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On Some Condensed Phosphates of Mono- and Polyvalent Metals and Spheres of Their Applications

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Abstract: A great multitude of condensed phosphates with different formula were synthesized and described in scientific literature since the end of the 20th and the beginning of the 21st cc. The presented work is the general overview concerning synthesis and systematic investigation of MI2O–MIII2 O3–P2O5–H2O systems at 100–600°C (where M^{I} represent alkali metals and Ag and M^{III} - various trivalent metals) summarizing experimental results and examination of possibilities of application of these condensed compounds.

More than 80 new previously unknown double condensed phosphates were obtained including one of the first representatives of double cyclooctaphosphates and cyclododecaphosphates classes. Therefore, presented data are the outcome of synthesis, analysis, examination of the experimental records, determination and evaluation of properties of synthesized by us compounds and correspondence with accomplishments and advancements in the area of inorganic polymers chemistry, especially, considering the possibilities of application of phosphates containing condensed phosphates.

Keywords: compounds synthesis and application, condensed phosphates, diphosphates, triphosphates, polyphosphates, cyclooctaphosphates, cyclododecaphosphates.

1 Introduction

Humans have been using phosphates since time immemorial. It's true – their composition was not known, their arrangement was not studied and their structure was not deciphered, but they were applied quite widely. There are many examples, but we give only one: the phosphates were used in the form of dyes, pigments, paints and were applied in the works of art in the context of the paintings art at least since 2nd century (for example some of the Fayum portraits dated by the 2nd–3rd cc.).The capability of condensation of phosphoric anions is recognized approximately to two and a half of centuries, but despite this fact the intensive development of the field of condensed phosphates has reached only in recent decades [1-4].

The chemistry of inorganic compounds of phosphorous has developed more intensively in the last few years for the cause that the phosphate compounds are most appropriate for further development of the inorganic polymers chemistry and also they are finding ever increasing practical application as phosphors, fertilizers, detergents, and as materialsь used in engineering and construction. At Present, there are available many acidic metal-phosphate adhesives, and of them aluminum dihydro-phosphate adhesives are most widely used [1–3].

Truly, the chemistry of condensed phosphates has taken a long time to progress, but last 10–20 years many important studies are recognized and published [2–6]. Starting from the innovator investigations of scientists a lot of number of condensed compounds called inorganic polymers was synthesized in the whole world, and the great number of innovative researches was really appreciated in 20th c. [3–10]. Based on the strength of varieties of phosphoric anions condensation processes, one of them leads to the predetermination of the compounds polymeric, cyclic oroligomeric structures [2–4, 11–17].

2 Experiments and Discussions

The fields of phosphates applications are very large and important and cannot be covered sufficiently widely in one

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article. Even a short enumeration of the spheres of application is quite diverse such as: raw materials for creation of phosphates glasses, thermo-resistant materials, effective applying fertilizers, detergents, cement substances, ion-exchange materials and also catalytic agents [3,11,15,18–25]. Some double condensed ammonium phosphates of polyvalent metals are effective flame retardants, phosphorus-containing compounds are also used as fillers. Due to certain characteristics, fire- and thermo-protective properties they are used in thermo-foaming polymeric composites with mineral fillers [18,19].
The configuration of compounds and thermal properties, as well as the vibrational and luminescent properties of condensed phosphates determine their large use in quantum electronics. The bio-materials appear on the base of hydroxyl-apatite and polyphosphates. Fundamental researches concerning double, triple, polymeric and substituted phosphates, where oxygen atoms are interchange by nitrogen, fluorine and sulfur atoms are executed [3,15]. The phosphates binding agents, phosphate-binders and laser materials are supplanted (replaced) by biomaterials, on the base of polyphosphates and hydroxyl apatite. Academician Ivan Tananaev always underlined the vital role of hydroxyl apatite, such as main corposant of the bio organisms comparable by their great importance with the DNA [15, 17].

