

An Unconventional Look at Sulfides and Selenides: anion-centred Polyhedra

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Lower sulfides of palladium, Pd₄S, Pd₃S, and Pd₁₆S₇, resemble alloys with “clathrated” S atoms and a very complex metal framework. In terms of anion-centred polyhedra, however, Pd₄S consists of corner-connected SPd₈ bisdisphenoids (CN=8), Pd₃S of corner-connected complex CN=6 polyhedra whereas Pd₁₆S₇ contains clusters of tetrahedrally arranged trigonal prisms SPd₆, interconnected by flattened SPd₄ tetrahedra. Edge- and corner-sharing SM₄ tetrahedra in various arrangements form the structures of PdS, PdSe and PtS. Clusters of tetrahedra as well as 4- and 6-petal rosettes of tall CN=5 coordination prisms SM₅ are in the structure of Rh₁₇S₁₅ and Ni₁₀Pd₇S₁₅; the same six-petal rosettes, interconnected by tetrahedra, form the structure of pentlandite Co₉S₈. Surprisingly simple structures formed by anion-centred polyhedra are found in tetrahedrite, Ag₂S, Cu₃Se₂, and also Bi₂S₃, Cu₂S and talnakhite.

The anion-centred configurations depend on the cation:anion ratio (metal-rich sulfides have higher CN) and on the type of cation. Especially Cu and Ag form typical anion-based polyhedra. Uniformity and small number of configurations suggest that the directional bonds of an anion may be equally important as those of the cation present. It means that an insight deeper than the usual anion-packing considerations might be necessary. Cation-lined interspaces between the anion-centred polyhedra and the contracted polyhedron edges with metal-metal bonds are of special interest.

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