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ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF SOLID Cu(II) COMPLEXES AND THE COURSE OF THEIR THERMAL DECOMPOSITION

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ABSTRACT

The relationship between the structures of coordination polyhedra of Cu(II) complexes and the kinetics of their thermal decomposition was studied for two series of isostructural compounds. It is shown that the activation energies decrease with increasing values of anisotropic temperature factors of released ligands' donor atoms, corrected for the thermal motion of central atom in the split bond direction.

INTRODUCTION

The study of the relationship between the structures of coordination compounds and the course of their thermal decomposition is frequently reduced to a comparison of the static structure data of the relevant compounds with the parameters of their thermal decomposition. However, the thermally induced bond splitting should be connected with the vibrational properties of the split bond. From all structure data, these properties are best reflected by the atomic anisotropic thermal factors, U_{ii} (pm^2). It was already shown that the values of activation energies (E^*) of decomposition reactions of some Cu(II) complexes increase with decreasing values of anisotropic thermal factors of split ligand donor atom (ref.1). When comparing the E^* values with those of "thermal movement" (ref.2) of the whole split bond Cu - ligand, even a better coincidence was found (ref.1). The thermal movement of a bond is defined by the equation

$$\Delta U_{ii}^{\frac{1}{2}} = (U_{ii}(L) - U_{ii}(Cu))^{\frac{1}{2}}$$

where L is the donor atom of the split-off ligand (ref.2).

In this paper the results concerning the kinetics of thermal decomposition of complexes $M_2^IM^{II}[Cu(NO_2)_6]$ are presented. The crystal structures of these complexes have been solved very precisely for cases M^I = K, M^{II} = Ca, Sr and Ba (type 1), and for M^{II} = Pb, M^I = K, Rb, Cs and Tl (type 2) (ref. in Table 1 and 2.)

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Due to the plasticity of the Cu(II) coordination sphere (ref.3), the coordination polyhedra $[Cu(NO_2)_6]^{4-}$ are differently distorted in the presence of different counter ions. The deformation is static for the complexes of type 1 and dynamic for those of type 2 (ref.4). Complexes, containing Pb^{II} (type 2) are called "fluxional" (ref.5) and when heated they change their structures (ref.6). It was of interest to find out, whether the mentioned relationship between the E^* values and those of $\Delta U^{\ddagger}_{ii}$ will also hold at these complexes.

EXPERIMENTAL PART

The thermo- analytical results were obtained on the series of isostructural complexes $M^{I}_{2}M^{II}[Cu(NO_2)_6]$ with known crystal structures. All studied complexes were prepared according to described procedures and their composition was checked analytically. The thermogravimetric curves were gained with a Perkin-Elmer thermobalance TGS-1, on the samples previously finely powdered and sieved to a mesh size of 0.05. Activation energy values were obtained according to the Coats - Redfern method (ref.7), using the least squares procedure.

RESULTS AND DISCUSSION

The stoichiometry of thermal decomposition for the complexes $M^{I}_{2}M^{II}[Cu(NO_2)_6]$ is complicated and all six Cu - NO_2 bonds are split in the first step of their decomposition (ref.8). The activation energies, found for this step were therefore compared with the bond lengths Cu - N as well as with the $\Delta U^{\ddagger}_{ii}$ values in the bond directions. For the complexes of type 1 (Table 1) the lowest activation energy was found for the decomposition of $K_2Ca[Cu(NO_2)_6]$. In this compound the interatomic distances Cu - N are the longest, and the $\Delta U^{\ddagger}_{ii}$ values are the highest (ref.9). The highest $E^{\ddagger}$ value was found for decomposition of $K_2Sr[Cu(NO_2)_6]$, having the shortest Cu - N bonds and the lowest $\Delta U^{\ddagger}_{ii}$ values in Cu - N bond directions (ref.10). The relatively small differences between the Cu - N bond lengths and $\Delta U^{\ddagger}_{ii}$ values of the compounds with M^{II} = Sr and Ba (ref.11) are reflected also in small differences between the E^* values of their thermal decomposition.

Complexes of type 2, when heated, undergo phase transitions from orthorhombic β- to cubic α-forms at different temperatures (ref.6). However, at the decomposition temperature, they are all present in cubic form with regular octahedral structure of anion

TABLE 1

Some structure data for $K_2M^{II}[Cu(NO_2)_6]$ complexes and the E^{*} values of the first step of their thermal decomposition

M^{II}	$Ca^{a)}$	$Sr^{b)}$	$Ba^{c)}$
$r(Cu - N_1)^{+}$	205.0	204.1	203.8
$r(Cu - N_2)$	231.3	231.0	231.1
$r(Cu - N_3)$	205.2	202.9	204.8
$\Delta U_{11}^{1/2}(Cu - N_2)$	4.1	4.0	2.5
$\Delta U_{22}^{1/2}(Cu - N_3)$	5.8	5.3	4.3
$\Delta U_{33}^{1/2}(Cu - N_1)$	6.6	3.0	5.9
E^{*} , kJ mol^{-1}	100 ± 5	130 ± 3	124 ± 3

$^{+}$ all data in pm; structure data from a) ref.9, b) ref.10, c) ref.11

$[Cu(NO_2)_6]^{4-}$. It is therefore comprehensible that the previously discussed interdependence between the E^{*} and $\Delta U_{ii}^{1/2}$ values was for these complexes valid only when the high temperature α-form structure data were compared (Table 2). As in other, former investigated cases (ref.1), no dependence between the bond lengths Cu - N and E^{*} values was found for type 2 complexes. This result

TABLE 2

Some structure data for the α-$M_2^IPb[Cu(NO_2)_6]$ and the E^{*} values of the first step of their thermal decomposition

M^{I}	r(Cu - N), pm	$\Delta U_{ii}^{1/2}$, pm	E^{*}, kJ mol^{-1}
$K^{a)}$	211.8	14.4	100 ± 3
Rb	-	-	117 ± 2
$Cs^{b)}$	217.4	5.6	118 ± 3
$Tl^{c)}$	211.8	12.6	109.± 1

Structure data from a) ref.12, b) ref.13, c) ref.14

can be considered as further evidence for the conception of near connection between the thermal decomposition of coordination compounds and the dynamic properties of their crystal structures.

However, the relationship presented holds only when differences in the composition and structure of studied complexes are not too expressive. This is quite understandable, when taking into account the number of factors, influencing the numerical values of activation energies. Moreover, the atomic anisotropic thermal factors are the most unprecisely determined structure data and they can be seriously considered only when the structure was solved with very high precision.

Nevertheless, it can be stated that in the series of isostructural complexes with analoguous composition the values of activation energies increase with decreasing thermal movement of the split bond.

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