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BRIEF COMMUNICATIONS

$Mo_3P_5SiO_{19}$: A Molybdenum Phosphate Containing a Confacial Bioctahedral Molybdenum(III) Dimer with a Mo–Mo Bond

S. L. WANG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

AND C. C. WANG AND K. H. LII*

Institute of Chemistry Academia Sinica, Taipei, Taiwan, Republic of China

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The crystal structure of $Mo_3P_5SiO_{19}$ has been determined from single-crystal X-ray diffraction data. $Mo_3P_5SiO_{19}$ crystallizes in the hexagonal space group $P6_3$ (No. 173) with $a = b = 14.692(4)$ Å, $c = 7.394(4)$ Å, $Z = 4$, $R = 0.043$ ($R_w = 0.034$) for 1477 reflections with $I > 3\,\sigma(I)$. The structure contains an unusual confacial bioctahedral Mo_2O_9 cluster with a Mo–Mo bond.

A large number of phosphorus–oxygen compounds of molybdenum containing molybdenum in oxidation states less than +6 have been reported (*1–11*), but only a few compounds exhibit metal–metal bonding. For example, the compound $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$ (*3*) contains a Mo–Mo triple bond, and a cubane-like Mo_4O_4 cluster with six molybdenum–molybdenum bonds has been observed in $Cs_3Mo_5P_6O_{25}$ (*9*). In an attempt to add new members to the family of molybdenum phosphate a new compound containing confacial bioctahedral molybdenum(III) dimer with a Mo–Mo bond was discovered. Although the confacial bioctahedral arrangement is common in the halide chemistry of transition metals, it appears unusual in oxygen lattice. In this report we present the crystal structure of $Mo_3P_5SiO_{19}$.

MoO_3 (99.9%), Mo metal (99.5%), SiO_2 (99.9%), and P_2O_5 (99.9%) were obtained from Cerac. A reaction aiming at "$NiMo_2P_4O_{14}$" at 1000°C in an evacuated fused silica tube yielded some brownish-yellow plates. An electron microprobe analysis on a few crystals showed that the crystals did not contain Ni, and the Mo : P : Si mole ratio was approximately equal to 2.6 : 4.4 : 1. The silicon content must be from the silica tube. The exact stoichiometry of the crystal was not known until its single-crystal X-ray structure was determined. A plate crystal having the dimensions of 0.20 × 0.15 × 0.05 mm was selected for X-ray structure deter-

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* To whom correspondence should be addressed.

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mination.[1] Attempts to prepare pure $Mo_3P_5SiO_{19}$ were performed by heating a mixture of proper stoichiometry of MoO_3, Mo, SiO_2, and P_2O_5 in an evacuated fused silica tube at 1000°C, but the X-ray powder patterns always showed a few unindexed reflections. A pure sample for magnetic susceptibility and spectroscopic studies has not been obtained.

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Mo_3P_5SiO_{19}$

Atom	x	y	z	U or U_{eq} (Å^2)
Mo1	−0.0085(1)	0.3272(1)	0.1250	0.0073(8)[a]
Mo2	0.0060(1)	0.3375(1)	0.4775(1)	0.0077(9)[a]
P1	−0.1900(4)	0.2462(4)	0.7902(6)	0.005(1)
P2	0.0853(4)	0.2291(4)	0.7969(7)	0.008(1)
P3	0.1026(5)	0.5210(4)	−0.2040(7)	0.008(1)
P4	0	0	0.272(6)	0.013(2)
P4′	0	0	0.346(8)	0.013(2)
Si1	$\frac{1}{3}$	$\frac{2}{3}$	−0.236(2)	0.002(2)
Si2	$\frac{1}{3}$	$\frac{2}{3}$	0.347(2)	0.005(2)
O1	0.085(1)	0.459(1)	−0.0306(2)	0.019(3)
O2	$\frac{1}{3}$	$\frac{2}{3}$	−0.442(4)	0.002(2)
O3	−0.098(1)	0.207(1)	0.322(2)	0.005(3)
O4	0.0323(8)	0.2346(8)	−0.035(2)	0.006(2)
O5	−0.1473(7)	0.2854(7)	−0.016(1)	0.000(1)
O6	0.736(1)	0.452(1)	0.777(2)	0.023(4)
O7	0.926(1)	0.882(1)	0.316(1)	0.011(3)
O8	0.2166(7)	0.6182(7)	−0.147(2)	0.000(2)
O9	0.103(1)	0.470(1)	0.621(2)	0.025(3)
O10	−0.1099(7)	0.3034(8)	0.647(1)	0.009(2)
O11	0.129(1)	0.323(1)	0.296(2)	0.009(4)
O12	0.045(1)	0.254(1)	−0.363(2)	0.024(3)
O13	0.962(1)	0.421(1)	0.307(1)	0.008(3)
O14	0	0	0.054(8)	0.15(2)

