

Description and crystal structure of vajdakite, $[(\text{Mo}^{6+}\text{O}_2)_2(\text{H}_2\text{O})_2\text{As}^{3+}_2\text{O}_5]\cdot\text{H}_2\text{O}$ —A new mineral from Jáchymov, Czech Republic

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ABSTRACT

Vajdakite, a new mineral from Jáchymov, NW Bohemia, Czech Republic, forms minute acicular, gray-green crystals associated with arsenolite, scorodite, parascorodite, kaňkite, annabergite, köttigite, pyrite, marcasite, nickelskutterudite, and löllingite. Microprobe analysis gave (in wt%): As = 27.72, Mo = 35.39, O = 36.66, total = 99.77. The simplified chemical formula is $[(\text{Mo}^{6+}\text{O}_2)_2(\text{H}_2\text{O})_2\text{As}^{3+}_2\text{O}_5]\cdot\text{H}_2\text{O}$. The mineral is monoclinic, $P2_1/c$, $a = 7.0515(6)$, $b = 12.0908(9)$, $c = 12.2190(14)$ Å, $\beta = 101.268(9)^\circ$, $V = 1021.7(2)$ Å³, $Z = 4$, $D_{\text{meas}} = 3.50(2)$ g/cm³, and $D_{\text{calc}} = 3.509$ g/cm³. The strongest lines in the powder X-ray diffraction pattern $d(I)(hkl)$ are: 6.046 (100)(020), 3.324 (59)(023), 6.915 (26)(100), 2.264 (19)(310), 3.457 (16)(200), 2.624 (15)(230), and 3.819 (10)(031). Vajdakite is optically positive, with $X \parallel b$ and $Z \wedge c = 12^\circ$; elongation is positive. Its birefringence is 0.28, with $2V_{\text{calc}} = 35.1^\circ$, $n_\alpha = 1.757(2)$, $n_\beta = 1.778(2)$, and $n_\gamma = 2.04(1)$. The pleochroic scheme is $X \sim Y =$ light greenish gray, and $Z =$ yellowish gray. Crystal size varies between 0.1 to 0.5 mm. TG curve and IR spectra show that vajdakite contains two distinct types of water molecules. The crystal structure was solved by direct methods (MoK α radiation) and refined using 1787 unique reflections to $R = 0.0455$, $R_w = 0.1143$. There are double chains built up by two individual chains with a sequence -O-As-O-Mo- interconnected by oxygen atoms from two triangular AsO₃ groups and two structurally non-equivalent MoO₅(H₂O) octahedra. The two vertex-sharing, triangular AsO₃ groups form an (As₂O₅)⁴⁻ diarsenite group. The first type of water molecule is not included in the coordination, but the second one is in octahedral coordination around Mo. The water molecules are linked by a complicated net of interlayer and intralayer hydrogen bonds.

INTRODUCTION

The city of Jáchymov (St. Joachimsthal) is located on the southern slope of the Krušné hory Mts. (Erzgebirge), approximately 20 km north of Karlovy Vary, NW Bohemia, Czech Republic, central Europe (Fig. 1). In this area, Mo anomalies associated with Ag + As + Co + Ni ± Bi and U mineralizations of the Geschieber vein of the Svornost mine have been studied in the framework of the project “Secondary minerals from the Jáchymov ore district,” which was supported by the Grant Agency of the Czech Republic. That study confirmed the occurrence of a new, natural Mo-bearing compound that we named vajdakite, which has been investigated in detail, including solution and refinement of its crystal structure (Ondruš et al. 1997a, 1997b, 1997c).

Holotype material has been deposited in the mineralogical collection of the National Museum, Prague, Czech Republic (the acquisition number P1p 19/98). The new mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the IMA in 1999 (98-031). The name is in honor of mineralogist Josef Vajdak (born 1930, Montana, U.S.A.), who drew our attention to this species, for his signifi-

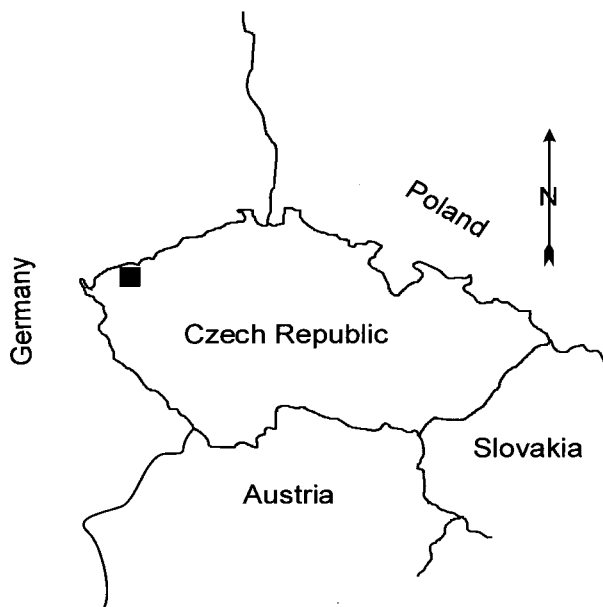


FIGURE 1. Sketch map showing the geographic localization of the Jáchymov ore district (black square).

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cant contributions to mineralogical research on the Jáchymov ore district.

Vajdakite belongs to a small group of diarsenites that includes such minerals as paulmooreite [with structure motif $(As_2O_5)^+$; Araki et al. 1980], gebhardite, fetiasite, leiteite, and manganarsite (Mandarino 1999).

DEPOSIT CHARACTERISTICS

The Jáchymov ore district coincides with the immediate area of the town and its close surrounding. The altitude of the ore district ranges from 450 to 850 m. The region is underlain by a complex of metamorphosed sedimentary rocks of Cambrian to Ordovician age, representing the cover of a Variscan granite pluton. The majority of the ore minerals were deposited during Variscan mineralization from mesothermal fluids.

