Flux Growth of Tungsten Oxychloride Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$

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Abstract: Mixed anion compounds can generate the emergence of novel properties that differ from those with mono-type anion due to the difference of electronegativities, ionic radii, polarizabilities, and oxidation states between unlike anions. Abundant research has been conducted on metallic mixed-anion materials with potential application in electronics, detectors of moisture, gas sensors, electrodes for solar batteries, etc. The flux method has been widely applied for mixed-anion crystal growth, which based on metathetical reaction with appropriate metal-salts flux under mild conditions. It is meaningful to synthesis the mixed anion compounds by the flux method. Single crystals of tungsten oxychloride Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ were prepared via CuCl$_2$ flux-growth method by two steps, which using high quality and phase-pure polycrystalline Li$_2$WO$_3$ as precursor. The crystal structure was determined by single-crystal X-ray diffraction analysis, which indicates that Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ crystallizes in P6$_3$/mcm space group (a = 1.02846(3) nm, c = 1.98768(9) nm, V = 1.82076(11) nm$^3$, and Z = 2). There are crystallographically independent five Li, two W, one Cu, two Cl, and five O atoms in the unit cell, where W(1) atoms are coordinated with one Cl and five O atoms in a distorted octahedra geometry, while W(2) atoms are connected with four O atoms in a tetrahedral coordination. The Cu atoms are connected with six O atoms forming [CuO$_6$] octahedra. Thus, the crystal structure of the titled compound consists of [CuO$_6$] and [W(1)O$_5$Cl] octahedra, and [W(2)O$_4$] tetrahedra. The success synthesis of tungsten oxychloride Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ through flux-growth method is meaningful for explore new mixed anion compounds in the future work.

Key words: tungsten oxychloride; CuCl$_2$ flux; crystal structure; X-ray diffraction

Mixed anion compounds, especially their unique structures and excellent physical properties, have been extensively studied and have great applications in military and civilization, they have attracted abundant attention since the difference of electronegativities, ionic radii, polarizabilities, and oxidation states between unlike anions can generate the emergence of novel properties that differ from those with mono-type anion$^{[1-4]}$. The active research of metallic mixed-anion materials with potential application in electronics, detectors of moisture, gas sensors, electrodes for solar batteries, etc. has been realized in several types of crystalline and thin film materials$^{[5]}$. It is meaningful to search a suitable method to synthesis aforementioned compounds. The main hotspot to research this kind of compounds lies in how to control the arrangement of anions to refine their electronic structures, such as the two-dimensional quantum antiferromagnetism in Sr$_2$CuO$_2$Cl$_2$ with trans-configuration of Cl ions in the CuO$_2$Cl$_2$ octahedra$^{[6]}$.

Recently, it has been reported that the incorporation of halides into oxides can strikingly change their electronic structures and modify the physical properties$^{[7-8]}$. Several novel transition-metal oxychlorides have been reported to date, such as MnSb$_2$O$_4$Cl$_2$,$^{[9]}$ PbCu$_2$(SeO$_3$)$_2$Cl$_2$,$^{[10]}$ Cu$_3$Bi(SeO$_3$)$_2$O$_2$Cl$^{[11]}$, FeTe$_2$O$_4$X (X=Cl, Br)$^{[12]}$, SrCu$_2$(SeO$_3$)$_2$Cl$^{[13]}$, SmSb$_2$O$_4$Cl$^{[14]}$, and MSb$_2$O$_4$(OH)Cl (M=Co, Fe, Mn)$^{[15]}$. Above-mentioned materials show novel structures and special magnetic properties due to their diversity structural which was more helpful to generate the magnetic ordering during low temperature. This was

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especially manifested in layered transition metal oxy-
halide FeTe₂O₅X (X = Br, Cl), where the layers are 
built by [FeO₆] octahedra, and then forming the 
[Fe₃O₁₆]²⁺ units which were linked via [Te₆O₁₆X₂]₆⁻ 
anionic groups. The magnetic properties are reported 
within a cluster approach of antiferromagnetically 
coupled tetramers including spin frustration and a fer-
romagnetic inter-tetramer interaction[12].

The flux method widely applied for mixed-anion 
crystal growth is based on metathetical reaction with 
appropriate metal-salts flux under mild conditions. 
Experimentally, zone melting and hydrothermal syn-
thesis methods are all comparatively complex and 
expensive for growing single crystals, and the flux 
method is at present one of the most economic and 
convenient methods for mixed anions compound[s][16].

