

MS15-P17 The structure directing role of Al and Cs in design of novel 3D open-framework compounds, $\text{Cs}_2\text{CuAl}_4\text{O}_8$ and $\text{CsAl}_2\text{BP}_6\text{O}_{20}$

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Of special interest in searching for new materials is the design of stable phases with open microporous structures based on mixed type frameworks. These kind of zeolite-like materials are promising not only as catalysts, sorbents, molecular sieves etc, but also as materials with magnetic, electronic, photoluminescence properties, to name a few. Two new compounds, $\text{Cs}_2\text{CuAl}_4\text{O}_8$ ($a=8.4551(7)$, $b=10.0118(9)$, $c=17.073(1)$ Å, $\beta=101.64(2)^\circ$, $V=1415.5(3)$ Å³, $P2_1/c$, $Z=4$) and $\text{CsAl}_2\text{BP}_6\text{O}_{20}$ ($a=11.815(2)$, $b=10.042(1)$, $c=26.630(4)$, $V=3159.6(3)$ Å³, $Pbca$, $Z=8$) have been obtained by the high temperature crystallization method in the phosphate system at the 1050° and 950°C, accordingly. Their crystal structures, determined by single-crystal X-ray diffraction, both are based on mixed anionic frameworks with caesium cations in the channels and cavities. The copper aluminate structure is built by double layers of corner-sharing AlO_4 tetrahedra interconnected by chains of edge-sharing CuO_4 square planes. The topology of a 2D aluminate layer is similar to those found in the ATT-type zeolites and isostructural silicate minerals armstrongite, davanite, and dalyite. A 3D mixed anionic framework of the borophosphate structure is assembled by based on BO_4 , PO_4 – tetrahedra and AlO_6 octahedra, sharing oxygen vertices. The Cs^+ cations play the templating role in the structure formation of both compounds. The aluminum atoms stabilize the mixed anionic framework in the $\text{CsAl}_2\text{BP}_6\text{O}_{20}$, and play the key role in the design of 2D layers in the $\text{Cs}_2\text{CuAl}_4\text{O}_8$ structure. A complex of physical characteristics for different future applications is possible in connection with new synthesized compounds.

Keywords: X-ray diffraction, crystal structure, properties, microporous, flux method

MS15-P18 H...H clashes in published carboxylic acid structures

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Being difficult to locate accurately from X-ray diffraction data, hydrogen atoms are often placed in calculated positions. However, the SHEXL manual warns about the possibility that “the automatic placing of hydrogen atoms has assigned the hydrogens of two different O-H or N-H groups to the same hydrogen bond” [1], and CheckCIF includes a test [2] of D-H...H-D contacts that gives a PLAT417 Class A alert if the H...H distance is less than 1.8 Å. Wood et al. [3] showed that even under high pressure, H atoms come no closer than 1.7 Å. The Cambridge Structural Database (version 5.35 updated to February 2014) was surveyed for structures with clashing carboxyl H atoms subject to the filters $R \leq 0.1$ and no gross (non-hydrogen) disorder. Initially the O=C-OH...HO-C=O arrangement was considered. Violations of the CheckCIF criterion were found in 32 such structures (one corrected in a subsequent redetermination). Making the sites partially occupied or substituting O---H---O interactions with the H atom at the midpoint eliminates the clashes. As a criterion for the latter situation a separate search for accurate and trouble-free structures in the CSD with this feature gave 89 observations with mean O...O distance 2.456 Å and standard deviation of the mean 0.017 Å; 24 of the above 31 structures fall within the range 2.40 to 2.51 Å. Making H atom sites partially occupied or placing a single H atom between O atoms reduces the hydrogen count. In most cases it is possible, based on geometric criteria, to suggest locations where the missing H atoms could be replaced. Of course, these remain hypothetical until they can be confirmed with structure factors. Clashing H atoms in a pair-bonded dimer can be resolved by exchanging one C=O for C-OH. Five dimers with CheckCIF violations had C-O distances identical within 0.027 Å, suggesting partially occupied H sites or 180° rotation of entire COOH groups. Two structures seem to have one C=O inappropriately protonated. It is evident that, even in this era of validation software, authors, referees and readers must be on guard against COOH...HOOC clashes.

[1] <http://shelx.uni-ac.gwdg.de/SHELX/shelx97.pdf>, page 2-7. Accessed 11 December 2014.

[2] <http://journals.iucr.org/services/cif/datavalidation.html>. Accessed 11 December 2014.

[3] P. A. Wood, J. J. McKinnon, S. Parsons, E. Pidcock & M. A. Spackman (2008) *CrystEngComm*, 10, 368-376.

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