Jáchymov is a classic deposit of both $Ag + As + Co + Ni \pm Bi$ and U mineralizations. The ore district is bounded by several faults, including the major northern fault zone. The fault pattern and location of several main mineral veins is shown in Ondruš et al. (1997b). The faults and veins are vertical or abrupt. The widths of the most important faults and fault zones are variable, reaching up to 20 m. For centuries, mineralized veins were classified according to their orientation as N-S trending veins (so-called "midnight veins") and E-W trending veins ("morning veins").

The mineralization is irregular. Barren parts of veins alternate with rich ore lenses and ore pillars developed at places. The N-S trending veins tend to be richer and wider, while the E-W trending veins show more variation in trend and dip as well as thickness. The richest parts of the deposit coincide with splitting of a vein into several branches. Toward contacts with granite, the veins become barren and disappear.

The mineralization of the deposit can be classified into five stages: (1) Sn-W stage connected with autometamorphism of younger granites, (2) quartz-sulfide stage, which is of minor importance, (3) carbonate-uraninite mineralization with fluorite, (4) carbonate-arsenide stage with native Ag and Bi, arsenides of Ni-Co, and minor uraninite, (5) sulfarsenide stage with native As in botryoidal aggregates up to 1 m, sulfarsenides, and sulfides of Ag. The uraninite, arsenide, and sulfarsenide stages are the most widespread ones in the district.

Mining of silver ores started in 1516 and the first rich discoveries (the largest recorded piece of native Ag was 280 kg) were followed by a strong silver fever. Jáchymov was rapidly developing and its population reached 18 200 in 1534. Over the centuries, mining of Ag was followed by mining of Co, Ni, Pb, As, and Bi, and later by mining of U and Ra. Mining activities continued with interruptions until 1962 when the last mines were closed.

Since 1992, extensive mineralogical research, focused chiefly on secondary minerals, has been carried out in the Jáchymov ore district. This research has shown that the Jáchymov district hosts about 340 minerals, and 30 new natural phases that formed there primarily because of diverse primary mineralization stages and the low overall content of carbonates resulting in the acidic character of the whole deposit.

OCCURRENCE AND PARAGENESIS

Vajdakite, one of the rarest secondary minerals at Jáchymov, has been found in only one place—on fractures in proximity to a vein approximately 5 cm thick. Vajdakite occurs with a strongly weathered, intimately intergrown mixture of pyrite, marcasite, nickelskutterudite, löllingite, and native As in the Geschieber vein, on the 12th level of the Svornost shaft. The mixture has partly to completely altered to a mixture of compact, gray-black scorodite (with a metallic luster) and arsenolite. Other associated secondary minerals are parascorodite, kaňkite, annabergite, and köttigite.

Vajdakite formed in an environment of concentrated sulfuric acid, in the presence of As_2O_3 in significant concentrations. No other minerals containing Mo were found in the assemblage. It is suggested that amorphous, finely dispersed Mo sulfides (jordisite) or oxides, soluble in the acid solutions, served as a source of Mo. The solutions carrying Mo probably attained elevated concentrations that resulted in crystallization of the new phase.

Vajdakite forms minute acicular crystals or continuous crusts, which form the border of a strongly corroded veinlet. The crystals are translucent and may easily be overlooked. Their color varies from gray-green to grass-green, and aggregates of yellow-green crystals were observed in some cases. Crystals are lath shaped, and their size varies from 0.1 to 0.5 mm. Their termination is highly irregular with needle-like features (Fig. 2). Rarely, crystal aggregates cover areas of several square centimeters. Laterally, the vajdakite gives way to gray-green scorodite in spherical and botryoidal aggregates.

PHYSICAL AND OPTICAL PROPERTIES

The streak of vajdakite is white to light gray-green, and its luster is vitreous. The density of crystal aggregates measured by the flotation method in Clerici solution is $3.50(2) \text{ g/cm}^3$ and the calculated crystal density (for $Z = 4$) is 3.509 g/cm^3 . Vajdakite is slightly soluble in water.

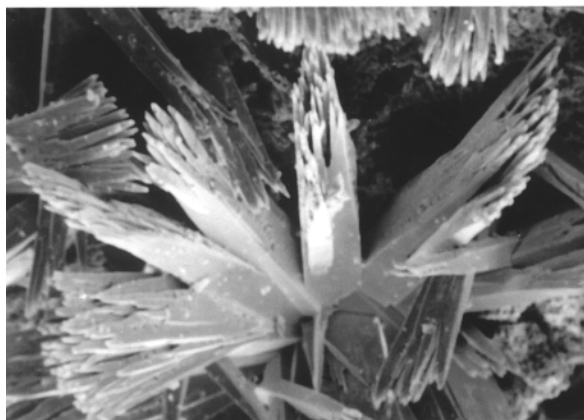


FIGURE 2. Scanning electron microscope photograph of aggregate of acicular vajdakite crystals. Note crystal terminations, which are highly irregular with an arrangement of radiating, parallel needle-like features. Magnification 300.

Vajdakite is optically positive ($2V_{\text{calc}} = 35.1^\circ$), with $X \parallel b$ and $Z \wedge c = 12^\circ$. The elongation is positive, and the birefringence is 0.28. The refractive indices, measured in Na-light, are $n_\alpha = 1.757(2)$, $n_\beta = 1.778(2)$, and $n_\gamma = 2.04(1)$. The pleochroic scheme is $X \sim Y = \text{light gray to light greenish gray}$ and $Z = \text{yellowish gray}$. The compatibility factor calculated from the Gladstone-Dale rule is -0.019 .

The orientation of optical and crystallographic directions in vajdakite is shown in Figure 3. The orientation of the cleavage was inferred from a comparison of optical and powder X-ray diffraction (XRD) data. Cleavage is perfect parallel to (100) and good parallel to (010).

