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ON THE THERMOLYSIS OF TRANSITION DIVALENT METAL AQUAAMMINE MONO- AND DI-PHOSPHATES

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Such special properties of phosphates as their photo- and electro luminophoric, catalytic, ferroelectric, and electret activities are developed in the result of a specific structure formation having stable enough by mechanical and thermal characteristics and simultaneous containing "useful defects" and highly mobile ions.

The research objective of this study is to examine the formation of the mixed-anion mono- and diphosphate complex compounds contained transition metals of individual material composition by their aqua ammine complex thermolysis.

It was investigated the thermal transformations of the Cobalt(II), Nickel(II), Copper(II), Zinc, and Cadmium aqua ammine mono- and/or diphosphates. The examined compounds were united into groups based on the cation composition (mono-, double, or triple).

The research steps are included i) the differential thermal analysis of the pointed compounds at a heating rate $2.5 \div 5$ $deg \cdot min^{-1}$ in capped platinum cylindrical crucibles; ii) sampling of the thermolysis intermediates in the DTA/TGA feature points; iii) examining of the intermediates by chemical elemental analysis, X-ray, IR, and the qualitative paper chromatography.

To compare the schemes of the mono-cation (Cu(II), or Zn, or Ni(II), or Cd) aqua ammine diphosphates thermal transformations it is noted that the nature of their thermolysis processes in whole are similar to the water removing of the corresponded divalent metal aqua ammine monophosphates. The steps of the transformation processes during the ammonia NH_3 and water H_2O evaporating include:

i) Intramolecular hydrolysis of metal cation and mainly diphosphate anion, it simultaneously proceeds by hydrogen phosphate condensing;
ii) Final stage may accompany by the evacuating of ammonia NH_3 traces when water removed completely. It means that coordinated ammonia is also involved in protolysis process;
iii) Partially protonated solid phosphates (x-ray amorphous or crystalline) are formed in the result of stepwise ammonia NH_3 and water H_2O removing from aqua ammine mono- or diphosphates during the thermolysis process;
iv) In the result of complete thermolysis of d-metal aqua ammine mono-diphosphates it was established the formation the crystalline products contained two phases in the ratio corresponded stoichiometrically to the

monophosphate and diphosphate anions content in the initial substances.

According to the thermal transformation schemes of the coordinated Cu(II), Co(II), Ni(II), Zn, and Cd cation double type aqua ammine mono-diphosphates it was determined that the mechanism of their thermolysis is very similar to the processes of gaseous evaporating at heating for monocation aqua ammine mono-diphosphates. The main definite regularities are: i) process of stepwise water H_2O and ammonia NH_3 from aqua ammine mono-diphosphates during intermediate thermolysis stages accompanies by intensive intramolecular hydrolysis of diphosphate anion with formatting of protonized monophosphates; ii) in most cases, two crystalline phases form on the final stage of water and ammonia removing.

In general, thermolysis mechanism of d-metal Cu(II), Zn, Co(II), Ni(II), and Cd triple complex aqua ammine mono-diphosphates is similar to the thermal transformations of double aqua ammine phosphates.

As a whole, based on the data about composition of starting, intermediate, and final compounds formed at heating of hetero-cation (double and triple) aqua ammine mono-diphosphates, it was established that the ammonia and water devolatilization is stepped process and it accompanies by amorphization of thermolysis intermediates. The concomitant characters are intramolecular hydrolysis and protonization of diphosphate anions with the next polycondensation of monophosphates. In the most cases end products of hetero-cation aqua ammine mono-diphosphates thermolysis no matter what their cation composition didn’t finish by the formation of phosphate with the stoichiometric mono/diphosphate ratio responded to their starting composition. From our viewpoint, the reasons of initial single-phase structure destroying at heating is: i) simultaneous existing of Cd(II) cation and other d-metal cations having large differences of ionic radii; ii) confirmation form of monophosphates and diphosphate anions, and iii) peculiarities of the bonding formation between groups of atoms in a crystal.