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THERMOGRAVIMETRIC INVESTIGATION OF THERMAL DECOMPOSITION OF COPPER(II) COMPLEXES WITH METHYLPYRIDO[2,3-d]IMIDAZOLE DERIVATIVES

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Abstract

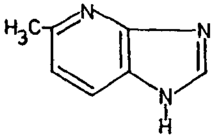
Solid-state complexes with the formulae $CuL_xX_2 \cdot nH_2O$, were L=2-methyl-, 5-methyl-, or 7-methylpyrido[2,3-d]imidazole, $X=NO_3^-$ or Cl^-, $x=2$ or 3, and $n=1$ or 2, were subjected to thermogravimetric analyses. The kinetic parameters were calculated according to the Coats-Redfern method. Reactions paths are proposed and their agreement with the data obtained from TG curves is checked.

Keywords: Cu(II) methylpyrido[2,3-d]imidazole complexes, thermal decomposition

Introduction

The presence of pyridine and imidazole rings in a number of substances existing in nature often determines their biological activity. N-Alkyl derivatives of imidazole were used as axial ligands in model haemoglobin compounds [1–3]. The benzimidazole system, complexed with cobalt(II), is found in vitamin B_{12}. Pyrido[2,3-imidazole derivatives exhibit antituberculotic activity [4, 5].

The pyrido[2,3-d]imidazole molecule contains an imidazole ring condensed with a pyridine ring. A methyl substituent located in close adjacency to a donor nitrogen atom can determine the number, stability and structure of the complexes formed. Moreover, anions may be expected to exert different effects on the strengths of interaction of organic ligands with the coordination centre.



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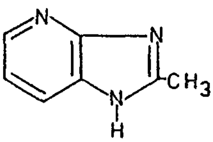

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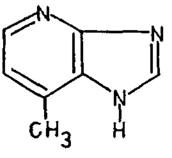

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The stabilities of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-methyl- and 7-methylpyrido[2,3-d]imidazole have been investigated in aqueous solution by means of potentiometry [6, 7]. However, no reports are so far available in the literature on the physico-chemical properties of the solid complexes with the ligands mentioned. The results of thermal stability determinations for crystalline Cu(II) complexes with 2-methyl-, 5-methyl- and 7-methylpyridol[2,3-d]imidazole (formulae 1–3) and also the kinetic parameters of thermal decomposition of those complexes are given in this work. As the kinetic parameters, the values of the activation energy (*E*), reaction order (*n*), and pre-exponential factor in the Arrhenius equation (ln*Z*) were calculated.

Experimental

Reagents and apparatus

The ligands 2-methylpyridol[2,3-d]imidazole (2-MPI) (*mp* 470 K), 5-methylpyrido[2,3-d]imidazole (5-MPI) (*mp* 499 K) and 7-methylpyridol[2,3-d]imidazole (7-MPI) (*mp* 529 K) were synthesized by methods reported previously [8, 9].

Elemental analyses (C, H, N, Cl) were carried out with a Perkin-Elmer CHN analyser Model 240. The copper content was determined in an EP-4 electrolyser (Nysa, Poland).

TG, DTG and DTA curves were recorded in air atmosphere in the range of temperature 293–1273 K, using a MOM (Budapest) derivatograph with a platinum crucible. The samples weighted from 0.09 to 0.16 g. A heating rate of 2.5 or 5°C min^{-1} was used. The sensitivity was 200 mg in TG. Calcined Al_2O_3 was used as reference material.

X-ray powder patterns were taken on a DRON-2 diffractometer (USSR) equipped with a scintillation counter and connected to an IBM computer. A step by step method over the 2θ angle range of 4–60° was used, with monochromatic CuK_α radiation and a Ni filter.

Synthesis of copper(II) complexes

A methanolic solution of 0.02 or 0.03 mol of ligand was added under stirring to an aqueous solution containing 0.01 mol of $Cu(NO_3)_2$ or $CuCl_2$. The precipitated blue crystals were filtered off, and washed with water and methanol. The samples were dried at 333 K and next at 383 K to constant mass.

Calculations

The thermogravimetric data provided a possibility to calculate the kinetic parameters of the decomposition processes. The method of Coats and Redfern was chosen [10]. The calculation procedure described in detail in [11–13] was used here.