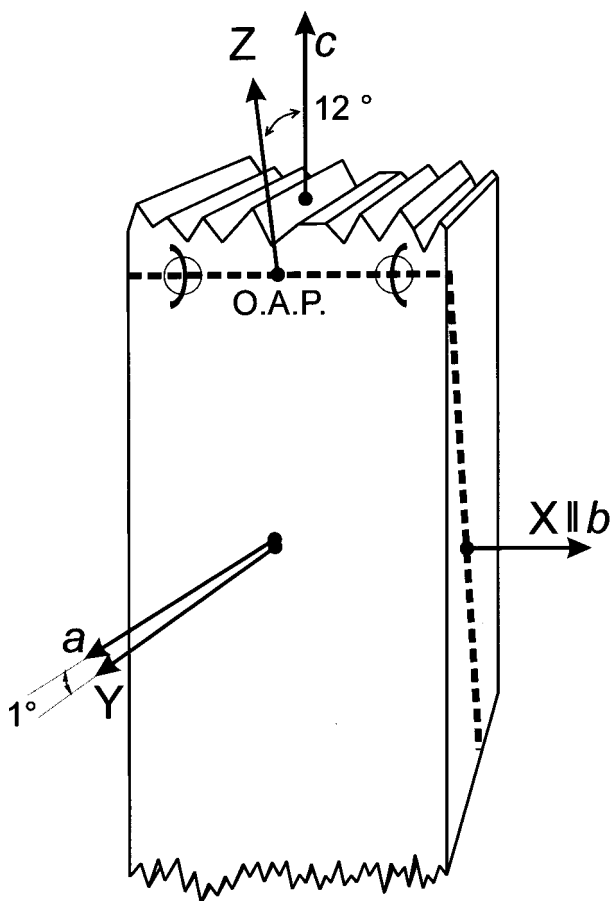


FIGURE 3. Optical orientation of vajdakite.

TABLE 1. Thermal analysis of vajdakite from Jáchymov

Temperature range (°C)	TG		Tentative assignment	DTA	
	Weight loss (wt%)	Temperature at loss maximum (°C)		Temperature at DTA maximum (°C)	Reaction type
50–145	3.5	105	1 H ₂ O	120, 135	Endo
145–240	7.2	180	2 H ₂ O	210, 225	Endo
240–285	3.0	255		265	Endo
285–330	1.5	320			
330–440	11.9	375	1 MoO ₃	385	Endo
440–520	9.5	470			
520–765	0.6	–			
765–		–	As ₂ O ₃ + MoO ₃	900	Exo

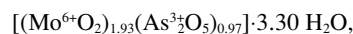
CHEMICAL COMPOSITION

The qualitative and quantitative chemical compositions of vajdakite were measured with a scanning electron microscope (CamScan 4) equipped with an energy-dispersive analyzer (LINK eXL) and a wavelength-dispersive analyzer (Microspec WDX-3PC). The qualitative X-ray spectrum of vajdakite indicated the presence of only two major elements—Mo and As.

Quantitative chemical composition was determined from three electron microprobe analyses. The following instrumental conditions were used: operating voltage = 20 kV, sample current = 20 nA, and specimen beam size = 5 × 5 μm. Arsenolite (As, O), molybdenum (Mo) were used as standards and the $\phi(\rho Z)$ correction procedure was used for calculation of all quantitative analyses. Quantitative determination of water was derived from oxygen content only.

Water and thus hydrogen were unambiguously detected by IR and TG. The thermal analysis could not be used because the individual decomposition reactions ran simultaneously, so the TG curve was extremely complicated (Fig. 4, Table 1).

Table 2 summarizes the results of three analyses and the ideal composition of the simplified formula. The empirical formula of vajdakite calculated on the basis of twelve oxygen atoms per formula unit is:



resulting in simplified formula $(\text{MoO}_2)_2 \text{As}_2\text{O}_5 \cdot 3 \text{ H}_2\text{O}$. This formula can be written also as $[(\text{Mo}^{6+}\text{O}_2)_2(\text{H}_2\text{O})_2 \text{As}^{3+}_2\text{O}_5] \cdot \text{H}_2\text{O}$, based on single-crystal and IR analyses. According to the inor-

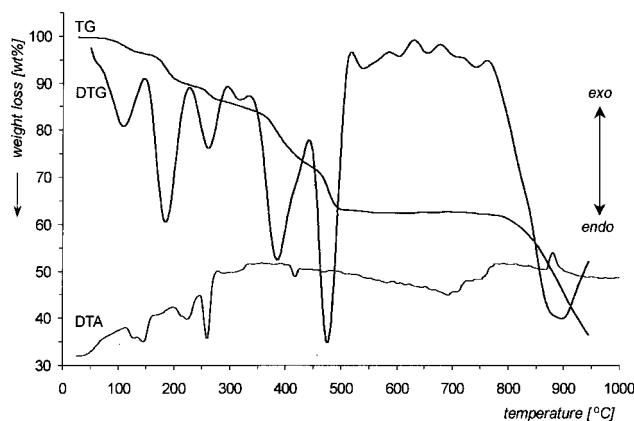


FIGURE 4. TG, DTG, and DTA curves of vajdakite from Jáchymov, Czech Republic.

