

Pauladamsite, $\text{Cu}_4(\text{SeO}_3)(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, a new mineral from the Santa Rosa mine, Darwin district, California, USA

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ABSTRACT

Pauladamsite (IMA2015-005), $\text{Cu}_4(\text{SeO}_3)(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, is a new mineral from the Santa Rosa mine, Darwin district, Inyo County, California, USA, where it occurs as a secondary oxidation-zone mineral in association with brochantite, chalcantite, gypsum, ktenasite, mimetite, schulenbergitte and smithsonite on limonitic gossan. Pauladamsite forms green, multiply twinned blades up to 0.5 mm long grouped in radial sprays. The streak is pale green. Crystals are transparent and have vitreous to silky lustre. The Mohs hardness is ~2, the tenacity is brittle, the fracture is irregular and crystals exhibit one perfect cleavage on [001]. The calculated density is 3.535 g/cm³. Electron microprobe analyses provided: CuO 48.96, ZnO 3.56, SeO₂ 18.82, SO₃ 13.90, H₂O 13.29 (calc.), total 98.53 wt.%. The empirical formula (based on 13 O apfu) is: $(\text{Cu}_{3.55}\text{Zn}_{0.25})_{\Sigma 3.80}\text{Se}_{0.98}\text{SO}_{13}\text{H}_{8.50}$. Pauladamsite is triclinic, $P\bar{1}$, $a = 6.0742(7)$, $b = 8.4147(11)$, $c = 10.7798(15)$ Å, $\alpha = 103.665(7)^\circ$, $\beta = 95.224(7)^\circ$, $\gamma = 90.004(6)^\circ$, $V = 533.03(12)$ Å³ and $Z = 2$. The eight strongest lines in the powder X-ray diffraction pattern are [d_{obs} in Å(hkl)]: 10.5(46)(011); 3.245(100)(001); 5.81(50)(011); 2.743(49)(112); 3.994(67)(012); 3.431(23)($\bar{1}12, \bar{1}\bar{2}1, \bar{1}20$); 2.692(57)(032, $\bar{1}22, \bar{2}\bar{1}2$); and 2.485(39)($2\bar{1}2, \bar{1}\bar{3}2, 0\bar{2}4$). The structure of pauladamsite ($R_1 = 10.6\%$ for 2086 $F_o > 4\sigma F$) contains Cu^{2+}O_6 octahedra, SO_4 tetrahedra and Se^{4+}O_3 pyramids. There are four different CuO_6 octahedra, each of which exhibits typical Jahn-Teller distortion, with four short equatorial Cu–O bonds and two much longer apical Cu–O bonds. The CuO_6 octahedra share edges to form five-octahedra-wide bands extending along [100]. Adjacent bands are connected in the [01 $\bar{1}$] direction by bridging SO_4 tetrahedra and in the [011] direction by bridging Se^{4+}O_3 pyramids, thereby forming a framework.

KEYWORDS: pauladamsite, new mineral, crystal structure, Santa Rosa mine, Darwin district, California, USA.

Introduction

THE Jahn-Teller distortion typically exhibited by Cu^{2+}O_6 octahedra results in structures which are rarely isostructural with non- Cu^{2+} oxysalts. This can be readily understood from a strictly bond-valence perspective. Eby and Hawthorne (1993) developed a hierarchical structural classification for Cu^{2+} -oxysalt minerals that divides them into four classes: isolated-polyhedron/finite-cluster, infinite-

chain, infinite-sheet and framework structures. Hawthorne and Schindler (2000) looked in more detail at the infinite-sheet Cu^{2+} -oxysalt mineral structures and, in particular, at those with sheets decorated by SO_4 groups.

The recent discovery of a new Cu-sulfate-selenite mineral at the Santa Rosa mine in California's Darwin mining district is of special interest because of its unusual combination of constituents, which include Se^{4+} with a lone-electron pair. The only other known Cu^{2+} -oxysalt mineral containing both SO_4^{2-} and SeO_3^{2-} groups is munakataite, $\text{Pb}_2\text{Cu}_2(\text{Se}^{4+}\text{O}_3)(\text{SO}_4)(\text{OH})_4$ (Kampf *et al.*, 2010), which also contains Pb^{2+} with a stereoactive lone pair.

