

The suppression of lone-pair stereoactivity in $[\text{Cu}^+(\text{As}^{3+}\text{O}_3)_4]$ clusters in dixenite: A tribute to Paul B. Moore

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ABSTRACT

The crystal structure of dixenite, ideally $\text{Cu}^+\text{Fe}^{3+}\text{Mn}_4^{2+}(\text{As}^{5+}\text{O}_4)(\text{As}^{3+}\text{O}_3)_5(\text{SiO}_4)_2(\text{OH})_6$, from Långban, Sweden, was refined to an R_1 -index of 1.58%, and the structure proposed by Araki and Moore (1981) was confirmed and details elucidated. The structure, crystallizing in space group $R\bar{3}$ with $a = 8.2204(3)$ and $c = 37.485(3)$ Å, consists of layers of $(\text{Mn}^{2+}, \text{Fe}^{3+})(\text{O}, \text{OH})_6$ octahedra linked by $(\text{As}^{5+}\text{O}_4)$ and (SiO_4) tetrahedra, $(\text{As}^{3+}\text{O}_3)$ trigonal pyramids, and $(\text{Cu}^+\text{As}_4^{3+})$ tetrahedra. There are five distinct layers in the repeat unit of the cell, four of which are very similar to the layers in mcgovernite. An unusual aspect of one of the trimers of octahedra is that there is a triangular-prismatic hole through the center of the cluster. The $(\text{Cu}^+\text{As}_4^{3+})$ tetrahedra are parts of larger clusters: $[\text{Cu}^+(\text{As}^{3+}\text{O}_3)_4]$ in which four $(\text{As}^{3+}\text{O}_3)$ groups link to a central Cu^+ that occupies the positions normally taken by the stereoactive lone-pairs of electrons that generally characterize As^{3+} in triangular-pyramidal coordination by O. Thus, the stereoactive lone-pair behavior that is characteristic of $(\text{As}^{3+}\text{O}_3)$ trigonal pyramids is suppressed by the coordination of Cu^+ by four As^{3+} ions.

Keywords: Dixenite, crystal structure, lone-pair electrons, Paul B. Moore