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$K_5Mo_4O_{14}F$: A Novel Fluorinated Polyoxomolybdate and Its Structural Stability

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Supporting Information

ABSTRACT: We successfully synthesized a novel fluorinated polyoxomolybdate, $K_5Mo_4O_{14}F$, in which the unusual polyanion $[Mo_4O_{14}F]^{5-}$ consists of face-sharing $[Mo_2O_8F]$ bioctahedra linked with $[MoO_4]$ tetrahedra. This unique structural feature provides the very rare case that simultaneously violates Pauling's electrostatic valence (II) and atomic coordination (IV) rules, as well as the stable tendency governed by the polyhedral sharing (III) rule. The structural stability of $K_5Mo_4O_{14}F$ was confirmed from thermal experiments over a wide temperature range and further elucidated by first-principles calculations.

In 1929, Linus Pauling proposed five rules[1] for governing the stability of microscopic atomic structures in ionic crystals, including the radius ratio rule (I), electrostatic valence rule (II), polyhedral sharing rule (III), atomic coordination rule (IV), and parsimony rule (V). After that, the very famous Pauling rules were adopted to predict and rationalize the structures for most crystals.[2] In fact, only a very few percentages (<1%) of newly discovered crystals violate one of Pauling's rules; no crystal has been reported to simultaneously break two or more of Pauling's rules because, in general, more violations of Pauling's rules would cause the atomic structure to be more unstable. As a result, the discovery of new compounds whose structures disobey Pauling's rules is crucial to enhancing the understanding of the structure−stability relationship and is of perpetual interest in solid-state chemistry.[3]

To study the relationship of structural diversity to stability, we focus our attention on the polyoxomolybdates because they are a special class of molybdates with unique topology and electronic versatilities of the molybdate anionic cluster.[4] Polyoxomolybdates have the general chemical formula $[Mo_xO_y]^{z-}$, with Mo cations most commonly five- or six-coordinated with O ions to form $[MoO_5]$ square pyramids or $[MoO_6]$ octahedra[5] (sometimes F ions replace some of the O ions). Because of the highly symmetrical core, high-nuclearity clusters, and relatively condensed three-dimensional structure, the coordination polyhedra of Mo−O(F) are multivariate, which would significantly extend the new structural possibilities of the crystal.

In this work, we synthesized a new anhydrous fluorinated polyoxomolybdate, $K_5Mo_4O_{14}F$, from melt. Its most unique structural feature is the $(Mo_4O_{14}F)^{5-}$ anionic groups, which consist of face-sharing $[Mo_2O_8F]$ bioctahedra linked with $[MoO_4]$ tetrahedra. The polyanion shows two significant features that are rarely exist in the crystal structures of related compounds. First, $[MoO_5F]$ octahedra and $[MoO_4]$ tetrahedra are interconnected in anhydrous polyoxomolybdates. Second, this anionic group shows a very special example that simultaneously violates Pauling's rules II and IV and the stable tendency governed by Pauling's rule III. To the best of our knowledge, cases that violate more than one of Pauling's rules in one crystal are very scarce. As a comparison, in $(NH_4)_8Mo_{10}O_{34}$ or $(Me_4N)_3[Mo_4O_{12}F_3]\cdot0.8H_2O$,[6,7] for example, the structure contains either face-sharing bioctahedra or the coexistence of $[MoO_4]$ and $[MoO_6]$ octahedra, which only violates one of Pauling's rules (the III or IV rule). The novel structural characteristics of $K_5Mo_4O_{14}F$ would enrich the knowledge for structural stability. The thermal experiments and first-principles calculations demonstrate that this structure is stable over a wide temperature range.

The crystals of $K_5Mo_4O_{14}F$ were obtained by a medium-temperature solution growth method using KNO_3 as the flux system. Normally, potassium nitrates are rarely adopted as flux to synthesize a single crystal with structure-soluble size (>0.05 mm) because of the acute decomposition of KNO_3 melt above the melting point. However, we found that the KNO_3−KBF_4 system is relatively stable as the melt at medium temperature (from 300 to 500 °C) and can be eutectic with MoO_3. In addition, KNO_3 melt has a quite low viscosity, which is beneficial to crystal nucleation and growth. So, we adopted a new synthesis method to obtain the title compound by using the KNO_3−KBF_4−MoO_3 ternary melt. The details of crystal growth are introduced in section S1 in the Supporting Information (SI). Transplant colorless single crystals with millimeter size were obtained through spontaneous crystallization. The crystal structure was solved and refined on the basis of single-crystal data. The X-ray diffraction (XRD) patterns of the obtained crystals show good agreement with the calculated results derived from the single-crystal data (XRD partterns shown in Figure S1 in the SI, and the crystal data, atomic coordinates, atomic displacement parameters, and bond distances are listed in Tables S1−S4 in the SI).

