

Crystal structure of $\text{Cu}_3\text{Mo}_2\text{O}_9$

$\text{Cu}_3\text{Mo}_2\text{O}_9$ has an orthorhombic structure which can be described by a space group $Pnma$ with lattice constants of $a=7.667 \text{ \AA}$, $b=6.862 \text{ \AA}$, and $c=14.6 \text{ \AA}$. There are four molecules in one unit cell, as shown in Figure S1. In this structure, there are three Cu sites labeled by Cu_1 , Cu_2 , Cu_3 , seven O sites by O_1 - O_7 , and two Mo sites by Mo_1 , Mo_2 . Also, included in this structure are two sorts of almost regular Mo_1 -4O and Mo_2 -4O tetrahedra, one sort of compressed Cu_1 -6O octahedra, one sort of Cu_2 -5O polyhedra, and one sort of Cu_3 -5O polyhedra. A Cu_2 -5O polyhedron can be taken as a pentahedron in which one Cu atom and four O atoms (O_1 , O_2 and 2O_5) are nearly coplanar. However, in the case of Cu_3 , a sixth O atom is situated at a distance of $\sim 2.56 \text{ \AA}$. Thus, Cu_3 -6O can also be regarded as a distorted octahedron. For this crystal structure an interesting feature is the unusual compressed Cu_1 -6O octahedral environment round the Jahn-Teller active ion Cu^{2+} . The Cu_1 -6O compressed octahedra are connected by corners to form strings running along the $[010]$ direction. Cu_2 -5O and Cu_3 -6O polyhedra are linked to the Cu_1 -6O octahedra of a string by edge sharing whereas the Mo-4O tetrahedra are linked to them by corner sharing, as Figure S1 shows. The Cu_1 - O_1 bonds along the $[010]$ direction are the shortest among all Cu-O bonds, suggesting the compression of Cu_1 -6O octahedra along this direction.

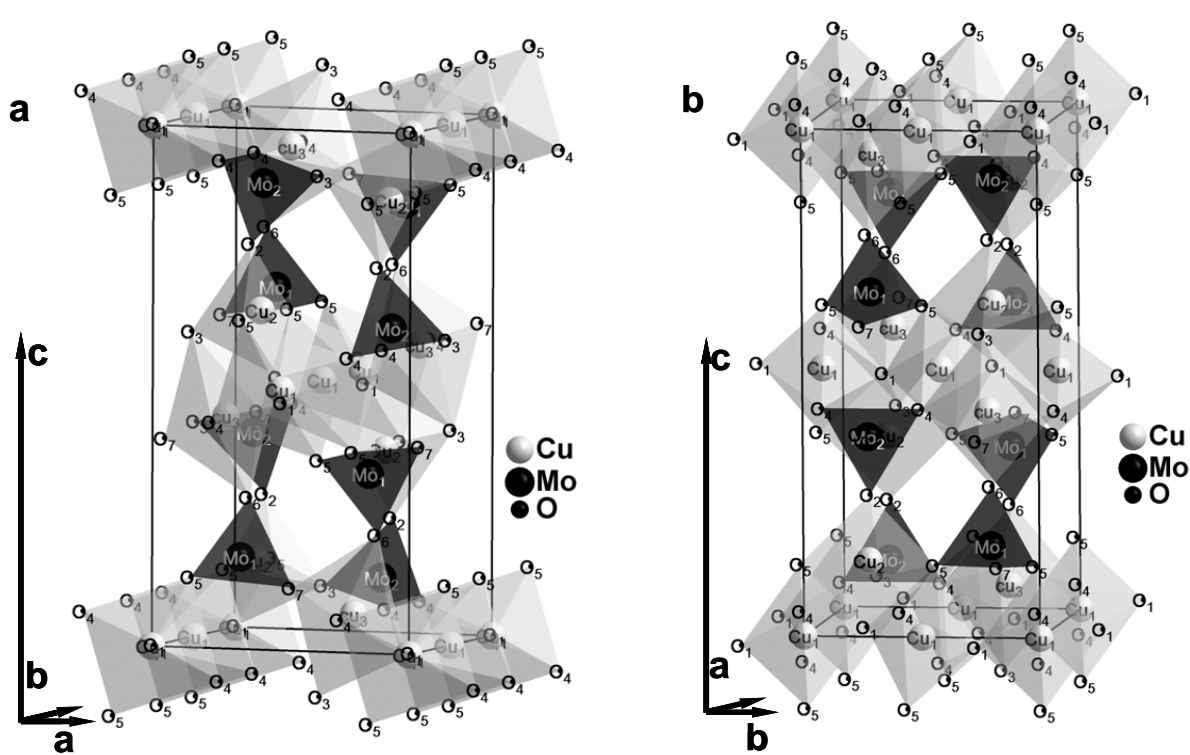


Figure S1 Schematic illustrations of a $\text{Cu}_3\text{Mo}_2\text{O}_9$ unit cell. Noting two sorts of Mo1,2-4O tetrahedra, one sort of compressed Cu1-6O octahedra forming strings running along *b*, one sort of Cu2-5O pentahedra in which a Cu atom and four O atoms are nearly coplanar, and one sort of Cu3-6O distorted octahedra.