In this paper, we report the single crystal growth of 
tungsten oxychloride Li₂₃CuW₁₀O₄₀Cl₅ in copper 
chloride (CuCl₂, melting point of 498 °C) flux, and 
analyze its crystal in details.

1 Experimental

1.1 Materials and Methods.

Regents were used as received: Li₂CO₃ (Macklin, 
99.99%), WO₃ (Aladdin, 99.99%), and CuCl₂ (Mack-
lin, 98%).

The tungsten oxychloride Li₂₃CuW₁₀O₄₀Cl₅ was 
synthesized through flux method in open-end quartz 
tubes. And the synthesis of Li₂₃CuW₁₀O₄₀Cl₅ adopt a 
two-step process. Firstly, precursor polycrystalline 
Li₄W₂O₇ were synthesized by reacting high-purity re-
gents in solid-state method. Li₂CO₃ and WO₃ was 
mixed with the mole ratio of 2:1. Then these raw 
materials were placed in a covered alumina crucible 
and calcinated at 890 °C for 12 h as described in refer-
cence[17]. Then, single crystal of Li₂₃CuW₁₀O₄₀Cl₅ was 
grown from CuCl₂ flux and precursor Li₄W₂O₇. 
Li₄W₂O₇ polycrystalline samples and ten times excess 
CuCl₂ was loaded into an open-end quartz tube, and 
put into a vertical pit furnace. The raw mixture was 
heated at 873 K for 2 d, and then cooling down to 573 
K with a cooling rate of 5 K/h before shutting down 
the furnace.

Finally, the reaction products were washed by hot 
demineralized water to eliminate the fluxing agents. 
After subsequent drying at 353 K, yellow, block 
shaped single crystals of the desired products were 
grown and suitable for subsequent single-crystal X-ray 
diffraction measurements.

1.2 Single-crystal structure determination

Block-shaped single crystal of Li₂₃CuW₁₀O₄₀Cl₅ was 
selected for single-crystal diffraction measurements. 
The R-AXIS Spider CCD diffractometer were 
used to collect data equipped with the graphite mono-
chromated Mo Kα radiation (λ = 0.071073 nm) at 293 
K.

The structure of Li₂₃CuW₁₀O₄₀Cl₅ was determined 
through direct method and refined by full-matrix 
least-squared methods on F² with SHELXL pack-
age[18], ADDSYM/PLATON was performed to studied 
with the final structure was for additional symmetry, 
and no other missed or higher symmetry was found[19].

Crystallographic data (including structure factors) for 
the structures in this paper have been deposited with 
the Cambridge Crystallographic Data Centre, CCDC, 
12 Union Road, Cambridge CB21EZ, UK. Copies of 
the data can be obtained free of charge on quoting the 
depository numbers CCDC-1952905.

2 Results and discussion

The tungsten oxychloride Li₂₃CuW₁₀O₄₀Cl₅ synthe-
sized from CuCl₂ flux in a vertical pit furnace crystal-
lizes hexagonally in space group of P6₃/mmc with 
the unit cell parameters of a = 1.02846(3) nm, c = 
1.98768(9) nm, and Z=2. There are crystallograph-
ically independent five Li, two W, one Cu, two Cl, and 
five O atoms in the unit cell, respectively, where W(1) 
atoms are coordinated with one Cl and five O atoms in 
a distorted octahedra geometry, while W(2) atoms are 
connected with four O atoms in a tetrahedral coordi-
nation. The Cu atoms are connected with six O atoms 
forming [CuO₄] octahedra.

Every two W(2)O₄ tetrahedra are in reverse sym-
metry along the c direction (Fig. 1 and 3). Three 
[W(1)O₆Cl] octahedra are connected with each other 
via sharing one Cl atom, and three O atoms with 
[CuO₆] octahedra to form the [W(1)₆CuO₂₅Cl₅] unit 
(Fig. 2). The three-dimensional (3D) structure of 
Li₂₃CuW₁₀O₄₀Cl₅ is assembled by the [W(1)₆CuO₂₅Cl₂] 
units sharing O and Cl atoms with Li. The Li atoms 
in Li₂₃CuW₁₀O₄₀Cl₅ present four kinds of environments 
(Fig. 4): Li(1) atoms are connected with two Cl atoms 
and four O atoms and Li(2) with one Cl atom and five 
O atoms, while Li(3) and Li(4) atoms are coordinated 
with six O atoms, and Li(5) atoms are surrounded by 
three Cl and four O atoms.