TABLE 2. Chemical analyses of vajdakite (wt%) from Jáchymov

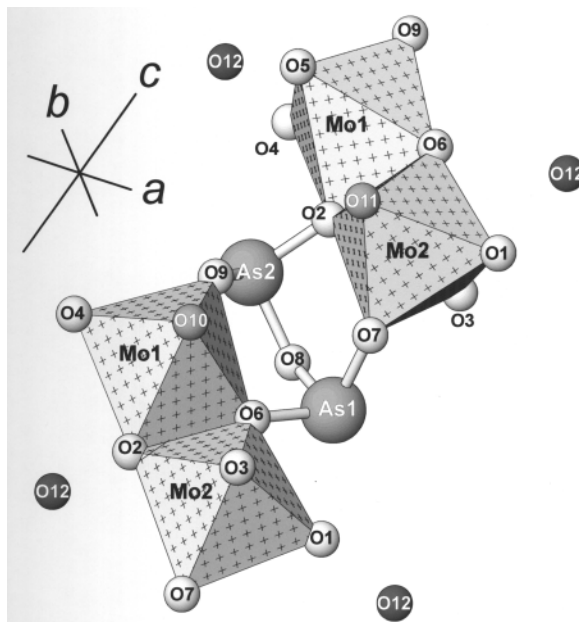
	1	2	3	4	5	
As	26.35–27.96	27.72	27.76	As ₂ O ₃	36.59	36.65
Mo	35.04–36.52	35.39	35.55	MoO ₃	53.09	53.34
O	36.02–37.15	36.66	35.57			
H		1.26*	1.11	H ₂ O	11.34	10.01
Total		101.03	100.00		101.03	100.00

Notes: 1 = range of three analyses, 2 = average of three microprobe chemical analyses, 3 = ideal composition as required by formula (Mo⁶⁺O₂)₂As₂³⁺O₅ · 3 H₂O, 4 = chemical analysis 1 recalculated to oxides, 5 = ideal composition as required by formula (Mo⁶⁺O₂)₂As₂³⁺O₅ · 3 H₂O.

* Value recalculated from electroneutral formula.

ganic chemical nomenclature, vajdakite can be named as bis[dioxomolybdenum(VI)]-diaqua-diarsenite hydrated (Block et al. 1990).

On the basis of the interpretation of the crystal structure of vajdakite, the calculated inter-atomic distances (Table 3) and bond valences (Table 4) unequivocally indicate the valences of Mo and As atoms in the mineral. Arsenic is trivalent whereas the valence of molybdenum (VI) may be inferred both from chemical formula keeping the compound electroneutral and from bond valence sums. Moreover, drawings displaying the crystal structure of vajdakite show that two arsenic atoms share one common oxygen forming the diarsenite group (As₂O₃)⁺ (see Fig. 5).

**FIGURE 5.** Basic structural motif found in the crystal structure of vajdakite, [(Mo⁶⁺O₂)₂(H₂O)₂As₂³⁺O₃]-H₂O.**TABLE 3.** Bond lengths (Å) and angles (°) for vajdakite

Mo1-O4	1.691(6)	O4-Mo1-O5	103.8(3)	O7-Mo2-O2	87.9(2)
Mo1-O5	1.706(6)	O4-Mo1-O9	106.2(3)	O6-Mo2-O2	70.4(2)
Mo1-O9	1.914(6)	O5-Mo1-O9	95.3(3)	O3-Mo2-O11	170.1(3)
Mo1-O2	2.055(5)	O4-Mo1-O2	94.3(3)	O1-Mo2-O11	86.3(3)
Mo1-O6	2.217(6)	O5-Mo1-O2	99.5(3)	O7-Mo2-O11	78.3(3)
Mo1-O10	2.309(6)	O9-Mo1-O2	151.0(2)	O6-Mo2-O11	78.0(2)
Mo2-O3	1.687(6)	O4-Mo1-O6	156.4(3)	O2-Mo2-O11	80.8(2)
Mo2-O1	1.710(6)	O5-Mo1-O6	96.4(3)	O7-As1-O8	99.4(3)
Mo2-O7	1.911(6)	O9-Mo1-O6	83.6(2)	O7-As1-O6#1	96.2(3)
Mo2-O6	2.018(5)	O2-Mo1-O6	70.1(2)	O8-As1-O6#1	97.0(3)
Mo2-O2	2.233(5)	O4-Mo1-O10	82.8(3)	O9-As2-O2#2	96.6(3)
Mo2-O11	2.289(7)	O5-Mo1-O10	173.2(3)	O9-As2-O8#2	97.6(2)
As1-O7	1.750(6)	O9-Mo1-O10	81.4(2)	O2#2-As2-O8#2	98.2(3)
As1-O8	1.786(5)	O2-Mo1-O10	81.1(2)	As2#1-O2-Mo1	124.1(3)
As1-O6#1	1.822(6)	O6-Mo1-O10	77.4(2)	As2#1-O2-Mo2	127.6(3)
As2-O9	1.778(6)	O3-Mo2-O1	103.6(3)	Mo1-O2-Mo2	108.3(2)
As2-O2#2	1.793(6)	O3-Mo2-O7	99.6(3)	As1#2-O6-Mo2	121.3(3)
As2-O8#2	1.817(5)	O1-Mo2-O7	102.8(3)	As1#2-O6-Mo1	126.7(3)
O2-As2#1	1.793(6)	O3-Mo2-O6	100.6(3)	Mo2-O6-Mo1	110.3(3)
O6-As1#2	1.823(6)	O1-Mo2-O6	93.7(3)	As1-O7-Mo2	129.9(4)
O8-As2#1	1.817(5)	O7-Mo2-O6	150.1(3)	As1-O8-As2#1	127.6(3)
		O3-Mo2-O2	89.5(3)	As2-O9-Mo1	119.9(3)
		O1-Mo2-O2	161.2(3)		

Note: Symmetry transformations used to generate equivalent atoms: x, -y + 1/2, z - 1/2; x, -y + 1/2, z + 1/2.

TABLE 4. Bond valences and their sums (v.u.) for vajdakite

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	S
Mo1		0.67		1.79	1.73	0.43			0.98	0.34			5.94
Mo2	1.71	0.41	1.81			0.74	0.99				0.36		6.02
As1						0.91	1.11	1.01					3.03
As2		0.99						0.93	1.03				2.95
H1										0.83		0.17	1
H2			0.15		0.22					0.63			1
H3											0.83	0.17	1
H4	0.05									0.17	0.78		1
H5				0.19								0.81	1
H6	0.21											0.81	1
Σ excluding H	1.71	2.07	1.81	1.79	1.73	2.09	2.10	1.94	2.01	0.34	0.36	0	
Σ including H	1.95	2.07	2.00	1.99	1.95	2.09	2.10	1.94	2.01	1.97	1.96	1.96	

THERMAL DATA

TG, DTG, and DTA curves were recorded on TG 750 Stanton Redcroft thermobalance. The operating conditions were: sample weight = 0.797 mg (TG analysis) and 32 mg (DTA analysis), heating rate = 10 °C/min, dynamic air atmosphere = 10 ml/min, and temperature range = 20–1000 °C (Fig. 4).

