

iii)  $R_N - R_X - d_{N-X}$  values for all N and X phases lie in a very narrow band, but with different slopes versus  $D_M$ : these averaging -0.46 for Mn, -0.38 for Co and -0.35 for Fe, Ni and Cu phases.

These results indicate that the relative cell dimensions are controlled by M-N or M-X contacts within the di-capped hexagon tetragonal prism about M (Fig. 1) as the M component is changed, whereas the overall size of a and c are such as to best satisfy the N-X distances (for CN 5) of the square pyramid framework (Fig. 2) (and to a lesser extent the [001] X-X dumbbell distances), this framework being the basis of the structure's stability. In addition, a and c are not independently variable in that they must provide an equitable unit-cell volume.

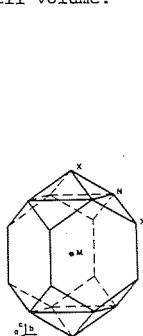
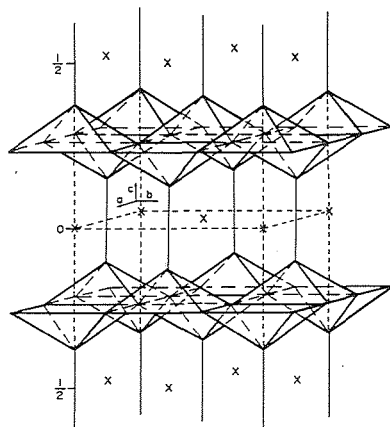


Fig. 1

Fig. 2 b..  $00\frac{1}{2} P_{222} [5py_4e] + F$  framework.

08.1-5 TOWARDS A GRAMMAR OF INORGANIC STRUCTURE. By Alan L. MACKAY, Dept. of Crystallography, Birkbeck College, London and Jacek KLINOWSKI, Dept of Physical Chemistry, University of Cambridge.

Pauling's Rules are only the first level of a hierarchic grammar of structure. The rules have been very successful for describing the immediate surroundings of atoms, especially if they are symmetrical, but they are less useful for handling large-scale structures, where cooperative movement may occur and large blocks, approaching crystallites in size, adjust themselves into position like colloidal crystals under electrostatic forces. HRTEM, SEM and XRD have recently provided information on "syntax" - these higher levels of structure. It is shown that hierarchisation minimises complexity and increases probability of formation. Complex silicates and lyotropic structures both parallel minimal surfaces (and can be modelled as membranes rather than lines of force). The concept of curved sheets can be extended in dimensionality to the distortion of polyhedra, leading to explanations of Loewenstein's Rule and such orderings in silicates, now being revealed by NMR. Through Delone's formalism; it becomes possible to treat ordered and disordered structures similarly. Also transformations of sheets to frameworks (such as kaolin to ultramarine) can be expressed in catastrophe theory terms.

08.1-6 COMPLEX TRANSITION METAL BORATES By H. Behm, Institut für Kristallographie, Universität Karlsruhe, D-7500 Karlsruhe, Germany. In the course of a systematic investigation of transition metal borates various chelate-complexes were synthesized. The crystal structures of several of these compounds have been completely determined; in other cases at least the complex borate anions could be identified. These chelates represent a novel type of borate which were not considered in former systematic classifications. The most important features of these complex borates are presented here and are discussed with the intention of predicting further hypothetical complex ions.

1. Borates can build up mono- or polynuclear chelates with transition metals.
2. Size, shape and topology of the borate molecules are fundamentally influenced by the coordination number and coordination polyhedron of the transition metal ion.
3. In mononuclear complexes the nuclei are coordinated to oxygen atoms which are either bonded to two boron atoms or to one boron atom and one hydrogen atom, but never to terminal oxygen atoms. In polynuclear complexes the bridging ligands are terminal oxygen atoms or oxide ions.
4. Additional coordinations may occur to ligands not belonging to the borate complex.
5. A satisfactory charge balance, as required by Pauling's rules, can be obtained by using the following charges for the ligand atoms:  $O^{2-} = -2$ ,  $>B-O = -1$ ,  $\begin{matrix} \text{O} \\ \parallel \\ \text{B} \\ \parallel \\ \text{O} \end{matrix} = -1/2$ ,  $\begin{matrix} \text{O} \\ \parallel \\ \text{B} \\ \parallel \\ \text{O} \end{matrix} = -1/4$  and  $\geq B-OH = -1/4$ .
6. Ring-like complexes must contain at least eight boron atoms.

Examples of ring-like mono-, di- and tetra-nuclear chelates are found in the compounds:  
 a)  $K_6[UO_2(B_{16}O_{24}(OH)_8)] \cdot 12H_2O$  (in press)  
 b)  $Na_6[Cu_2(B_{16}O_{24}(OH)_{10})] \cdot 12H_2O$  (A.C.1983,C39)  
 c)  $Na_5Cu_{0.5}[Cu_4O(B_{20}O_{32}(OH)_8)] \cdot 26H_2O$  (in press)  
 These ring-like complexes can be regarded as being derived from a simple cyclic  $B_8O_8$  unit. Neighbouring tetrahedral boron atoms may be connected by additional  $BO_3$  groups. In the polynuclear chelates the  $B_8O_8$  unit may be widened by insertion of  $BO_2$  units. With this method new hypothetical complex anions can be generated. The stability of such complexes must then be checked by experiment.