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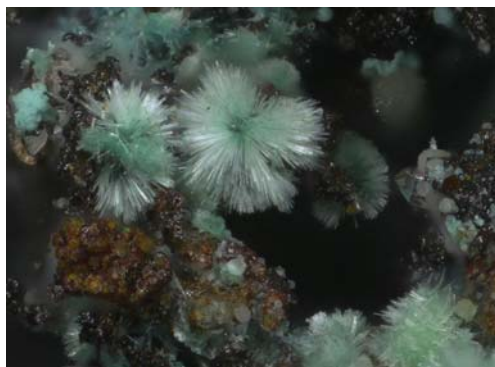


FIG. 1. Sprays of pauladamsite laths (Field of view: 2 mm across).

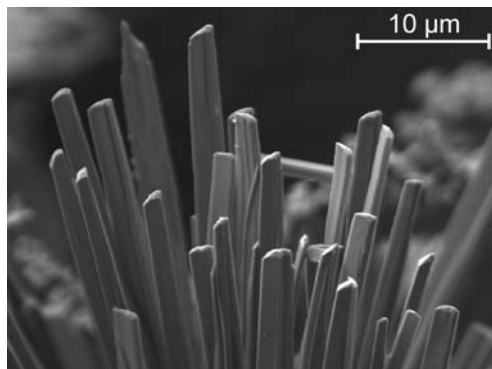


FIG. 2. SEM image of pauladamsite laths. Note the grooves along the lengths of the laths, which are an indication of the twinning.

The new mineral is named pauladamsite in honour of Paul M. Adams (b. 1954) who discovered/collected the mineral. Mr. Adams has a B.S. in geology from the State University of New York at Albany (1976) and an M.S. in geology from the University of Southern California (1979). He has been employed as a spectroscopist and microscopist in the aerospace industry for 37 years and has been field collecting minerals for over 40 years. He was coauthor of seven other new mineral descriptions: ferrisurite, meurigite-Na, iangreyite, krásnoite, fluorowardite, ferribushmakinite and crimsonite. He has agreed to the naming of the mineral.

The new mineral and name have been approved by the Commission on New Minerals, Nomenclature

and Classification of the International Mineralogical Association (IMA2015-005). The description is based upon five cotype specimens that are deposited in the collections of the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA, catalogue numbers 65569, 65570, 65571, 65572 and 65573.

Occurrence and paragenesis

The new mineral occurs at the Santa Rosa mine, Darwin district, Inyo County, California, USA.

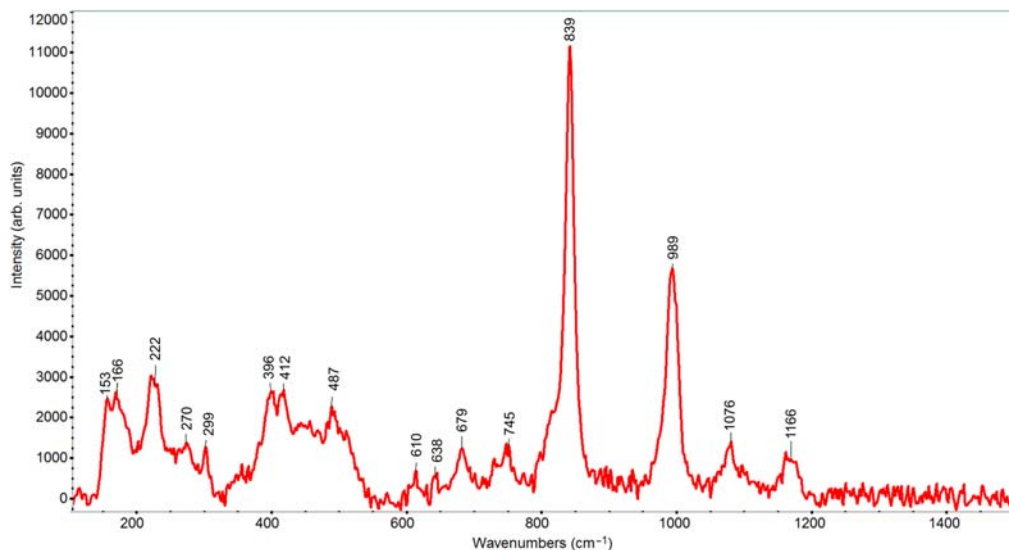


FIG. 3. Raman spectrum for pauladamsite.

