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## COMMUNICATION

# $K_3MoPO_7$ : the first molybdenum phosphate with edge-sharing $MoO_6$ octahedra and $PO_4$ tetrahedra

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S. Luo,<sup>a,b</sup> L. Kang,<sup>a,b,c</sup> Z. Lin<sup>\*a,b</sup> and C. Chen<sup>a,b</sup>

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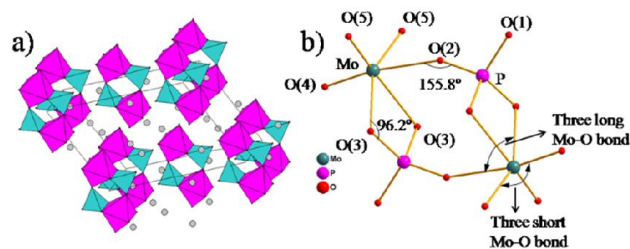
Herein we report the discovery of a novel molybdenum phosphate  $K_3MoPO_7$ , in which the basic building unit,  $[P_2Mo_2O_{14}]^{6-}$  ring cluster anions, contains the unique edge-sharing  $MoO_6$  and  $PO_4$  polyhedra. The structural stability of  $K_3MoPO_7$  is confirmed by both experimental and first-principles studies.

Corner-, edge- and face-sharing patterns are three basic polyhedra connection modes in inorganic chemistry.<sup>1</sup> These three linkage ways and their combinations significantly enrich the structural chemistry and result in diverse polymorphisms. In fact, the linkage ways mainly depend on the ionic charge, ionic radii and coordination number.<sup>2</sup> In inorganic oxides, the corner-sharing pattern is the most common way to be adopted by the  $M_xO_y$  (M is cation) polyhedra, such as in borates<sup>3</sup>, silicates,<sup>4</sup> aluminates<sup>5</sup> and phosphates<sup>6</sup>. The edge- or face-sharing patterns, on the other hand, are much less likely to exist in the above compounds. In general, both patterns could be obtained in extreme conditions only.<sup>7</sup>

The molybdenum phosphate system also has rich crystal chemistry with a large number of structures containing tunnels, cages and micropores.<sup>8</sup> Till now hundreds of molybdenum phosphate have been synthesized, and many of them have large surface areas which can be used in ion exchange, catalysis, and separations.<sup>9</sup> It is observed that in all discovered molybdenum phosphates the  $MoO_6$  octahedra always share their corners with  $PO_4$  tetrahedra to build up frameworks.<sup>8</sup> According to the Pauling's third and fourth rules,<sup>2</sup> polyhedra with high charge cations and low coordination numbers would be more stable if they are connected by sharing vertices while less stable if sharing edges or faces, due to the cation-cation electrostatic repulsion between centroids. Thus, for  $MoO_6$  octahedra and  $PO_4$  tetrahedra they are very likely to share minimal vertices (i.e., corner-shared) to build framework since the  $Mo^{6+}$  and  $P^{5+}$  cations have quite high positive charges. The edge- or face-sharing of  $MoO_6$  octahedra and  $PO_4$  tetrahedra have not been

found yet. In this work we synthesize the first molybdenum phosphate  $K_3MoPO_7$  in which the  $MoO_6$  octahedra are sharing-edged with  $PO_4$  tetrahedra so form the unique  $[P_2Mo_2O_{14}]^{6-}$  anion rings. The structural stability is investigated by thermal measures and first-principles calculations.

$K_3MoPO_7$  was synthesized through solid-state reaction in stoichiometric ration with  $K_2CO_3$ ,  $MoO_3$  and  $K_2HPO_4$  as the starting materials. It can also be obtained from stoichiometric composition melt of above raw materials with slow cooling since it is a congruent compound. The proof will show in thermal characterization aspect below. Small transplant single crystals with light yellow color were obtained through spontaneous crystallization. The crystal structure was solved and refined on the basis of single-crystal data. The XRD patterns of as-synthesized samples show good agreement with the calculated one derived from the single crystal data.



**Fig. 1** (a) Polyhedral view of the  $K_3MoPO_7$  structure projected along the  $b$  axis. Pink octahedrons and cyan tetrahedrons stand for  $MoO_6$  anion groups and  $PO_4$  anion groups, respectively. (b) ball-and-stick model for a  $[P_2Mo_2O_{14}]^{6-}$  anion. The K, Mo, P, O atoms are shown as gray, teal, pink and red, respectively

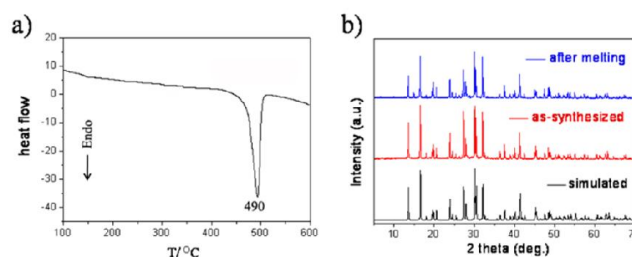
$K_3MoPO_7$  crystallizes in a monoclinic system with the centrosymmetric space group  $C2/m$ . In an asymmetric unit, K, Mo, P and O occupy three, one, one, and five crystallographically unique positions, respectively. The

structure of  $\text{K}_3\text{MoPO}_7$  is featured by isolated  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  anions, with  $\text{K}^+$  cations filled up the space around the anions (Fig. 1a). The  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  anion is constructed by two  $\text{MoO}_6$  octahedra and two  $\text{PO}_4$  tetrahedra in which the Mo and P atoms are coplanar. These polyhedra alternately connect with each other *via* either corner-sharing or edge-sharing patterns to form an 8-membered polyanion ring with the symmetry of  $C_{2h}$  point group (Fig. 1b). The simple  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  fundamental building unit is first found in all inorganic compounds.

