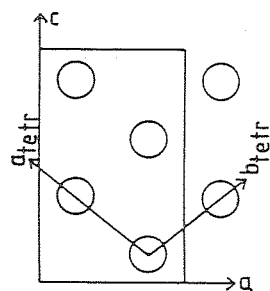


08.2-1 THE CRYSTAL STRUCTURE OF $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ AND $\text{AgBF}_4 \cdot \text{H}_2\text{O}$. By W. Ludwig and R. Wartchow, Institut für Anorganische Chemie der Universität, Callinstr. 9, D-3000 Hannover 1, Germany.

A structure analysis of $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ and $\text{AgBF}_4 \cdot \text{H}_2\text{O}$ using powder data showed that both compounds crystallize orthorhombic with lattice constants $a = 8.123$, $b = 7.829$, $c = 13.562$ and $a = 7.966$, $b = 7.794$, $c = 13.416$ Å resp., probably being isotypic to $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$, space group Pbca , $Z=8$. Upon obtaining single crystals, structure refinements with three dimensional X-ray intensity data were carried out yielding $R = 0.06$ and 0.05 resp. and confirming the original assumption on the structure type. Like $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ (O. Bars et al., Acta Cryst. (1977) B33, 3751) the structure of the title compounds of general formula $\text{ABX}_4 \cdot \text{H}_2\text{O}$ is built up of BX_4 tetrahedra and irregularly shaped AX_6O_2 polyhedra, which share corners and edges. The water molecule is coordinated by two A-cations and the A-cation by two water molecules. However, in contrast to $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ the A-O distances in the silver compounds are distinctly shorter than the A-X distances. This difference leads to a new description of the structure: There are zigzag chains of $-\text{Ag}-\text{O}-\text{Ag}-\text{O}-\text{Ag}-$ lying parallel to $[010]$.

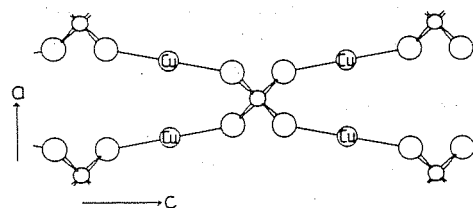


Regarding them as cylinders they form a pseudotetragonal packing with the chain axis corresponding to $c_{\text{tetr.}}$, $a_{\text{tetr.}}$ parallel to $[201]$ and $b_{\text{tetr.}}$ parallel to $[20\bar{1}]$. The BX_4 tetrahedra fill the empty channels of the packing ($1/2 \ 1/2 \ z$, in the pseudotetragonal cell), thus completing the coordination

of the Ag atoms. An exact description of the structure (shape and connection of the polyhedra, hydrogen bonds and other aspects) will be given. Also some problems, which arise in the structure determination (realised by means of Patterson synthesis and direct methods) as well as in the refinement process, will be discussed.

08.2-2 THE CRYSTAL STRUCTURE OF COPPER(I) SULFATE Cu_2SO_4 . By H.J. Berthold and J. Born, Institut für Anorganische Chemie der Universität, Callinstr. 9, D-3000 Hannover, Germany.

The crystal structure of Cu_2SO_4 has been investigated using X-ray powder diffraction data. Cu_2SO_4 crystallizes in the orthorhombic space group Fddd ($Z=8$) with $a = 474.8(3)$, $b = 1396(1)$ and $c = 1086(1)$ pm. Least squares refinement using 21 well resolved reflections yielded $R = 6.4$ %. Although Ag_2SO_4 also crystallizes in the space group Fddd , there is a remarkable difference between the structures of Cu_2SO_4 and Ag_2SO_4 . Due to the strong tendency of Cu(I) to form two collinear sp bonds to oxygen the structure contains short O-Cu-O groups ($\text{Cu}-\text{O} = 196$ pm), lying almost parallel to the c axis. In Ag_2SO_4 the corresponding O-Ag-O interactions are much more ionic and hence the Ag-O distance (241 pm) in this group does not differ much from the other Ag-O distances. Thus, in Ag_2SO_4 each Ag^+ is surrounded by six oxygen atoms at 241, 243 and 269 pm in a strongly distorted octahedral arrangement, while the coordination sphere of Cu^+ contains only four oxygen atoms at 196 and 250 pm and in addition two copper atoms at 291 pm. The structure of Cu_2SO_4 can best be described as being built up of layers of composition Cu_2SO_4 parallel to (010) , in which the four oxygen atoms of each SO_4 group are bonded to four other SO_4 groups of the same layer via O-Cu-O bridges. The structure of the layers in



Cu_2SO_4 is different from that of the layers in Ag_2SO_4 parallel to (001) described by Mehrotra, Hahn et al. (N. Jahrbuch Mineralogie, Monatshefte 1978, 409). With respect to the bonding between different SO_4 groups the structure of Cu_2SO_4 is closely related to that of crystalline H_2SO_4 , where, in layers of composition H_2SO_4 , each SO_4 group is bonded to four SO_4 groups of the same layer via $\text{O}-\text{H}\cdots\text{O}$ hydrogen bridges with $\text{O}\cdots\text{O} = 262$ pm. To compensate for the denser packing of the SO_4 groups the stacking of the layers differs from that in Cu_2SO_4 leading to the lower monoclinic symmetry of crystalline H_2SO_4 (space group C2/c , $Z=4$) (Yu and Mak, J. Cryst. Molecul. Structure 8, 193 (1979)). The structure of Cu_2SO_4 can be regarded as being intermediate between the structures of Ag_2SO_4 and H_2SO_4 .