American Mineralogist, Volume 85, pages 1816–1821, 2000

Elyite, $Pb_4Cu(SO_4)O_2(OH)_4·H_2O$: Crystal structure and new data

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ABSTRACT

The crystal structure of elyite, $Pb_4Cu(SO_4)O_2(OH)_4·H_2O$, a = 14.233(2), b = 11.532(1), c = 14.611(2) Å, β = 100.45(1)°, V = 2358.4(5) Å^3, Z = 8, was solved by direct methods and refined in space group $P2_1/c$ to $R1$ = 3.64% and w$R2$ = 5.10% for the 5861 independent reflections. Data were collected on a tiny untwinned crystal fragment with a four-circle diffractometer (Mo$K\alpha$ radiation, CCD area detector). The structure contains eight unique Pb atoms, two isolated Cu atoms in planar fourfold-coordination (<Cu-O> = 1.933, 1.927 Å) and two isolated, almost ideal SO_4 tetrahedra. All anions coordinating Cu are OH groups. Two H_2O molecules are weakly bound to Pb atoms. The Pb atoms show highly variable coordinations due to variable stereochemical activities of the Pb^{2+} lone electron pairs. The connectivity of the structure is based on Pb-O polyhedra which are closely linked by common O ligands to form rod-like structure elements parallel to the b axis. The structure framework is held together by sharing ligands with CuO_4 squares and SO_4 tetrahedra. The CuO_4 squares can be considered as struts connecting the Pb-O rods along the c axis and, intermittently, along the a axis. A complex hydrogen bond system provides additional strengthening. The non-merohedral twinning parallel to {100} reported previously is explained by the presence of a pseudo-mirror plane in the structure. Comparisons are drawn with the structures of the related Pb-Cu-sulfates chenite, $Pb_4Cu(SO_4)_2(OH)_6$, and linarite, $PbCu(SO_4)(OH)_2$. The violet color of elyite and other Cu compounds might be related to the planar fourfold-coordination of Cu.

INTRODUCTION

Elyite is a rare Pb-Cu-sulfate forming tiny elongate laths with an unusual lavender to violet color. The mineral was originally described from Nevada by Williams (1972) who gave the formula as $Pb_4Cu(SO_4)(OH)_8$. Several additional occurrences have been reported in anthropogenic ore slags and, much more rarely, in oxidation zones of lead-zinc deposits. Based on rotation and Weissenberg photographs, Williams (1972) reported a monoclinic unit cell a = 14.248(2), b = 5.768(2), c = 7.309(2) Å, β = 100.43(2)°, V = 590.7 Å^3, space group $P2_1/a$, with Z = 2, and D_{calc} = 6.321, D_{meas} ~ 6 g/cm^3. A recent single-crystal study of a sample from a Japanese locality gave a larger monoclinic cell, a = 14.244(1), b = 11.536(1), c = 14.656(1) Å, β = 100.45(1)°, V = 2368.3 Å^3, and a different space group, $P2_1/c$ (Miyawaki et al. 1997). The b- and c-edges are doubled compared to those of Williams (1972). The platy form of the elyite laths was determined to be {100}, whereas Williams (1972) considered it to be {001}, on which he observed common, non-repetitive mirror twinning. Miyawaki et al. (1997) also provided an improved and indexed X-ray powder pattern, and gave the results of a new electron microprobe analysis leading to the formula $Pb_{4.00}Cu_{0.94}(SO_4)_{1.07}[O_{0.73}(OH)_{6.28}]_{\Sigma 7.01}$, which indicated a lower oxygen content. They noted that the powder diffraction pattern of Williams (1972) contains six reflections which violate the a glide plane in space group $P2_1/a$. The present work was conducted to establish the correct unit cell of elyite and determine its crystal structure.