Results and discussion

The results of elementary analysis of the complexes investigated are shown in Table 1. The compounds obtained proved to be monohydrates usually containing two molecules of organic ligand. Only in the case of 2-MPI were complexes with two water molecules isolated: Cu(2-MPI)$_2$(NO$_3$)$_2$·2H$_2$O and Cu(2-MPI)$_3$(NO$_3$)$_2$·2 H$_2$O.

Table 1 Analytical data for the complexes

Compound	Found (calcd.)/%				
	C	H	N	Cu	Cl
Cu(2-MPI)$_2$(NO$_3$)$_2$·2H$_2$O	34.44	3.25	24.38	12.44	–
	(34.32)	(3.71)	(22.88)	(12.97)	
Cu(2-MPI)$_3$(NO$_3$)$_2$·2H$_2$O	38.22	4.18	24.04	10.24	–
	(40.48)	(4.04)	(24.73)	(10.20)	
Cu(5-MPI)$_2$(NO$_3$)$_2$·H$_2$O	35.81	3.26	23.96	13.85	–
	(35.64)	(3.42)	(23.75)	(13.47)	
Cu(5-MPI)$_2$Cl$_2$·H$_2$O	41.88	3.36	20.93	15.95	17.30
	(40.15)	(3.85)	(20.07)	(15.17)	(16.93)
Cu(7-MPI)$_2$(NO$_3$)$_2$·H$_2$O	35.39	3.10	23.90	14.52	–
	(35.63)	(3.42)	(23.75)	(13.47)	
Cu(7-MPI)$_2$Cl$_2$·H$_2$O	40.25	3.73	20.01	16.53	16.95
	(40.15)	(3.85)	(20.07)	(15.17)	(16.93)

The TG and DTA curves for the Cu(II) complexes with 5-MPI are shown in Figs 1 and 2. The thermoderivatographic plots of the remaining nitrate and chloride complexes displayed the same features as the curves given in Figs 1–2. The data given in Table 2 illustrate the process of thermal decomposition of the compounds investigated. Kinetic parameters for these reactions are listed in Table 3.

Decomposition processes of nitrate complexes

In the DTA curve obtained for the complex Cu(5-MPI)$_2$(NO$_3$)$_2$·H$_2$O (Fig. 1), an endothermic peak was followed by an exothermic one in the temperature range 408–493 K. The peak in the DTA curve was accompanied by a rapid (cf. the almost vertical part in the TG curve in Fig. 1) 46.74% mass loss from the sample investigated. In the temperature range 553–753 K, a very strong exothermic peak, accompanied by a 37.20% mass loss, was observed in the DTA curve. The thermal decomposition of the complex Cu(7-MPI)$_2$(NO$_3$)$_2$·H$_2$O also proceeded according to α two-step mechanism. During the first step, the DTA exothermic peak was accompanied by a rapid, 46.51%, mass loss. Subsequent, intensive exothermic decomposition of the complex occurred at 598–653 K, followed by a mass loss of 36.54%.