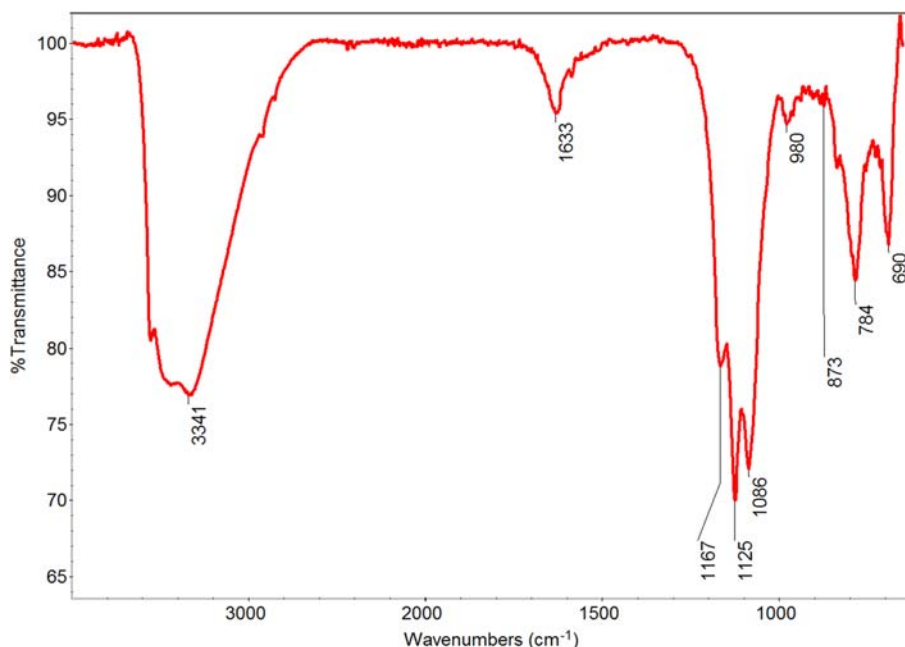


FIG. 4. FTIR spectrum for pauladamsite.

(36°25'7"N, 117°43'26"W). The Santa Rosa mine is located in the SE portion of the Inyo Mountains ~18 km NW of Darwin. The most detailed description of the Santa Rosa mine is by Mackevett (1953), summarized and somewhat modified by Hall and Mackevett (1958 and 1963).

The Santa Rosa mine was discovered in 1910 and by the early 1950s was the 8th largest Pb producer in California. The mine is located within an inlier of the lower limestone member of the Permian-age Owens Valley Formation, which has been metamorphosed to calc-hornfels. The inlier is surrounded by

Tertiary and Quaternary volcanic rocks and is cut by andesite porphyry dykes. Later basalt dykes cut both the limestone and aforementioned volcanic rocks. The ore-bearing veins occur in faults that predate the volcanic rocks. The veins are highly oxidized and consist mainly of cerussite and hemimorphite in a gangue of limonite, jasper and calcite. The small amount of remaining primary ore contains mainly galena, sphalerite, pyrite, chalcopryrite and arsenopyrite (in order of decreasing abundance).

Samples containing the new mineral were collected by Paul M. Adams in late 2012 in a 1.5 m × 1.5 m area of what is referred to by

TABLE 1. Electron microprobe data for pauladamsite.

Constituent	Wt. %	min	max	SD	Probe Standard
CuO	48.96	46.51	51.30	1.71	Cu metal
ZnO	3.56	1.86	5.07	1.39	Zn metal
SeO ₂	18.82	18.26	19.83	0.61	syn. ZnSe
SO ₃	13.90	13.44	14.17	0.32	celestine
H ₂ O*	13.29				
Total	98.53				

*Based upon S = 1, charge balance and 13 O apfu.

SD – standard deviation.