CRYSTAL STRUCTURE SOLUTION AND REFINEMENT

Two elyite specimens were selected for the present study. The first specimen, from the locality Altemannfels, Badenweiler, Black Forest, Germany (Walenta 1992), contains a spray of acicular to lath-shaped, transparent crystals up to 1 mm long, in association with partly altered cerussite and anglesite. The second specimen, from a small slag dump in the Kleines Drecktal, Lauthental, Harz mountains, Germany, contains elyite in voids of a black slag. The lath-shaped, transparent crystals are up to 1.5 mm in length; they are closely associated and partly intergrown with bright bluish chenite [$Pb_4Cu(SO_4)_2(OH)_6$] crystals and a whitish spray of an unidentified Pb sulfate.

Preliminary investigations of crystals from both specimens were done with a Nonius KappaCCD single-crystal diffractometer equipped with a 300 mm diameter capillary-optics collimator to provide increased resolution. The investigations revealed a good to very good crystal quality and a primitive monoclinic cell identical to that reported by Miyawaki et al. (1997). The cell given by Williams (1972) was found to represent only a subcell, also confirming the conclusions of Miyawaki et al. (1997). Optical studies showed the crystals studied to be untwinned. For the intensity data collection, a suitable crystal fragment was cut from a lath-shaped lavender

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0003-004X/00/1112–1816$05.00

transparent crystal taken from the first specimen. The fragment with the approximate dimensions 0.10 × 0.016 × 0.013 mm^3 was mounted on the mentioned diffractometer and 323 frames were acquired (see Table 1 for details). The intensity data were processed with the Nonius program suite DENZO-SMN, corrected for Lorentz and polarization, and empirically corrected for absorption and background effects. No superstructure reflections were seen on the recorded frames. A further absorption correction based on the numerical simulation of the crystal shape, was applied and gave a minor improvement (the $R1$ value dropped by 0.4%). The data were averaged to give 5864 symmetry-independent reflections (R_{int} = 2.5%).

The positions of eight Pb and two Cu atoms were found by direct methods (SHELXS-97, Sheldrick 1997a) and those of two S and 22 O atoms were located from subsequent difference Fourier maps. A full-matrix anisotropic least-squares refinement on F^2 (SHELXL-97, Sheldrick 1997b) in space group $P2_1/c$ proceeded smoothly. Three low-angle reflections, 200, 002, and 020, whose intensities were strongly affected by the experimental conditions, were then omitted in the refinement process. Subsequently, the positions of ten H atoms, belonging to eight OH groups and two H_2O molecules, were detected from difference Fourier maps and considerations of probable hydrogen-bond geometries. Two H atoms, each belonging to one of the two H_2O molecules, could not be located. Unrestrained refinements of the H positions gave O-H distances ranging between ~0.50 and ~0.97 Å. The isotropic and equivalent displacement parameters of the H and O atoms belonging to the two H_2O molecules were higher than those belonging to OH groups. The 10 O-H distances were then restrained at 0.9(1) Å. The refinement converged to the final discrepancy factors $R1$ = 3.64% and w$R2$ = 5.10%, for 5861 reflections, that reduce to $R1$ = 2.75% and w$R2$ = 4.93%, when taking into account the 5155 reflections with $F_o > 4\sigma(F_o)$. The maximum peaks in the final difference-Fourier maps were 1.78 and –1.74 e/Å^3, respectively, the most positive peaks being all close to Pb atoms. The final atomic positions and displacement parameters are given in Table 2, selected bond lengths and angles, and calculated bond valences in Table 3, and suggested hydrogen bonds are listed in Table 4. A list of observed and calculated structure factors has been deposited (Table 5).[1]

DESCRIPTION OF THE STRUCTURE

Cation polyhedra and structure connectivity

The elyite structure contains eight unique Pb atoms, two isolated Cu atoms in planar fourfold-coordination (<Cu-O> = 1.933 and 1.927 Å) and two isolated SO_4 tetrahedra with almost ideal tetrahedral symmetry [<S-O> = 1.478 and 1.461 Å, O-S-O angles = 107.9(3) to 110.5(4)°]. As mentioned above, ten H atoms were found although the actual number of H atoms is 12 (see below). All detected atoms lie on general positions (Table 2).

