JOURNAL OF SOLID STATE CHEMISTRY 73, 274–277 (1988)

$Cs_3Mo_5P_7O_{24}$: A Molybdenum Phosphate Containing a Cubane-like Mo_4O_3P Cluster Unit with Six Mo–Mo Bonds

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Received May 26, 1987

The crystal structure of $Cs_3Mo_5P_7O_{24}$ has been determined from single-crystal X-ray diffraction data. $Cs_3Mo_5P_7O_{24}$ crystallizes in the trigonal space group $P31c$ (159) with $a = 11.940(4)$ Å, $c = 9.292(2)$ Å, $V = 1147.1(7)$ Å^3, $Z = 2$, $R = 0.0218$ ($R_w = 0.0258$) for 2850 reflections with $I > 3\,\sigma(I)$. The structure consists of large tunnels where the cesium atoms are located. The framework is built up from unusual cubane-like Mo_4O_3P cluster units with six Mo–Mo bonds, isolated MoO_6 octahedra, and pyrophosphate groups.

The investigation of the system M–Mo(v)–P–O (M = metal cation) has shown the formation of $K_4Mo_8P_{12}O_{52}$ (*1*), $Cs_2Mo_4P_6O_{26}$ (*2*), $Cs_4Mo_8P_{12}O_{52}$ (*2*), and $AgMo_5P_8O_{33}$ (*3*). Interestingly, $Cs_2Mo_4P_6O_{26}$, which has the same chemical compositions as $Cs_4MO_8P_{12}O_{52}$, adopts a markedly different structure. The phosphate containing Mo^{4+} has been observed in $T1Mo_2P_3O_{12}$ (*4*). In contrast to the Mo(V)-containing compounds which exhibit isolated MoO_6 octahedra only linked to PO_4 tetrahedra, $T1Mo_2P_3O_{12}$ contains corner-sharing Mo_2O_{11} units and PO_4 groups. As the formal oxidation state of the Mo atom is further reduced, one might expect the formation of metal–metal bonds which were found in the cubane-like Mo_4O_4 cluster unit in the remarkable compound $Cs_3Mo_5P_6O_{25}$ (*5*). However, the interconnection between the building units is governed by several factors such as the nature of the counter cations, the oxidation state of the Mo atom, and the nonmetal to metal ratio. Therefore, the compound $CsMoP_2O_7$ containing isolated highly reduced Mo^{3+} can be obtained by adjusting the nonmetal to metal ratio (*6*).

The investigation of phases formed in the molybdenum phosphorus oxide system has shown the great ability of PO_4 tetrahedra and P_2O_7 groups to form various frameworks with molybdenum polyhedra. Four different structural types have been isolated and elucidated in detail in the system

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0022-4596/88 $3.00

of Cs–Mo–P–O, suggesting a large number of new structures in the system of molybdenum phosphate. In this paper we present the crystal structure of a new molybdenum phosphate, $Cs_3Mo_5P_7O_{24}$, which contains an unusual cubane-like Mo_4O_3P cluster unit with six Mo–Mo bonds.

MoO_2 (99.9%), Mo metal (99.9%), MoO_3 (99.9%), Cs_2MoO_4 (99.9%), and P_2O_5 (99.9%) were obtained from Cerac. Cs_2MoO_4 was dried at 200°C under dynamic vacuum overnight before being used. The reactants were weighed and intimately mixed in a N_2-atmosphere glove box. In an attempt to prepare a compound with the nominal composition of $Cs_3Mo_6P_{10}O_{38}$ at 920°C in an evacuated quartz ampule for 7 days, columnar crystals with greenish tint were isolated from the reaction products. Both the color and the morphology of the columnar crystal are distinct from those of $Cs_3Mo_5P_6O_{25}$. Although reactions to prepare a pure phase of $Cs_3Mo_5P_7O_{24}$ under different conditions have been performed, the X-ray powder patterns of the products always showed reflections due to other phases.