TABLE 2. Powder X-ray diffraction data for pauladamsite. Calculated lines with intensities <2 are not shown.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
100	10.5	10.4286	100	0 0 1			2.2094	2	0 3 2
9	8.1	8.1745	9	0 1 0	12	2.177	2.1824	11	2 0 3
		6.0475	5	1 0 0	16	2.097	2.1106	2	1 1 4
50	5.81	5.8001	34	0 1 1			2.1018	6	0 $\bar{4}$ 1
7	5.43	5.4582	5	$\bar{1}$ 0 1	8	2.052	2.0729	9	2 0 4
8	4.58	4.5640	4	1 $\bar{1}$ 1			2.0436	4	0 4 0
14	4.17	4.1459	14	$\bar{1}$ 0 2			2.0021	2	2 3 0
67	3.994	3.9880	53	0 1 2			1.9665	2	2 $\bar{3}$ 1
12	3.774	3.7778	13	1 0 2	7	1.9275	1.9231	2	1 4 0
11	3.670	3.6667	7	0 2 2			1.9213	3	0 4 1
		3.5132	3	0 $\bar{1}$ 3			1.8889	2	2 0 4
23	3.431	3.4633	5	$\bar{1}$ 1 2			1.8242	2	$\bar{3}$ $\bar{2}$ 1
		3.4483	3	$\bar{1}$ $\bar{2}$ 1			1.7974	2	2 0 5
		3.4219	10	$\bar{1}$ 2 0	6	1.7713	1.7697	4	2 1 4
		3.3519	4	1 2 0			1.7657	2	0 4 2
15	3.219	3.2097	15	1 1 2	10	1.7371	1.7381	6	0 0 6
6	3.013	3.0259	7	0 $\bar{2}$ 3	14	1.6880	1.6937	3	0 3 4
5	2.936	2.9563	6	0 1 3			1.6891	5	2 1 5
		2.9000	4	0 2 2			1.6803	2	2 $\bar{4}$ 3
		2.8418	2	2 $\bar{1}$ 1			1.6778	2	0 5 2
		2.8340	2	2 0 1			1.6759	2	2 4 0
11	2.808	2.8156	2	2 1 0	15	1.6288	1.6349	2	0 5 0
		2.8040	7	0 $\bar{3}$ 1			1.6321	4	2 $\bar{4}$ 3
16	2.755	2.7592	5	2 1 1			1.6235	4	0 1 6
		2.7513	15	2 $\bar{1}$ 1	10	1.6026	1.6049	2	2 2 4
57	2.692	2.6912	31	0 $\bar{3}$ 2			1.6006	5	2 $\bar{4}$ 4
		2.6871	2	$\bar{1}$ 2 2			1.5808	2	2 3 3
		2.6735	13	2 $\bar{1}$ 2	6	1.5599	1.5595	3	0 5 1
		2.6071	3	0 0 4			1.5528	3	2 $\bar{3}$ 5
		2.5304	2	$\bar{1}$ $\bar{1}$ 4	10	1.5348	1.5368	6	2 $\bar{4}$ 4
		2.5154	2	2 0 2			1.5272	2	2 $\bar{3}$ 4
		2.5053	2	$\bar{1}$ 3 0	20	1.5135	1.5165	8	4 0 1
39	2.485	2.4994	17	2 $\bar{1}$ 2			1.5119	2	4 0 0
		2.4832	2	$\bar{1}$ $\bar{3}$ 2	12	1.4905	1.4993	7	2 $\bar{4}$ 5
		2.4810	8	0 $\bar{2}$ 4			1.4920	3	2 4 2
		2.4638	3	1 3 0			1.4898	2	0 0 7
		2.4572	2	2 2 0			1.4716	2	2 $\bar{5}$ 2
32	2.396	2.4053	7	2 2 0	13	1.4585	1.4535	4	2 $\bar{4}$ 3
		2.3948	18	2 $\bar{1}$ 3	3	1.4090	1.4070	2	2 $\bar{3}$ 6
		2.3692	3	1 $\bar{1}$ 4			1.3967	2	4 1 3
		2.3570	6	2 $\bar{2}$ 1	6	1.3650	1.3683	2	0 $\bar{4}$ 7
		2.3190	2	2 1 2			1.3631	2	0 5 6
8	2.234	2.2422	4	$\bar{1}$ 1 4	8	1.3331	1.3295	3	4 $\bar{3}$ 1
		2.2367	3	1 $\bar{2}$ 4	4	1.3137	1.3131	2	4 $\bar{3}$ 3
		2.2132	2	2 1 3					

collectors as the sulfate stope. This portion of the underground workings corresponds to an adit driven in 1953. Of this adit, Hall and Mackevett (1958) wrote: "An adit was driven under the mine workings by the Anaconda Company to explore the veins at depth. The adit was driven westerly 1,800

feet at an altitude of 6580 feet from the sharp bend in the road at the foot of tramway from the upper Sanger workings (see Mackevett, 1953, pl. 2). The adit is completely in calc-hornfels. The ore showings in the adit are sparse. Most of the veins have pinched out above the level of the adit, but

PAULADAMSITE, A NEW COPPER SELENITE SULFATE

TABLE 3. Data collection and structure refinement details for pauladamsite.