As often observed for Pb-O polyhedra, most of the eight Pb atoms show three to five shorter Pb-O bonds (2.20 to 2.70 Å) and a variable number of longer bonds within 3.30 Å, based on the (somewhat arbitrary) assumption that all Pb-O distances <3.30 Å can still be considered as bonds with non-negligible bond strengths (Table 3). This gives approximate Pb coordination numbers of 6 (for six Pb atoms) up to 7 and 8 (one Pb atom, respectively). The presence of the three short Pb-O bonds is most obvious in the coordination of Pb1, Pb2, Pb3, and Pb4, and is due to stereochemical activity of the lone electron pair of Pb^{2+}, which is always located opposite the three shortest Pb-O bonds. Although a detailed description of the eight Pb-O polyhedra is outside the scope of this work, we point out that the coordination geometry of the Pb1-O polyhedron is fairly unusual: the six O neighbors of Pb1 are all in the same hemisphere with respect to the cation and the polyhedron can be described as a slightly distorted pentagonal pyramid with the Pb atom just outside of the pentagonal base.

The average S-O bond lengths in the two sulfate tetrahedra, 1.478 and 1.461 Å, are in satisfactory accordance with the commonly observed value, 1.473 Å (Baur 1981), considering the involvement of some of the respective O ligands in H bonding

TABLE 1. Crystal data, data collection information, and refinement details for elyite

Space group, Z	$P2_1/c$, 8		
a,b,c (Å)	14.233(2), 11.532(1), 14.611(2)	ρ_{calc} (g/cm^3)	6.232
β (°)	100.45(1)	μ (mm^{-1})	58.91
V (Å^3)	2358.4(5)	Transmission factors	0.103–0.504
Diffractometer	Nonius KappaCCD system	Total reflections measured	51340
λ (Mo*K*α) (Å), *T* (K)	0.71073, 293	Unique reflections	5864
Detector distance (mm)	28	*R*(*F*), w*R*(*F*^{2})*	3.64%, 5.10%
Rotation axis	φ, ω	Extinct. Factor	0.00028(1)
Rotation width (°)	2.0	No. of refined parameters	348 (with 10 restraints)
Total no. of frames	323	GooF	1.132
Collect. time per frame (s)	350	$(\Delta/\sigma)_{max}$	0.001
$2\theta_{max}$ (°)	56.75	$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	–1.74, 1.78
h, k, l ranges	–19 → 19, –15 → 15, –19 → 19		

* $w = 1/[\sigma^2(F_o^2) + (0.012P)^2 + 13.6P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$.

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[1] For a copy of Table 5, document item AM-00-056, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (http://www.minsocam.org or current web address).

TABLE 2. Fractional atomic coordinates and displacement parameters (×10^4) for elyite (s.u.s in parentheses)