It is worthy to note that the  $\text{MoO}_6/\text{PO}_4$  edge-sharing configuration in the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  ring is unique and distinguished to any other microscopic pattern in molybdenum phosphates. Our comprehensive survey for all transition-metal phosphates in inorganic crystal structural database reveals that indeed the edge-sharing structure with  $\text{MO}_6$  octahedra is very rare as the M cations are  $d^0$  transition-metal ( $M = \text{Ti}^{4+}, \text{Nb}^{5+}, \text{Mo}^{6+}, \text{W}^{6+}, \text{Ta}^{5+}, \text{V}^{5+}$ ). There is only one phosphovanadate,  $\text{Li}_2\text{VPO}_6$ , having the similar edge-sharing structure.<sup>10</sup> On the other hand, for the non- $d^0$  transition-metal  $\text{MO}_6$  octahedra ( $M = \text{Co}^{3+}, \text{Mn}^{2+}, \text{Cr}^{3+}, \text{V}^{3+}, \text{V}^{2+}$  etc.) they are relatively easy to form the edge-sharing structure with  $\text{PO}_4$  tetrahedra; tens of these compounds containing this connection pattern have been found. This result actually agrees with the Pauling's rules since the non- $d^0$  transition metals have relatively lower charge which could reduce the electrostatic repulsion between  $\text{M}^{n+}$  and  $\text{P}^{5+}$  cations. Therefore, the discovery of  $\text{K}_3\text{MoPO}_7$  provides a very rare example that violates the common rules for structural stability, which has significant implications to explore the molybdenum phosphates with new structures and new functions.

In  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  anion ring the  $\text{Mo}^{6+}$  cation of  $\text{MoO}_6$  octahedron is located in the distorted environments due to second-order Jahn-Teller (SOJT) effect.<sup>11</sup> The centroid shifts toward a vertex of the octahedron (local  $C_3$  [111] direction), which results in the formation of three short (1.749(2) Å - 1.754(2) Å) and three long (2.186(2) Å - 2.353(3) Å) Mo-O bonds, as shown in Fig. 1b, and all the three short bonds are outwards from the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  anion ring. As a comparison, in the  $\text{PO}_4$  group P-O bond lengths are ranged from 1.52 to 1.57 Å, and this group almost keeps the regular tetrahedral shape. In  $\text{K}_3\text{MoPO}_7$  all bond lengths are comparable to those in other reported molybdenum phosphates. The calculated total bond-valences sums on Mo and P are 5.82 and 4.85, respectively. These values match well with the expected oxidation states.<sup>12</sup>

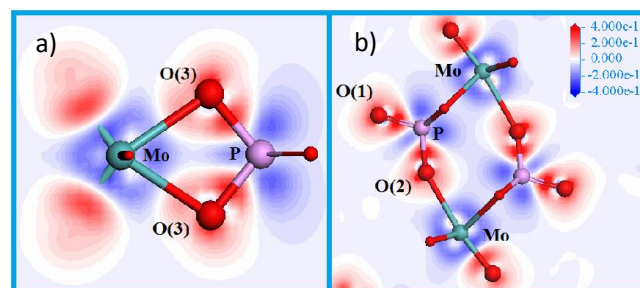
It is interesting that each  $\text{MoO}_6$  octahedron in the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  cluster anion contains three free vertices. This is also very rarely observed in molybdates. In general, the formation of the structures with  $\text{MO}_6$  octahedra that contain three (or more) free vertices is very unfavorable due to the strong *trans* influence of the terminal M-O bonds (i.e., the *Lipscomb* restriction).<sup>13</sup> In  $\text{K}_3\text{MoPO}_7$  the ring-like  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  groups are very different from all other microscopic structures in molybdenum phosphates where the  $\text{MoO}_6$  groups are usually connected to other groups as chain, layer or three-dimensional network. The zero-dimensional topological structure of the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  cluster anion results in more dangling oxygen ions existed in the  $\text{MoO}_6$  octahedra. Therefore, this simple group might be an ideal starting building unit to further polymerize with other groups for the construction of more complex solids, e.g., open-framework structures or polyoxometalates, for the applications of catalysis, luminescence, magnetism, medicine, etc.<sup>14</sup>



**Fig. 2.** (a) DSC curves of  $\text{K}_3\text{MoPO}_7$ . (b) X-ray powder diffraction patterns of  $\text{K}_3\text{MoPO}_7$ . The middle curve is powder of as-synthesized. The top one is powder after melting. The bottom curve is simulated XRD derived from the single crystal data.