Diffractometer	Rigaku R-Axis Rapid II	
X-ray radiation	MoK α ($\lambda = 0.71075$ Å)	
Temperature	298(2) K	
Ideal formula	Cu ₄ (SeO ₃)(SO ₄)(OH) ₄ ·2H ₂ O	
Space group	$P\bar{1}$	
Unit-cell dimensions	$a = 6.0742(7)$ Å $b = 8.4147(11)$ Å $c = 10.7798(15)$ Å	$\alpha = 103.665(7)^\circ$ $\beta = 95.224(7)^\circ$ $\gamma = 90.004(6)^\circ$
Z	2	
V	533.03(12) Å ³	
Absorption coefficient	11.551 mm ⁻¹	
F(000)	540	
Crystal size (μm)	165 × 10 × 5	
θ range	1.95 to 25.05°	
Index ranges	0 ≤ h ≤ 7, -9 ≤ k ≤ 10, -12 ≤ l ≤ 12	
Reflections collected	2986	
Reflections with $F_o > 4\sigma(F)$	2086	
Completeness to $\theta = 25.05^\circ$	97.0%	
Refinement method	Full-matrix least-squares on F^2	
Parameters refined	129	
Goof	1.104	
Final R indices [$F_o > 4\sigma(F)$]	$R_1 = 0.1060$, $wR_2 = 0.3013$	
R indices (all data)	$R_1 = 0.1404$, $wR_2 = 0.3221$	
Largest diff. peak/hole	+3.43/-2.54 e Å ⁻³	

$$R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]. \text{Goof} = S = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}. R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}. w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } a \text{ is } 0.1958, b \text{ is } 8.5151 \text{ and } P \text{ is } [2F_c^2 + \text{Max}(F_o^2, 0)] / 3.$$

some zinc-rich primary ore was discovered and was being mined in 1955”.

The mineral occurs on limonitic gossan matrix consisting mainly of goethite, hematite, hemimorphite, hetaerolite, K-feldspar and quartz. The occurrence is along the margin of a massive sulfide body in contact with coarse-grained marbles and garnet skarn. Galena in the sulfate stope is rich in Se (up to 15 at.%) and locally was observed altering to cerussite and native selenium. A number of trace accessory phases that contain selenium also occur as inclusions in sphalerite. These include aguilarite, bohdanowiczite, clausthalite, geffroyite, krut’aitite, naumannite and tetradymite (Adams, 2016). Pyrite, with minor amounts of Se-containing covellite and traces of clausthalite, is the primary sulfide most closely associated with pauladamsite and may be the source of selenium. Other secondary minerals found associated closely with pauladamsite are brochantite, chalcantite, gypsum, kobyashevite, ktenasite, mimetite, schulenbergitte, smithsonite and another potentially new Cu selenite-sulfate. Other secondary minerals identified in the general assemblage are antlerite, boyleite, brianyoungite,

devilline, hydrozincite, lahnsteinite, osakaite and posnjakite.

Physical and optical properties

Pauladamsite occurs as green blades grouped in radial sprays (Fig. 1). The blades are elongate on [100] and flattened on {001}, and are up to 0.5 mm long. Besides the {001} form, one or more other forms in the {0kl} zone are indicated in scanning electron microscopy (SEM) images (Fig. 2); however, none could be measured. Multiple twinning is ubiquitous, probably by rotation on [100]. The mineral has a pale green streak. Crystals are transparent and have vitreous to silky lustre. Pauladamsite does not fluoresce in longwave or shortwave ultraviolet light. The Mohs hardness is estimated to be ~2, the tenacity is brittle, the fracture is irregular and crystals exhibit one perfect cleavage on {001}. The density could not be measured because individual blades were too difficult to see in Clerici solution and aggregates of blades tended to trap air bubbles. The calculated

TABLE 4. Fractional coordinates, occupancies and atom displacement parameters (Å) for pauladamsite.