Site	x	y	z	U_{eq}/U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.76199(2)	0.24357(2)	0.167887(18)	160.1(0.7)	217.3(1.6)	142.4(1.4)	115.8(1.4)	8.3(1.0)	17.7(1.1)	–5.7(1.0)
Pb2	0.886214(19)	–0.02750(2)	0.07928(2)	152.5(0.7)	117.7(1.4)	135.3(1.3)	211.8(1.6)	–12.4(1.1)	49.1(1.1)	1.8(0.9)
Pb3	0.882928(19)	0.01208(2)	0.54651(2)	161.2(0.7)	109.2(1.4)	152.8(1.3)	215.2(1.6)	5.9(1.1)	12.0(1.1)	–17.1(1.0)
Pb4	0.73814(2)	–0.24952(2)	0.405103(18)	142.4(0.7)	161.9(1.5)	142.5(1.3)	130.6(1.4)	18.0(1.0)	47.7(1.1)	9.5(1.0)
Pb5	0.75268(2)	0.23200(2)	–0.075258(19)	154.9(0.7)	174.2(1.5)	160.8(1.3)	139.8(1.4)	–24.3(1.0)	55.3(1.1)	0.5(1.0)
Pb6	0.74581(2)	–0.23237(2)	0.652309(19)	153.4(0.7)	170.6(1.5)	153.8(1.3)	131.0(1.4)	–27.4(1.0)	14.6(1.1)	1.6(1.0)
Pb7	0.627551(19)	0.00700(2)	0.49958(2)	146.5(0.7)	113.0(1.4)	134.4(1.3)	197.7(1.5)	–4.2(1.0)	42.7(1.1)	17.5(0.9)
Pb8	0.629953(19)	–0.00198(2)	0.03815(2)	150.4(0.7)	113.8(1.4)	133.4(1.3)	199.7(1.5)	–5.6(1.0)	17.0(1.1)	–9.6(0.9)
Cu1	0.75912(6)	0.00198(7)	0.29219(6)	159.4(1.9)	191(5)	145(4)	146(5)	–15(3)	40(4)	0(3)
Cu2	0.49357(6)	–0.24673(7)	0.47751(6)	124.5(1.8)	113(5)	124(4)	140(4)	–4(3)	29(3)	–24(3)
S1	0.59143(14)	–0.00318(15)	–0.23283(13)	172(4)	196(10)	198(9)	121(9)	–25(7)	25(7)	32(7)
S2	0.01662(13)	0.22104(15)	0.08822(14)	174(4)	128(9)	189(8)	202(10)	7(7)	27(8)	–3(7)
O1	0.5301(4)	0.0978(5)	–0.2246(4)	264(13)	270(30)	300(30)	200(30)	–50(20)	–20(20)	130(20)
O2	0.6535(4)	0.0213(5)	–0.3017(4)	269(13)	270(30)	340(30)	230(30)	–20(30)	120(30)	–50(20)
O3	0.5304(4)	–0.1047(5)	–0.2629(4)	285(14)	280(30)	290(30)	310(30)	–60(30)	100(30)	–90(20)
O4	0.6539(4)	–0.0264(5)	–0.1421(4)	283(14)	320(30)	310(30)	170(30)	–50(20)	–90(30)	150(30)
O5	0.0696(4)	0.3283(5)	0.0835(5)	426(17)	270(40)	200(30)	760(50)	50(30)	–10(30)	–70(20)
O6	0.0842(4)	0.1247(5)	0.1069(4)	302(14)	230(40)	220(30)	420(40)	100(30)	–10(30)	60(20)
O7	0.9610(5)	0.2271(7)	0.1629(4)	462(19)	250(40)	930(50)	220(30)	–80(30)	80(30)	90(30)
O8	0.9519(4)	0.2019(5)	–0.0006(4)	253(13)	170(30)	350(30)	230(30)	40(20)	20(20)	00(20)
O9	0.7601(3)	0.3546(4)	0.0454(3)	135(10)	160(30)	110(20)	130(30)	–05(19)	10(20)	–12(18)
O10	0.7642(3)	0.0999(4)	0.0629(3)	138(10)	120(30)	110(20)	180(30)	–09(19)	10(20)	22(18)
O11	0.7547(3)	–0.1465(4)	0.0347(3)	131(10)	160(30)	120(20)	130(30)	–18(19)	40(20)	–15(18)
O12	0.7562(3)	–0.1038(4)	0.5176(3)	133(10)	100(30)	110(20)	180(30)	–30(19)	00(20)	–15(18)
OH1	0.6679(4)	–0.0752(4)	0.1993(4)	194(11)	230(30)	210(30)	150(30)	–40(20)	40(20)	–30(20)
OH2	0.6662(4)	0.0746(4)	0.3539(4)	183(11)	170(30)	190(30)	190(30)	–20(20)	40(20)	–20(20)
OH3	0.8523(4)	0.0751(4)	0.3882(4)	183(11)	170(30)	180(20)	200(30)	–20(20)	50(20)	–30(20)
OH4	0.8569(4)	–0.0609(5)	0.2282(4)	256(13)	250(30)	330(30)	190(30)	10(20)	30(30)	100(20)
OH5	0.5766(4)	–0.1780(4)	0.4030(3)	157(11)	140(30)	220(30)	110(30)	–20(20)	20(20)	–50(20)
OH6	0.4056(4)	–0.3004(4)	0.5536(4)	178(11)	140(30)	240(30)	160(30)	20(20)	40(20)	–30(20)
OH7	0.5880(4)	–0.2011(4)	0.5833(4)	189(11)	140(30)	270(30)	170(30)	–20(20)	50(20)	20(20)
OH8	0.4041(4)	–0.3094(4)	0.3733(4)	184(11)	160(30)	250(30)	150(30)	–50(20)	50(20)	–60(20)
OW1	0.0390(5)	0.2145(6)	0.3520(5)	398(16)	340(40)	570(40)	310(40)	50(30)	130(30)	120(30)
OW2	0.8493(5)	0.4822(6)	0.2363(5)	410(17)	400(40)	390(40)	440(40)	–180(30)	70(30)	–80(30)
H1	0.638(7)	–0.090(9)	0.233(7)	600(400)	–	–	–	–	–	–
H2	0.634(7)	0.114(8)	0.328(7)	400(300)	–	–	–	–	–	–
H3	0.898(6)	0.078(9)	0.363(7)	500(300)	–	–	–	–	–	–
H4	0.912(6)	–0.073(9)	0.271(6)	500(300)	–	–	–	–	–	–
H5	0.565(8)	–0.177(10)	0.352(5)	700(400)	–	–	–	–	–	–
H6	0.441(7)	–0.303(10)	0.596(6)	600(400)	–	–	–	–	–	–
H7	0.547(6)	–0.184(8)	0.614(6)	400(300)	–	–	–	–	–	–
H8	0.440(7)	–0.308(9)	0.336(7)	600(300)	–	–	–	–	–	–
H9	0.995(7)	0.224(9)	0.376(7)	500(300)	–	–	–	–	–	–
H10	0.889(7)	0.522(8)	0.283(7)	600(300)	–	–	–	–	–	–

