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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Crystal Structure of $Cu_4UO_2(MoO_4)_2(OH)_6$

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Abstract – The formation of $Cu_4UO_2(MoO_4)_2(OH)_6$ in the UO_3–CuO–MoO_3–H_2O system was established by the method of hydrothermal synthesis. The obtained crystals are monoclinic; the unit-cell parameters are: a = 19.8392(11) Å, b = 5.5108(3) Å, c = 6.1009(4) Å; γ = 104.477°; Z = 2; space group $B2/m$, ρ_{calcd} = 4.864 g/cm^3. The structure was calculated from 1393 independent nonzero reflections. Further least-squares refinements resulted in the value R = 0.030. The layers of copper coordination octahedra sharing edges can be distinguished in the framework structure. The symmetric uranyl groups are linked by tetrahedral molybdate anions into endless straight ribbons aligned in the c axis. The coordination polyhedron of the uranium atoms can be described as a tetragonal bipyramid. MoO_4 groups link the copper octahedra and compensate for the charge of the copper layer.

During the investigation of uranyl compounds with molybdate groups and divalent cations, the synthesis of compounds in the UO_3–CuO–MoO_3–H_2O system was performed under hydrothermal conditions over a period of 14 days (T = 280°C, p = 500 bar). Among the individual phases formed in the above mentioned system, we found compounds in the form of bright green crystals. The results of X-ray analysis of these crystals correspond to the formula $Cu_4UO_2(MoO_4)_2(OH)_6$ (I). The determination of the structure of I is obviously interesting because it represents a rare case of high content of divalent cations in the compounds of this group, and because it provides new information about secondary uranium minerals. The crystals of I are monoclinic, the unit-cell parameters are: a = 19.8392(11) Å, b = 5.5108(3) Å, c = 6.1009(4) Å; γ = 104.477(4)°;

Table 1. X-ray diffraction data for $Cu_4UO_2(MoO_4)_2(OH)_6$

d, Å	I	hkl	d, Å	I	hkl	d, Å	I	hkl	d, Å	I	hkl
9.614	7	200	3.252	100	501	2.637	15	$\bar{2}12$	2.127	10	301
5.797	5	101	3.203	30	600	2.627	60	$\bar{4}20$	2.119	5	420
5.333	6	010	3.196	20	410	2.575	10	402	2.090	5	711
4.804	85	400	3.110	30	$\bar{6}10$	2.503	50	701	2.077	5	$\bar{7}21$
4.419	40	301	3.080	50	$\bar{5}11$	2.475	85	212	2.058	15	$\bar{8}20$
4.240	30	210	3.050	70	002	2.428	30	$\bar{8}10$	2.043	10	$\bar{2}22$
4.091	100	$\bar{1}11$	2.907	70	202	2.359	20	$\bar{6}20(121)$	2.015	15	901
3.797	10	111	2.649	7	012	2.177	85	$\bar{6}12$	1.991	15	$\bar{4}22$
3.733	100	$\bar{3}11$									

Table 2. Atomic coordinates and individual thermal parameters of atoms in the structure of $Cu_4UO_2(MoO_4)_2(OH)_6$

Atom	x/a	y/b	z/c	B, Å^2	Atom	x/a	y/b	z/c	B, Å^2
U	0	0	0	0.681(5)	O_2	0.0498(3)	0.378(1)	0.500	1.5(1)
Mo	0.41922(3)	0.2977(1)	0	0.700(8)	O_3	0.3007(3)	0.1689(9)	0.500	0.82(8)
Cu_1	0.24959(5)	0.5046(2)	0	0.77(1)	O_4	0.0677(3)	0.286(1)	0	1.5(1)
Cu_2	0.250	0	0.250	0.75(1)	O_5	0.4339(2)	0.1461(8)	0.2492(7)	1.38(6)
O_1	0.2040(2)	0.2873(6)	0.2455(7)	0.82(6)	O_6	0.3282(3)	0.250(1)	0	1.18(9)

$Z = 2$; space group $B2/m$, $\rho_{calcd} = 4.864$ g/cm^3. The X-ray diffraction data for compound I are presented in Table 1. The refinement of the parameters was carried out for 24 reflections. The experimental data for structure determination were obtained on a CAD-4 automated diffractometer. After the absorption correction was applied, the structure was calculated from 1393 independent nonzero reflections satisfying the criterion $I > 3\sigma(I)$. The X-ray powder diffraction pattern was obtained using a camera-monochromator of the Guinier type (CuK_α radiation). All calculations were performed on a Micro Vax II computer.

Further least-squares refinement of atomic coordinates and anisotropic thermal parameters led to the values $R = 0.030$, $R_w = 0.031$. Atomic coordinates and individual thermal parameters, main interatomic distances and bond angles are listed in Tables 2, 3, and 4, respectively. The structure of the compound is presented in Fig. 1.

In the structure of $Cu_4UO_2(MoO_4)_2(OH)_6$, it is possible to distinguish the layers of copper octahedra aligned in the (011) plane. It is possible to divide these octahedra into two groups according to coordination type. The Cu_2 atom (located at the center of symmetry) is coordinated to four oxygen atoms of the hydroxyl groups (O_1 and O_3) and to two oxygen atoms of the molybdate groups (O_6). These last are separated from the copper atom by a much longer distance. All oxygen atoms of the hydroxyl groups are tridentate-bridged; oxygen atoms of the molybdate groups are tetradentate-bridged.