	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu1	0.4796(5)	0.2478(4)	0.8656(3)	0.0192(9)	0.0161(16)	0.0149(17)	0.031(2)	0.0138(14)	0.0004(13)	0.0017(12)
Cu2	0.2495(5)	-0.0019(3)	1.0003(3)	0.0168(8)	0.0123(14)	0.0173(16)	0.0249(18)	0.0117(14)	0.0047(12)	0.0021(13)
Cu3	0.1746(6)	0.4288(4)	0.6865(3)	0.0223(9)	0.0260(18)	0.0149(16)	0.029(2)	0.0123(14)	0.0019(15)	0.0007(14)
Cu4	0.9706(5)	0.2479(4)	0.8663(3)	0.0174(8)	0.0142(15)	0.0135(16)	0.030(2)	0.0148(14)	0.0048(13)	0.0043(12)
Se	0.7188(4)	0.5881(3)	0.8206(3)	0.0181(7)	0.0165(13)	0.0144(13)	0.0271(15)	0.0115(10)	0.0043(11)	0.0037(11)
S	0.1229(13)	0.7602(8)	0.5990(7)	0.0251(17)	0.038(4)	0.011(3)	0.026(4)	0.004(3)	0.002(3)	0.003(3)
O1	0.110(4)	0.669(3)	0.470(2)	0.041(6)	0.042(14)	0.054(15)	0.031(13)	0.020(11)	0.005(10)	0.014(11)
O2	0.275(4)	0.897(3)	0.617(2)	0.039(6)	0.034(12)	0.036(13)	0.040(14)	-0.006(11)	0.006(10)	-0.009(10)
O3	0.205(4)	0.659(2)	0.6879(19)	0.036(5)	0.059(14)	0.026(11)	0.022(11)	0.007(9)	-0.006(11)	0.015(11)
O4	0.892(4)	0.814(3)	0.632(2)	0.032(5)	0.031(12)	0.029(11)	0.034(12)	0.005(9)	0.003(9)	0.010(9)
O5	0.750(3)	0.711(2)	0.9692(17)	0.022(4)						
O6	0.502(3)	0.462(2)	0.8287(18)	0.022(4)						
O7	0.945(3)	0.460(2)	0.8227(17)	0.020(4)						
OH8	0.469(3)	0.015(2)	0.8835(17)	0.016(4)						
OH9	0.982(3)	0.017(2)	0.8832(16)	0.013(4)						
OH10	0.256(3)	0.732(2)	1.0177(17)	0.021(4)						
OH11	0.202(3)	0.225(2)	0.7505(17)	0.023(4)						
OW12	0.377(4)	0.366(3)	0.548(2)	0.039(6)						
OW13	0.320(4)	0.866(3)	1.325(2)	0.033(5)						

TABLE 5. Selected bond lengths (Å) in pauladamsite.

Cu1–OH10	1.931(19)	Cu3–O3	1.94(2)	Se–O5	1.682(18)	Hydrogen bonds	
Cu1–O6	1.942(19)	Cu3–OW12	2.00(2)	Se–O6	1.713(18)	OH8···O2	2.94(3)
Cu1–OH11	1.98(2)	Cu3–OH11	1.998(18)	Se–O7	1.746(18)	OH9···O4	2.85(3)
Cu1–OH8	2.015(18)	Cu3–O7	2.089(18)	<Se–O>	1.714	OH10···O6	3.15(3)
Cu1–O5	2.321(19)	Cu3–O1	2.31(2)			OH11···O2	2.84(3)
Cu1–OW13	2.48(2)	Cu3–O6	2.371(19)	S–O1	1.42(2)	OW12···O4	2.60(3)
<Cu1–O _{eq} >	1.967	<Cu3–O _{eq} >	2.007	S–O2	1.45(2)	OW12···O1	3.15(3)
<Cu1–O _{ap} >	2.401	<Cu3–O _{ap} >	2.341	S–O3	1.48(2)	OW13···O2	3.09(3)
				S–O4	1.52(2)	OW13···O4	2.94(3)
				<S–O>	1.47		
Cu2–OH8	1.940(17)	Cu4–OH10	1.921(19)				
Cu2–OH9	1.991(17)	Cu4–OH11	1.945(19)				
Cu2–OH9	1.997(16)	Cu4–O7	1.956(19)				
Cu2–OH8	2.046(18)	Cu4–OH9	1.993(17)				
Cu2–OH10	2.293(18)	Cu4–O5	2.304(19)				
Cu2–O5	2.394(18)	Cu4–OW13	2.59(2)				
<Cu2–O _{eq} >	1.994	<Cu4–O _{eq} >	1.954				
<Cu2–O _{ap} >	2.344	<Cu4–O _{ap} >	2.447				

density based on the empirical formula and the unit cell refined from the single-crystal data is 3.535 g/cm³ and that based on the ideal formula is 3.621 g/cm³. Pauladamsite is rapidly soluble in room-temperature, dilute HCl.

