

Crystal structure of dicaesium oxopentachloromolybdate(V), $\text{Cs}_2(\text{MoOCl}_5)$

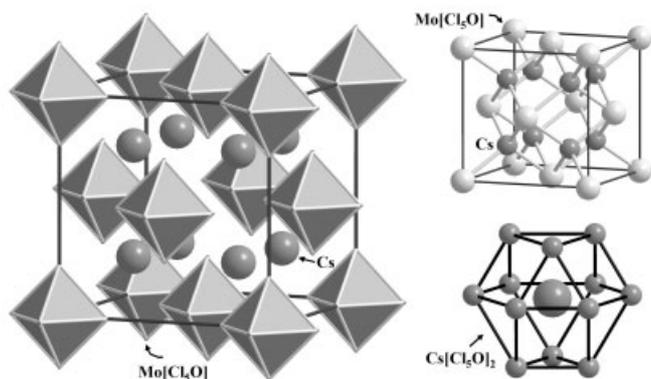
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Abstract

$\text{Cl}_5\text{Cs}_2\text{MoO}$, cubic, $Fm\bar{3}m$ (No. 225), $a = 10.2276(2)$ Å, $V = 1069.8$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.058$, $T = 295$ K.

Source of material

The title compound was synthesized in aqueous solution. The reaction was carried out with the mixture of MoCl_5 (4.098 g), $\text{Cs}(\text{OH}) \cdot \text{H}_2\text{O}$ (3.358 g) and 30 ml 37% HCl with molar ratio of $\text{Mo} : \text{Cs} = 3 : 4$. The mixture was heated on the electric stove to boiling point while it was stirring. After it was cooled down and evaporated in air for several days, two kinds of crystals were obtained. One in the shape of octahedron with dark green corresponded to the title compound and was used in structure determination. The composition of formula was confirmed by chemical analysis (ICP) with $\text{Cs} : \text{Mo} : \text{O} = 2.20(6) : 1.00(9) : 0.8(2)$.

Discussion

The title compound was first synthesized by Brown [1]. But its structure was not reported yet until now. The crystal structure of the title compound is isotopic to $\text{Cs}_2(\text{NbOCl}_5)$. It is characterized by isolated $[\text{MoCl}_5\text{O}]$ octahedra linking caesium cations with chlorine or oxygen anions to form a three-dimensional structure. The title com-

pound has some common structural characteristics with typical structure of CaF_2 which have same space group ($Fm\bar{3}m$) with it. Its crystal structure can be deduced from fluorite structure. $[\text{MoCl}_5\text{O}]$ octahedra locate at every corner and face-center sites of the cubic cell as calcium (Ca^{2+}) cations in the fluorite structure. Caesium cations occupy all of eight subcells (which have half of cubic cell edge) body-center sites as fluorine (F^-) anions do in the fluorite structure. The structure can be understood as $[\text{MoCl}_5\text{O}]$ close-packing in face-centered cubic (fcc) and caesium filling its all tetrahedra holes (see the topological drawing in the right upper of the figure). Each caesium cation is linked with four $[\text{MoCl}_5\text{O}]$ octahedra by 12 chlorine or oxygen anions with bond distance ($\text{Cs}-\text{Cl}(\text{O})$) of 3.622 Å, so its coordination number is 12 (see the caesium coordination polyhedron in the bottom of the figure). Each $[\text{MoCl}_5\text{O}]$ octahedron is linked with 8 caesium cations in cubic shape. The bond distance of $\text{Mo}-\text{Cl}(\text{O})$ in $[\text{MoCl}_5\text{O}]$ octahedron is 2.346 Å. Chlorine and oxygen anions are of disorder in the structure and occupy in the same equational positions. Caesium's ionic radius is larger than potassium's, so its structure is different from $\text{K}_2(\text{MoOCl}_5)$ in which chlorine and oxygen anions are of order and occupy their own positions [2]. For this cause, the title compound has higher symmetry in structure than $\text{K}_2(\text{MoOCl}_5)$ does.

Table 1. Data collection and handling.

Crystal:	dark green octahedron, size $0.08 \times 0.08 \times 0.08$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	91.16 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis RAPID, ω/ϕ
$2\theta_{\text{max}}$:	72.26°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	225, 166
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 120
$N(\text{param})_{\text{refined}}$:	7
Programs:	SHELXL-97 [3], DIAMOND [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	8c	1/4	1/4	1/4	0.0418(3)	U_{11}	U_{11}	0	0	0
Mo(1)	4a	0	0	0	0.0661(7)	U_{11}	U_{11}	0	0	0
Cl/O(1) ^a	24e	0	0.7707(2)	0	0.0424(6)	U_{11}	U_{11}	0	0	0

a: $\text{Cl/O}(1) = 0.83\text{Cl} + 0.17\text{O}$

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