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THERMOLYSIS OF THE TRANSITION DIVALENT METAL AQUA AMMINE DIPHOSPHATES AS A METHOD FOR NEW MATERIALS OBTAINING

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To establish the regularities of dehydration processes at heating of hydrated phosphates is necessary for determining the stability temperature ranges for the certain compounds and the acquisition of certain phosphates forms such special properties as stoichiometric composition and structure, color, dispersion, catalytic activity, proton conductivity etc.

The objects of thermolysis research were aqua ammine diphosphates of transition bivalent metals (Co, Ni, Cu, Zn, and Cd), combined in groups on the basis of salt types (monocation, double, or triple).

The suggested methodology for detecting of chemical transformations happening during diphosphate thermolysis includes the differential thermal analysis of bivalent Co, Ni, Cu, Zn, and Cd aqua ammine diphosphates at a heating rate $2.5 \div 5$ deg·min^{-1} in capped platinum crucibles; sampling of the thermolysis intermediates heated to temperatures corresponded to the DTA/TGA feature points; analysis of the obtained thermolysis intermediates by chemical elemental analysis, X-ray, IR, and the qualitative paper chromatography.

To compare the thermal transformation block diagrams obtained for Cu(II), Zn, Co(II), Ni(II), and Cd monocation aqua ammine diphosphates complexes enables to conclude that their thermal transformation mechanisms as a whole are similar to the processes of water removing of the corresponded bivalent metal hydrated neutral diphosphates. Thermal transformations of the complex diphosphates are characterized by the following features: step-by-step removing of ammonia and water from aqua ammine diphosphate complexes; which ends by the formation of the final products – crystalline neutral diphosphates; during thermal NH_3 and H_2O removing from aqua ammine diphosphate complex the intramolecular hydrolysis of a cation and an diphosphate anion taken place; this process was accompanied by the simultaneous destruction and condensation of phosphate anions of different conversion degree depending on the nature of the d-metal cation; the final stage of thermolysis accompanied by the removing of a ammonia NH_3 insignificant amount at the total lack of water. This fact demonstrated that the protolysis been not only by water but ammonia too.

According to the developed block schemes of the thermal transformations for complex salts – double cation-containing Cu(II), Zn, Co(II), Ni(II), and Cd aqua ammine diphosphates it is established that the their thermolysis mechanism is similar to the dehydrating processes of monocation aqua ammine diphosphates. The general regularities are:

i) In the most cases, thermolysis of the double aqua ammine diphosphates independently their cation composition ends by the crystallization of the double diphosphates having cation stoichiometric ratio remained from initial complexes;

ii) Thermolysis process consists in step-by-step ammonia NH_3 and water H_2O removing from aqua ammine diphosphate complexes with formation of end-products – neutral diphosphates – at temperature which depends on cation composition of calcinating compound;

iii) Condensation depth of monophosphates anion at thermolysis process depends on cation composition of aqua ammine diphosphate complexes too and, as a result, intensity of donor-acceptor interaction between d-metal cations with water/ammonia ligands.

Analyzed the block diagrams of the thermal transformations developed for triple complex salts - Cu(II), Zn, Co(II), Ni(II), and Cd aqua ammine diphosphates – we concluded that their thermolysis mechanisms are similar in general to the dehydration processes of double aqua ammine phosphates. The major trends are: i) in the most cases, triple aqua ammine diphosphate thermolysis ends or formation of triple diphosphate having cation stoichiometric ratio remained from initial complex, or mix of double diphosphates, when one of the three initial metal cations is included to the composition of the individual diphosphate.