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Crystal structure of deloryite, $Cu_4(UO_2)[Mo_2O_8](OH)_6$

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Abstract

Deloryite, $Cu_4(UO_2)[Mo_2O_8](OH)_6$, $M = 946.10$, monoclinic, space group $C2/m$, $a = 19.94(1)$, $b = 6.116(2)$, $c = 5.520(3)$ Å, $\beta = 104.18(5)°$, $V = 652.8(1)$ Å^3, $Z = 2$, $\rho_c = 4.78$ g cm^{-3}, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 200.22$ cm^{-1}, dimensions $0.15 \times 0.1 \times 0.1$ mm^3, $F(000) = 852$, room temperature, $R = 0.064$ for 402 reflections with $|F| > 3\sigma(F)$. The crystal structure of deloryite, like its synthetic analogue as well as chemically and crystallographically related derriksite $Cu_4(UO_2)(SeO_3)_2(OH)_6$, contains layers formed by distorted $[Cu(O,OH)_6]$ octahedra with shared edges. The octahedral layers are linked by columns, built up of alternating pseudotetragonal $U^{[2+4]}O_6$ bipyramids and pseudotrigonal $Mo^{[4+1]}O_5$ bipyramids. Two MoO_5 bipyramids with shared edge form $[Mo_2O_8]$ dimers with Mo–Mo distances = 3.456(4) Å. The five-fold coordination of Mo revealed leads to a different description of the structural model of deloryite with respect to the earlier XRD study of its synthetic analogue. $Mo_2^{[4+1]}O_8$ dimers in deloryite replace the pairs of tetrahedra SeO_3E (E = lone-pair electrons) in derriksite.

Keywords: Deloryite; Crystal structure; Molybdate

1. Introduction

The new complex oxide deloryite, $Cu_4(UO_2)[Mo_2O_8](OH)_6$, was recently discovered in the southern part of the Cap Garonne mine near Le Pradet, Var, France [1] and approved by the CNMMN of IMA before publication. This preliminary X-ray diffraction study of deloryite reveals that the mineral is monoclinic, with $a = 19.83$; $b = 6.112$; $c = 5.529$ Å; $\beta = 103.9°$; space group $C2$, $C2/m$ or Cm and $Z = 2$. Concerning the dimensions of the unit cells and their composition there is a definite similarity between deloryite and orthorhombic derriksite, $Cu_4(UO_2)(SeO_3)_2(OH)_6$, which structure was reported in Ref. [2]. According to Ref. [1] the difference in space group symmetry between both minerals can be explained by the replacement of the trigonal pyramids SeO_3 in derriksite by the MoO_4 tetrahedra in deloryite. This idea has been confirmed by the structure determination of the synthetic analogue of deloryite, $Cu_4UO_2(MoO_4)_2(OH)_6$ [3]. However, such a model assumes a significant deficiency in the sum of the bond strength on the non-bridging oxygen which participates in the MoO_4 tetrahedron. Thus, our intention is to study the structure of deloryite and to characterize its relationship to derriksite.

2. Experimental

The parameters of the monoclinic unit cell of deloryite were refined on an Enraf-Nonius CAD-4F diffractometer using eight reflections collected in the interval $\theta = 15$–$20°$ (monochromated Mo Kα radiation, $\lambda = 0.71073$ Å): $a = 19.94(1)$, $b = 6.116(2)$, $c = 5.520(3)$ Å, $\beta = 104.18(5)°$, $V = 652.8$ Å^3. A total of 709 reflections with $|F_0| > 3\sigma(F_0)$ was collected in half of the reciprocal space, $\sin\theta/\lambda < 0.74$ Å^{-1}, from a crystal of deloryite with linear dimensions $0.15 \times 0.1 \times 0.1$ mm^3. There were 402 unique observations obtained after reflection averaging ($R_{\text{int}} = 0.044$). The software package AREN [4] was used for all calculations. The positions for U, Mo and Cu atoms were determined by a direct method on the basis of the centrosymmetric space group $C2/m$ with no systematic absences beyond those due to lattice centring. 171 normlized structure amplitudes E_{hkl} from the whole set (252) of the strongest E_{hkl} were included into 9000

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Table 1
Atomic coordinates and equivalent thermal parameters B_{eq}[a] for cations and isotropic U_j for anions in deloryite

