08.2-35 STRUCTURAL CHEMISTRY OF CYCLOPHOSPHATE ANIONS AND STRUCTURE OF THE FIRST DECAMETAPHOSPHATE, by M. Bagieu and J.C. Guillet, Laboratoire de Cristallographie, C.N.R.S., 166 X, 38042 - Grenoble Cedex, France.

Ring anions with the general formula \((P_2O_7)_n\) are known for \(n = 3, 4, 5, 6\) and 8. With the structure of the barium-zinc decametaphosphate \(Ba_2Zn_3P_{10}O_{40}\), we describe the first example of a cyclophosphate with \(n = 10\). The symmetry is monoclinic, space group \(Pn\), with \(a = 21.738, b = 5.556, c = 10.748\) Å, \(\beta = 99.647^\circ\) and \(Z = 2\).

The refinement yielded \(R = 0.052\) for 4998 intensities and 406 parameters.

The dimensions of the isolated rings found in this compound are about 11 x 10 Å; they form arrays along \(b\), linked by \(ZnO_4\) tetrahedra; such arrays are further connected by \(ZnO_6\) and \(BaO_9\) polyhedra.

Main geometrical features of the \((P_2O_7)_n\) group are compared with those observed in already described metaphosphates such as \(Cu_2Li_2P_6O_{18}\), \(Cr_2P_6O_{18}\), \(Cr_2(NH_4)_2P_8O_{24}\) and numerous tetra- and trimetaphosphates. Comparison is also made with other \(XO_3\) ring-anions, where \(X = Si, Ge\) and As.

08.2-36 X-RAY AND INFRARED SPECTRAL STUDIES OF CSREP\(_{0.12}\) CRYSTALS, by T.I. Plyusmina, K. Byrappa and G.I. Dorokhova, Department of Crystallography and Crystal Chemistry, Moscow State University, Leningrad Gori, Moscow, USSR 117234.

The discovery of unusual spectral characteristics in the rare earth phosphates has attracted the attention of crystallographers, physicists and chemists. It has been found that these unusual spectral characteristics are connected with the internal structures. Among the rare earth phosphates the ultraphosphates and metaphosphates of rare earth elements are of great importance.

The crystal chemistry of RE ultraphosphates has been studied in detail by many workers. But the investigations of the RE metaphosphates are incomplete in many aspects.

We have obtained CSREP\(_{0.12}\) crystals from highly concentrated phosphoric acid solutions. The X-ray study reveals that the CSREP\(_{0.12}\) crystals can be divided into five structural types. A brief description of the morphology of CSREP\(_{0.12}\) crystals with reference to the temperature of growth is given. Based on the structures of these crystals, they can be divided into three types viz. ring type, chain type and ribbon type. The crystal chemistry of CSREP\(_{0.12}\) crystals has been discussed in brief. We have determined the absorption peaks characteristic for all the three types in the IR-spectra taken in the range of 1800-400 cm\(^{-1}\). It was found that the angle \(\angle\text{PO}_4\) in the ring type is less than in the chain type. The splittings \(u, v\) and \(w\) are higher for the chain type than in the ring type. The absorption \(\Delta\nu\) for the ring type \((\Delta\nu = 170 \text{ cm}^{-1})\) and the ribbon type \((\Delta\nu = 150 \text{ cm}^{-1})\) of CSRE metaphosphates. Therefore, it can be considered that the ring type of CSRE metaphosphates are nearer to the ring type of CSE metaphosphates in their \(\angle\text{PO}_4\) values.

08.2-37 PLANAR Ca - PO\(_4\) SHEET STRUCTURES, by M. Mathew, S. Takagi and W. E. Brown, American Dental Association Health Foundation, Research Unit, National Bureau of Standards, Washington, DC 20234.

A number of calcium phosphates are known to have Ca-PO\(_4\) chains constituting sheet-type structures, corrugated or planar. As part of a program to correlate the stability of these sheet-type structures with the nature of bonding, we have determined the crystal structures of CaBr\((H_2P_2O_7)_2\), 4H\(_2\)O (I) and Ca\((H_2P_2O_7)_2\), 4H\(_2\)O (II). Crystals of I are monoclinic, \(C2/c\), \(Z = 4\), \(a = 20.314(1), b = 6.556(1), c = 6.973(1)\) Å and \(\beta = 90.02(3)^\circ\). The structure was refined to \(R = 0.054\). Crystals of II are monoclinic, \(B2/c\), \(Z = 4\), \(a = 21.416(4), b = 6.550(1), c = 7.000(1)\) Å and \(\beta = 91.05(2)^\circ\). The structure was refined to \(R = 0.032\).

The two structures are nearly isomorphous despite the difference in space group. Both compounds have a planar sheet-type structure consisting of edge-sharing Ca-PO\(_4\) chains. The interlayer contents, Br or I (X) and the water molecules form \(X(H_2O)\) octahedra via O - H...X hydrogen bonds. Two types of sheet, Ca\((H_2P_2O_7)_2\) and CaBr\((H_2P_2O_7)_2\), connected together by Ca...O ion-bonds and O - H...O hydrogen bonds. Relationship with other calcium phosphates with sheet-type structures will be discussed.

This research was supported in part by NIDR Grant DE 60030-02.