The stability of  $\text{K}_3\text{MoPO}_7$  was experimentally demonstrated by the thermal behaviour measured with a differential scanning calorimetry (DSC). No obvious endo- or exothermic peak was observed until the melting point of the compound was reached near 490 °C (Fig. 2a). This demonstrates that the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]^{6-}$  anionic structure keeps stable in ambient atmosphere from room temperature to the melting point. After melting, the cooled solid remains were characterized by XRD and were identified that it crystallized into  $\text{K}_3\text{MoPO}_7$  (Fig. 2b). A few weak extra peaks were observed since the volatilization of melt and component deviation. The DSC and XRD results clearly reveal that this compound melts congruent.

To further investigate the mechanism of the structural stability of the edge-sharing  $[\text{PO}_4]$  and  $[\text{MoO}_6]$  in the  $[\text{P}_2\text{Mo}_2\text{O}_{14}]$  ring, the first-principles studies on the electronic density difference and Mulliken atomic/bond populations<sup>15</sup> were performed<sup>16</sup> by the plane-wave pseudopotential method implemented in the CASTEP package<sup>17</sup>. The electronic density difference calculation produces a density difference field which shows the changes in the electron distribution as all chemical bonds are formed in the system. Fig. 3(a) and 3(b) exhibit the electronic density difference in the edge-sharing and corner-sharing  $\text{MoO}_6/\text{PO}_4$  groups, respectively, which shows a different charge redistribution among the edge-sharing O(3) and corner-sharing O(2). In detail, the O(3) atoms obtain more electronic charges from the neighboring Mo atoms compared with the O(2) atoms, but the charge transfer from the neighboring P atoms to the O(3) is less than to the O(2) atoms. This indicates a necessary migration of electronic charges from P-O bond to Mo-O bond due to the modification of the chemical environment around the oxygen atoms as they are charged from corner-sharing to edge-sharing.



**Fig. 3.** Contour plots of the electronic density difference on the planes formed by (a) Mo, P and edge-sharing O(3) atoms and (b) Mo, P and corner-sharing O(2) atoms. The off-plane O atoms are represented by small red balls.

The more quantitative results come from the Mulliken analysis; P-O(3) and P-O(2) bond populations are 0.59 and 0.74, respectively, while those on the Mo-O(3) and Mo-O(2) population is 0.28 and 0.23, respectively. Thus, the increase (decrease) of bond covalence between Mo (P) and edge-sharing O compared with those around the corner-sharing O account for the stability of the whole [Mo<sub>2</sub>P<sub>2</sub>O<sub>14</sub>] group. It should be noted, however, that the Mulliken analysis reveals that the effective charges on O(3) (-0.96) is less than that on O(2) (-1.03). This implies that indeed the edge-sharing oxygen atoms are less stable than the corner-sharing oxygen, in consistence with the Pauling's second rule (i.e., the oxygen anion having more charge tends to be more stable). We suggest that the zero-dimensional closed-ring configuration of the [Mo<sub>2</sub>P<sub>2</sub>O<sub>14</sub>] group would be beneficial to the formation of edge-sharing structure compared with the chain, layer or three-dimensional network.

## Conclusions

A unique [P<sub>2</sub>Mo<sub>2</sub>O<sub>14</sub>]<sup>6-</sup> ring-shape anion containing edge-sharing MoO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra has been discovered in a novel molybdenum phosphate K<sub>3</sub>MoPO<sub>7</sub>. The basic building unit with edge-sharing MoO<sub>6</sub> and PO<sub>4</sub> polyhedra was first found. K<sub>3</sub>MoPO<sub>7</sub> is a congruent compound with melting point at about 490 °C. The first-principles calculations reveal that the unusual edge-sharing feature attributes to the migration of electronic charges from P-O bond to Mo-O bond. In other words, the edge-sharing Mo-O bond is of larger covalence than that of the corner-sharing Mo-O bond. Our studies presented in this work, therefore, would greatly prompt the development of molybdenum phosphates and have implications on the progress of structural chemistry.

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## Notes and references

<sup>a</sup> Beijing Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Email: zslin@mail.ipc.ac.cn

<sup>b</sup> Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

<sup>c</sup> University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

† The CCDC number of K<sub>3</sub>MoPO<sub>7</sub> is 996800. Crystal data for K<sub>3</sub>MoPO<sub>7</sub>: M=712.42 g/mol, monoclinic, a=13.990(3) Å, b=5.8600(12) Å, c=9.6157(19) Å, β=111.68(3)°, Z=2, V=732.54(87) Å<sup>3</sup>, space group C2/m. 5379 reflections measured, 1545 independent reflections ( $R_{int} = 0.0261$ ). The final  $R_1$  value was 0.029. The final  $wR(F^2)$  value was 0.0776 ( $I > 2\sigma(I)$ ). The final  $R_1$  value was 0.0311 (all data). The final  $wR(F^2)$  value was 0.0790 (all data). The goodness of fit on  $F^2$  was 1.064

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