(see below). Calculated bond valences for the Pb, Cu, and S atoms are all close to expected values (Table 3).

The connectivity of the elyite structure is based on Pb-O polyhedra which are closely linked by common O ligands to form rod-like structure elements parallel to [010] (Fig. 1). The structure framework is held together by sharing ligands with CuO_4 squares and, to a lesser extent, with SO_4 tetrahedra. The CuO_4 squares can be considered as struts connecting the Pb-O rods along [001] and, intermittently, along [100] (Fig. 1). A complex hydrogen bond system provides additional strengthening (see below for details).

The reported twinning of elyite parallel to the platy {100} pinacoid ({001} in the original description) is easily explained by the presence of a pseudo-mirror plane in the structure shown in a view down [001] (dashed line in Fig. 2). The cleavage is also parallel to {100}, and may preferentially occur at the planes defined by the two H_2O molecules and the weakly bound $S2O_4$ tetrahedra (Figs. 1 and 2). The morphological elongation is parallel to [010], i.e., parallel to the "rods" composed of Pb-O polyhedra. Elyite has a Mohs' hardness of two and is sectile; both properties are explained by the weak bonds between the different polyhedra and the presence of a flexible hydrogen bond system (see below). It is noteworthy that the structure arrangement in elyite is in agreement with the findings of Eby and Hawthorne (1993) that Cu oxysalt mineral structures, which are based on isolated Cu-O polyhedra, are all exclusively represented by sulfates.