Condensed phosphates or that is to say inorganic polymers of polyvalent metals, notably double condensed phosphates of rare earth metals with alkali or other monovalent metals have a number of remarkable valuable and appreciable properties, which explicate scenarios of their wide application [1–3, 12–19].
A great number of multitude double poly- and cyclophosphates with different formula was synthesized and described in scientific literature since the end of the 20th and the beginning of the 21st cc. A number of certain objects was investigated from the structural point of view and the anion character was finally confirmed [2,4–6,8,10,11,14,20–22,26,27].
Our group of scientists was synthesized numerous new double condensed oligo- and cyclophosphates, whose general properties we have examined [5,10–12,19–23,26,27]: systematic investigation of M^{I}_2O–$M^{III}_2O_3$–P_2O_5–H_2O at 100–600°C (where M^{I} = alkali metals and Ag, and M^{III} - various trivalent metals) at the molar ratio of initial components $n=M^{I}_2O/M^{III}_2O_3$: from 1 to 12 was executed. Over 80 new, formerly unknown, double condensed phosphates have been obtained, including the one of the first representatives of double cyclooctaphosphates and cyclododecaphosphates classes: $K_2Ga_2P_8O_{24}$ and $Rb_2Ga_2P_8O_{24}$ (these compounds were obtained by Avaliani & Chudinova [5,14,22] and $Cs_3Ga_3P_{12}O_{36}$ was obtained by Avaliani [5]).

Therefore, presented data are the outcome of synthesis, analysis, examination of the experimental records, their analysis, determination and evaluation of properties of obtained compounds and correspondence with accomplishments and advancements in the area of inorganic polymers chemistry [2,3–6,7], especially, considering the fact that crystal structure was examined and described. A numerous number of compounds was wholly studied and observed by X-ray structural techniques and the possibility of their application were studied as well [5, 8,10,14,20,21].

The utmost interesting and mostly preferred main representatives of mentioned classes [4–6,10,12] are presented below, in the Figures 1, 2, and 3.

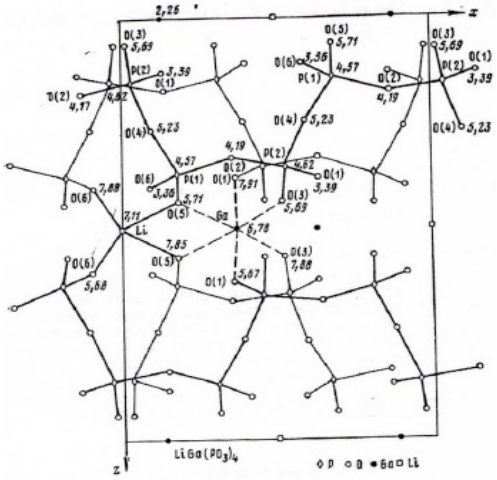

Fig. 1: Scheme of structure of double polyphosphate $(LiGa(PO_3)_4)_x$.

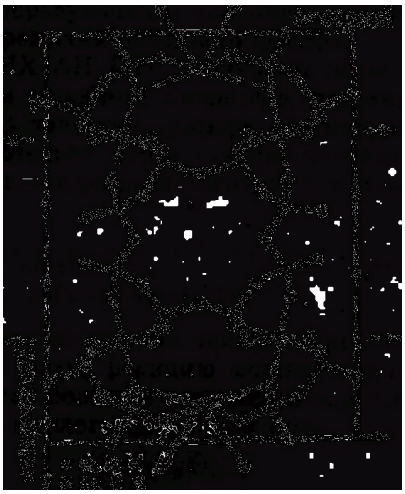

Fig. 2: The P_8O_{24} group observed in $Ga_2K_2P_8O_{24}$ [5,28].

