

08.2-33 ON THE STRUCTURES OF TRIPHOSPHATE COMPLEXES OF METAL IONS IN CRYSTALS AND IN AQUEOUS SOLUTION.

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The triphosphate group, $P_3O_{10}^{5-}$, and its complex formation with metal ions have been extensively investigated by spectroscopic methods (Brintzinger, Helv. chim. acta(1965) 48, 47; Remy, Fraissard, Bouille, Bull. Soc. Chim. France(1972) N5, 2222; Doremieux-Morin, J. Magn. Res.(1976) 21, 419; Lutsko, Prodan, Žurnal Prikladn. Spektroskop.(1976) 25, 455). In the limited number of known crystal structures of hydrated and anhydrous triphosphates the bonding to the metal ions has always been found to be bidentate. Hydrates of acidic salts of the type $H_2M(III)P_3O_{10} \cdot 2H_2O$, which contain water molecules not coordinated to the metal ion (Averbuch-Pouchot, Guitel, Acta Cryst.(1977) B33, 1613; Lutsko, Nikanovich, Lapko, Neorganicheskie Materialy(1980) 16, 1613) show ion exchange properties in contrast to the anhydrous salts in which ion exchange does not seem to take place. Water plays an important role in the structures of the triphosphates and the hydrates are generally less hydrolytically, thermally and mechanically stable than the anhydrous salts. In order to relate the properties of the triphosphates with their structures we have determined some crystal structures of mono-, di- and trivalent metals. $K_3H_2P_3O_{10} \cdot H_2O$: orthorhombic(Pbca) with $a=7.588(2)$, $b=11.163(4)$, $c=26.697(8)$ Å, $Z=8$, final R value 0.051. $CdNa_3P_3O_{10} \cdot 12H_2O$: monoclinic($P2_1/n$), $a=14.835(12)$, $b=9.397(8)$, $c=15.244(9)$ Å, $\beta=90.20(6)^\circ$, $Z=4$, final R value 0.047. $FeH_2P_3O_{10}$: monoclinic($P2_1/c$), $a=7.381(2)$, $b=8.808(4)$, $c=12.399(3)$ Å, $\beta=112.68(2)^\circ$, $Z=4$, final R value 0.031. $VH_2P_3O_{10}$: monoclinic($P2_1/c$), $a=7.397(5)$, $b=8.822(6)$, $c=12.384(7)$ Å, $\beta=112.58(4)^\circ$, $Z=4$. The bonding to the metal ions is bidentate in $FeH_2P_3O_{10}$ but tridentate in $CdNa_3P_3O_{10} \cdot 12H_2O$ with one oxygen from each phosphate group bonded to the cadmium ion (Cd-O bond lengths are 2.236(4) and 2.239(4) Å to the terminal and 2.330(4) Å to the central PO_4 -tetrahedron of the triphosphate group). A tridentate bonding also occurs in $K_3H_2P_3O_{10} \cdot H_2O$. The K-O distances are 2.787(4), 2.771(4) and 2.793(5) Å to the terminal and central PO_4 -tetrahedron respectively.

With the use of diffraction methods the structures of triphosphate complexes in aqueous solution have also been studied. From X-ray scattering curves on aqueous thallium(I) solutions precise values for the Tl-O and Tl-P distances within the complexes can be determined because of the dominant contributions to the scattering from the heavy Tl atoms. The distances found in a preliminary investigation (2.9 Å for Tl-O and 3.8 Å for Tl-P) are close to those found for the K-O and K-P distances in the $K_3H_2P_3O_{10} \cdot H_2O$ crystals, possibly indicating a similar type of bonding for these two monovalent metal ions.

08.2-34 ON TOPOTAXIC THERMAL TRANSFORMATIONS OF ACID ORTHO-PHOSPHATE SERIES $NaH_2PO_4 \cdot XH_2O$ ($X=1,2$). By N.M. Mustafayev, Sh.D. Osmanzade and Kh.S. Mamedov, Institute of Inorganic Physical Chemistry, Academy of Sciences of Azerb. SSR, Baku, USSR.

The mechanism of topotaxic transformation in the series of $NaH_2PO_4 \cdot 2H_2O$ — $NaPO_4 \cdot H_2O$ — NaH_2PO_4 — $NaPO_3$ by dehydration is defined. The cation pack $NaH_2PO_4 \cdot 2H_2O$ (H. Bartl et al., Acta Cryst. (1976) B32, 987) is characterized by a chain of Na-octahedra, but the anion pack represents a framework of PO_4 -tetrahedra connected to each other by strong hydrogen bridges: $OH-O=2.537$ and 2.585 Å. Space in this framework is restricted by six tetrahedra and is filled with atoms of Na and H_2O (see Fig.). The distinctive feature of this framework, in comparison with the common ones, is its participation in the formation of pinion rings of oxygen atoms (double quantity), and it influences the sizes of the working pores (3.15 – 3.70 Å against 2.3 Å in the common ones). The cation pack is preserved in all three phases of thermal transformation products; only the method of conjugation is altered. This is indirect proof of the topotaxic transformation, as the anion pack undergoes significant changes (M. Catti et al., Acta Cryst. (1976) B32, 359; M. Catti et al., Acta Cryst. (1974), B30, 1). As the water goes out, the anion pack is diminished, while the condensation degree is preserved. Moreover, the water loss from the opposite packs of octahedra leads to the fact that the framework contraction becomes anisotropic in character, so that the elongation parallel to the octahedral chain prevails. In the first two stages of dehydration (175°C and 280°C), the transformations are similar to those of zeolite dehydration, which traces strong hydrogen bridges. Loss of the hydroxyl group in the last stage (320–330°C) leads to the degeneration to two from four tetrahedron packs. As a result, the three-fold framework of PO_4 -tetrahedra transforms into a chain radical.