Tentative assignment and interpretation of the TG and DTA curves of vajdakite are as follows (Table 1). Vajdakite dehydrates in two steps, with one water molecule (probably corresponding to lattice water with O12, see crystal structure) liberated first at 50–145 °C, and two additional water molecules (probably corresponding to water with O10 and O11, see crystal structure) released in the range of 145–240 °C. Stepwise release of one MoO₃ molecule is observed at 240–765 °C. The remaining MoO₃ and As₂O₃ are released at temperatures higher than 765 °C. Schematically, the thermal decomposition of vajdakite is characterized by the following sequence of reactions: (MoO₃)₂As₂O₅ · 3 H₂O (–1 H₂O/105 °C) → (MoO₃)₂As₂O₅ · 2 H₂O (–2 H₂O/180 °C) → (MoO₃)₂As₂O₅ (–1 MoO₃/320–375–470 °C) → MoO₂As₂O₄ → MoO₃↑ + As₂O₃.

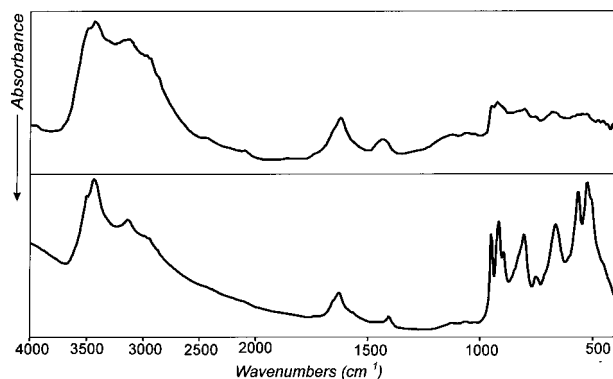


FIGURE 6. The infrared spectra of vajdakite from Jáchymov, Czech Republic. (a) DRIFT-diffusion reflectance spectrum (above), (b) KBr pellet (below).

INFRARED ABSORPTION SPECTRA

Infrared absorption spectra in the 400–4000 cm⁻¹ range were recorded with a Nicolet 740 FTIR spectrometer using KBr pellets and the diffusion reflection mode, and the results are shown in Figure 6. The IR spectrum of vajdakite measured in the KBr pellet is interpreted in Table 5.

Papers by Cotton and Wing (1965), Selbin (1966), Baran et al. (1981), and Tossell (1997) were used for the interpretation of the IR spectrum of vajdakite. Bands at 951, 917, and 895 cm⁻¹ were assigned to ν Mo-O_t (terminal oxygen), ν Mo-O_{br} (bridging oxygen), and ν Mo-O-Mo stretching vibrations, respectively. Bands at 803 and 750 cm⁻¹ are connected with ν AsO₂ and ν As-O-As stretching vibrations. A band at 664 cm⁻¹ is also assigned to ν As-O-As stretching vibration. Finally, the bands at 566, 526, 510sh (where the abbreviation “sh” means shoulder), and 465sh may be assigned to δ AsO₂, δ As-O-As, and δ MoO₂ bending vibrations and ν Mo-H₂O stretching vibrations.

Characteristic ν OH stretching vibrations at 3478sh, 3417, and 3117 cm⁻¹, δ H₂O bending vibrations at 1650sh and 1623 cm⁻¹, and H₂O libration modes at 830sh, 720sh, and 610sh have also been observed. The values of wave-numbers of these vibrations indicate that some hydrogen bonds are involved in the crystal structure of vajdakite. The presence of two kinds of structurally different water molecules may be inferred from the band at 1623 cm⁻¹ (with a shoulder at 1650 cm⁻¹) relating to the δ H₂O bending vibration. This interpretation is supported and confirmed by thermogravimetric analysis.

POWDER X-RAY DIFFRACTION

Powder XRD data were collected using a Philips X'Pert MPD diffractometer equipped with a sealed copper tube and a graphite secondary monochromator. The high voltage was set to 40 kV and the tube current was set to 40 mA. Diffraction data were collected in the range from 3 to 130.005 °2 θ using CuK α radiation, with a step size of 0.015 °2 θ and an exposure time of 10 sec per step. To minimize the complicated background shape caused by the glass sample holders, the sample studied was placed atop a flat silicon wafer in an alcohol suspension and allowed to dry.

TABLE 5. Infrared absorption spectrum of vajdakite

ν (cm ⁻¹)		Tentative assignment
3478	s, sh	ν OH stretching vibrations of hydrogen bonded water molecules
3417	vs	
3117	s	
1650	sh	δ H ₂ O bending vibrations of hydrogen bonded water molecules
1623	w-m	
1401	w	overtone or combination band ?
951	s	ν MoO _t stretching vibrations
917	s	ν MoO _{br}
895	m-s	ν Mo-O-Mo
830	sh	L H ₂ O libration mode
803	s	ν AsO ₂ , As-O-As stretching vibrations
750	m	
720	sh	L H ₂ O libration mode
664	s	ν As-O-As stretching vibrations
610	sh	L H ₂ O libration mode
566	vs	δ AsO ₂ , As-O-As, and MoO ₂ bending vibrations, ν Mo-H ₂ O stretching vibrations
526	vs	
510	s, sh	
465	w,sh	

Notes: Used intensity scale: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, character of absorption maxima: sh = shoulder, b = broad, t = terminal, br = bridging.

