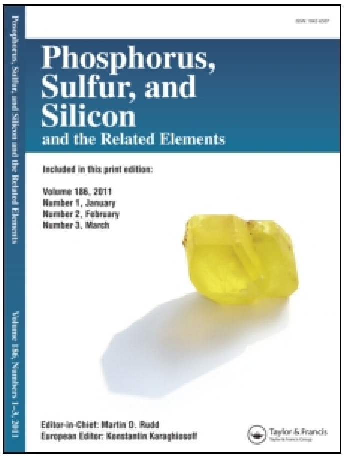

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Main Types of Condensed Phosphates of Alcaline and Trivalent Metals Obtained from Polyphosphoric Acid Melts

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MAIN TYPES OF CONDENSED PHOSPHATES OF ALCALINE AND TRIVALENT METALS OBTAINED FROM POLYPHOSPHORIC ACID MELTS

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Theoretically predicted[1] large variety of forms of condensed phosphates (CP), which contain chain, ring and branch anions, have practically not been completely realized till now. That is why the new compound synthesis remains the actual task in CP chemistry. A number of known CP types increases sharply due to the application of reactions in melts of condensed phosphoric acids (CPA) for synthetic purposes (usually called "polyphosphoric acids"). Among CP of metals the double phosphates are characterized by extreme variability of composition and structure. The compounds made an essential addition to series of poly- and cyclophosphates, but attempts to obtain double ultraphosphate were unsuccessful. This paper generalizes the results of our investigations in the field of preparative and structural chemistry of double CP, namely: CP of alcaline (Li, Na, K, Rb, Cs, NH_4^+) and trivalent (Al, Ga, Fe, Cr) metals. These compounds were prepared in CPA melts in a wide temperature range (corresponding data for rare earth elements have been published earlier[2]). The double phosphates classification from the chemical and structural point of view is given, and for the first time the synthesis of double ultraphosphates $Na_3M^{III}P_8O_{23}$ is reported.

Preparation principles

According to the rearrangement theory of Van Wazer[3], phosphate anions in CPA melts continuously exchange their fragments (monophosphate-, terminal-, and middle groups and branching points) along the P-O-P bonds. Incorporation of metal cations into the melt shifts this mobile equilibrium towards the formation of the anion, which satisfies the following conditions: 1) its geometric form is the most convenient one for the present cations; 2) it should form with the present cations the least soluble compound which is precipitated. So, CPA are the source of various phosphate anion forms from mono- to ultraphosphates; at the same time CPA are solvents in reactions of CP synthesis. Variation of reaction temperature and cation combinations in CPA melts yield many new CP types.

Preparation method

Mixtures of $M_2^ICO_3+M_2^{III}O_3$ (or $M^{III}(NO_3)_3 \cdot 9H_2O$) with components ratio from 2.5:1 to 10:1 were heated with 30-fold excess of phosphoric acid in the temperature range of 170-450°C. It takes from 7 to 60 days for the synthesis to complete. The crystals were washed with water, then they were analyzed by chemical and X-ray methods.

Eight groups of double oligo- and polyphosphates of M^I-M^{III}

The study of 24 alcaline and trivalent metal combinations yielded more than 60 new CP which are divided into 8 groups according to their anion structures (see also [4]):

Diphosphates: $M^IM^{III}(H_2P_2O_7)_2$, $M^IM^{III}H_3(P_2O_7)_2$, $M^IM^{III}P_2O_7$
Triphosphates: $M^IM^{III}HP_3O_{10}$
Polyphosphates: $M^IM^{III}(PO_3)_4$
Anion-mixed compounds: $M^IM_2^{III}(H_2P_3O_{10})(P_4O_{12})$
Cyclotetraphosphates: $M^IM^{III}P_4O_{12}$
Cyclooctaphosphates: $M_2^IM_2^{III}P_8O_{24}$
Cyclododecaphosphates: $M_3^IM_3^{III}P_{12}O_{36}$
Ultraphosphates: $M_3^IM^{III}P_8O_{23}$