Atom	x	y	z	B_{eq}, U_j (Å^2)
U	0	0	0	1.86(6)
Mo	0.4188(1)	0	0.2975(7)	1.14(8)
Cu(1)	0.2497(2)	0	0.505(1)	0.53(9)
Cu(2)	0.25	0.25	0	0.74(9)
O(1)	0.066(2)	0	0.289(6)	1.8(6)
O(2)	0.322(2)	0	0.254(6)	2.3(7)
O(3)	0.433(1)	0.250(4)	0.146(4)	1.9(4)
O(4)	0.448(1)	0	0.617(6)	1.2(6)
OH(1)	0.198(1)	0	0.831(6)	1.4(6)
OH(2)	0.203(1)	0.250(3)	0.281(4)	1.0(3)

[a] B_{eq} calculated from the anisotropic temperature factor corrections: $B_{eq} = 4/3 \Sigma_i \Sigma_j \beta_{ij} a_i a_j$.

triple productions of Sayre. The refinement of cationic positions and isotropic temperature factors led to $R_{hkl} = 0.16$. Subsequent F synthesis allowed us to localize six O atoms. The isotropic refinement by least-squares decreased R_{hkl} to 0.082 and the absorption correction (absorption coefficient μ = 200.22 cm^{-1}) [5] to 0.074. The final $R_{hkl} = 0.064$ was calculated with anisotropic temperature factors for cations and isotropic temperature factors for all O atoms. The relatively high value of R-factor obtained for the structure of deloryite with respect to its synthetic analogue ($R = 0.030$ for 1393 reflections) is due to several reasons: (i) the small size of available monocrystal obviously causes the low intensity of reflections, their small number and, consequently, the lower accuracy of their estimation. This conclusion can be confirmed by the extremely low value of the ratio $|F|_{max}/|F|_{min} = 8.4$ for deloryite; (ii) deloryite, as a natural product, contains some chemical impurities (e.g. SO_3, Al_2O_3) [1], which certainly create the structural imperfections. Refined atomic coordinates, selected interatomic distances and the sum of the bond strengths on the anions [6] are given in Tables 1, 2 and 3 respectively. The intensity calculations [7] for deloryite (Table 4) demonstrated a good correspondence with powder diffraction data.

3. Discussion

The main conclusion, found out as a result of the present study, is that the atomic arrangements in the structures of deloryite and its synthetic analogue are the same; however, the description of a tetrahedral coordination of Mo, accepted in Ref. [3], does not permit the achievement of a balance of the bond strengths on non-bridging O(4), which is 1.56 v.u. Therefore, we propose another description of the structure of deloryite.

Similarly to derriksite, the most specific feature of the structure is the layers parallel to (100), built by the distorted Cu octahedra with shared edges (Figs. 1, 2). Thus all O vertices belong to three Cu atoms, and brucite-like layers with hexagonal closest packing of O(2), OH(1) and OH(2) are formed. Cu(O,OH)$_6$ octahedra with two elongated distances Cu–O (Cu(1)–O(2) = 2.23; –OH(1) = 2.27; Cu(2)–O(2) = 2.32 Å × 2) exhibit typical Jahn–Teller distortion. The octahedral layers are connected by the polyhedral columns, formed by the alternating [Mo_2O_8] dimers and pseudotetragonal UO_6 bipyramids. The coordination of U with two relatively short U–O bonds (1.80 Å) and four elongated U–O bonds (2.30 Å) can be described as a compressed tetragonal bipyramid similar to the environment of U^{6+} in derriksite. According to Ref. [8] this configuration can also be

Table 2
Selected interatomic distances (Å) in deloryite[a]

Mo polyhedron	U polyhedron	Cu octahedra	
Mo–O(4) 1.71(3)	U–O(1) 1.80(3) × 2	Cu(1)–OH(2) 2.02(1) × 2	Cu(2)–OH(1) 1.94(1) × 2
O(3) 1.79(2) × 2	O(3) 2.30(2) × 4	OH(2) 2.04(1) × 2	
O(2) 1.88(4)	Average 2.13 {2.127}	O(2) 2.23(4)	OH(2) 1.99(2) × 2
O(4) 2.58(3)	Q.E. 1.015 {1.014}	OH(1) 2.27(3)	O(2) 2.32(2) × 2
	O(1)–O(3) 2.85(3) × 4	Average 2.10 {2.114; 2.101}	Average 2.08 {2.110}
Average [5] 1.96	O(1)′–O(3)′ 3.00(3) × 4	Q.E. 1.006 {1.009; 1.007}	Q.E. 1.010 {1.010}
O(2)–O(3) 2.86(4) × 2	O(3)–O(3) 3.05(3) × 2	O(2)–OH(2) 2.85(4) × 2	O(2)–OH(2) 2.85(4) × 2
O(4) 2.79(4)	O(3) 3.45(3) × 2	OH(2) 3.12(3) × 2	OH(1) 2.95(4) × 2
O(3)–O(4) 2.86(3) × 2	Average 3.03		
O(4) 2.96(3) × 2		OH(1)–OH(2) 2.67(3) × 2	OH(1) 3.11(1) × 2
O(3) 3.06(3)		OH(2) 3.41(3) × 2	OH(2)–OH(1) 2.67(3) × 2
O(4)–O(4)′ 2.70(4)			
Average 2.87		OH(2)–OH(2) 2.66(2) × 2	OH(1) 2.90(3) × 2
		OH(2) 3.05(3) × 2	O(2) 3.25(3) × 2
		Average 2.96	Average 2.45

[a] Figures in curly brackets represent the values of quadratic elongation and average bond lengths in the structure of derriksite.