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$K_5Mo_4O_{14}F$ crystallizes in a monoclinic system with the centrosymmetric space group $C2/c$, and its structure is illustrated in Figure 1. In an asymmetric unit, K, Mo, O, and F occupy three, two, seven, and one crystallographically unique positions, respectively. The crystal structure is built up of isolated $(Mo_4O_{14}F)^{5-}$ anions in the symmetry group of C_2, and K^+ cations filled up the space around the anions (Figure 1a). In a $(Mo_4O_{14}F)^{5-}$ anionic group (Figure 1b), two Mo atoms (Mo2 and Mo2′) are octahedrally coordinated respectively with five O and one F atoms to form two distorted [MoO_5F] octahedra, whereas the other two Mo atoms (Mo1 or Mo1′) are respectively surrounded by four O atoms in a tetrahedral fashion ([MoO_4]). Very interestingly, the two [MoO_5F] octahedra are interconnected by sharing a common face, which contains one F (F1) and two O (O1 and O1′) atoms, so forming a face-sharing bioctahedron. Meanwhile, each of the two [MoO_4] tetrahedra laterally connects with a [Mo_2O_8F] bioctahedron by sharing the bridging O atoms (O1 and O1′) from the right and left sides, respectively. The coexistence of both Mo−O(F) octahedra and tetrahedra in a crystal is very rarely observed. The only exception in the anhydrous polyoxomolybdates was just discovered in $(NH_4)_8[Mo_{10}O_{34}]$,[6] which consists of edge-sharing MoO_6 octahedra and MoO_4 tetrahedra. In fact, the structure with face-sharing bioctahedra and MoO_4 tetrahedra in the title compound, to our best of knowledge, was found for the first time in molybdates.

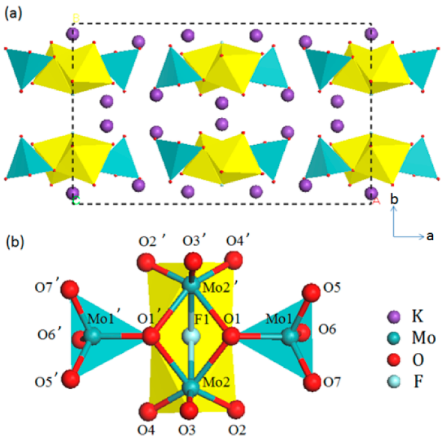

Figure 1. (a) Polyhedral view of the $K_5Mo_4O_{14}F$ structure projected along the *c* axis. Yellow octahedra and light-green tetrahedra represent the $[MoO_5F]^{5-}$ and $[MoO_4]^{2-}$ anionic groups, respectively. (b) Ball-and-stick model for a $(Mo_4O_{14}F)^{5-}$ anionic group.

The metal−ligand bond lengths in the $(Mo_4O_{14}F)^{5-}$ group are varied according to the local atomic environments: in the [Mo_2O_8F] bioctahedra, the bond lengths between Mo atoms (Mo2 or Mo2′) and the three bridged atoms (O1, O1′, and F1) are 2.184(4), 2.187(4), and 2.191(4) Å, respectively, whereas in the [MoO_4] tetrahedra, the bond lengths between the three-coordinated O atoms (O1 or O1′) and the four-coordinated Mo atoms (Mo1 or Mo1′) are all equal to 1.886(4) Å. For all Mo−O polyhedra, the terminal Mo−O bond lengths are in the range from 1.732(4) to 1.756(4) Å. All of these Mo−O or Mo−F bond lengths are comparable to those in other known fluorooxomolybdate anions.[8] The Mo−Mo distance [3.2510(9) Å] inside the bioctahedron is relatively small because of the face-sharing connected pattern of the [MoO_5F] octahedra. All Mo atoms, similar to those in the other polymolybdates,[7] are displaced from the central sites of the polyhedra toward the terminal O atoms. The [MoO_5F] octahedra are seriously distorted because the O−Mo−O/F bond angles vary in the range from 70.72(12)° to 105.3(2)°. As a comparison, in the [MoO_4] groups, the O−Mo−O bond angles vary from 108.5(2)° to 112.37(18)°, almost keeping the regular tetrahedral configuration.

The atomic configurations in the $(Mo_4O_{14}F)^{5-}$ anionic group violate Pauling's rules II and IV. The details are shown as follows: (i) The electrostatic valence rule (rule II) indicates that the sum of the electrostatic bond strength[8] to an anion should be equal or nearly equal to the normal charge on the anionic atom. However, in $(Mo_4O_{14}F)^{5-}$, the sum of the electrostatic bond strength on the bridged O anion (O1 or O1′) is about −3.25, much larger than the normal charge on the oxygen anion (−2), so the local charge balance is broken and Pauling's rule II is violated. (ii) The connection of the [MoO_5F] and [MoO_4] groups also violates the atomic coordination rule (rule IV), which states that the polyhedra with high valency and small coordination number tend to not share polyhedral elements with one another.