The XRD pattern was indexed on the basis of the refined crystal structure data (see below). Peak positions and intensities were calculated using an asymmetric Pearson VII profile shape function by program package ZDS v. 6.01 (Ondruš 1993). The powder pattern is presented in Table 6.

Because there are a large number of peak overlaps in the powder pattern of vajdakite, we refined the unit-cell parameters from the powder data using the Rietveld method as $a = 7.0515(6)$, $b = 12.0908(9)$, $c = 12.2190(14)$ Å, $\beta = 101.268(9)^\circ$, $V = 1021.7(2)$ Å³, and the space group is $P2_1/c$. The axial parameter ratio is $a:b:c = 0.583:1:1.0106$, and number of formula units per unit cell is $Z = 4$.

CRYSTAL STRUCTURE

For the crystal-structure solution, a needle-shaped fragment of vajdakite was investigated using a CAD4-MACHIII four-circle single crystal diffractometer with MoK α radiation. The crystallographic data obtained are summarized in Table 7. The crystal structure was solved by direct methods (SHELXS86, Sheldrick 1990) and refined by a full-matrix, least-squares procedure based on F^2 (SHELXL93, Sheldrick 1993). Scattering factors were those employed in the SHELX programs. Absorption factors were neglected because of the small dimensions of the crystal and minimal length of the diffraction path through the crystal during the measurement.

TABLE 6. X-ray powder diffraction pattern of vajdakite from Jáchymov ($I_{rel} \geq 1$)

I_{rel}	d_{obs}	d_{calc}	h	k	l	I_{rel}	d_{obs}	d_{calc}	h	k	l	I_{rel}	d_{obs}	d_{calc}	h	k	l
3	8.524	8.511	0	1	1	2	2.3658	2.3666	1	2	4	3	1.5499	1.5498	2	7	$\bar{1}$
26	6.915	6.916	1	0	0			2.3644	1	4	$\bar{3}$			1.5473	1	6	$\bar{5}$
100	6.046	6.045	0	2	0	2	2.3047	2.3052	3	0	0	4	1.5162	1.5172	3	6	0
4	5.776	5.774	1	1	$\bar{1}$	8	2.2824	2.2827	2	3	2			1.5150	1	1	$\bar{8}$
2	5.040	5.042	1	0	$\bar{2}$			2.2826	1	5	0			1.5158	2	7	1
		5.036	1	1	1	19	2.2642	2.2644	3	1	0	3	1.4998	1.4995	0	8	1
7	4.551	4.551	1	2	0	2	2.2425	2.2429	1	2	$\bar{5}$	2	1.4728	1.4734	4	1	$\bar{3}$
8	4.458	4.449	1	2	$\bar{1}$			2.2424	0	5	$\bar{2}$			1.4729	1	8	$\bar{1}$
2	4.081	4.084	1	2	1	2	2.1850	2.1907	3	2	$\bar{1}$			1.4703	3	5	$\bar{5}$
6	3.922	3.921	1	1	2			2.1849	2	4	1	2	1.4587	1.4589	4	4	1
4	3.874	3.872	1	2	$\bar{2}$	3	2.0890	2.0887	1	5	$\bar{2}$	2	1.4011	1.3987	1	1	8
10	3.819	3.820	0	3	1	7	2.0011	2.0028	3	3	$\bar{2}$			1.4009	4	4	2
16	3.457	3.458	2	0	0			2.0010	3	3	0	2	1.3920	1.3930	4	3	$\bar{3}$
4	3.434	3.436	1	3	$\bar{1}$	5	1.9866	1.9872	0	6	$\bar{1}$			1.3919	3	7	$\bar{1}$
59	3.324	3.333	0	2	3	3	1.9264	1.9266	1	6	$\bar{1}$	6	1.3835	1.3831	5	0	0
		3.325	2	1	0			1.9246	3	3	$\bar{3}$	4	1.3485	1.3483	5	2	0
2	3.260	3.259	1	3	1	7	1.9201	1.9208	2	5	$\bar{1}$	2	1.20027	1.20166	2	1	$\bar{10}$
7	3.000	3.002	2	2	0	3	1.8710	1.8712	1	6	$\bar{2}$			1.20218	0	6	8
		2.996	0	0	4	3	1.8342	1.8343	3	4	$\bar{2}$	2	1.16663	1.16635	3	9	$\bar{1}$
2	2.930	2.931	0	4	1	3	1.7289	1.7289	4	0	0			1.16618	5	1	4
3	2.909	2.908	0	1	4	5	1.7115	1.7115	4	1	0	2	1.15313	1.15287	5	6	$\bar{1}$
5	2.887	2.890	1	3	2			1.7094	2	4	4			1.15365	6	2	$\bar{2}$
		2.887	2	2	$\bar{2}$	4	1.6757	1.6758	1	7	0	2	1.14840	1.14867	6	2	$\bar{3}$
		2.883	1	1	4			1.6756	3	0	4			1.14872	6	1	4
9	2.801	2.802	2	2	1	3	1.6696	1.6695	3	5	$\bar{2}$	2	0.99595	0.99607	4	9	3
2	2.768	2.770	2	0	$\bar{2}$	3	1.6621	1.6647	3	1	$\bar{6}$			0.99593	6	5	$\bar{2}$
3	2.745	2.746	1	4	$\bar{1}$			1.6597	3	1	4			0.99592	1	12	$\bar{1}$
15	2.624	2.624	2	3	0			1.6623	4	2	0			0.99567	3	11	$\bar{1}$
12	2.593	2.593	1	4	$\bar{2}$	2	1.6060	1.6059	4	2	1			0.99566	4	10	$\bar{2}$
5	2.515	2.518	2	2	2	2	1.5763	1.5768	4	3	$\bar{3}$	3	0.98470	0.98474	4	3	$\bar{11}$
		2.516	1	1	4			1.5757	0	3	7			0.98527	0	2	12
2	2.4871	2.4876	2	3	1			1.5757	3	4	3			0.98459	0	7	10

Note: Peak positions and intensities refined from powder data using the asymmetric Pearson VII PSF.