Note. The occupancy factors for P4 and P4′ are 0.55 and 0.45, respectively.

[a] Atoms were refined anisotropically, and the equivalent isotropic thermal parameter is given by $U_{eq} = (\Sigma_i \Sigma_j B_{ij} a_i \cdot a_j)/6\pi^2$.

The atomic coordinates and thermal parameters are listed in Table I. Only molybdenum atoms were refined anisotropically. The thermal parameters of a few oxygen atoms had no physical significance when they were anisotropically refined. P4, P4′, and O14 are at 2a special positions (0, 0, z). Si1, Si2, and O2 are at 2b special positions ($\frac{1}{3}$, $\frac{2}{3}$, z). All other atoms are at 6c general positions. As shown in Fig. 1 the structure is formed of PO_4 tetrahedra, Si_2O_7 groups, and confacial bioctahedral Mo_2O_9 clusters. The basic framework of $Mo_3P_5SiO_{19}$ is essentially the same as that of $V_3P_5SiO_{19}$ (*12*) except that the Mo–Mo bond distance (2.613(1) Å) is considerably shorter than the V–V distance (2.90 Å), the local structure at the 2a special positions (0, 0, z) appears different, and the disilicate group in the molybdenum compound exhibits a staggered configuration rather than a semieclipsed configuration. The arrangement of V_2O_9, PO_4, and Si_2O_7 groups in the vanadium compound has been described in detail (*12*). The Si_2O_7 groups sit on the 2b special positions which are each surrounded by Mo_2O_9 units. In contrast to the vanadium compound, a model with disordered PO_4 tetrahedra was used in the structure refinement for $Mo_3P_5SiO_{19}$ in order to fit the elongated electron densities at the 2a special positions. The refinement resulted in two closely spaced phosphorus atoms (P4 and P4′, 0.55 Å apart) with reasonable thermal parameters and about the same occupancy factors (about 50% for each). No attempt was made to include two oxygen atoms to fit the elongated electron density for the disordered oxygen atom (O14) at the 2a special position. Each of the PO_4 tetrahedra at the 2a special position is linked to three PO_4 tetrahedra in the *ab* plane to form a P_4O_{13} unit. Leclaire *et al.* (*12*) pointed out that a simple migration of one phosphorus atom out of two would lead to the formation

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[1] Crystallographic data for $Mo_3P_5SiO_{19}$: hexagonal space group $P6_3$ (No. 173), a = 14.692(4), c = 7.394(4) Å, V = 1382(1) Å^3, Z = 4, ρ_{calc} = 3.72 g/cm^3, $\lambda(MoK\alpha)$ = 0.71073 Å, $\mu(MoK\alpha)$ = 33.92 cm^{-1}. Of the 3700 reflections measured at room temperature on a Nicolet R3/V diffractometer, 1609 reflections were unique and 1477 reflections were considered observed ($I > 3.0\ \sigma(I)$) after LP and empirical absorption corrections (transmission factor 0.970–0.727). The structure was solved by direct methods and refined by full matrix least-squares refinement. R = 0.043, R_w = 0.034, GOF = 3.47. Highest peak on final difference map = 2.1 e/Å^3. All calculations were performed on a MicroVax II based Nicolet Shelxtl Plus system.