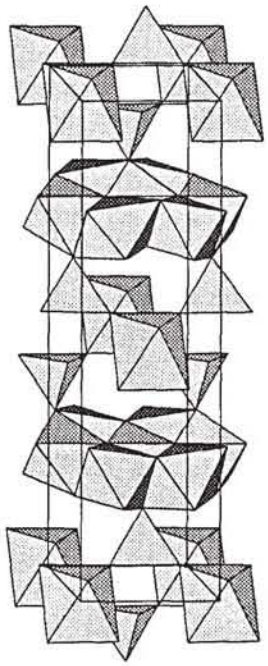

Fig. 1. *The structure of $Cu_4UO_2(M_6O_4)_2(OH)_6$.*

The coordination sphere of the Cu_1 atom (in the *m*-planes) involves five oxygen atoms of the hydroxyl groups and one oxygen atom of the molybdate group.

Table 3. The basic interatomic distances (Å) in the structure of $Cu_4UO_2(MoO_4)_2(OH)_6$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
U	2O(4)	1.796(3)	Cu(1)	2O(1)	2.012(2)	O(1)	O(1)	2.588(4)	O(2)	O(5)	2.786(4)
U	4O(5)	2.288(2)	Cu(1)	O(3)	2.265(3)	O(1)	O(1)	2.995(4)	O(2)	O(5)	2.978(4)
Mo	O(2)	1.738(3)	Cu(1)	O(6)	2.343(3)	O(1)	O(3)	2.908(3)	O(2)	O(6)	2.753(5)
Mo	2O(5)	1.793(2)	Cu(2)	2O(1)	2.016(2)	O(1)	O(3)	2.674(3)	O(3)	O(6)	2.988(4)
Mo	O(6)	1.759(3)	Cu(2)	2O(3)	1.933(2)	O(1)	O(6)	2.934(3)	O(4)	O(5)	2.992(4)
Cu(1)	2O(1)	1.989(2)	Cu(2)	2O(6)	2.359(2)	O(2)	O(2)	2.652(7)	O(4)	O(5)	2.823(4)
									O(5)	O(6)	2.765(3)

Table 4. The basic bond angles in the structure of $Cu_4UO_2(MoO_4)_2(OH)_6$

Atom 1	Atom 2	Atom 3	Angle, deg	Atom 1	Atom 2	Atom 3	Angle, deg
O(4)	U	O(4)	180(0)	O(1)	Cu(1)	O(1)	87.7(1)
O(4)	U	O(5)	93.4(1)	O(1)	Cu(1)	O(1)	101.0(1)
O(5)	U	O(5)	84.0(1)	O(1)	Cu(1)	O(1)	177.81(7)
O(5)	U	O(5)	96.0(1)	O(3)	Cu(1)	O(6)	165.1(1)
O(5)	U	O(5)	180(0)	O(1)	Cu(2)	O(1)	180.0(0)
O(2)	Mo	O(5)	114.96(9)	O(1)	Cu(2)	O(6)	83.83(9)
O(2)	Mo	O(6)	103.8(2)	O(3)	Cu(2)	O(3)	180.0(0)
O(5)	Mo	O(5)	115.9(2)	O(3)	Cu(2)	O(6)	92.37(8)
O(5)	Mo	O(6)	102.2(9)	O(6)	Cu(2)	O(6)	180.0(0)
O(1)	Cu(1)	O(1)	80.61(8)				

The distortion of the octahedron is attributed to the different kinds of oxygen atoms surrounding the Cu(1) atom and to the Jahn–Teller effect, as in the case of Cu_2. All CuO_6 octahedra are joined into sheets by shared edges. The linear and symmetric uranyl groups are united by the tetrahedral molybdate anions into endless straight ribbons composed of $[UO_2(MoO_4)_2]_n^{2n-}$, and aligned in the *c* axis. The coordination polyhedron of the uranium atom can be described as a tetragonal bipyramid that is rarely encountered in the structures of similar compounds. Four oxygen atoms belonging to four molybdate groups are arranged in the equatorial plane of the bipyramid, and the oxygen atoms of the uranyl group are located in the axial positions.

The molybdate anions of tetrahedral coordination are located between two neighboring uranyl groups aligned in the *c* axis. These link the sheets of copper octahedra and compensate the sheet charge. Two oxygen atoms of the MoO_4 tetrahedron coordinate two different uranyl groups, the third oxygen atom is included in the coordination sphere of three copper atoms, and the fourth is terminal.

The structure of the naturally occurring mineral derriksite $Cu_4UO_2(SeO_3)_2(OH)_6$ was reported in the literature [1]. Despite the difference in the composition, the parameters of the structure are close to the synthesized compound (a = 5.570(2) Å, b = 19.088(8) Å, c = 5.965(2) Å) with allowance for the rearrangement of the cell vectors. The difference in the space groups, however, indicates significant differences in these structures: the pattern of layer alternation is retained, but appear to be shifted in the structure of derriksite as compared to the structure of $Cu_4UO_2(MoO_4)_2(OH)_6$.

Moreover, the terminal oxygen atom in the MoO_4 tetrahedron is absent in the SeO_3 group in the derriksite (the coordination number of Se is reduced to three). This accounts for the structural differences between the two compounds.

REFERENCES

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