Optically, pauladamsite is biaxial (–), with indices of refraction, based on measurements in white light: $\alpha = 1.667(\text{calc})$, $\beta = 1.723(2)$ and $\gamma = 1.743(2)$. Conoscopic observation using a spindle stage provided $2V = 60(2)^\circ$ and strong $r > v$ dispersion. The optical orientation is $X \approx c^*$, $Y \approx b$, $Z \approx a$. The pleochroism is X light yellowish green, Y bluish green, Z nearly colourless; $Y > X > Z$. Note that α was difficult to measure because of the thinness of the blades; consequently, it was calculated from β , γ and $2V$. The Gladstone-Dale compatibility index $1 - (K_p/K_c)$ is -0.014 using the empirical formula and 0.002 using the ideal formula, in both cases indicating superior compatibility (Mandarino, 2007).

Raman spectroscopy

The Raman spectrum of pauladamsite was recorded with a Renishaw inVia microprobe using a 514 nm laser. The nominal spot size was 2 μm . The Fourier transform infrared (FTIR) spectrum was recorded using a Thermo Nicolet model 6700 spectrometer equipped with a Continuum microscope. The sample was analysed in transmission mode with a micro diamond compression cell.

The Raman spectrum (Fig. 3) shows a number of SO₄ bands at 1166 (ν_3 antisymmetric stretch), 1076

(ν_3 antisymmetric stretch) and 989 (ν_1 symmetric stretch) cm^{–1}, and SeO₃ bands at 839 (ν_1 symmetric stretch), 745 (ν_3 antisymmetric stretch), 487 (ν_2 bending mode) and 396 (ν_2 bending mode) cm^{–1}. Additional low wavenumber bands are due to Cu–O modes. The SeO₃ bands are very similar to those found in other low-symmetry phases containing SeO₃, such as favreauite (Mills *et al.*, 2014). The bands at 1633 and 3341 cm^{–1} in the FTIR spectrum of pauladamsite (Fig. 4) confirm the presence of H₂O and OH within the structure. Additional bands in the region 1167–980 cm^{–1} are due to the SO₄, while bands between 873 and 690 are due to SeO₃.

Chemical composition

Quantitative analyses (five) were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current and a beam diameter of 8 μm . No other elements were detected by energy dispersive spectroscopy. Other likely elements were sought by electron microprobe analysis, but none were found to be above the limit of detection. Raw X-ray intensities were corrected for matrix effects with a $\phi(\rho z)$ algorithm (Pouchou and Pichoir, 1991). There was insufficient material for CHN analyses, so H₂O was calculated on the basis of $S = 1$, charge balance and 13 O apfu, as determined by the

TABLE 6. Bond-valence sums for pauladamsite. Values are expressed in valence units.*

	O1	O2	O3	O4	O5	O6	O7	OH8	OH9	OH10	OH11	OW12	OW13	Σ
Cu1					0.18	0.49		0.40		0.51	0.44		0.11	2.14
Cu2					0.14			0.49	0.43	0.19				2.05
Cu3	0.18		0.49			0.15	0.33				0.42	0.42		2.00
Cu4					0.18		0.47		0.43	0.52	0.49		0.09	2.18
S	1.74	1.60	1.48	1.32										6.14
Se					1.42	1.30	1.19							3.91
H8		0.13						0.87						1.00
H9				0.17					0.83					1.00
H10						0.03				0.97				1.00
H11		0.17									0.83			1.00
H12a				0.25								0.75		1.00
H12b	0.03											0.97		1.00
H13a		0.06											0.94	1.00
H13b				0.13									0.87	1.00
Σ	1.95	1.96	1.97	1.87	1.92	1.98	2.00	2.14	2.11	2.19	2.18	2.14	2.01	

*Bond-valence parameters are from Brown and Altermatt (1985).