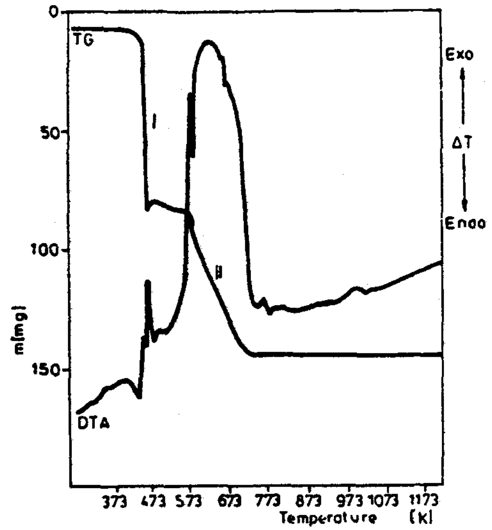

Fig. 1 TG and DTA curves for Cu(5-MPI)$_2$(NO$_3$)$_2$·H$_2$O

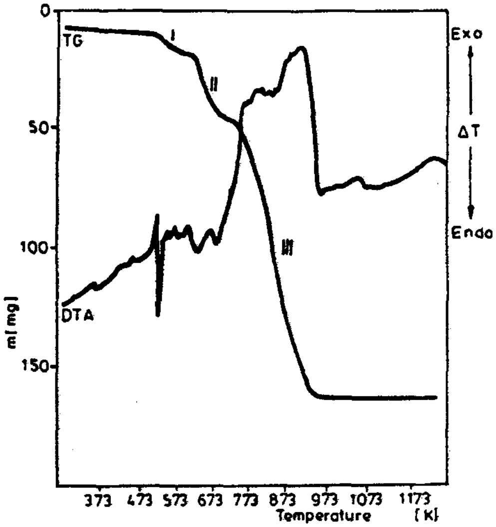

Fig. 2 TG and DTA curves for Cu(5-MPI)$_2$Cl$_2$·H$_2$O

The TG and DTA curves of Cu(2-MPI)$_2$(NO$_3$)$_2$·2H$_2$O exhibited a distinct exothermic peak at 453 K, accompanied by an extremely rapid 51.35% mass loss. A very strong exothermic peak, accompanied by a TG mass loss of 35.94%, was observed at 668 K in the DTA curve.

For the complex containing three molecules of 2-MPI, Cu(2-MPI)$_3$(NO$_3$)$_2$·2H$_2$O, a very strong endothermic peak could be seen at 358 K in the DTA curve, followed

Table 2 Thermal decomposition process characteristics

Stable phase or thermal reaction	T_{range} / K	Effect	Total mass loss/ % found	theory
$Cu(5\text{-}MPI)_2(NO_3)_2 \cdot H_2O \rightarrow Cu(5\text{-}MPI)_{0.5}(NO_3)_2$	408–493	endo, exo	46.74	46.14
$Cu(5\text{-}MPI)_{0.5}(NO_3)_2 \rightarrow CuO$	553–753	exo	37.20	37.00
			83.9	83.1
$Cu(7\text{-}MPI)_2(NO_3)_2 \cdot H_2O \rightarrow Cu(7\text{-}MPI)_{0.5}(NO_3)_2$	493–523	exo	46.51	46.14
$Cu(7\text{-}MPI)_{0.5}(NO_3)_2 \rightarrow CuO$	598–653	exo	36.54	37.00
			83.05	83.14
$Cu(2\text{-}MPI)_2(NO_3)_2 \cdot 2H_2O \rightarrow Cu(2\text{-}MPI)_{0.5}(NO_3)_2$	448–483	exo	51.35	48.12
$Cu(2\text{-}MPI)_{0.5}(NO_3)_2 \rightarrow CuO$	582–843	exo	35.94	35.64
			87.29	83.76
$Cu(2\text{-}MPI)_3(NO_3)_2 \cdot 2H_2O \rightarrow Cu(2\text{-}MPI)(NO_3)_2$	333–438	endo, exo	48.63	48.52
$Cu(2\text{-}MPI)(NO_3)_2 \rightarrow CuO$	653–833	exo	40.78	38.71
			89.41	87.23
$Cu(5\text{-}MPI)_2Cl_2 \cdot H_2O \rightarrow Cu(5\text{-}MPI)_2Cl_2$	513–603	endo	4.50	4.30
$Cu(5\text{-}MPI)_2Cl_2 \rightarrow Cu(5\text{-}MPI)_{1.5}Cl_2$	603–743	endo, exo	16.23	15.90
$Cu(5\text{-}MPI)_{1.5}Cl_2$	743–963	exo	66.34	–
			87.37	
$Cu(7\text{-}MPI)_2Cl_2 \cdot H_2O \rightarrow Cu(7\text{-}MPI)_2Cl$	493–603	endo	12.31	12.76
$Cu(7\text{-}MPI)_2Cl \rightarrow Cu(7\text{-}MPI)_{1.5}Cl$	603–723	endo, exo	14.36	15.90
$Cu(7\text{-}MPI)_{1.5}Cl$	723–893	exo	65.64	–

by an exothermic peak at 438 K. These effects were accompanied by a rapid, 48.63% mass loss from the sample investigated. In the temperature range 653–833 K, three adjacent exothermic peaks, accompanied by a 40.78% mass loss, were observed in the DTA curve.