TABLE 7. Crystal data and structure refinement for vajdakite

Empirical formula	H ₆ As ₂ Mo ₂ O ₁₂	Diffractometer	Enraf-Nonius CAD4-MACHIII
Formula weight	539.77	Measured reflections	1935
Crystal system	Monoclinic	Independent reflections	1787 [$R(int) = 0.0489$]
Space group	$P2_1/c$	Absorption correction	none
a (Å)	7.0398(4)	Refinement method	Full-matrix least-squares on F^2
b (Å)	12.0682(13)	F(000)	1008
c (Å)	12.210(2)	Data / restraints / parameters	1786 / 0 / 145
β (°)	101.265(9)	Temperature (K)	293(2)
Volume (Å ³)	1017.4(2)	Final R indices [$I > 2\sigma(I)$]	$R = 0.0455$, $Rw = 0.1143$
Z	4	R indices (all data)	$R = 0.0580$, $Rw = 0.1243$
D_x (calculated) (g/cm ³)	3.524	GOF	1.07
μ (1/mm)	8.98	Δ/σ (max)	1.745
Crystal size (mm)	0.10 × 0.14 × 0.39	$\Delta(\rho)$ (e/Å ³)	-1.728
Scanning mode	$\theta/2\theta$		
Data collection range (2θ)	2.40 to 24.99		
h	0; 8		
k	0; 14		
l	-14; 14		
Wavelength (Å)	0.71069		

All non-H atoms were found. Atomic coordinates and anisotropic displacement parameters for them are given in Tables 8 and 9. A list of interatomic distances in As and Mo coordination polyhedra is given in Table 3.

The basic motif of the structure of vajdakite (Figs. 5 and 8) consists of double chains built up by individual chains with the sequence -O-As-O-Mo. The latter are interconnected by bridging oxygen atoms and additional oxygen atoms belonging to a common apex of two symmetrically independent AsO₃ triangles and two structurally non-equivalent MoΦ₆ octahedra (where Φ is an unspecified ligand). Repetition of the basic motif yields a continuous chain. The projection of those chains onto (100) gives independent parallel oriented layers (see Fig 7). In the interstitial spaces of these layers, there is one water O12, not included in the coordination.

Two almost symmetrical vertex-sharing triangles of AsO₃ represent an (As₂O₃)⁺ diarsenite group. Atomic distances of these triangles are very close to those in paulmooreite (Pb₂As₂O₅) (see Table 10 and Araki et al. 1980).

The MoΦ₆ octahedra are slightly distorted (see Table 11), as inferred from structure data applying the program VOLCAL (Finger 1996). The Mo1Φ₆ octahedron has a larger volume and its quadratic elongation and bond-angle variance have higher

values indicating more severe distortion than in the case of the Mo2 octahedron. Octahedra around Mo1 and Mo2 share a common edge defined by oxygen atoms O2 and O6 within a single

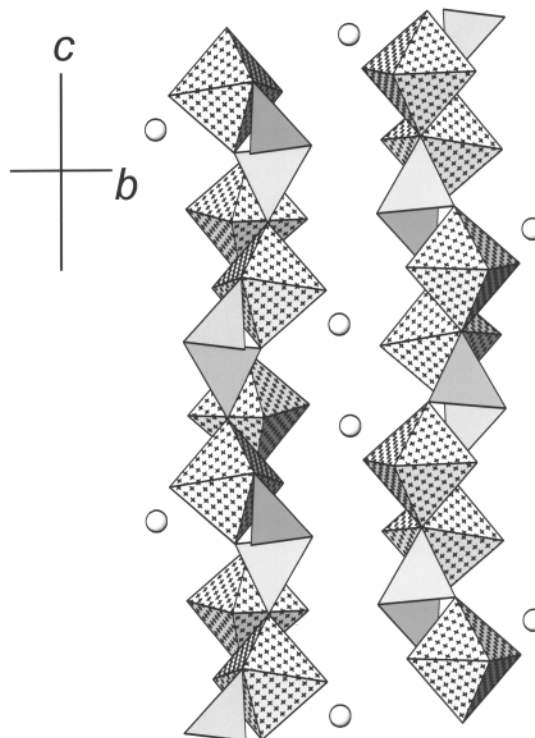


FIGURE 7. Projection of the vajdakite crystal structure onto (100).

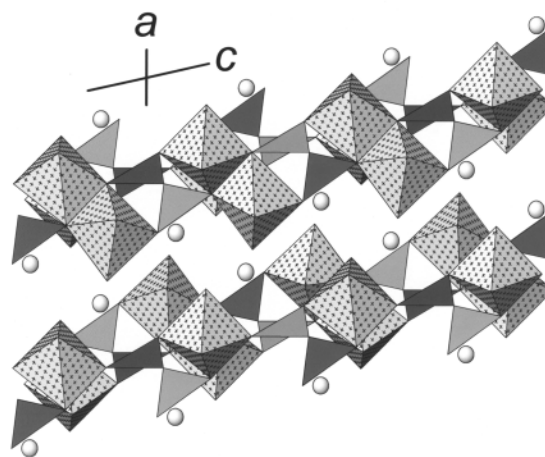


FIGURE 8. Projection of the vajdakite crystal structure onto (010).

TABLE 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
Mo1	6214(1)	2121(1)	2757(1)	12(1)
Mo2	1799(1)	2321(1)	905(1)	13(1)
As1	2066(1)	1418(1)	-1626(1)	13(1)
As2	6245(1)	3440(1)	5030(1)	13(1)
O1	-333(9)	2915(5)	1068(5)	24(2)
O2	4963(8)	1976(5)	1095(4)	14(1)
O3	1387(10)	951(5)	1006(5)	26(2)
O4	8084(9)	1267(5)	2671(5)	22(1)
O5	7186(9)	3414(5)	2745(5)	22(1)
O6	3147(8)	2659(5)	2485(4)	14(1)
O7	1681(9)	2432(5)	-668(5)	19(1)
O8	4275(8)	840(5)	-875(4)	14(1)
O9	6029(9)	2158(5)	4300(5)	18(1)
O10W	4588(9)	470(5)	2832(5)	22(1)
O11W	2886(11)	4090(6)	742(6)	34(2)
O12W	1477(9)	137(6)	3705(5)	25(2)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_j tensor.

