08-Inorganic and Mineralogical Crystallography

The crystal structure of jaffeite, Ca mex[{SiO4}] (OH) ₂, from Kombat mine, Namibia (Sarp. H., Power. D. R. Amer. Mineral., 1989, 74, 1203-1206) has been determined by X-ray methods (hexagonal, P6 3, lattice constants a=10.035, c=7.499 Å, Z=2, 871 reflections). Jaffeite and its synthetic analogue are isotypic with fluorohelite B ₂[Mg,F,(OH),O₆]₂, jeffreypite B₂[Be(Al₂)(OH)₃O₆] and paleite CaZrB₆ [Al₂O₆]. All these structures contain octahedral frameworks, formed by double bands, in which octahedra share edges. At the contacts of these bands there are trigonal and hexagonal channels. The trigonal channels are filled by pyrogenous [SiO₄]₂⁻ (jaffeite), by trigonal Zr-trimers and B-triangles (paleite) or by [BO₃]-triangles and fluorohelite, jeffreypite type. The type of the fillers (Si,O-Si, Zr with 8 or two B-atoms) determine the similarity of a (b) cell parameters and the difference of c parameter in the considered structures.

The crystal structure of aluminum dicumene disulfate fluoride dichloride tetrahydrate, Al₄Ca₆(SO₄)₂FCl·4H₂O has been determined. Space group P 4/m, a=6.875 (1), c=13.42 (2) Å, Z=2, Dₐ=2.553 g/cm³. The 447 unique reflections were obtained with Syntax P2₂, diff. F/2θ meter with Mo radiation for 0.1x0.1x0.5mm colorless plate square crystal. The structure has been solved by direct methods and refined by full-matrix leastsquares to R-factor 0.046 (Rw=0.048). Hydrogen atoms have been located in difference synthesis.

In the crystal structure of Al₄Ca₆(SO₄)₂FCl·4H₂O the chains of polyhedra are arranged along [001]. These chains consist of pairs of CaO₄ClF polyhedra alternated with single AlO₄F₂ polyhedra which are rotated along [001] with a difference of 24°. The chains are combined by SO₄-tetrahedra so that all four sulphate oxygen atoms take part in coordinating Ca atoms to form with Cl and F atoms distorted octahedra, which are two non-equivalent tetragonal pyramids with common base. The stretched one has Cl atom on top, the flattened one an F atom. The Al coordination sphere consists of two F atoms and four oxygen atoms of water molecules as flattened perfect tetragonal dipyramide. The Al coordination polyhedron has not direct contacts with SO₄-tetrahedra but interatomic distances analysis perform that in spite of the long distance between oxygen atoms (2 815 Å), a distance from water hydrogen atom to tetrahedral oxygen atom is shortened (H-O≈2.92 Å) and so these atoms have the specific interaction by hydrogen bond to penetrate crystal structure (Fig).

Bond distances (Å and angles (deg.) in structure, Ca polyhedron: Ca-C≡2 5.89 (4), Ca-F=2 233 (5), Ca-O=2 356 (3), CaCl=F=180. 0 (1), CaClO₄=84. 9 (1), FC=O=95. 0 (1), O=Ca-Cl=89. 6 (1), O=CaO₄=169. 9 (1), Al polyhedron: Al-F=1 750 (5), Al-O=1 918 (6), PA=180. 0 (2), FAIO₃=90. 0 (2), O=AlO₄=180. 0 (2), O=AlO₄=90. 0 (2). S tetrahedron; S=O–1 474 (4), O=S=O =109. 1 (2), O=S=O =109. 1 (2).

Revealed are laws of compounds (oxi- salts, oxides) in which the strongest structure fragments are tetrahedra [TO₄] [OCu₄] in particular. Here O is "monatomic" oxygen not present in and residues SO₄, SeO₄, Cl⁻ etc. hydroxyl groups OH⁻ water molecules H₂O. Such oxygen ions are the most highly charged negative particles, O⁻ and that is why in gaseous phase, liquids and crystal structures they collect cations around these.

It is known that classic tetrahedra [TO₄] (valency of central atom 7, 6, 5, 4, 3) are polymerized under atmospheric conditions only through their vertices. At the same time tetrahedra [TO₄] (valency of the central atom 2) may be polymerized both through the vertices (up to 4 tetrahedra in a vertex) and through the common edge. This sharply increases the diversity of formed polymers [OCu₄] (S. K. Filatov, T. F. Semenova, Doklady Ac. Sc. USSR, 1982, Vol. 322, No. 3, 536-539). By now there are the following known types of polymers from tetrahedra [OCu₄] isolated tetrahedra [OCu₄]⁴⁺ (e. g. sponomevite K₂Cu₄OCl₄); couples of tetrahedra interconnected through the common edge, [OCu₄]⁴⁺ (sudotovite K₂Cu₄O₅SO₄); chains of tetrahedra interconnected through the vertices, [OCu₄]²⁺ (kameharite K₂Cu₄OCl₄ (SO₄)); chains of tetrahedra interconnected through the edges, [OCu₄]²⁺ (pipit K₂Cu₄O₅ (SO₄) MeCl);chains of tetrahedra interconnected by turns through the