At the same time, according to Pauling's rule III, polyhedra tend to be most interconnected by sharing minimal vertices (i.e., corner-sharing), and the structural stability would be significantly decreased if edges or faces are shared because of the increased cation−cation electrostatic repulsion between centroids. However, in $K_5Mo_4O_{14}F$, the [MoO_5F] octahedra are interconnected through common faces to form $(Mo_2O_8F)^{5-}$ bioctahedra and so disobey the tendency of structural stability. Although several face-sharing polyoxomolybdates have been synthesized from the hydrothermal or aqueous solution method,[9] it is the first time that the anhydrous face-sharing polyoxomolybdate has been obtained through the melt method. In addition, it should be noted that for each [MoO_5F] octahedron three oxygen vertices are free-standing. According to the Lipscomb restriction,[10] this atomic configuration is very rarely observed in polyoxomolybdates because, in general, a [MoO_5F] octahedron that contains three (or more) free vertices is very likely to facilitate dissociation of a neutral [MoO_3] molecule from the group[11] because of the strong trans influence of the terminal Mo−O bonds.

The unusual structural characteristics described above seem to suggest that the structure of $K_5Mo_4O_{14}F$ could be very unstable. In order to investigate the stability of this compound, differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) was performed to determine the thermal behavior. As shown in Figure S2a in the SI, it is clear that no obvious endo- or exothermic peak was observed until near 400 °C. The TGA curve demonstrates that the compound in an ambient atmosphere varied from room temperature to 600 °C without weight loss. Moreover, the XRD patterns measured at 23 and 300 °C (Figure S2b in the SI) demonstrate that the structure of the compound remains unchanged (stable) over a wide temperature range. These results show that this compound is very stable over a large range of temperature. Above 400 °C, the title compound gradually decomposes. After melting, the solid remains are a combination of $K_2Mo_2O_7$ and K_2MoO_4 (XRD patterns in Figure S1 in the SI), revealing that it melts incongruently. In addition, to further learn about the solution stability of the polyanions in $K_5Mo_4O_{14}F$, the ^{19}F NMR spectrum was measured in D_2O. The ^{19}F NMR spectrum exhibits three resonances at −122.38, −150.47, and −150.52 ppm, respectively (Figure S3 in the SI). The major resonance at −122.38 ppm can be assigned to the characteristic peak of aqueous F ions,[12] indicating that the $(Mo_4O_{14}F)^{5-}$ polyanions are decomposed in water.

The mechanism of the structural stability of the $K_5Mo_4O_{14}F$ crystals can be elucidated by first-principles calculations. The electronic density difference in the $(Mo_4O_{14}F)^{5-}$ anionic groups was calculated by the plane-wave pseudopotential method implemented in the *CASTEP* package.[13] Figure 2 displays the contour of electronic density difference in the Mo1−O1−Mo2′ plane, which illustrates charge redistribution due to the formation of chemical bonds. Clearly, the charge densities are more accumulated on the Mo2′−O1 bond compared with those on the Mo1−O1 bond, indicating that migration of electronic charges from the [MoO_4] tetrahedron to the [Mo_2O_8F] bioctahedron accounts for the stability of the whole $(Mo_4O_{14}F)^{5-}$ group. This conclusion can also be verified by Mulliken analysis[14] (see Table S5 in the SI): the Mulliken population on the terminal O atoms (e.g., O5) in the tetrahedron is 7.6, less than that on the bridging O1/O1′ (7.9); thus, the charge is transferred from the former to the latter ions. We deem that distortion of the Mo−O(F) octahedra prompts charge redistribution in the $(Mo_4O_{14}F)^{5-}$ anionic groups to stabilize the crystal structure. Meanwhile, the existence of the [MoO_4] tetrahedron enlarges the Mo−Mo distance in the bioctahedra to some degree, so that the electrostatic repulsion is reduced. Therefore, $K_5Mo_4O_{14}F$ can stably exist under ambient conditions. The further phonon calculations[15] obtained by the linear response method[16] also demonstrate that no imaginary mode has been observed in the phonon spectrum (see Figure S4 in the SI), verifying the kinetic stability of the title crystal.

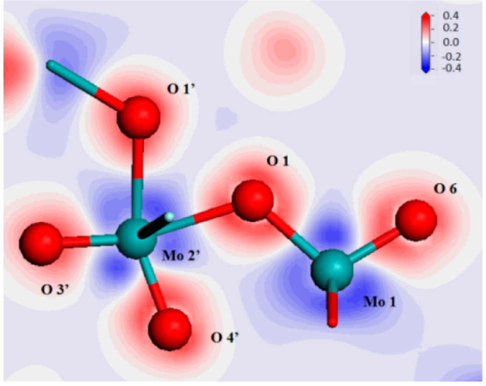

Figure 2. Contour plots of the electronic density difference on the plane formed by Mo1−O1−Mo2′.

In summary, a fluorinated molybdenum $K_5Mo_4O_{14}F$ was synthesized, in which the novel polyanion $(Mo_4O_{14}F)^{5-}$ is constructed by the face-sharing bioctahedra and [MoO_4] tetrahedra. This structure seems to be very unstable according to Pauling's II, III and IV rules, but the experiment measurements show that it is very stable over a large range of temperature. The first-principles calculations reveal that its stability is mainly contributed from the charge migration from the tetrahedra to the bioctahedra. We believe the present studies would have great implications for the development of solid state chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Methods, X-ray crystallographic data in CIF format (CCDC 997415 for $K_5Mo_4O_{14}F$), and additional data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00643.

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Notes

The authors declare no competing financial interest.

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