Table 3
Bond strengths on the anions in deloryite

Anions	Cations				H(d)	H(a)	V_i	$I\Delta I_i$
	U	Mo	Cu(1)	Cu(2)				
O(1)	2.10						2.10	0.10
O(2)		1.08	0.23	0.18 × 2		1/6	1.84	0.16
O(3)	0.54	1.37				1/6	2.08	0.08
O(4)		1.7 + 0.16					1.86	0.14
OH(1)			0.20	0.49 × 2	5/6		2.01	0.01
OH(2)			0.41 × 2	0.43	5/6		2.08	0.08
Σ								0.57

Table 4
X-ray powder diffraction data of deloryite[a]

h	k	l	d_{calc}	d_{meas}	I_{calc}	I/I_{vis}
2	0	0	9.666	9.63	7	5
0	0	1	5.352	5.367	17	20
4	0	0	4.833	4.815	86	80
3	1	0	4.436	4.425	33	40
2	0	1	4.261	4.276	47	40
−1	1	1	4.097	4.100	100	100
1	1	1	3.805	3.804	20	10
−3	1	1	3.739	3.734	99	90
5	1	0	3.268	3.254	52	40
6	0	0	3.222		15	
4	0	1	3.216	3.214	28	25
−6	0	1	3.118	3.095	13	10
−5	1	1	3.088	3.074	24	5
0	2	0	3.058	3.053	26	10
2	2	0	2.916	2.915	30	35
−4	0	2	2.630	2.628	33	40
7	1	0	2.517		23	
−1	1	2	2.503	2.502	12	35
6	0	1	2.503		5	
2	2	1	2.484	2.482	49	60
−3	1	2	2.484			
1	1	2	2.367	2.365	24	25
−6	2	1	2.183	2.177	34	35
4	0	2	2.130	2.135	13	5
−8	0	2	2.062	2.051	20	10
−2	2	2	2.048		4	
9	1	0	2.027	2.021	7	5
−4	2	2	1.994	1.992	16	10
6	2	1	1.937	1.937	32	25
−1	3	1	1.912	1.907	11	10
−3	3	1	1.872		13	
−6	2	2	1.870	1.868	10	25
−9	1	2	1.832		8	
−4	0	3	1.825	1.825	2	5
−10	0	2	1.788	1.789	2	5
9	1	1	1.765	1.757	8	5
4	2	2	1.748		2	
−8	2	2	1.710	1.704	2	5
−10	2	1	1.662	1.655	21	10

[a] XRD pattern performed with a Guinier-Hagg camera (Cu Kα_1 radiation), d_{calc} and I_{calc} calculated using the program LAZY PULVERIX [7].

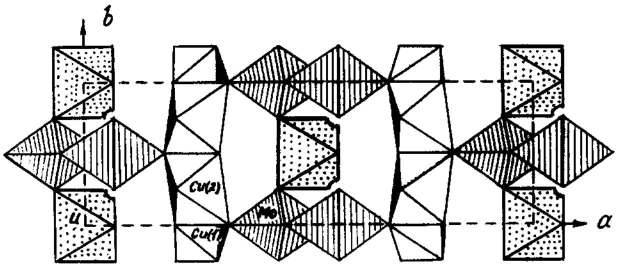

Fig. 1. Projection of deloryite on (001).

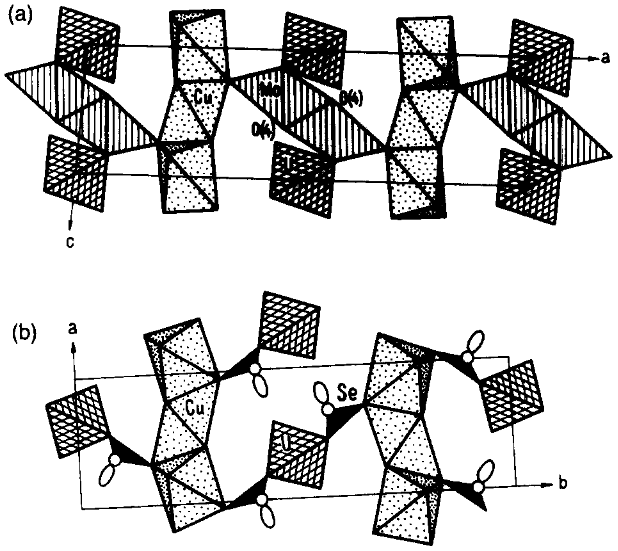

Fig. 2. Projections of (a) deloryite on (010) and (b) derriksite on (001).

considered as a uranyle cation UO_2 in square planar coordination.