TABLE 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vajdakite. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hk a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	9(1)	17(1)	7(1)	0(1)	-4(1)	2(1)
Mo2	10(1)	19(1)	7(1)	-1(1)	-4(1)	1(1)
As1	11(1)	18(1)	8(1)	-1(1)	-4(1)	-3(1)
As2	10(1)	20(1)	7(1)	0(1)	-3(1)	-3(1)
O1	18(3)	38(4)	10(3)	-2(3)	-8(3)	8(3)
O2	9(3)	25(3)	6(3)	2(2)	-1(2)	3(2)
O3	30(4)	19(3)	28(4)	0(3)	-1(3)	-1(3)
O4	18(3)	31(4)	14(3)	-4(3)	-5(2)	5(3)
O5	23(3)	20(3)	24(3)	3(3)	5(3)	-2(3)
O6	10(3)	26(3)	5(3)	-2(2)	-5(2)	4(2)
O7	16(3)	29(3)	8(3)	1(2)	-4(2)	4(3)
O8	15(3)	15(3)	11(3)	0(2)	-4(2)	3(2)
O9	15(3)	28(3)	6(3)	0(2)	-8(2)	1(3)
O10W	20(3)	20(3)	22(3)	2(2)	-7(3)	-1(3)
O11W	38(4)	25(4)	31(4)	0(3)	-10(3)	-11(3)
O12W	17(3)	26(4)	27(3)	-11(3)	-8(3)	-3(3)

TABLE 10. Comparison of atomic distances (\AA) of AsO₃ triangles within diarsenite group As₂O₅ in vajdakite and paulmooreite

vajdakite		paulmooreite (ICSD 100229)			
As1	As2	As1	As2	O1	O2
O7	1.750	O9	1.778	O2	1.747
*O8	1.786	O2	1.793	O1	1.750
O6	1.822	*O8	1.817	*O3	1.826
				O5	1.733
				O4	1.772
				*O3	1.843

* Bridging oxygen.

layer.

Because no H atoms could be found in the ΔF map due to insufficient resolution of the X-ray data, the concept of bond valences (Brown and Wu 1976) was used to propose the possible hydrogen bonds. The data of Brese and O'Keeffe (1991) were used to calculate the bond valences for all non-H atoms. Possible hydrogen bonds are inferred based on the relation of H...O bond valence and O...O distance as published by Brown and Altermatt (1985).

In vajdakite, there are two distinct types of water molecules. Calculation of bond valences (see Table 4) gives the bond valence sum for the O12 as 0 v.u. Hence, this site represents an H₂O molecule not included in the coordination of cations. The bond valence sums for O10 (0.34 v.u.) and O11 (0.36 v.u.) suggest that they represent H₂O molecules in octahedral coordination with Mo (the atomic distances Mo-O are about 2.2 Å). The bond valence sums for atoms O1, O3, O4, and O5 range from 1.71 to 1.81 v.u. indicating that all of them form H...O bridges. These oxygen atoms are bound in the double covalent bond Mo-O. Although we do not know the actual positions of the H atoms, it is possible to infer localization of H...O bridges from inter-atomic distances between oxygens O10, O11, and O12 and their closest oxygen neighbors with lower bond valence sums (O1, O3, O4, O5). From the data in Table 12, it can be deduced that these H...O bridges form a very complicated net of interlayer and intralayer hydrogen bonds. The O10, O11, and O12 atoms from H₂O molecules contribute by their hydrogen bonds mainly to the bonding between two MoO₆ octahedra in the neighboring layers. The O1, O3, O4, and O5 atoms form interlayer hydrogen bonds with H atoms of O10, O11, and O12. The mean bond valence sums for atoms O2, O6, O7,

O8, and O9 (i.e., those in single covalent bonds of As-O-As or As-O-Mo) is 2.04 v.u. This result indicates that there are no H...O bridges involving these oxygen atoms, as the values of bond valence sum nearly equal to the formal oxidation number for oxygen. Bond valence sums for both As and Mo are in good agreement with their corresponding formal oxidation numbers.

Based on the expected localization of all three water molecules within the vajdakite crystal structure, and comparing the bond valence sums and inter-atomic distances for Mo-O and As-O, it is obvious that there are no acid groups like As-OH or Mo-OH in the structure of this mineral.

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TABLE 11. Summary of atomic distances (Å) of MoO₆ octahedres in vajdakite and their comparison to those in molybdate(V) deuterophosphate(V) dideuterium oxide (ICSD 65014)

vajdakite				ICSD 65014	
Mo1		Mo2		Mo1	
O4	1.691	O3	1.687	O6	1.673
O5	1.706	O1	1.710	O4	1.747
O9	1.914	O7	1.911	O1	2.021
O2	2.055	O6	2.018	O1	2.021
O6	2.217	O2	2.233	O2	2.071
O10	2.309	O11	2.289	O5	2.271

Note: Distance Mo-O of about 2.3 Å corresponding to coordinated water in both examples.

TABLE 12. Inter-atomic distances (Å) between oxygen O10 (and O11) and other oxygen atoms for which bond valence sum lies in the range from 0.5 to 1.85 v.u.

O10		O11		O12	
O1	>3.5	O1	2.767	O1	2.829
O3	2.902	O3	>3.5	O4	2.825
O4	2.685	O4	>3.5	O5	2.999
O5	2.805	O5	>3.5	O10	2.647
O11	2.785	O10	2.785	O11	2.660

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