In Li₂₃CuW₁₀O₄₀Cl₅, the W–O distances ranging from 
0.1778(9) to 0.2154(5) and the bond lengths of
W–Cl are 0.2141(5) nm, which are comparable to those in Ba$_3$WO$_3$Cl$_2$[20], K$_2$W$_3$O$_{10}$[21], WCl$_6$[22], and WOC$_4$[23], the Cu-O distances are 0.1993(8) nm in good agreement with Ba$_3$Cu$_2$O$_4$Cl$_2$[23], and BaCuSi$_2$O$_6$[24], from bond valence sums (BVS, Table 3) calculations in Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$, Cu displays +2 formal oxidation states according to charge balance.

The Li–O and Li–Cl distances range from 0.2012(6) to 0.249(3) nm and 0.248(3) to 0.287(4) nm, which are closed to those in Li$_2$MnCl$_4$[25], Li$_2$ZnCl$_4$[26], Li$_2$WCl$_6$[27], Li$_2$CaTa$_2$O$_7$[28]. The crystallographic data and structural refinements for Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ are summarized in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond distances and atomic BVS are displayed in Table 3.

**Table 1 Summary of Crystallographic Data and Structure Refinement Parameters for Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$**

| Chemical Formula | Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ |
|------------------|----------------------------------|
| Formula weight   | 2878.91                          |
| Crystal size (mm$^3$) | 0.162 × 0.115 × 0.090           |
| Crystal system   | Hexagonal                        |
| Space group      | P6$_3$/mcm                       |
| a/nm             | 1.02846(3)                       |
| c/nm             | 1.98768(9)                       |
| V/nm$^3$         | 1.82076(11)                      |
| Z                | 2                                |
Table 2 Atomic coordinates and equivalent isotropic displacement parameters of Li$_2$CuW$_{10}$O$_{40}$Cl$_5$

| Atom | Site | x     | y     | z     | $U_{eq}$(nm$^2$) |
|------|------|-------|-------|-------|-----------------|
| W(1) | 12k  | 0.1904(1) | 0 | 0.6257(1) | 0.6(1) |
| W(2) | 8h   | 2/3 | 1/3 | 0.5947(1) | 0.6(1) |
| Cu(1)| 2b   | 0   | 0   | 1/2 | 2.0(1) |
| Cl(1)| 6g   | 0.4831(4) | 0.4831(4) | 3/4 | 1.6(1) |
| Cl(2)| 4e   | 0   | 0   | 0.6693(6) | 7.9(3) |
| O(1) | 12k  | 0.3077(8) | 0 | 0.5594(4) | 1.1(2) |
| O(2) | 12k  | 0.3077(8) | 0 | 0.5594(4) | 1.1(2) |
| O(3) | 24l  | 0.3150(6) | 0.1562(6) | 0.6766(3) | 1.1(1) |
| O(4) | 24l  | 0.5092(7) | 0.3447(6) | 0.5644(3) | 1.2(1) |
| O(5) | 8h   | 2/3 | 1/3 | 0.6842(5) | 1.2(2) |
| Li(1)| 12j  | 0.2060(40) | 0.2060(40) | 3/4 | 1.4(2) |
| Li(2)| 12k  | 1/2 | 1/2 | 1/2 | 2.2(6) |
| Li(3)| 12i  | 0.3510(20) | 0.1755(12) | 1/2 | 2.3(5) |
| Li(4)| 6f   | 0.3520(30) | 0.3520(30) | 0.6319(1) | 4.2(7) |
| Li(5)| 6g   | 0.4800(30) | 0.2210(30) | 3/4 | 2.8(5) |

