

Mo₄O₄⁶⁺ Cubes in Cs₃Mo₄P₃O₁₆

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A single crystal X-ray structural analysis reveals that black cubes of Cs₃Mo₄P₃O₁₆, synthesized from Cs₂MoO₄, MoO₃, Mo, and P₂O₅ at 950 °C, contain isolated Mo₄O₄⁶⁺ cubes, with six short Mo–Mo bonds, with the cubes bridged together into a three dimensional array by PO₄³⁻ groups.

The tendency for the lower oxidation states of molybdenum to form metal–metal bonds has been observed in a wide variety of materials, such as dimers and trimers in small organometallic type molecules¹ and in many Mo₄S₄ⁿ⁺ cubes.² Molybdenum–molybdenum bonds have also been observed in several lower valent ternary oxides of general formula

M_xMo_yO_z with many different M.³ However, when the oxygen content of these ternary oxides is sufficiently reduced for the low oxidation state of the Mo necessary for the formation of Mo–Mo bonds to be obtained, then the relatively small number and size of the oxide ligands causes a close approach of the Mo atoms which results in edge, corner, or

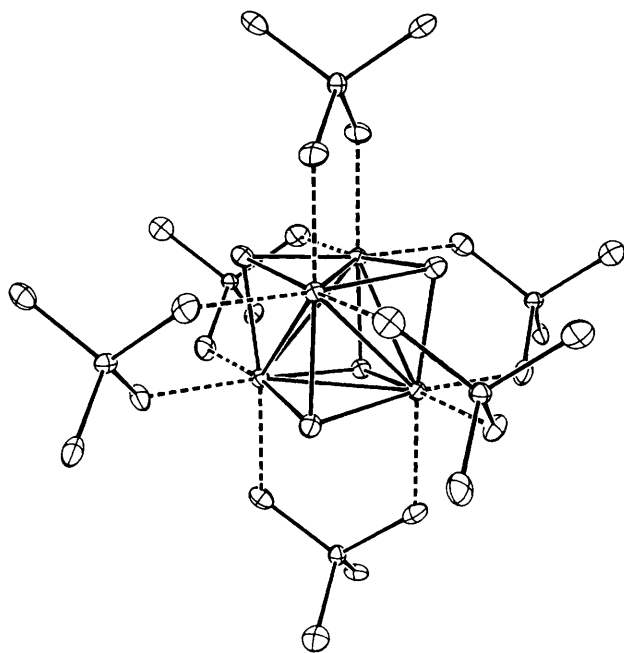


Figure 1. The co-ordination of the PO_4^{3-} groups to a single $\text{Mo}_4\text{O}_4^{6+}$ cube in $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$.

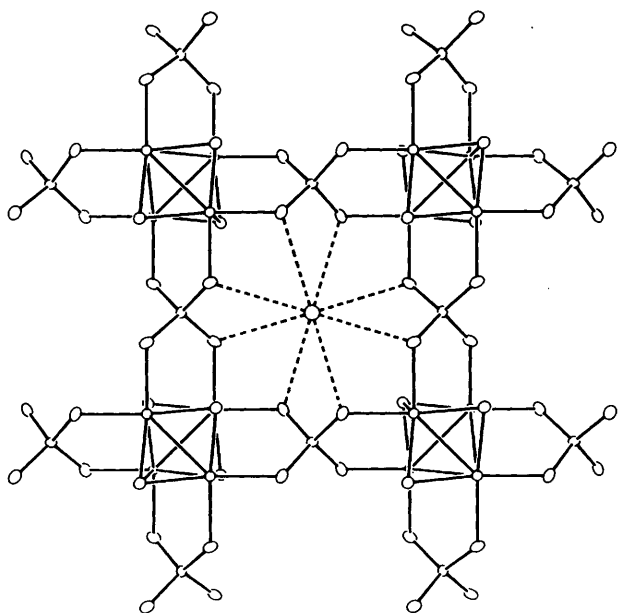


Figure 2. The co-ordination environment of the Cs^+ ion in $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$. The Cs^+ shown is at $z = 0.5$ while the other Cs^+ cations not shown in this view are centred above and below the P atoms at $z = 0$ and 1.

face sharing of the metal-metal bonded Mo polyhedra. It therefore seemed reasonable that it may be possible to synthesize isolated Mo polyhedra by using phosphate or pyrophosphate groups⁴ in place of oxide ligands. We report here the synthesis and structure of $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$, which, along with our recent discovery of $\text{Cs}_3\text{Mo}_5\text{P}_6\text{O}_{25}$,⁵ constitute the only examples of metal-metal bonded Mo_4O_4 cubes.