The planar fourfold-coordination of Cu and the violet color in elyite and other Cu compounds

The exclusively planar fourfold-coordination of the Cu atoms makes elyite one of the few natural examples of this coordination. The review on Cu oxysalt minerals by Eby and Hawthorne (1993) points out that Cu predominantly shows a Jahn-Teller-distorted [4+2]-coordination, with a very strong bimodal distribution of Cu-O distances and maxima at 1.97 and 2.44 Å (ratio 2:1). The <Cu-O> bond lengths in elyite are in accordance with the average bond distance of planar four-

TABLE 3. Selected interatomic distances (Å), bond angles (°) and calculated bond valence sums (v.u.) for the coordination polyhedra in elyite

Bond distances in the Pb-O, Cu-O, and S-O polyhedra					
Pb1-O9	2.197(5)	0.80	Pb5-O9	2.248(5)	0.69
Pb1-O10	2.262(4)	0.67	Pb5-OH6	2.360(5)	0.50
Pb1-OH8	2.410(5)	0.44	Pb5-O10	2.511(5)	0.34
Pb1-O7	2.852(6)	0.14	Pb5-OH2	2.664(5)	0.23
Pb1-OW2	3.109(6)	0.07	Pb5-OH3	2.742(5)	0.18
Pb1-O2	3.191(5)	0.05	Pb5-O8	2.869(6)	0.13
<Pb1-O>	2.670	2.17 v.u.	<Pb5-O>	2.566	2.07 v.u.
Pb2-O10	2.253(4)	0.68	Pb6-O11	2.235(5)	0.72
Pb2-O11	2.317(5)	0.58	Pb6-OH7	2.317(5)	0.57
Pb2-OH4	2.322(5)	0.56	Pb6-O12	2.490(5)	0.36
Pb2-O6	3.041(6)	0.08	Pb6-OH1	2.628(5)	0.25
Pb2-O8	3.104(5)	0.07	Pb6-O4	2.962(6)	0.10
Pb2-OW1	3.257(7)	0.05	Pb6-OW1	3.082(7)	0.07
Pb2-O6	3.282(6)	0.04	<Pb6-O>	2.619	2.06 v.u.
Pb2-O7	3.282(7)	0.04			
<Pb2-O>	2.857	2.10 v.u.	Pb7-O12	2.209(4)	0.77
			Pb7-OH2	2.422(5)	0.43
Pb3-O12	2.223(4)	0.74	Pb7-O9	2.469(5)	0.38
Pb3-O9	2.325(4)	0.56	Pb7-OH5	2.588(5)	0.27
Pb3-OH3	2.388(5)	0.47	Pb7-OH7	2.797(5)	0.16
Pb3-OW2	2.899(7)	0.12	Pb7-O2	2.865(6)	0.13
Pb3-O5	3.004(6)	0.09	<Pb7-O>		2.14 v.u.
Pb3-OW1	3.108(7)	0.07			
Pb3-O5	3.196(6)	0.05	Pb8-O10	2.216(5)	0.75
<Pb3-O>	2.735	2.10 v.u.	Pb8-O11	2.442(5)	0.41
			Pb8-OH1	2.468(6)	0.38
Pb4-O11	2.218(5)	0.75	Pb8-OH8	2.658(5)	0.23
Pb4-O12	2.332(4)	0.55	Pb8-OH6	2.685(5)	0.21
Pb4-OH5	2.438(5)	0.42	Pb8-O4	2.731(6)	0.19
Pb4-O5	2.856(6)	0.14	<Pb8-O>	2.533	2.16 v.u.
Pb4-O4	2.880(5)	0.13			
Pb4-O6	2.948(6)	0.11			
<Pb4-O>	2.612	2.08 v.u.			
Cu1-OH1	1.918(5)	0.52	S1-O1	1.473(5)	1.50
Cu1-OH2	1.922(5)	0.52	S1-O3	1.476(5)	1.49
Cu1-OH3	1.940(5)	0.49	S1-O4	1.480(6)	1.48
Cu1-OH4	1.951(5)	0.48	S1-O2	1.481(5)	1.47
<Cu1-O>	1.933	2.02 v.u.	<S1-O>	1.478	5.94 v.u.
Cu2-OH5	1.917(5)	0.53	S2-O5	1.456(6)	1.58
Cu2-OH6	1.922(5)	0.52	S2-O6	1.462(5)	1.55
Cu2-OH7	1.929(5)	0.51	S2-O7	1.462(6)	1.55
Cu2-OH8	1.939(5)	0.50	S2-O8	1.465(6)	1.54
<Cu2-O>	1.927	2.05 v.u.	<S2-O>	1.461	6.21 v.u.