A columnar crystal of $Cs_3Mo_5P_7O_{24}$ having the dimensions of 0.5 × 0.1 × 0.1 mm was selected for single-crystal X-ray structure determination.[1] The structure, which is viewed along the trigonal *c* axis, is shown in Fig. 1(a) and contains tunnels where the cesium atoms are located. The cesium atom is coordinated by 11 oxygen atoms at distances ranging from 3.016 to 3.616 Å. Figure 1(b) is a projection of the structure onto the (110) plane and shows the arrangement of the tetrahedral Mo_4 clusters and $Mo(1)O_6$ octahedra. The Mo_4 tetrahedra all point in the $-z$ direction. As shown in Fig. 1(c), the four faces of the Mo_4 tetrahedron are capped with three oxygen and one phosphorus atoms, three corners of the tetrahedron base are each coordinated by a bidentate P_2O_7 ligand, and the three slant edges (Mo2–Mo3) are each bridged by a μ-pyrophosphate group. The four Mo, three O, and one P atoms form a distorted cube. Each pyrophosphate group is coordinated to a corner of the Mo_4 tetrahedron as a bidentate ligand, bridges an edge of a neighboring Mo_4 cluster, and also forms a bridge between two neighboring Mo1 atoms. The structural formula is $Cs_3Mo(Mo_4O_3P)(P_2O_7)_3$. Therefore, the basic framework of $Cs_3Mo_5P_7O_{24}$ is essentially the same as that of $Cs_3Mo_5P_6O_{25}$ except that the μ_3-oxygen atom on the 3-fold axis in $Cs_3Mo_5P_6O_{25}$ is replaced by a phosphorus atom and the Mo_4 tetrahedra in the $Cs_3Mo_5P_7O_{24}$ crystal all point in the $-z$ direction.

The (μ_3-P)–Mo distance (2.390(3) Å) is considerably longer than the (μ_3-O)–Mo bond distances (2.007(6)–2.045(6) Å) and is comparable with that in MoP (2.451 Å) (7). During the least-squares refinement, the μ_3-atom on the 3-fold axis was initially assigned to be an oxygen atom. Subsequent refinements resulted in a nonpositive thermal parameter and a large residual electron density (10 $e^-/Å^3$) on the difference map, indicating the presence of a heavier atom than oxygen. A few cycles of refinement including a μ_3-phosphorus atom yielded a significantly better agreement factor (2.18% vs 3.14%) and small residual electron density at the μ_3-P position (<1 $e^-/Å^3$). Therefore, the compound is formulated as

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[1] Crystallographic data for $Cs_3Mo_5P_7O_{24}$: trigonal space group $P31c$ (159), a = 11.940(4) Å, c = 9.292(2) Å, V = 1147.1(7) $Å^3$, Z = 2, ρ(calc) = 4.28 g/cm^3, λ(Mo$K\alpha$) = 0.71073 Å, μ(Mo$K\alpha$) = 79.43 cm^{-1}. Of the 3090 unique reflections measured at room temperature on an Nicolet R3/V diffractometer, 2850 reflections were considered observed ($I > 3\ \sigma(I)$) after LP and empirical absorption corrections (transmission factor 0.793–0.908). The structure was solved by direct methods and refined by full matrix least-squares refinement. All atoms except O1 were refined anisotropically. The absolute direction of the z axis was also determined. R = 0.0218, R_w = 0.0258, GOF = 2.74. The highest peak in final difference map = 1.4 $e^-/Å^3$. All calculations were performed on a MicroVax II based Nicolet SHELXTL PLUS system.