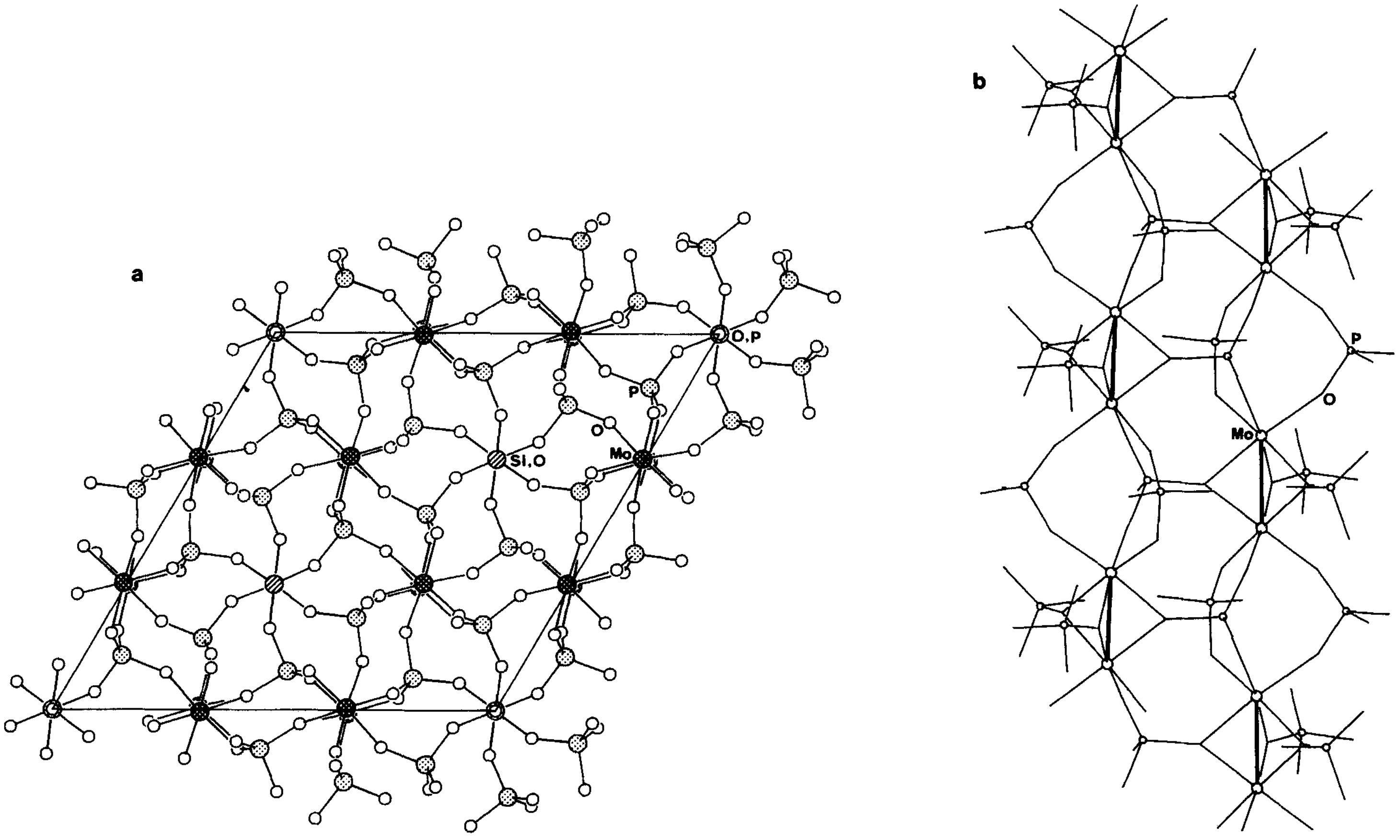

FIG. 1. (a) A view of the structure of $Mo_3P_5SiO_{19}$ parallel to the *c* axis. The Mo, P, Si, and O atoms are represented by cross-hatched circles, dotted circles, shaded circles, and open circles, respectively. (b) A section of infinite chains built up from corner-sharing Mo_2O_9 clusters and PO_4 tetrahedra. For clarity, the radii for O atoms are set equal to zero.

