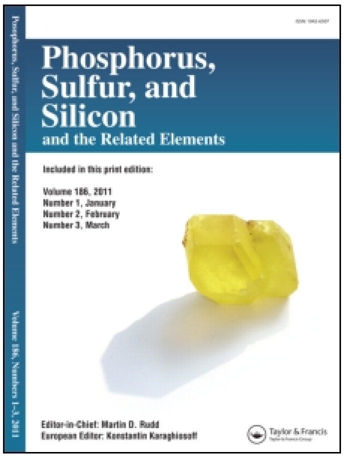

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Crystal Chemistry of Condensed Phosphates of Trivalent Metals

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CRYSTAL CHEMISTRY OF CONDENSED PHOSPHATES OF TRIVALENT METALS

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Research into the crystal chemistry of condensed phosphates is of paramount importance for an understanding of the chemistry of inorganic polymers. It opens up wide possibilities both in terms of theory and practical application. Phosphates of trivalent metals as starting materials are of great practical value. It is known that phosphates of rare-earth elements are characterized by high quantum yields. The phosphates of Ca, Fe, Cr, V, and Al are used as high-temperature binders and adsorbents.

The following classes of condensed phosphates have been investigated:

1. Oligophosphates (simple oligophosphates, olgigophosphate acids, binary diphosphates, triphosphate acids);
2. Polyphosphates (simple polyphosphates, polyphosphate acids, binary polyphosphates);
3. Cyclic phosphates (simple and binary);
4. Ultraphosphates (binary);
5. Phosphates consisting of mixed anions;
6. Hypophosphates.

The purpose of our investigation is following:

1. A structural analysis of the anion radical; an analysis of the changes in the form of the anion depending on the dimension of the cation of the trivalent metal, the dimension of the cation of the alkali metal, the ratio between the dimensions of the given cations, and the presence of a hydrogen bond;
2. Establishment of the criterion for assessing the quantitative probability of the formation of anions in the form of simple chains, complex chains and cyclic structures.

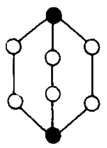
3. Determination of the interrelationship between the structural peculiarities and properties.

A structural analysis of binary condensed phosphates of trivalent and alkali metals of the $M^{I}M^{III}(PO_3)_4$ type has shown that in the case of constant trivalent and variable alkali metal the form of the polyphosphate chain becomes more complex and the identity period increases with an increase in the dimension of the cation of the alkali metal. In the case where M^{I}-Li, Na the chains are of a simple form, with four PO_4 tetrahedrons for the identity period. In compounds containing NH_4^+, Rb^+, Cs^+, Tl^+ the identity period of the chain and the degree of its curvature increase. This is explained by the fact that the larger cations of alkali metals in their coordination include both the end and the bridging oxygen atoms. In this way the cations not only change the configuration of their chain at the expense of the rotation around the P-O-P bond, but they also bend the chain making its form more complex owing to the movement of the bridging oxygen atom. In the limiting case at the moment of crystallization this can result in the breaking of the chain and in the formation of cyclic structures.

An analysis of the structure of a number of compounds in which the alkali metal remains constant while the trivalent metal is varied the same regularity is observed: with a decrease in the size of the cation of trivalent metal the degree of curvature of the polyphosphate chain increases owing to an increase in the number of tetrahedrons during the identity period; and the number of structural types (polymorphism) also increases. This occurs as a result of a decrease in the ratio of the average distance $d(M^{III}\text{-}O)$ Å/$d(M^{I}\text{-}O)$ Å. When this ratio, which we designate by K, is greater than or equal to one, the polymer anion has the form of a simple chain; when K equals to or is less than 0.85, the polymer anion has the form of complex chains or cycles; and when K is less than or equal to 0.69, the polymer anion consists of cycles only. Since in compounds consisting of large cycles (octa- and dodeca-cycles) terminal oxygen atoms are present which do not take part in the coordination of trivalent metal, systems with a higher concentration of alkali metal, $M^{I}_{n}M^{III}(PO_3)_{n+3}$ (where n > 1), are more likely to form large cyclic structures. Thus, there are two possible approaches to elucidating the formation of cyclic compounds:

1. A quantitative criterion, characterized by K;
2. Compounds with a greater content of alkali metal.

Of special interest is a binary ultraphosphate of iron and sodium, $Na_3FeP_8O_{23}$. Until now binary ultraphosphates were unknown. The presence in a compound of two metals having different valences offers the possibility of obtaining a great variety of forms of anion grouping and of locating the coordinational polyhedrons relative to one another. Such a compound does not repeat the forms of anions that are known to exist in simple ultraphosphates. The $(P_8O_{23})^{6-}$ anions consisting of three interlinked hexacycles are oligomers that are isolated from one another (Fig. 1).



● - branch points
o - middle tetrahedra

FIGURE 1. The structure of an ultraphosphate anion in $Na_3FeP_8O_{23}$.

Since in the ultraphosphate of sodium and iron the FeO_6 polyhedrons are isolated not only from one another but also from the NaO_6 polyhedrons we have here unusually large distances between the iron atoms, $(Fe\text{-}Fe)_{min} = 7.296(3)$ Å.

An analysis of the atomic structure of binary condensed phosphates of rare-earth elements and alkali metals shows that LnO_8 polyhedrons are everywhere isolated from ona another. The distances between the cations, $(Ln\text{-}Ln)_{min}$, are quite large. This explains the increase in the probability of emission transitions of Nd^{3+} ions from a metastable state.

We have carried out an analysis of theoretically possible cases of the association of $M^{III}O_n$ polyhedrons in simple oligophosphates depending on the degree of the condensation of the anion. It has been found that linear anion groupings are inherent only in simple diphosphates where terminal oxygen atoms in the anion groups are functionally equivalent.

A relationship has been established between the length of the P-P bond and the atomic number of the lanthanide in a new type of compounds: crystallohydrates of rare-earth hypophosphates having the composition $LnHP_2O_6 \cdot nH_2O$.

An elucidation of the said dependence is of basic importance for a study of the nature of the chemical bond in the $(P_2O_6)^{4-}$ anion.

The results of an x-ray diffraction analysis and an investigation of the luminescence make it possible to recommend binary phosphates of neodymium and rare-earth metals as active media in designing minilasers.