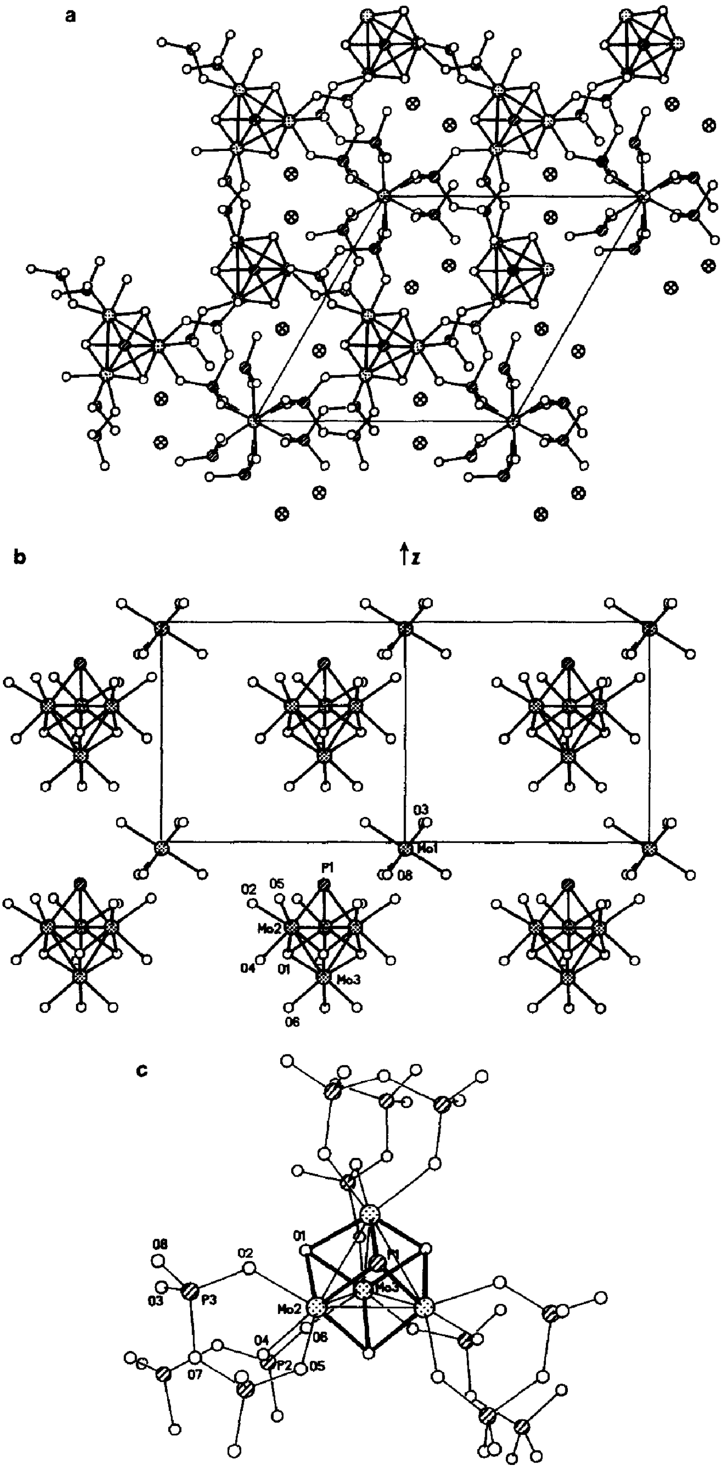

FIG. 1. (a) A view of the structure of $Cs_3Mo_5P_7O_{24}$ parallel to the 3-fold axis. The Cs, Mo, P, and O atoms are represented by circles with crosses, dotted circles, circles with slashes, and open circles, respectively. (b) A projection of the structure onto the (110) plane showing the arrangement of $Mo(1)O_6$ octahedra and tetrahedral Mo_4 clusters. The Cs, P2, P3, and O7 atoms are omitted for clarity. (c) A cubane-like Mo_4O_3P cluster with the pyrophosphate ligands in a direction approximately along the 3-fold axis.

$Cs_3Mo_5P_7O_{24}$. The bond distances between the unique Mo atom (Mol) and its six surrounding oxygen atoms in $Cs_3Mo_5P_7O_{24}$ (2.034(6) (3×) and 2.045(6) Å (3×)) are significantly shorter than the corresponding distances in the isotypic compound (2.067(6) (3×) and 2.090(5) Å (3×)), indicating that the unique Mo atom in the former compound is in a higher oxidation state. The Mo_4 tetrahedron in $Cs_3Mo_5P_7O_{24}$ is also compressed along the 3-fold axis with d(Mo2–Mo2) = 2.702(1) (3×) and d(Mo2–Mo3) = 2.612(1) Å (3×). The bond lengths in the tetrahedron base (Mo2–Mo2) are essentially the same as the corresponding distances in $Cs_3Mo_5P_7O_{24}$ (2.697(1) Å). But the three edges (Mo2–Mo3), which are each bridged by a μ-pyrophosphate ligand, are significantly longer than those in the isotypic compound (2.558(1) Å), suggesting less electrons available for metal–metal bonding in the Mo_4O_3P cluster unit. The observed changes in the bond distances are expected, since the μ_3-P atom should be considered as phosphide (P^{3-}) and therefore the formal charge per Mo_5 unit in $Cs_3Mo_5P_7O_{24}$ is higher than that in $Cs_3Mo_5P_6O_{25}$ by 1 unit. However, the charge distribution between the unique Mo atom and the Mo_4O_3P cluster unit is not clear to us at present. Magnetic susceptibility measurements on a pure sample would be informative. The synthesis of analogous molybdenum phosphates containing μ_3-S or As on the 3-fold axis will also be investigated.

Acknowledgments

The authors thank the National Science Council of the Republic of China for financial support of this study under Contracts NSC76-0208-M007-79 and NSC76-0208-M001-47. K.-H. Lii would also like to express thanks for support from the Institute of Chemistry Academia Sinica.

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