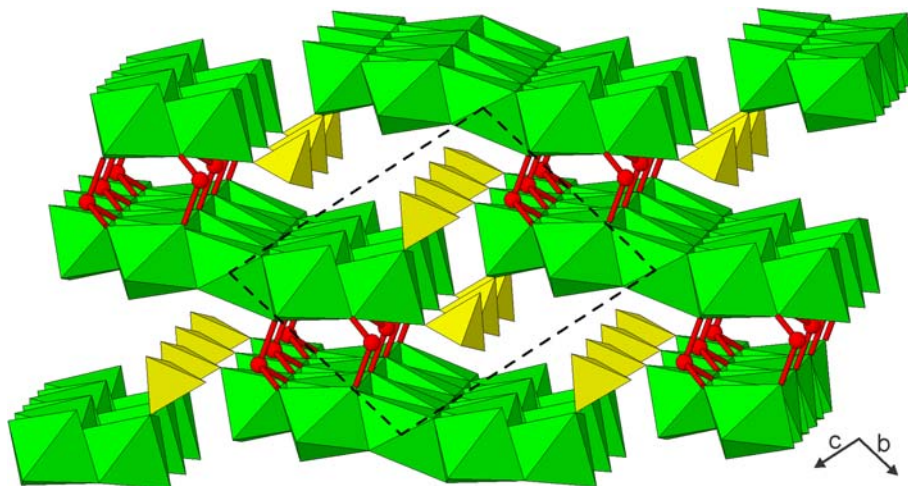


FIG. 5. The structure of pauladamsite viewed slightly canted down [100]. CuO_6 octahedra are green, SO_4 tetrahedra are yellow and Se atoms and Se–O bonds are red. The unit-cell outline is shown with dashed lines.

crystal structure analysis (see below). The tiny crystals do not take a good polish, which contributes to the low analytical total. Analytical data are given in Table 1. The empirical formula for pauladamsite (based on 13 O apfu) is $(\text{Cu}_{3.55}\text{Zn}_{0.25})_{\Sigma 3.80}\text{Se}_{0.98}\text{SO}_{13}\text{H}_{8.50}$. The simplified formula is $\text{Cu}_4(\text{SeO}_3)(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, which requires CuO 54.74, SeO_2 19.09, SO_3 13.77, H_2O 12.40, total 100 wt.%.

X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized $\text{MoK}\alpha$ radiation. For the powder-diffraction study, a Gandolfi-like motion on the ϕ and ω axes was used to randomize the sample and observed d values and intensities were derived by profile fitting using *JADE 2010* software (Materials Data, Inc.). The powder data are presented in Table 2. Unit-cell parameters refined from the powder data using *JADE 2010* with whole pattern fitting are: $a = 6.0895(16)$, $b = 8.4104(17)$, $c = 10.7828(16)$ Å, $\alpha = 103.641(6)$, $\beta = 95.299(7)$, $\gamma = 89.903(8)^\circ$ and $V = 534.26(19)$ Å³.

Crystals of pauladamsite are ubiquitously twinned, often multiply. The best crystal found consisted of three twin components (probably related by rotation on [100]). The *TwinSolve*

program in the *Rigaku CrystalClear* software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction. The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005) and was refined using *SHELXL-97* (Sheldrick, 2008) employing neutral atom scattering factors. Details of data collection and structure refinement are provided in Table 3. Fractional coordinates and atom displacement parameters are provided in Table 4, selected interatomic distances in Table 5 and bond valences in Table 6.

The structure of pauladamsite (Fig. 5) contains Cu^{2+}O_6 octahedra, SO_4 tetrahedra and Se^{4+}O_3 pyramids. There are four different CuO_6 octahedra, each of which exhibits typical Jahn-Teller distortion, with four short equatorial Cu–O bonds and two much longer apical Cu–O bonds (Table 5). The CuO_6 octahedra share edges to form wide bands extending along [100]. The bands are five-octahedra-wide in the [011] direction. Adjacent bands are connected in the [011] direction by bridging SO_4 tetrahedra and in the [011] direction by bridging Se^{4+}O_3 pyramids, thereby forming a framework. An extensive network of hydrogen bonds further binds the framework together. This framework is unique, as far as we can tell, among minerals and synthetic phases, and only superficially has similarities with other structures with ribbons of edge-sharing octahedra, such as felsöbányaite (Farkas and Pertlik, 1997).

The only other minerals containing both selenite and sulfate groups are olsacherite, $\text{Pb}_2(\text{SeO}_3)(\text{SO}_4)$

and munakataite, $\text{Pb}_2\text{Cu}_2(\text{Se}^{4+}\text{O}_3)(\text{SO}_4)(\text{OH})_4$. Although the structure of olsacherite has not been solved, it is probably closely related to that of anglesite, which has a structure quite different from that of pauladamsite. The structure of munakataite (Kampf *et al.*, 2010) contains edge-sharing chains of CuO_6 octahedra; however, these chains are only one octahedron wide. The chains of octahedra in munakataite are decorated by SO_4 tetrahedra and Se^{4+}O_3 pyramids; however, the SO_4 tetrahedra and Se^{4+}O_3 pyramids do not link the chains to one another.

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