08.1–7 THE CRYSTAL STRUCTURE OF \([\text{[(CH}_3\text{)}_3\text{NH}]_2\text{Cu}_4\text{Br}_6\text{]}^{2-}\)

STACKING PATTERNS OF QUASI-PLANAR BIBRIDGED \(\text{Cu}_n\text{X}_2\text{L}_2\) OLMIGOMERS. By Roger D. Willett and Urs Geiser, Department of Chemistry, Washington State University, Pullman, WA 99164–4030 USA.

The title compound crystallizes in the monoclinic space group \(P2_1/a\) with \(a = 19.054(9)\) Å, \(b = 14.713(7)\) Å, \(c = 9.566(3)\) Å, and \(\beta = 109.87(3)^\circ\). The compound contains nearly planar bibridged \(\text{Cu}_4\text{Br}_6\) anions with \(\text{Cu-Br}\) distances of \(2.3-2.56\) Å. For the bromide ions in neighboring units, the bromide ions alternate to cover three and four bromide 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 \((n_1d)\) and perpendicular \((n_2d)\) to the \(\text{Cu-Br}\) direction, yielding a vector notation, \(\langle n_1d\rangle\). Thus the dimer stacking in \((a)\) is specified by \((1/2,1/2)\), while that in \((b)\) is given by \((3/2,1/2)\).

As another example, the stacking of \(\text{Cu}_4\text{Br}_6\) trimers in \([\text{[(CH}_3\text{)}_3\text{NH}]_2\text{Cu}_4\text{Br}_6\text{]}^{2-}\) 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 \([\text{[(CH}_3\text{)}_3\text{NH}]_2\text{Cu}_4\text{Cl}_6\]^{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 \(\text{EPh}_4^-\)-SALZEN.

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Verbindungen \(\text{EPh}_4^\pm\) \((R = P, As; X^- = \text{anorganisches Anion})\) kristallisieren häufig unter Ausbildung von Säulen aus übereinandergestapelten \(\text{EPh}_4^-\)-Ionen. Die \(\text{EPh}_4^-\)-Ionen erfüllen exakt oder näherungsweise die Symmetrie \(4\). Je nach Symmetrie des Anions ist die Raumgruppe \(P4/n\) oder \(I\) oder eine Untergruppe davon. Beispiel: \(\text{PPh}_4^\pm\text{MoOCl}_4\) \((P4/n)\) — \(\text{PPh}_4^\pm\text{AsCl}_3\) \((P2/n)\) — \(\text{PPh}_4^\pm\text{SnCl}_3\) \((P1)\).

In Verbindungen \((\text{EPh}_4^\pm)\) \(2\)

ordnen sich je zwei \(\text{EPh}_4^-\)-Ionen um ein Inversionszentrum, indem drei Phenylgruppen einen Ionen in die Lücken zwischen drei Phenylgruppen des anderen ragen. Die \((\text{EPh}_4)\) -Paare können zu Stabkristallen und dabei gebündelt sind (Typ I), oder es werden Schichten gebildet, die Schichten sind unterwander elementar aufeinander gestapelt (Typ II) oder zwischen ihnen befinden sich weitere \((\text{EPh}_4)\) -Einzelpaare (Typ III).

08.1–9 A STRUCTURE CLASSIFICATION OF CONDENSED MODES IN \(\text{ABX}_4\) COMPOUNDS. By R. Deblieck, J. Van Landuyt and S. Amelioox, Universität Antwerpen, RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.

Some \(\text{ABX}_3\) (pervoskite) compounds such as \(\text{CaTiO}_3\) and \(\text{NaNbO}_3\) undergo phase transitions due to the condensation of soft phonons. The structure of the lower temperature phases can be described in terms of the tilting of the \(\text{X}\) 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 \(\text{B}\) cations at right angles.


Consequently Glazer’s classification was extensively used for the description of the structures of the lower temperature phases of \(\text{ABX}_4\)-compounds as well.

It is however quite obvious that this description will be degenerate when applied to \(\text{ABX}_4\) 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 \(\mathbf{R}\) with four distinct possibilities: \(\mathbf{R} = (0,0,0); \mathbf{R} = (a,0,0); \mathbf{R} = (0,b,0); \mathbf{R} = (a,b)\), 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 \(\text{ABX}_4\)-case, including a schematic representation of the structure and a structure factor calculation of all relevant reflections for each possible structure.