The type of compounds in each specific case depends on the reaction temperature, nature of M^I and M^{III} cations, and M^I/M^{III} ratio, but not all combinations of M^I and M^{III} cations yield all the 8 groups of above mentioned CP. Diphosphates $M^IM^{III}(H_2P_2O_7)_2$ are formed if Li, Na, K, and Rb cations combine with Al, Ga, Fe (but not with Cr) at rather low temperatures (170-200°C). The large Cs cation substitutes for an additional proton in this compound and $Cs_2M^{III}H_3(P_2O_7)_2$ are formed, their structure was determined in [5]. Double hydrodiphosphates can be used as starting materials for synthesis of a series of double cyclo- and polyphosphates by solid state methods: $M^IM^{III}(H_2P_2O_7)_2^- \xrightarrow{-2H_2O} M^IM^{III}(PO_3)_4$.

Diphosphates $M^IM^{III}P_2O_7$ are well known. They are formed in CPA melts at high alcaline metal concentrations and high temperatures. The largest number of compounds was obtained for Fe in combination with Li, Na, K, Rb, Cs.

Triphosphates $M^IM^{III}HP_3O_{10}$ form the most numerous group of condensed M^I and M^{III} phosphates. Combinations of K, Rb, Cs, and NH_4^+ cations with trivalent cations produce such compounds in a wide temperature range from 200 to 350-400°C. Their structures can be devided into 2 types (I and II): the first one consists of layers[6] and the second has framework structure[7]. Type I is preferred for Al and Cr compounds, and type II for Fe compounds. The compounds are stable up to 400°C, then they are decomposed as follows:

$$M^IM^{III}HP_3O_{10} \longrightarrow M^IM^{III}P_2O_7 + M^IM^{III}(PO_3)_4$$

Thermal decomposition of ammonium-contained triphosphates at 400°C results in one earlier unknown type of Al, Cr, and Fe cyclotriphosphates $M^{III}P_3O_9$ (form G).

Anion-mixed compounds-triphosphatecyclotetraphosphates $M^IM_2^{III}(H_2P_3O_{10})(P_4O_{12})$ are formed if K, Rb, and Cs cations combine with Al or Fe in the temperature range of 250-300°C under not very high alcaline metal concentrations. In their structures were discovered triphosphate chains which are connected with tetraphosphate rings by hydrogen bonds[8].

The class of substances having analytical composition $M^IM^{III}(PO_3)_4$ demonstrates the largest variety of anion forms. These substances were obtained for all the 24 combinations of M^I and M^{III}, but in a rather narrow temperature range (300-400°C) and under ratio M^I:M^{III} = 5 + 7.5. In this series of compounds the alcaline metal nature strongly influences the form of the anion: Li forms polyphosphates $LiM^{III}(PO_3)_4$, Na-cyclotetraphosphates $NaM^{III}P_4O_{12}$ (M^{III} = = Ga, Fe), K-cyclooctaphosphates $K_2M_2^{III}P_8O_{24}$, Cs-cyclododecaphosphates $Cs_3M_3^{III}P_{12}O_{36}$. In $M_2^{I}M_2^{III}P_8O_{24}$ structure there are hollow rings P_8O_{24}[9]; and in $M_3^{I}M_3^{III}P_{12}O_{36}$ structure trivalent metal cations are placed inside the rings $P_{12}O_{36}$[10]. Firstly obtained double ultraphosphates $Na_3M^{III}P_8O_{23}$ are formed in the temperature range of 300-400°C if mixtures, beside Na and M^{III} cations, also contain an excess of ammonium. These compounds contain a new form of isolated "cage-like" anion, which one can imagine as a hexaphosphate ring with diphosphate bridge which connects the two opposite phosphorus atoms in this ring. They are extremely inert to acids. While heated, $Na_3FeP_8O_{23}$ is stable up to 660°C, then it is melted with $Fe(PO_3)_3$ formation.

Present data demonstrate variability of double phosphate oligomers and polymers. Probably there are several reasons for this. 1) Availability of "building materials" in CPA melts allows to form any type of phosphate anions. 2) Availability of several cations (alcaline and trivalent metals and hydrogen in this case) having different dimensions and coordinative possibilities makes the packing of complex phosphate anions easier.

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