Table 3 Kinetic parameters[a] for thermal decomposition reaction

Compounds	Decomposition[b]	E_a/kJ mol^{-1}	n	lnZ	R^c
$Cu(5\text{-}MPI)_2(NO_3)_2 \cdot H_2O$	I	–	–	–	–
	II	67.9	1.67	2.5	0.990
$Cu(7\text{-}MPI)_2(NO_3)_2 \cdot H_2O$	I	–	–	–	–
	II	291.1	2.53	22.4	0.997
$Cu(2\text{-}MPI)_2(NO_3)_2 \cdot 2H_2O$	I	–	–	–	–
	II	193.8	6.34	12.9	0.989
$Cu(2\text{-}MPI)_3(NO_3)_2 \cdot 2H_2O$	I	–	–	–	–
	II	48.2	1.23	0.2	0.904
$Cu(5\text{-}MPI)_2Cl_2 \cdot H_2O$	I	141.1	2.28	10.7	0.996
	II	191.2	2.11	12.6	0.995
	III	90.3	1.03	2.3	0.994
$Cu(7\text{-}MPI)_2Cl_2 \cdot H_2O$	I	87.2	1.06	5.5	0.996
	II	154.9	2.50	10.1	0.994
	III	72.0	0.23	1.0	0.999

[a] E_a is activation energy, n is reaction order and Z is the pre-exponential factor
[b] Peaks are numbered according rising temperature, Figs 1 and 2
[c] R – correlation factor

XRD measurements showed [14] that the composition of the final product of thermal decomposition of the samples investigated corresponded to CuO. The results obtained, and also the similar curve shapes, allowed the conclusion that the thermal decompositions of the Cu(II) complexes with 2-MPI, 5-MPI and 7-MPI proceeds according to the same mechanism. Elimination of crystalline water and partial deamination take place during the first step of sample decomposition. The strong exothermic peaks observed at higher temperatures in the DTA curves most probably denote the combustion of the remaining organic ligand and the decomposition of the nitrate groups. Table 2 contains the proposed mechanisms for decomposition of the copper(II) complexes investigated. Similar behaviour was observed during heating of nitrate complexes of copper(II) with the amines of bipy, alkyl derivatives of imidazole, ethylenediamine and benzimidazole [15–18]. Those compounds also decomposed exothermally to CuO, but the elimination of organic ligand molecules was in that case the main process during the first step of decomposition. The proposed sequence of decomposition of the ligands examined is supported by a discussion of the curves free ligand. It results from these that decomposition of the ligands, followed by a sharp mass loss (ca 90%), occurs in the temperature range 473–653 K. Hence, decomposition of the complexes in this temperature region must mainly involve ligand elimination, and must proceed without participation of the coordination centres. No influence of the positions of the methyl groups in the ligand molecules on the thermal stabilities of the complexes containing such ligands was observed in this work.

Decomposition processes of chloride complexes

The endothermic peak observed at 533 K in the curve for $Cu(5\text{-}MPI)_2Cl_2{\cdot}H_2O$, accompanied by a 4.5% mass loss, corresponds to elimination of the water molecule (theor. 4.3%). Further heating of the complex (in the range 603–743 K) resulted in elimination of the ligand, probably followed by $Cu(5\text{-}MPI)_{1.5}Cl_2$ formation; this supposition is suggested by the value of the mass loss, which is 16.23% (theor. 15.90%). The highest mass loss, 66.34%, was observed in the TG curve in the temperature range 743–963 K. This was accompanied by an intense, broad exothermic peak in the DTA curve, probably illustrating the combustion of the remaining part of the organic ligand. Similar three-stage decomposition was observed during heating of the complex $Cu(7\text{-}MPI)_2Cl_2{\cdot}H_2O$ (cf. Table 2) similarly as in [16], the final compositions of the products of thermal decomposition of the two complexes were, not identified because of their volatility.

Replacement of NO_3^- by Cl^- in the complexes investigated led to qualitative changes in the derivatographic plots. A comparison of the corresponding steps of thermal decomposition of the nitrate and chloride complexes shows that elimination of the organic ligand is slower and occurs at higher temperatures for the chloride complexes than for the nitrate complexes. This suggests that the above replacement must cause an increase in thermal stability of the complex [15, 16, 19]. This is consistent with the general observation that 'changing the anion has a pronounced effect on the thermal stability of a complex' [15]. The difference in thermal stability between the nitrate and chloride complexes of Cu(II) is probably a result of the stability of the electron structure of the chloride anion (octet). By reason of this, the participation of the electrons of the organic ligands in the coordinate bond is enhanced, which causes an increase in the strength of the metal-organic ligand bonding in the chloride complexes.

Thermogravimetric results permitted calculation of the kinetic parameters for the individual steps of the process of total decomposition of the complexes investigated (Table 3). Calculations for the steps of decomposition characterized by point-type decomposition (i.e. when a vertical section is observed in the TG curve) could not be accomplished, however.

* * *

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