Table 3 Selected bond lengths and atomic BVS for Li$_2$CuW$_{10}$O$_{40}$Cl$_5$

| Bond         | Bond lengths/nm | Bond         | Bond lengths/nm | Bond         | Bond lengths/nm |
|--------------|-----------------|--------------|-----------------|--------------|-----------------|
| W(1)−O(3)   | 0.1786(6)       | Li(1)−O(3)   | 0.2075(2)       | Li(4)−O(4)   | 0.2086(5)       |
| W(1)−O(3)   | 0.1786(6)       | Li(1)−O(3)   | 0.2075(2)       | Li(4)−O(4)   | 0.2086(5)       |
| W(1)−O(2)   | 0.1787(7)       | Li(1)−O(5)   | 0.213(2)        | Li(4)−O(4)   | 0.2086(5)       |
| W(1)−Cl(2)  | 0.2141(5)       | Li(1)−O(5)   | 0.213(2)        | Li(4)−O(4)   | 0.2086(5)       |
| W(1)−O(1)   | 0.2154(5)       | Li(1)−Cl(1)  | 0.248(3)        | Li(4)−O(2)   | 0.2303(8)       |
| W(1)−O(1)   | 0.2154(5)       | Li(1)−Cl(1)  | 0.268(3)        | Li(4)−O(2)   | 0.2303(8)       |
| W(2)−O(5)   | 0.1778(9)       | Li(2)−O(3)   | 0.2056(2)       | (Li(4)−O)    | 0.2158(3)       |
| W(2)−O(4)   | 0.1785(6)       | Li(2)−O(3)   | 0.2056(2)       | BVS          | 0.096           |
| W(2)−O(4)   | 0.1785(6)       | Li(2)−O(1)   | 0.2490(3)       | Li(5)−O(3)   | 0.2054(8)       |
| W(2)−O(4)   | 0.1785(6)       | Li(2)−Cl(1)  | 0.2710(3)       | Li(5)−O(3)   | 0.2054(8)       |
| W(2)−O(2)   | 0.1784(2)       | Li(2)−O(4)   | 0.213(2)        | Li(5)−O(3)   | 0.2054(8)       |
| BVS         | 0.574           | Li(2)−O(4)   | 0.213(2)        | Li(5)−O(3)   | 0.2054(8)       |
| Cu(1)−O(1)  | 0.1992(8)       | Li(3)−O(2)   | 0.2012(6)       | Li(5)−Cl(2)  | 0.266(3)        |
| Cu(1)−O(1)  | 0.1992(8)       | Li(3)−O(2)   | 0.2012(6)       | Li(5)−Cl(2)  | 0.266(3)        |
| Cu(1)−O(1)  | 0.1992(8)       | Li(3)−O(1)   | 0.2346(2)       | Li(5)−Cl(1)  | 0.285(4)        |


3 Conclusion

In summary, new single crystals Li$_{23}$W$_{10}$CuO$_{40}$Cl$_5$(1) have been successfully grown by flux growth method in open-end silica tubes. The crystal structure of Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ has been characterized by single crystal diffraction method. The 3D framework is built by [CuO$_6$] octahedra, [W(1)O$_5$Cl] octahedra and [W(2)O$_4$] tetrahedra. The adjacent [W(1)O$_5$Cl] octahedra are connected with each other via sharing one Cl atom, and further sharing three O atoms with [CuO$_6$] octahedra to form the [W(1)$_6$CuO$_{23}$Cl$_2$] unit. The success synthesis of Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ through flux-growth method is meaningful for explore new mixed anion compounds in the future work.

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中文翻译

助熔剂法合成钨氧氯化合物 Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$

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摘 要：由于不同阴离子之间的电负性、离子半径、极化率和氧化态之间的差异，混合阴离子化合物可以产生不同于单一类型阴离子的新特性。混合阴离子金属材料在电子、湿度探测器、气体传感器、太阳能电池电极等领域有着广泛的应用前景。助熔剂法是一种广泛应用到合成阴离子的生长的方法，其以适当的金属盐作为助熔剂，在较温和的条件下进行复分解反应。助熔剂法在合成阴离子化合物的合成中具有重要意义。钨氧氯化合物 Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ 单晶以高质量的 Li$_2$WO$_4$ 为前驱体，以 CuCl$_2$ 为助熔剂通过两步法合成。通过 X 射线单晶衍射确定其晶体结构。结果表明，Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ 结晶于 $P6_3/mmc$ 空间群，晶胞参数分别为 $a = 1.02846(3)$ nm, $c = 1.98768(9)$ nm, $V = 1.82076(11)$ nm$^3$, $Z = 2$。单胞中分别包含五个晶体学独立的 Li 原子，两个 W 原子，一个 Cu 原子，两个 Cl 原子以及五个 O 原子。结构中，W(1) 原子和一个 Cl 原子及五个 O 原子相连，形成畸变八面体，而 W(2) 原子与四个 O 原子相连接形成四面体，Cu 原子与六个 O 原子相连形成八面体。因此，Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ 的晶体结构主要由 [CuO$_6$] 和 [W(1)O$_5$Cl] 八面体以及 [W(2)O$_4$] 四面体构成。助熔剂法合成钨氧氯化合物 Li$_{23}$CuW$_{10}$O$_{40}$Cl$_5$ 对今后探索新型的混合阴离子化合物具有重要意义。

关 键 词：钨氧氯化合物；CuCl$_2$ 助熔剂；晶体结构；X 射线衍射

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