded in the range 4000–250 cm^{-1} with a Beckman IR 20A infrared spectrometer, using KBr discs.

Solid-state electronic spectra were recorded with a Cary 14 spectrophotometer provided with an automatic recording system. The spectra were taken in Nujol mull.

Magnetic susceptibility measurements were carried out by the use of Gouy's method. Molecular susceptibility was corrected for the diamagnetism of the component atoms by means of Pascal's constant [6].

Thermal studies were made as reported earlier [7].

Results and discussion

The elemental analysis results on the complex agreed with the molecular formula $[(N_2H_4CO)Cu(OH)_2]$. The complex has a room-temperature magnetic moment (1.52 BM) lower than the spin-only value (1.73 BM). The decrease in magnetic moment indicates an antiferromagnetic exchange interaction. The electronic spectrum of the complex shows a *d*-*d* transition absorption band at 15,600 cm^{-1}, which corresponds to square-planar stereochemistry [8, 9] for the copper(II). The band is assigned to the transition $^2B_{1g} \leftrightarrow {}^2E_g$ in a ligand field of D_{4h} symmetry. The presence of an additional weak absorption band at 17,000 cm^{-1} $[^2A_{1g} \leftrightarrow {}^2B_{1g}]$ suggests partial tetragonal distortion in the molecule.

The IR active vibrational frequencies of urea have been reported previously [10]. The most important IR absorption bands of diagnostic value and their tentative assignments for urea and the complex $[OC(NH_2)_2Cu(OH)_2]$ are listed in Table 1. The spectrum of the complex molecule differs significantly from that of the urea molecule. The ν_{NH} stretching frequencies in urea have been found to be sensitive to coordination to copper. This leads to a shift in ν_{asym}NH (3450 cm^{-1}) and a deformation in ν_{sym}NH (3350 cm^{-1}) for the urea molecule. The $\nu_{C=O}$ (1670 cm^{-1}) and bending NH + $\nu_{C=O}$ (1600 cm^{-1}) of the urea molecule are observed at almost the same frequencies in the complex. However, due to the intramolecular hydrogen-bonding in the free urea molecule, the shift in νNH is not nearly as great as in the case of the carbonyl $[\nu_{C=O}]$ coordinated complex [8]. The absorption band at around 3570 cm^{-1} (indicative of the OH stretching frequency) and another at around 1570 cm^{-1} (indicative of the bending mode of OH) both confirm the presence of the hydroxyl group in the complex. The far IR region of the complex shows the presence of additional bands at 410 cm^{-1} and 480 cm^{-1}, due to Cu—O and Cu—N. The values of the force constant (*K*) for Cu—O and Cu—N bonds have been calculated [11] and are found to be 2.48×10^5 dyne/cm and 2.62×10^5 dyne/cm, respectively.

Thermal studies

From the experimental data it can be concluded that the decomposition of the complex $[OC(NH_2)_2Cu(OH)_2]$ can be described by the following reactions:

$$[OC(NH_2)_2Cu(OH)_2] \rightarrow Cu(OH)_2 + OC(NH_2)_2 \qquad \text{(i)}$$

$$Cu(OH)_2 \rightarrow CuO \qquad \text{(ii)}$$

$$CuO \rightarrow Cu_2O \qquad \text{(iii)}$$

Figure 1 shows the TG curves obtained for the complex under dynamic nitrogen and oxidizing atmospheres. These thermal curves were recorded at a heating rate of 10 deg/min. The natures of the TG curves in the two atmospheres are analogous. The complex shows a first decomposition stage between 200° and 450°, in which a weight loss occurs corresponding to one urea molecule. The DTG curve in air (Fig. 2) shows two distinct decomposition peaks, at 300° and 450°, which reveals that the loss of the urea molecule is complex in nature. The broad endotherm at 425° in the DTA curve (Fig. 3) indicates the loss of ligand in the gas phase. The above findings can be used to speculate on the reaction pathway in the thermal loss of gaseous NH_3 from urea. The schematic representation of urea decomposition involves rearrangement through a cyclic urea structure:

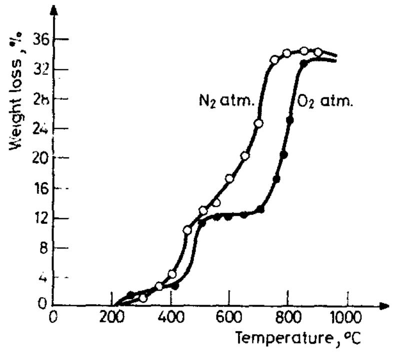
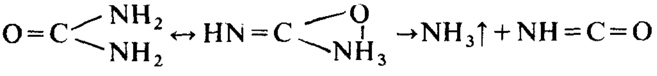


