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ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF DOUBLE HEXAAQUA-Cu(II) AND Ni(II) SELENATES AND THE COURSE OF THEIR DECOMPOSITION

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ABSTRACT

Stoichiometry and kinetics of the thermal decomposition of the double hexaaquacopper(II) and nickel(II) selenates with counter cations M(I) = NH_4, K, Rb, Cs and Tl were studied. The stoichiometry of their decomposition depends on the M(II), the Cu(II) compounds (except of Cs salt) being decomposed in two steps (- 4, - 2 water molecules), the nickel (II) compounds (except of K salt) in one step. The loss of water molecules is accompanied by the coordination of selenato groups, as indicated in their electronic and IR spectra. The activation energies for the first step of the Cu(II) complexes decomposition increase with increasing counter ion's diameter. No similar dependence was found for Ni(II) complexes. Macromechanistic studies showed that the most probable decomposition mechanism is the reaction on the phase boundary with spherical symmetry.

INTRODUCTION

Compounds of the type $M_2^IM^{II}(H_2O)_6(SeO_4)_2$, as far their crystal structures are known, are isostructural with the parrent sulphates [1]. In the series of $M_2^ICu(H_2O)_6(SO_4)_2$ complexes, the deviations from regular octahedral structures of the $Cu(H_2O)_6^{2+}$ cation increase with the size of the counter ion [2,3]. The activation energies for the first step of $M_2^ICu(H_2O)_6(SO_4)_2$ dehydration increase with increasing degree of Cu(II) coordination polyhedra deformation. For compounds, containing Ni(II) as central atom no similar correlation between the E^* values and the counter ion's size was found[4]. This was attributed to the different properties of coordination compounds of these central atoms, caused by their different electronic structure [5,6].

In the series of $M_2^IM^{II}(H_2O)_6(SeO_4)_2$ are for Cu(II) compounds known the crystal structures with $M^I = NH_4$ [7] and K [8], for Ni(II) compounds only the structure with $M^I = NH_4$ [9].

The aim of the present work was therefore to find out, whether similar dependences between the Cu(II) coordination polyhedra de-

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formation and the values of E^* for the first step of thermal decomposition will hold at selenate compounds as found for sulphato complexes, as well.

MEASURING METHODS

The $M_2^IM^{II}(H_2O)_6(SeO_4)_2$ compounds were prepared from water solutions. The composition of prepared compounds was checked analytically. IR and electronic spectra were taken in nujoll mulls on the Specord IR-75 (4000 - 400 cm^{-1}), PYE Unicam (400 - 200 cm^{-1}), Unicam (6000 - 20 000 cm^{-1}) and Specord M-40 (18 000 - 31 000 cm^{-1}). Thermal decomposition of all complexes was carried out on the derivatograph OD - 102 in air atmosphere. The sample weight was 200 mg, the temperature increase 3^o min^{-1}. The studied compounds were before measurements finely powdered, and sieved. The activation energies and preexponential factors were calculated according to [10], from TG curves using the least-square procedure. The macromechanism of studied reactions was evaluated according to [11].

RESULTS AND DISCUSSION

According to TG curves of studied compounds, the Cu(II) and Ni(II) complexes are decomposed generally with the same stoichiometry as found for sulphato complexes [4]. The copper(II) compounds decompose in two steps (- 4 H_2O, - 2 H_2O) with the exception of Cs salt. Because of it´s quite different decomposition stoichiometry, we did not pay any more attention to this compound. Nickel (II) compounds, except of K salt, decompose in one step (- 6 H_2O). During the decomposition of K salt the $K_2Ni(H_2O)_2(SeO_4)_2$ is formed.

The electronic spectra of starting compounds and those of $M^IM^{II}(H_2O)_2(SeO_4)_2$ showed that the coordination number 6 is preserved during the decomposition for both central atoms. This has to be connected with the coordination of selenato groups, originally attached to the $M(H_2O)_6^{2+}$ via hydrogen bonds only [7 - 9]. The coordination of the selenato groups is reflected in the IR spectra of the thermal decomposition intermediates. The lowering of the SeO_4^{2-} symmetry, due to their coordination was concluded on the basis of the differences in the IR spectra of compounds with the same counter ion, but different amount of coordinated water molecules.

The results of kinetic study of the first step of Cu(II) compounds decomposition, as well as the results on the Ni(II) compounds are given in Table 1. The activation energies found for Cu(II) complexes decomposition are higher than those, found for sulphato complexes [4]. On the contrary the activation energies, found for Ni(II) selenato compounds are lower (with exception of K salt) than those, found for sulphato compounds.

Table 1. Results of the kinetic analysis of the studied reactions

M^{II}	M^{I}	T_d °C	Coats - Redfern E^* kJ mol^{-1}	Coats - Redfern log A	Škvára - Sesták E^* kJ mol^{-1}	Škvára - Sesták log A
Cu	NH_4	54	139 ± 7	17.8 ± 1.0	128 ± 4	15.7 ± 0.6
	K	55	121 ± 2	15.9 ± 0.3	82 ± 2	22.4 ± 1.0
	Rb	55	174 ± 8	23.3 ± 1.0	126 ± 4	17.5 ± 0.3
	Tl	55	197 ±15	27.1 ± 2.2	156 ± 7	20.9 ± 1.1
Ni	NH_4	89	91 ± 3	8.9 ± 0.5	128 ∓ 3	13.5 ± 0.3
	K	90	190 ± 9	23.8 ± 1.3	144 ± 8	17.0 ± 1.0
	Rb	97	84 ± 5	7.8 ± 0.7	124 ± 6	12.8 ± 0.8
	Cs	93	75 ± 6	7.0 ± 0.7	106 ± 4	10.8 ± 0.5
	Tl	88	100 ± 4	10.1 ± 0.6	115 ± 5	11.7 ± 0.7

The evaluation of TG curves according to [10] (the reaction order was found to be 1 for all Cu(II) and Ni(II) compounds) gave for Cu(II) complexes decomposition the E^* values, which increase with increasing size of the counter ion. However, the crystal structure data on NH_4^+ and K^+ copper(II) salts, as well as the electronic spectra of the other Cu(II) complexes does not confirm the increase of the coordination polyhedra deformation with the increasing counter ion radius. Anyway, no similar dependence was found for Ni(II) complexes.

The results of kinetic analysis according to [11] gave the E^* and log A values different to those, calculated according to [10]. For Cu(II) complexes decomposition the trend in the E^* values changes is preserved, however. The E^* values, found for Ni(II) compounds decomposition according to [11] decrease with increasing diameter of outer sphere cation. The only exception is $Tl_2Ni(H_2O)_6(SeO_4)_2$.

For all studied decomposition reactions the best fitting with the experimental data was found for R_3 mechanism (reaction on the phase boundary with spherical symmetry).

Cocluding, we have to say that the trend of the E^* values changes, found for the first step of $M_2^ICu(H_2O)_6(SeO_4)_2$ thermal decomposition is analogous to that found for sulphato complexes, however its interpretation needs more detailed studies. Comparing the results, gained for studied Ni(II) and Cu(II) compounds, we can say that the different stereochemical properties of the coordination polyhedra of these two central atoms are of significant meaning for the hexaaquacopper(II) and nickel(II) thermal decomposition.

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