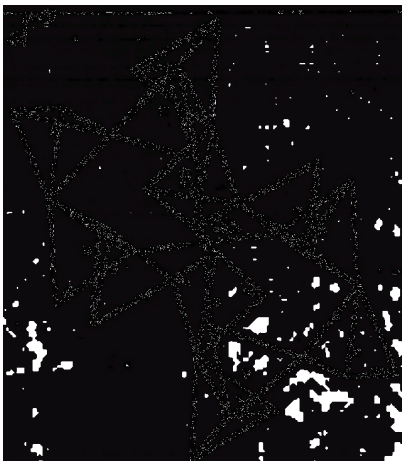

Fig.3: Projection of Cs3Ga3P12O36 on plane xy. Structure is similar with $Cs_3V_3P_{12}O_{36}$. Octahedron VO6 is inserted at center of the ring [2,4–5].

One of primary synthesized cyclododecaphosphates, e.g. $Cs_3Ga_3P_{12}O_{36}$, $Cs_3Sc_3P_{12}O_{36}$, $Cs_3In_3P_{12}O_{36}$ have been obtained by us during investigation of systems Cs_2O–$M^{III}_2O_3$–P_2O_5–H_2O at the molar ratios of P:Cs:M^{III} = 15:5:1 and 15:7.5:1 [5,10–12,21,22] (see also interesting detailed publication [13]). By means of experiments were synthesized many double oligophosphates such as: $Me^{I}Me^{III}(H_2P_2O_7)_2$, $Me^{I}Me^{III}(H_2P_2O_7)_2{\cdot}H_2O$, double acidic triphosphates $Me^{I}Me^{III}HP_3O_{10}$, cyclotetraphosphates $Me^{I}Me^{III}P_4O_{12}$, cyclooctaphosphates $M^{I}_2M^{III}_2P_8O_{24}$ and ultra-phosphate $M^{I}_3M^{III}P_8O_{23}$, cyclododecaphosphates $M^{I}_3M^{III}_3P_{12}O_{36}$, long chain polyphosphates $M^{III}(P0_3)_3$, etc.

It's clearly justified that cyclooctaphosphates $M^{I}_2M^{III}_2P_8O_{24}$ are the best catalysts in the process for receiving of olefin hydrocarbons and diene compounds. The properties of this compound in the model dehydration reaction of n-butyl alcohol by the impulsion method were studied. Based on the conducted experiments, it was found that the overall conversion was from 52 to 65%. Studied sample was comparable by the activity with BPO_3 (50%) sample obtained by mixing the starting components and exceeded the activity of the zeolite catalyst sample NaZr–A (32%) tested under comparable conditions. It has also been found that the C4 olefinic hydrocarbons were firmly retained by the catalyst under the experimental conditions.

Thus, the conducted tests give grounds to believe that potassium and gallium cyclooctahosphates can be used as catalysts in organic synthesis reactions – the preparation of olefinic C2–C6 hydrocarbons and diene compounds. The cyclic compound $K_2Ga_2P_8O_{24}$ has structurally large cavities with a 5.2Å in diameter, which gives a good opportunity to use this and analogue phosphates as an adsorbent for the separation of low molecular weight gases (see Figure 1). It should be noted that synthesized by us double cyclooctaphosphates of potassium-gallium, rubidium-gallium, and potassium-scandium are isomorphs to each other.

During investigations it was established that synthesized by us gallium and/or indium acidic triphosphates $M^{III}H_2P_3O_{10}{\bullet}(1–2)H_2O$ are finest ion-exchange agents and

this property prove the effectiveness of application of mentioned compounds as ion-exchangers. Analogically, the similar scandium acid triphosphate may be used as an ion-exchange agent [5,28–30].

High thermal resistance and thermo-stability of polyphosphates of polyvalent metals, great content of phosphorus determined their use as one of components and/or basic materials for development of phosphate glasses receiving process. Highly condensed ultraphosphates and double polyphosphates of multivalent and monovalent metals are used in quantum electronics and for the design of a mini laser device that is predetermined by vibrational and luminescent properties of mentioned condensed compounds [3,5,28–32]. Very high catalytic activity characterizes vanadium phosphates, similar to gallium phosphates used in organic synthesis reactions. Condensed europium phosphates are equally promising, they can be used as photos and cathode-luminescent materials.