Fig. 1 TG plots for the complex in N_2 and O_2 atmospheres



$$O{=}C\begin{matrix}NH_2\\NH_2\end{matrix} \leftrightarrow HN{=}C\begin{matrix}O\\|\\NH_3\end{matrix} \rightarrow NH_3\uparrow + NH{=}C{=}O$$

No intermediate is isolable, due to the complicated nature of the decomposition of

Table 1 Magnetic susceptibility and electronic spectral data of the complex and IR data of urea and complex

Complex	μ_{eff}, B.M.	Electronic bands, cm^{-1}	Assignment	IR spectral data			
				urea, cm^{-1}	complex, cm^{-1}	assignment	force constant × 10^5, dyne/cm
$[OC(NH_2)_2Cu(OH)_2]_2$	1.52	15,600	$^2B_{1g} \rightarrow {}^2E_g$	3450(bs)	3570(s)	ν_{OH}	
				3350(bs)		$\nu_{asym}NH$	
					3320(w)	$\nu_{sym}NH$	
		17,000	$^2A_{1g} \rightarrow {}^2B_{1g}$	1670(ms)	1680(s)	ν_{CO}	
				1600(bs)	1615(bs)	NH_2 bending+CO	
					1570(s)	bending OH	
				1450(s)	1420(ms)	ν_{CN}	
				1150(s)	1145(s)	NH_2 rocking	
				790(s)	480(w)	Cu—N	2.62 KCu—N
					410(w)	Cu—O	2.48 KCu—O

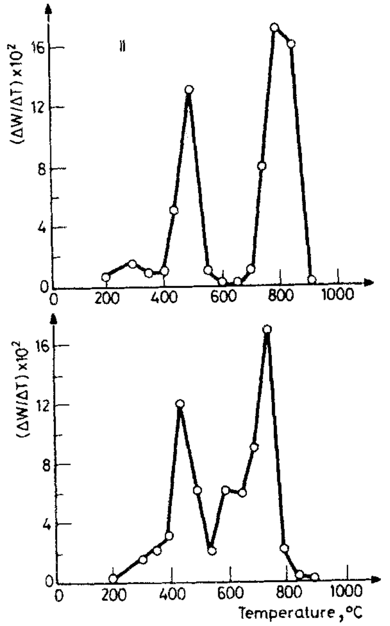


Fig. 2 DTG curves for the complex in (I) N_2 and (II) O_2 atmospheres

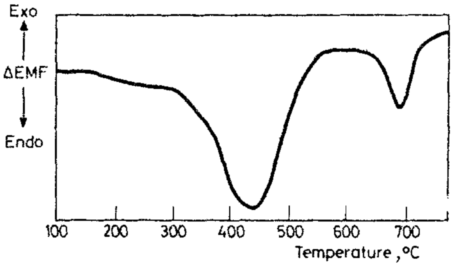


Fig. 3 DTA curves for the complex

the complex. The second and third steps of the decomposition reaction show continuous weight loss up to 850°, and the final residue corresponds to Cu_2O (weight loss: experimental 34%, theoretical 34.2%).

Kinetic parameters

The thermogravimetry data have been used to study the kinetics of the thermal decomposition. The methods of Satava [12] and Coats–Redfern [13] were applied to evaluate the activation energy and reaction order in the process (urea)$Cu(OH)_2 \rightarrow Cu_2O$. Deduction of the mechanism of reaction by means of nonisothermal kinetic methods has been discussed by Satava. In this programme, the experimental TG data are analysed via the linearity of the function $\log g(\alpha)$ versus $\frac{1}{T}$. Plots of $\log g(\alpha)$ against $1/T$ are found to be non-linear (Fig. 4), pointing to a heterogeneous decomposition. The plots are all curved, with comparatively sharp turning points. The characteristics of the plots do not provide an accurate understanding of the reaction mechanism that controls the thermal decomposition of the complex over the considerable temperature range. From the curves it can be said that the complex decomposes first with a large slope, corresponding to a high activation energy, followed by a second step of decomposition, associated with a small activation energy. In no case can the entire course of the reaction be described by a single rate equation.

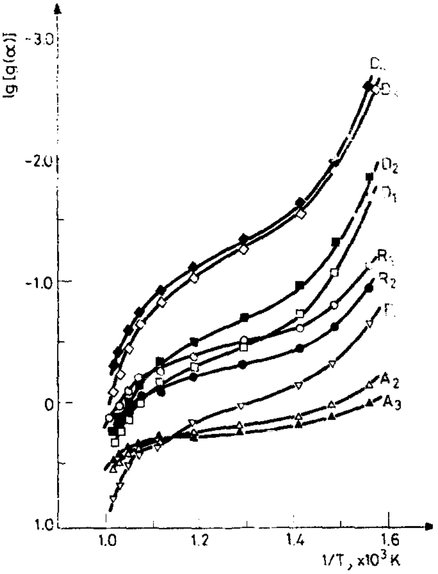


Fig. 4 Satava's plots for the complex

For a reaction in which the order is known, the final equation described by Coats and Redfern has the form

$$\log\frac{[1-(1-\alpha)^{1-n}]}{T^2(1-n)} = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT}$$

where α is the sample fraction decomposed at time t and a is the heating rate. This has been applied here to obtain the activation energy for the decomposition of the complex. The plot of $\log[1-(1-\alpha)^{1-n}/[T^2(1-n)]$ against $\frac{1}{T}\times 10^3$ (Fig. 5) showed