of P_8O_{25} unit. Since our microprobe analysis suggests a higher silicon content, the possibility of formation of $P_6Si_2O_{25}$ unit at the 2a special positions in $Mo_3P_5SiO_{19}$ cannot be ruled out. A complete replacement of the phosphorus atoms at (0, 0, z) by silicon would lead to the hypothetical compound $Mo_{12}O_{18}Si_6O_{75}$. The average oxidation state (+3) of the molybdenum atoms remains the same because the replacement of the phosphorus atoms by silicon is compensated for by the decrease in oxygen content. As indicated by the O–O distances (2.81(2)–3.16(2) Å for Mo1; 2.71(2)–3.00(2) Å for Mo2), both octahedra are markedly distorted probably due to the confacial bioctahedral arrangement. Both MoO_6 octahedra exhibit three slightly shorter Mo–O distance (2.07(1)–2.10(1) Å for Mo1; 1.96(1)–2.05(1) Å for Mo2) and three slightly longer ones (2.12(1)–2.21(1) Å for Mo1; 2.07(1)–2.13(1) Å for Mo2). The slightly longer distances correspond to the distances from Mo^{3+} cation to the common oxygen atoms. The most notable feature of the Mo_2O_9 cluster is the short Mo–Mo distance of 2.613(1) Å. The bond length is comparable to that in $Cs_3Mo_2Cl_9$ (d(Mo–Mo) = 2.66 Å) (*13*) despite the larger size of bridging chlorine vs oxygen. The six valence d electrons available from the two metal atoms in Mo_2O_9 fill the a_1' and degenerate e' bonding orbitals, thus producing a formal metal–metal bond order of 3 (*14*). Because SCF − $X\alpha$ − SW calculation on $[Mo_2Cl_9]^{3-}$ (*15*) shows that the e' bonding orbitals have very little bonding effect, it is not surprising that the Mo–Mo distance in $Mo_3P_5SiO_{19}$ is distinctly longer than the double bond in species of edge-sharing bioctahedral dimer such as MoO_2 (d(Mo–Mo) = 2.52 Å). The presence of bridging ligands in $[M_2X_9]^{n-}$ complicates the treatment of the bonding and thus an assessment of bond order. The consideration of the Mo_2O_9 cluster as formally possessing a metal–metal triple bond seems inappropriate because of little bonding effect of the e' orbitals.

Since the metal–metal distances decrease sharply in going from $[Cr_2Cl_9]^{3-}$ to $[W_2Cl_9]^{3-}$ (*13*), it would be of great interest to see if the Cr–Cr and W–W bond lengths in oxygen lattice differ so markedly. Reactions to prepare pure phases of "$W_3P_5SiO_{19}$" and $Cr_3P_5SiO_{19}$ under similar reaction conditions to those for $Mo_3P_5SiO_{19}$ have been performed. On the basis of X-ray powder analysis, the tungsten analog was not obtained, but the chromium compound was obtained in polycrystalline form.

The discovery of a confacial bioctahedral Mo_2O_9 cluster in $Mo_3P_5SiO_{19}$ and a cubane-like Mo_4O_4 cluster in $Cs_3Mo_5P_6O_{25}$ provides a new route for the preparation of novel molybdenum clusters in oxygen lattice. A more systematic approach to discover new structures in the system of early transition metal phosphates has been initiated along with an examination of their properties.

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