In the present discussion, we speak shortly about the use of the mentioned phosphate systems of hardening, which are used in fine arts also. The procedure of thermo-phosphate painting is very simple [15]. The base material (asbestos – cement sheeting, fiber, cardboard, glass, ceramics, metals) is first coated with phosphate which is fixed by heating, then with phosphate colors (by a brush or by spraying). Thereafter, the color layer is treated (for example, pulverized) with a fixative containing phosphate adhesive. According to academician Tananaev, finally it is heated for 2–3min at 200–400°C using an electric shield for large size paintings, or an ordinary gas burner, or other modes of heating. The painting obtained in such way is moisture- and heat-proof, and does not need the special conditions necessary for prolonged storage. Certain details concerning thermo-graphic painting – in fact a new trend in the art avowed as "Thermo-phosphate Pictorial Art" developed by O. Pavlov [33] – are also available in the work [15]. Summarizing in brief, O. Pavlov has developed mineral as well as phosphate paints in three forms: thermo-phosphate paints, powder colors, pastel and artistic colors. The thermo-phosphates pastels are represented by 63 crayons. The picture obtained is protected from moisture and thermal impact. It's not required special conditions necessary for long-term storage.

At present time, the sufficient experience has already been acquired in "cold technology" without heat treatment of ready-made art paintings (see more details in the work [15]). It is possible that in the further some researches in this field of inorganic chemistry should be interesting for scientists working in this field, particularly with a view to expanding the scope of application of condensed phosphates.

I. P. Dobrovolsky et. al.[34] report that, there are revealed interesting perspectives for obtaining of bindings and pigments from technogenic raw materials for phosphates facade colors. In the mentioned work, some requirements for industrial waste appropriate for obtaining phosphate paints are formulated. Methods for phosphate bindings and pigments on the basis of industrial waste are given as well. Multiple possibilities for oligomeric and polymeric condensed phosphates as inorganic polymers in various technological domains and everyday life were examined in [35,36]. The development of phosphates and silicates chemistry and high-melting nonmetallic materials technology are predetermined by physical-chemical properties of the condensed states of the phases and substances in a colloid dispersed state and to the great possibility of using mentioned materials in various fields of new technical domains.

3 Conclusions

During investigations it is established that synthesized by us gallium and/or indium acidic triphosphates $M^{III}H_2P_3O_{10}\bullet(1–2)H_2O$ are the finest ion-exchange agents and this property prove the effectiveness of application of mentioned compounds as ion-exchangers. Analogically, the similar scandium acid triphosphate $M^{III}H_2P_3O_{10}\bullet(1–2)H_2O$ may be used as an ion-exchange agent.

It is undoubtedly justified that cyclooctaphosphates $M^{I}{}_2M_2{}^{III}P_8O_{24}$ are the best catalysts in the process for receiving of olefin hydrocarbons and diene compounds. The properties of this compound in the model dehydration reaction of n-butyl alcohol by the impulsion method are studied. It was found that the overall conversion was from 52 to 65%. Studied sample is comparable to the activity of the sample BPO3 (50%) obtained by mixing the starting components and exceeded the activity of the zeolite catalyst sample (32%) tested under comparable conditions. It has also been found that the C4 olefin hydrocarbons were firmly retained by the catalyst under the experimental conditions. On this basis, the potassium-gallium cyclooctahosphate can be used as a catalyst in organic synthesis reactions – for the preparation of olefine $C_2–C_6$ hydrocarbons of diene compounds.

The cyclic compound $K_2Ga_2P_8O_{24}$ has structurally large cavities with diameter 5.2Å, which gives a good opportunity to use this and analogue phosphates as an adsorbent for the separation of low molecular weight gases.

Comparing the results for double phosphates of gallium, indium and monovalent metals with other condensed compounds synthesized by us and various literary data, we conclude that condensed composites of Ga and In according to their configuration and structure, are isomorphs with similar phosphates of scandium and are not analogous to corresponding compounds of trivalent rare earth elements.

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