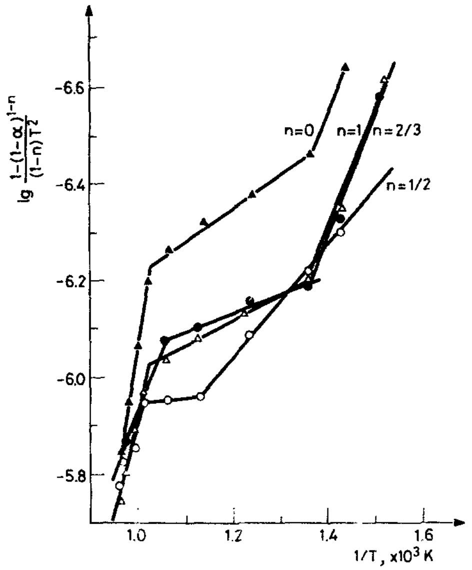


Fig. 5 Coats and Redfern's plots for the complex

two breaks for each value of n. A number of such relationships are plotted for a number of assumed values of n = 0, 0.5, 0.66, and 1.0. The activation energy for each line is calculated from the equation $E = 2.3\ R \tan \beta$ (where $\tan \beta$ = the slope of the straight line and R = the gas constant). The decomposition of the complex is a three-step process, since two breaks are observed in the Coats and Redfern plots, and thus three values for the activation energy are reported (Table 2). The activation energy for the first curve corresponds to the gaseous decomposition of the ligand, while the activation energies of the second and third curves are due to the decomposition of the hydroxyl groups and the conversion of CuO to Cu_2O.

Table 2 Values of activation energy

n	E_1, kJmol^{-1}	E_2, kJmol^{-1}	E_3, kJmol^{-1}
0	9.00	7.03	49.50
0.50	5.30	2.68	60.12
0.66	9.20	10.04	35.14
1.00	11.00	13.80	132.6

References

1 R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, J. Am. Chem. Soc., 79 (1957) 1575.

2 M. Kishita, M. Inoue and M. Kubo, Inorg. Chem., 3 (1964) 237.

3 J. Bullock, J. Inorg. Nucl. Chem., 29 (1967) 257.

4 B. K. Banerji and P. C. Srivastava, Fert. Techn., 16 (1979) 264.

5 A. Sengupta, P. C. Srivastava, C. Aravindakshan and B. K. Banerjee, J. Phys. Chem. Solids., 43 (1982) 645.

6 N. N. Eiggis and J. Lewis, Modern Coordination Chemistry, Interscience, New York, 1959, p. 403.

7 P. C. Srivastava, B. N. singh, S. K. Adhya and K. C. Banerji, J. Thermal Anal., 27 (1983) 263.

8 B. N. Figgis, Introduction to Ligand Fields, Interscience, N.Y., 312.

9 D. W. Smith, Inorg. Chem., 5 (1966) 2236.

10 P. C. Srivastava, B. N. Singh, C. Aravindakshan and K. C. Banerji, Thermochim. Acta, 71 (1983) 227.

11 K. Nakamoto, Infrared spectra of Inorganic and Coordination compounds, Wiley, New York, 1962.

12 V. Satava, Thermochim. Acta, 2 (1971) 423.

13 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.

Zusammenfassung — Der zweikernige Kupfer(II)-Harnstoff-Komplex wurde dargestellt. Durch Elementaranalyse, Spektroskopie im IR-, UV- und sichtbaren Bereich sowie Messung der magnetischen Suszeptibilität wurde die der Formel $[OC(NO)_2Cu(OH)_2]_2$ entsprechende Struktur ermittelt. Die Kinetic der thermischen Zersetzung des Komplexes in Stickstoff und Sauerstoff wurde aus thermmogravimetrischen Kurven bestimmt, die drei Hauptzersetzungsttufen erkennen lassen. Endprodukt der thermischen Zersetzung ist Cu_2O.

Резюме — Синтезирован двухядерный комплекс медь(II) — мочевина и на основании элементного анализа, ИК спектроскопии, электронных спектров поглощения и измерений магнитной восприимчивости установлено, что состав его соответствует формуле $[OC(NH_2)_2 \cdot Cu(OH)_2]_2$. Кинетика термического разложения комплекса была изучена путем термогравиметрических измерений в потоке азота и кислорода. Разложение комплекса протекает в три стадии с образованием закиси меди в качестве конечного продукта реакции.