**08.1–7   THE CRYSTAL STRUCTURE OF $[(CH_3)_3NH]_2Cu_4Br_{10}$:**

STACKING PATTERNS OF QUASI-PLANAR BIBRIDGED $Cu_nX_{2n+2}^{2-}$

AND $Cu_nX_{2n}L_2$ OLIGOMERS. By Roger D. Willett and Urs

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The title compound crystallizes in the monoclinic space group $P2_1/a$ with $a = 19.054(9)Å$, $b = 14.719(7)Å$, $c = 9.566(3)Å$, and $\beta = 109.87(3)°$. The compound contains nearly planar bibridged $Cu_4Br_{10}^{2-}$ anions with Cu-Br distances of 2.3-2.5Å and bridging Cu-Br-Cu angles from 93° to 96°. In addition to the four normal
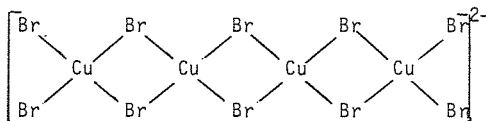
Cu-Br bonds, each copper forms one or two additional semi-coordinate Cu-Br bonds, yielding a final 4 + 1 or 4 + 2 coordination geometry, and forming chains parallel to the c axis. Although an analogous tetramer exists in the corresponding chloride salt, the stacking of the tetramers is different. In the latter, a uniform stacking arrangement is attained, with three of the four copper ions forming long Cu-Cl bonds to chloride ions in neighboring units. For the bromide salt, the bromide ions alternately cover three and four copper ions in adjacent tetramers.

We introduce a notation where we specify the relative displacement of adjacent oligomers in terms of the ligand-ligand distance, d, along the edges. It is necessary to specify both the translation parallel $(n_{||}d)$ and perpendicular $(n_{\perp}d)$ to the Cu-Cu direction, yielding a vector notation, $(n_{||},n_{\perp})$. Thus the dimer stacking in (a) is specified by (1/2,1/2), while that in (b) is given by (3/2,1/2).

(a)   (b)
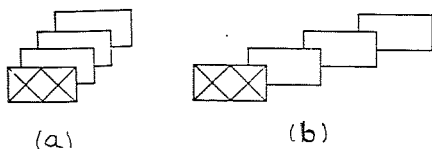
As another example, the stack of $Cu_3Br_8^{2-}$ trimers in $[(C_2H_5)_2NH_2]_2Cu_4Br_{10}\cdot C_2H_5OH$ is given by the pair of vectors (1/2,1/2)(-1/2,-1/2) - e.g. - alternate trimers stack exactly on top of each other.

In this notation, the uniform stacking in $[(CH_3)_3NH]_2Cu_4Cl_{10}$ is given by (3/2,1/2) while the alternate stacking in the title compound is specified by the pair (3/2,1/2)(1/2,-1/2).

08.1–8   KRISTALLPACKUNG IN EPh_4^+-SALZEN.
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Verbindungen $EPh_4^+X^-$ (E = P, As; X^- = anorganisches Anion) kristallisieren häufig unter Ausbildung von Säulen aus übereinandergestapelten EPh_4^+-Ionen. Die EPh_4^+-Ionen erfüllen exakt oder näherungsweise die Symmetrie $\bar{4}$. Je nach Symmetrie des Anions ist die Raumgruppe P4/n oder I$\bar{4}$ oder eine Untergruppe davon. Beispiel: PPh_4MoOCl_4 (P4/n) ——— $PPh_4ReCl_4N_2S_2$ (P2/n) ——— PPh_4SnCl_3 (P$\bar{1}$).
In Verbindungen $(EPh_4^+)_2X^{2-}$ ordnen sich je zwei EPh_4^+-Ionen um ein Inversionszentrum, indem drei Phenylgruppen des einen Ions in die Lücken zwischen drei Phenylgruppen des anderen ragen. Die $(EPh_4^+)_2$-Paare können zu Stäben aneinandergereiht sein, die parallel gebündelt sind (Typ I), oder es werden Schichten gebildet. Die Schichten sind entweder unmittelbar aufeinander gestapelt (Typ II) oder zwischen ihnen befinden sich weitere $(EPh_4^+)_2$-Einzelpaare (Typ III). Dabei bleiben in jedem Fall Hohlräume, welche die Anionen aufnehmen. Beispiel: $(AsPh_4)_2UCl_6\cdot2\ CH_2CL_2$ mit zwei Modifikationen vom Typ I und III.

08.1–9   A STRUCTURE CLASSIFICATION OF CONDENSED MODES IN ABX_4 COMPOUNDS. By R. Deblieck, J. Van Landuyt and S. Amelinckx. Universiteit Antwerpen, RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.

Some ABX_3 (perovskite) compounds such as $CaTiO_3$ and $NaNbO_3$ undergo phase transitions due to the condensation of soft phonons. The structure of the lower temperature phase can be described in terms of the tilting of the BX_6 octahedra around one or some of their tetrad axes. Glazer (Acta Cryst.(1972). B28, 3384), classified these structures in tilting schemes using the correlation of tilting of the octahedra along the "pseudocubic" axes connecting the B-cations at right angles.
In ABX_4-compounds, although the octahedra are not vertex-shared in the third dimension, phase transitions involving soft modes do occur also (M. Hidaka et al., J.Phys.C.Sol. St. Phys.(1979). 12, 2737; J.Phys.C.Sol.St.Phys.(1979).12, 1799; Phys. stat.sol. (a) (1982). 72, 809).
Consequently Glazers' classification was extensively used for the description of the structures of the lower temperature phases of ABX_4-compounds as well.
It is however quite obvious that this description will be degenerate when applied to ABX_4 compounds, because of the supplementary degrees of freedom present in these compounds : i.e. when a particular tilting scheme has been applied consistently to two successive layers of vertex-shared octahedra these layers may still be shifted relative to one another over a vector $\bar{R}$ with four distinct possibilities : $\bar{R} = (o,o)$; $\bar{R} = (a,o)$; $\bar{R} = (o,b)$; $\bar{R} = (a,b)$, yielding possible new structures.
It is our aim to present a similar non degenerate classification whereby an exhaustive count is made of all possible structures in the ABX_4-case, including a schematical representation of the structure and a structure factor calculation of all relevant reflections for each possible structure.