08.1-3 STRUCTURAL CHEMISTRY OF HEXAOXOGERMANATES: By W. Eysel, U. Lambert, C. Sussieck and B. Nuber, Mineralogisch-Petrographisches Institut and Anorganisch-Chemisches Institut, Universitat Heidelberg, FRG.

The crystal structure of a new compound $CuPb_3Ge^{VI}[Ge_4^{IV}O_{12}]O_2$, was determined. Structural data are: $I2/a$; $a = 14.828\text{Å}$, $b = 8.161\text{Å}$, $c = 10.383\text{Å}$, $\beta = 90.91°$; $Z = 4$. The GeO_4 tetrahedra form Ge_4O_{12} rings, which are connected by GeO_6-octahedra to a three-dimensional framework. Cu exhibits a Jahn-Teller octahedral, Pb an irregular 8-fold coordination. For crystallo-chemical comparisons GeO_6-polyhedra from hexaoxogermanates as well as mixed tetraoxo-germanates were evaluated statistically.
Various oxygen coordination polyhedra are known for germanium, namely GeO_n with $n = 4$, 5 and 6. A literature search revealed several hundred structures with $n = 4$ (tetraoxogermanates), four with $n = 5$ and 37 with $n = 6$ (hexaoxogermanates). In addition, 51 mixed structures with both, $n = 4$ and $n = 6$ and even one with $n = 4$, 5 and 6 were found.
85 GeO_6-polyhedra from 64 structures, i.e. 510 distances Ge-O, were considered. All are more or less regular octahedra. The bond strength formula

$$s_i = s_o(D_i/D_o)^{-n}$$

by Shannon and Brown (Acta Cryst. A29, 266, 1973) was used with $s_o = 4/6$. As a result $D_o = 1.895\text{Å}$ and $N = 0.5$ were obtained. This defines an average regular octahedron with a Ge-O distance of 1.895Å; in the various structures the distances range from 1.68 to 2.20 Å.
Under normal conditions the GeO_4-tetrahedron represents the stable coordination. GeO_6 is favoured by both high pressures and high Ge contents: Out of 92 structures with GeO_6 octahedra, 54% have Ge:cation ratios >1, 30% a ratio = 1 and 15% ratios <1.
In the mixed tetraoxo-hexagermanates, GeO_6 octahedra can be combined with most tetrahedral arrangements from isolated GeO_4-polyhedra to three-dimensional frameworks; isolated tetrahedra, rings and groups, however, predominate.
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08.1-4 A COMPARISON OF EFFECTIVE IONIC CATION RADII OF NITRIDES, SULFIDES AND OXIDES. By Werner H. Baur, Institut für Kristallographie und Mineralogie, Johann Wolfgang Goethe-Universität Frankfurt am Main, Senckenberganlage 30, D-6000 Frankfurt am Main 1, Bundesrepublik Deutschland

Effective ionic radii have been useful crystal chemical tools since the 1920's. Modern, self-consistent sets of such radii valid for oxides and for sulfides were published by Shannon (Acta Cryst., A32, 751, 1976, and in 'Structure and Bonding', vol. 2, p. 53, 1981). Recently a set of 102 empirical effective ionic radii applicable to nitrides has been derived from over 500 experimental interatomic distances observed in 324 crystal structure determinations of nitrides, amides, ammines, cyanides, azides, imides, nitrosyls, nitryls and of organometallic compounds (Baur, Crystallography Reviews, 1, in press, 1987). These radii take into account the oxidation numbers and the electronic spin states of the cations, and the coordination numbers of both the cations and the nitride ions. The radii are available for 50 chemical elements and apply to compounds which are ionic or ionic-covalent, not to the semi-metallic interstitial nitrides. Interatomic distances cation-nitride can be estimated from the sums of the appropriate radii on average within less than 0.02Å of the observed experimental distances. These radii are empirically useful, but no physical significance should be attached to them. The dependence of the nitride ion radius on coordination number is greater than for the oxide ion: it varies from 1.42Å for two-coordinated, to 1.54Å for eight-coordinated nitride ions. Effective ionic radii are useful, among other things, for checking the results of crystal structure determinations for reasonableness, and for predicting cation-anion distances to be used as observations in the computer simulation of crystal structures. Nitrides can often be prepared only in powder form, thus this latter possibility should be particularly useful when trying to solve their crystal structures from powder diffraction data.
Contrary to earlier expectations individual cation radii can assume different values depending on whether they are bonded to oxide, sulfide or nitride ions. This finding is true even though absolute values cannot be assigned to ionic radii. Of the 95 cation radii for nitrides 59 can be compared with both the corresponding radii in oxides and in sulfides, 23 more can be compared only with the oxide radii, and for 13 no counterpart is available among the other two sets of radii. The extreme deviations between nitride and oxide radii are -0.14Å (for Ce^{+4} in six coordination) and 0.17Å (for square planar four coordinated Fe^{+2}), for a maximum range of 0.31Å. The corresponding extreme values between nitride and sulfide radii are -0.14Å (for Pt^{+2} in square planar four coordination) and 0.08Å (for eight coordinated Sr^{+2} and for four coordinated P^{+5}), for a maximum range of 0.22Å. The maximum range in differences of oxide and sulfide radii was found by Shannon (1981) to be 0.33Å, thus it is larger than between nitride radii and either oxide or sulfide radii. The average deviation of the sets of radii from each other between any of the three sets is about 0.05Å. The mean deviations between experimentally observed bond lengths and those estimated using any of the three sets of radii are less than half as large. The differences in the radii can be pronounced for one and the same cation depending on which anion it is bonded to. Divalent iron in low spin configuration and six coordination has a radius of 0.41Å against sulfur, 0.51Å against nitrogen and 0.61Å in an oxide. Large differences between nitride and oxide radii are found also for first and second row ions. Shannon (1981) made a corresponding observation when comparing oxide and sulfide radii. A theoretical explanation for these effects is lacking. Some, but not all of these radius differences might be attributable to covalency effects.