The main difference between deloryite and derriksite is the formation of the pseudotrigonal MoO_5 bipyramids (Fig. 1) in the former instead of SeO_3 trigonal pyramids in the latter. The higher valency of Mo^{6+} with respect to Se^{4+} assumes the replacement of pairs of tetrahedra SeO_3E (E = lone-pair electrons) by $Mo_2^{[4+1]}O_8$ dimers with equal negative charges. Thus, additional oxygen O(4) in the structure of deloryite substitutes the lone-pair electrons of the Se^{4+}. As a consequence, the five-fold coordination of Mo atoms occurs, with the central cation removed in the direction of one apex, and in the first approach Mo atoms have pseudotrigonal pyramidal coordination with four short distances Mo–O (average 1.81 Å). However, it must be completed to a bipyramid by the additional O(4)′ on elongated distance 2.58 Å, which improves the sum of the bond strengths. As a result, the contacts of two pseudotrigonal Mo bipyramids through one short edge O(4)–O(4)′ = 2.70 Å lead to the formation of the dimers [Mo_2O_8]. Because calculations of quadratic elongation [9] and average bond lengths (Table 2) show no change in overall distortion of UO_6 bipyramids and Cu octahedra, the increase of unit cell volume in deloryite (652.8 $Å^3$) with respect to derriksite (634.0 Å) must be caused solely by the larger volumes of [Mo_2O_8] dimers in comparison with the groups [SeO_3]. The difference in space group symmetry between deloryite and derriksite determines the distinctions in arrangement of [Mo_2O_8] dimers and tetrahedral pairs [SeO_3E]$_2$ in their structures. Fig. 2 shows that [Mo_2O_8] dimers have a parallel orientation along [100] since the neighbouring tetrahedral pairs [SeO_3E]$_2$ along [010] are rotated by approximately 90°.

The five-fold coordination of Mo is relatively rare with respect to more typical Mo octahedra and tetrahedra [10]. According to Ref. [11] it can be considered as a tetrahedron with additional vertex located over the stretched triangle face. The Mo polyhedra in deloryite correspond to this model, as the edges of the trigonal faces, opposite to the additional vertices O(4)′, are elongated (2.96 × 2 and 3.06 Å) with respect to three others (2.86 × 2 and 2.79 Å). The five-fold coordination of Mo in combination with Mo octahedra is found in $K_2Mo_3O_{10}$ [12], where five bonds Mo–O are within the interval 1.66–2.00 Å, as well as in $Ce_{16}Mo_{21}O_{56}$ [13], where Mo atoms are surrounded by five O atoms in an approximately square pyramidal environment with Mo–O distances of 1.949–2.164 Å, and in some other structures.

Structural similarities between deloryite and derriksite confirm the conclusion that cationic frameworks dominate in the structures with heavy and high-valence cations [11,14]. Since there is a tendency to regular arrangement of these cations, which must lead to the formation of fixed and equal distances between them, their real interatomic distances often correlate to the type of linkage between their coordination polyhedra. In connection with Mo-containing compounds it is worth noting that in structures of Mo oxides [15] the distances Mo–Mo = 3.60–4.05 Å assume contact between Mo polyhedra through the vertices; 3.20–3.44 Å through the edges; 3.50–3.86 Å attributed to contacts between Mo octahedra and tetrahedra through shared vertices; and 3.24–3.40 Å between Mo octahedra and pentagonal pyramids with shared edges. Similar correlations were revealed in the Mo-containing structures with another type of cation (besides Mo) [16]. However, the presence of other cations leads to the formation of more isolated Mo polyhedra with respect to the framework of "pure" Mo oxides, since the distances Mo–Mo do not increase. Moreover, the five-fold coordination of Mo was found specifically in these structures. Thus, the contact of two five-fold Mo polyhedra through the edge assumes a distance Mo–Mo = 3.41 Å [11]. In this context the formation of isolated dimers [Mo_2O_8] with rather short distances Mo–Mo = 3.456(4) Å in the structure of deloryite, close to the values given above, does not seem to be an exception.

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