Black cubes of $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$ were originally discovered in the products resulting from the reaction of Cs_2MoO_4 , Mo,

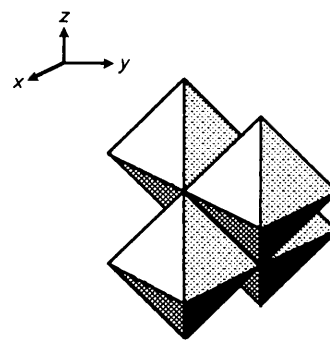


Figure 3. Polyhedral representation of the Mo_4O_{16} fragment in $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$. The corner of each octahedron represents an oxygen atom while the Mo atoms are at the centre of each octahedron.

MoO_3 and P_2O_5 (mole ratio 1:3:2:1). Preliminary X-ray examination of these cubes showed that the crystal system was cubic, with no systematic absences, and a statistical analysis of the intensity distribution very strongly suggested an acentric space group. Of the two space groups fulfilling these requirements, $P43m$ and $P23$, the former was chosen because of the presence of a site of symmetry $\bar{4}2.m$ which is the symmetry of a phosphate tetrahedron.

The solution of the X-ray data[†] showed that the black cubes had the composition $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$ and had a structure built up from Cs^+ cations, $\text{Mo}_4\text{O}_4^{6+}$ cubes, and PO_4^{3-} groups arranged as shown in Figure 1. The Mo atom was found at the e site (symmetry $.3m$) in $P43m$ at x, x, x with $x = 0.3820(2)$ which generated a perfect tetrahedron with Mo at the vertices, six Mo-Mo distances of 2.579(6) Å, and a metal-metal bond parallel to the face diagonal on each side of the cubic unit cell. Each triangular face of the Mo_4 tetrahedron was capped by a μ^3 oxo ligand at an e site (symmetry $.3m$) which, when combined with the Mo atoms, forms the Mo_4O_4 cube. The phosphorus atom was located at the c site (symmetry $\bar{4}2.m$), which is at the centre of the unit cell face at (0,0.5,0.5), while the O atom of the phosphate group resides at the i site (symmetry $.m$) and thus each PO_4^{3-} group bridges two Mo_4 tetrahedra together. The Cs^+ cation was located at the centre of each of the twelve unit cell edges and is symmetrically bonded to eight phosphate oxygens, involving four phosphate groups, at 3.210(8) Å (Figure 2).

Each Mo atom is co-ordinated to six O atoms [three μ^3 O ions at 2.03(3) Å and three phosphate O at 2.073(7) Å] to give a distorted MoO_6 octahedron. If one considers just the four Mo atoms with their surrounding sixteen oxygen atoms, then this Mo_4O_{16} core can be visualized as four MoO_6 octahedra each sharing three edges with three other MoO_6 units giving the array with tetrahedral symmetry shown in Figure 3. One can also consider the anionic framework of the $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$ structure as these Mo_4O_{16} units connected into a three

[†] Crystal data for $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$: space group $P43m$ (No. 215), $a = 7.728(4)$ Å, $U = 461.7(7)$ Å³, $Z = 1$, $D_c = 4.07$ g cm⁻³. A total of 820 reflections were recorded and equivalent reflections averaged to give a total of 176 reflections of which 173 had $I > 3.00\sigma I$ (98% observed) giving a data:parameter ratio of 173:17 and $R = 3.4\%$, $R_w = 4.7\%$, and G.O.F. = 1.229. For Mo- K_α radiation, $\mu = 88.48$ cm⁻¹ and an empirical absorption correction was applied. Since $P43m$ is an acentric space group, refinements were carried out for both possible configurations. The residuals for the other configurations not reported here were $R = 4.05\%$, $R_w = 5.41\%$, and G.O.F. = 1.411. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

dimensional array by P^{5+} ions. It should be noted that there is a rather large 'hole' in this structure at the origin position in the unit cell at (0,0,0) and if the structure is examined along the [100], [010], or [001] directions, one finds Cs^+ cations and the 'holes' equally spaced.

Once the stoichiometry was determined from the structural analysis it was possible to synthesize $Cs_3Mo_4P_3O_{16}$ as an X-ray pure, single phase material from the reaction of Cs_2MoO_4 , Mo, MoO_3 , and P_2O_5 in a mole ratio of 1 : 1.111 : 0.556 : 1 in an evacuated silica tube at 950 °C for 48 h.

Since the charges on Cs^+ , P^{5+} and O^{2-} are fixed, the oxidation state of the Mo in this material is +3.5 indicating that there are 10 electrons available for bonding in the Mo_4 tetrahedron. Magnetization measurements in the range 4.2 to 300 K indicate that $Cs_3Mo_4P_3O_{16}$ has an $S = 0$ ground state. At $T > 200$ K there is an indication that an excited state with $S > 0$ is starting to be populated although confirmation of this has to await magnetization measurements above room temperature. This is in contrast to magnetic measurements on the $Mo_4O_4^{6+}$ cubes in $Cs_3Mo_5P_6O_{25}$ which, although not totally unambiguous owing to the presence of additional magnetically active

Mo^{3+} ions in the lattice and complicated ordering phenomena at low temperatures, seemed to indicate a $S = 1$ ground state.

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