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Note

THERMOGRAVIMETRIC STUDY OF THE THERMAL DECOMPOSITION OF THE MIXED COMPLEX: Cu^{II}(L-TRYPTOPHANATE)(DL-METHIONINATE)·$3H_2O$

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Till now, few thermal studies in the solid phase of metal complexes with aminoacids have been reported [1]. In a previous work [1], we showed the kinetics of the thermal decomposition of the complex bis-L tryptophanato-copper(II) in the solid phase, determining the activation energies of the decomposition steps.

In this line of work, we describe for the first time in this paper the kinetics of thermal decompositon of the mixed complex Cu^{II}(L-tryptophanate)(DL-methioninate)·$3H_2O$ (abbreviated Cu(L-Trp)(DL-Met)·$3H_2O$).

Kinetic parameters are calculated using the theoretical model of Šatava [3] and including the equation used by Johnson and Gallagher [4]: $1/(1-\alpha)-1=kt$. The results are compared with those obtained for the simple complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$.

EXPERIMENTAL

The compound Cu(L-Trp)(DL-Met)·$3H_2O$ was prepared in accordance with ref. 5. It was obtained with a higher hydratation than previously reported [5].

The copper was determined by gravimetry and C, H and N with a Carlo Erba (Model 1102) automatic analyser. Calcd. for $Cu(C_{11}H_{11}N_2O_2)(C_5H_{10}NO_2S)\cdot 3H_2O$: Cu, 13.55; C, 40.97; H, 5.80; N, 8.96; Found: Cu, 13.41; C, 40.72; H, 5.79; N, 9.03%.

X-ray powder analysis confirmed that this material was free from simple complexes and the ligands.

The infrared spectrum of Cu(L-Trp)(DL-Met)·$3H_2O$ shows bands at 3240, 3130 and 2910 cm^{-1} corresponding to the NH_2 group of the aminoacids and indicates the coordination of this group to the metal. The infrared spectrum affords indirect evidence that the sulphur atom is not involved in coordination to the metal at room temperature [5].

The thermogravimetric measurements were carried out on a Perkin Elmer (Model TGS-2) thermobalance with an FDC first-derivative computer in a

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nitrogen atmosphere at a heating rate of 5°C min^{-1}. Each run was repeated twice and the experimental reproducibility was good for each mass used.

RESULTS AND DISCUSSION

The thermogravimetric curve and its derivative show three stages in the thermal decomposition of the mixed complex as in the simple complex Cu(L-Trp)$_2$ [1], but copper is not obtained at 943 K as final product. The complex Cu(DL-Met)$_2$ [2] shows one stage and copper is not obtained at 800 K.

For the first stage, the representation of the degree of decomposition (α) vs. T (K) indicates a process of short acceleration followed by one of deceleration, with a short interval of temperature between both. For the second and third steps the processes of acceleration are longer and both end with a short period of deceleration.

The mass loss indicates that the pathway is not simple and, therefore, we cannot predict a clear pattern for each step. Compounds containing Cu–S are probably formed.

To obtain the kinetic paramenters (activation energy and pre-exponential factor) we have used the equations of ref. 3 and included the equation $1/(1-\alpha)-1=kt$ [4]. The logarithms of all the functions G(α) [3,4] have been calculated from the values and have been represented against $1/T$ K. For the correct kinetic mechanism log G(α) will be a linear function of $1/T$ (K).

The behaviour observed for the first decomposition step could not be explained by the equations used, because the values of correlation factors in the adjustment to a straight line by least squares of log G(α) vs. $1/T$ (K) are low.

For the second and third steps it is found that the functions: $G(\alpha) = -\ln(1-\alpha)$; $G(\alpha)=[-\ln(1-\alpha)]^{1/2}$ and $G(\alpha)=[-\ln(1\text{-}\alpha)]^{1/3}$ present high correlation factors, the function $[-\ln(1-\alpha)]^{1/2}$ being slightly higher. This function corresponds to a random nucleation mechanism (Avrami–Erofeev, equation I).

For the simple complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$ the equations $G(\alpha)=[-\ln(1-\alpha)]^{1/3}$ and $G(\alpha)1/(1-\alpha)-1$ were found, respectively [1,2].

The activation energies and pre-exponential factors for each decomposition step have been calculated and the results are given in Table 1. The data referring to the complexes Cu(L-Trp)$_2$ and Cu(DL-Met)$_2$ have been taken from refs. 1 and 2. In accordance with the values of initial temperatures of decomposition, the order of thermal stability is: Cu(L-Trp)$_2$ < Cu(L-Trp)(DL-Met)$\cdot 3H_2O$ < Cu(DL-Met)$_2$. The linear chain of methionine produces a higher thermal stability. In both complexes Cu(DL-Met)$_2$ and Cu(L-Trp)(DL-Met)$\cdot 3H_2O$, the interaction S–Cu probably occurs at high temperatures in

TABLE 1

T_i (initial temperature), T_f (final temperature), E_a (activation energy) and Z (pre-exponential factor) for the thermal decomposition of the complexes studied

Compound	T_i (K)	T_f (K)	E_a (kJ mol^{-1})	Z (s^{-1})	Reference
Cu(L-Trp)(DL-Met)·$3H_2O$	500 (1st step)	538 (1st step)	–	–	This work
	633 (2nd step)	673 (2nd step)	232.8	1.43×10^{16}	This work
	843 (3rd step)	923 (3rd step)	232.1	6.47×10^{10}	This work
Cu(L-Trp)$_2$	498 (1st step)	541 (1st step)	–	–	1
Cu(DL-Met)$_2$	523 (one step)	563 (one step)	600.7	1.28×10^{56}	2

accordance with the mass loss. The indole group of L-tryptophane is probably responsible for the existence of three steps in the decomposition of the complexes Cu(L-Trp)$_2$ and Cu(L-Trp)(DL-Met)·$3H_2O$.

The water molecules of the compound Cu(L-Trp)(DL-Met)·$3H_2O$ are removed at 500 K. This fact suggests that the water molecules are coordinated to the copper ion in the complex [6].

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