Bond angles in the planar CuO$_4$ squares			
OH1-Cu1-OH2	95.7(2)	OH5-Cu2-OH6	174.3(2)
OH1-Cu1-OH3	178.1(2)	OH5-Cu2-OH7	86.0(2)
OH2-Cu1-OH3	84.8(2)	OH6-Cu2-OH7	93.2(2)
OH1-Cu1-OH4	86.5(2)	OH5-Cu2-OH8	95.3(2)
OH2-Cu1-OH4	176.0(2)	OH6-Cu2-OH8	86.0(2)
OH3-Cu1-OH4	93.1(2)	OH7-Cu2-OH8	173.8(2)

Bond-valence sums (v.u.) for O atoms (excluding H contributions)							
O1	1.51	O7	1.71	OH1	1.12	OH7	1.23
O2	1.65	O8	1.74	OH2	1.16	OH8	1.16
O3	1.48	O9	2.43	OH3	1.14	OW1	0.19
O4	1.79	O10	2.45	OH4	1.14	OW2	0.19
O5	1.84	O11	2.45	OH5	1.20		
O6	1.79	O12	2.42	OH6	1.23		

Note: Bond-valence parameters used are from Brese and O'Keeffe (1991). Bond valence sums (v.u.) are derived from unrounded bond-valence contributions.

fold-coordinated Cu, 1.933(3) Å (Lambert 1988). Eby and Hawthorne (1993) listed only two minerals with exclusively planar fourfold-coordination of Cu: henmilite and cuprorivaite. In both, the CuO$_4$ polyhedra are isolated.

TABLE 4. Suggested hydrogen bonding system for elyite

Involved atoms	D-H···A (°)	D-A (Å)
OH1-H1···O1	134	2.920(8)
OH2-H2···O3	133	2.893(8)
OH3-H3···OW1	139	3.230(9)
OH4-H4···O5	129	3.042(9)
OH5-H5···O1	146	2.918(8)
OH6-H6···O1	139	2.762(8)
OH6-H6···OH7	113	2.799(7)
OH7-H7···O3	142	2.761(7)
OH8-H8···O3	153	3.077(7)
OW1-H9···O8	143	2.841(8)
OW2-H10···O6	154	2.839(9)

Notes: D = donor, A = acceptor.

Henmilite, Ca$_2$Cu(OH)$_4$[B(OH)$_4$]$_2$ (Nakai et al. 1986), also shows a bluish violet color, very similar to that of elyite. The Cu atom in henmilite has four Cu-O bonds at ~1.944 Å. Another example of a blue-violet Cu oxysalt mineral, whose atomic arrangement is also characterized by Cu in planar fourfold-coordination (<Cu-O> 1.931 Å), is johillerite, Na(Mg,Zn)$_3$Cu(AsO$_4$)$_3$ (Keller and Hess 1988), which is not included in the review by Eby and Hawthorne (1993). A synthetic compound with the same structure type, Zn$_3$Cu$_2$(AsO$_4$)$_3$, is violet-blue and macroscopically pleochroic (blue, violet) (Fleck 1998). It contains both divalent fourfold-coordinated Cu and monovalent linearly twofold-coordinated Cu. The fourfold-coordinated Cu atom has two Cu-O bonds at 1.907 and two at 1.931 Å. The above observations suggest that the more or less violet color of some Cu oxysalt compounds might be related to a planar fourfold-coordination of Cu in their structures, involving short and strong Cu-O bonds. However, there are also examples which are not in accordance with this hypothesis: cuprorivaite, CaCuSi$_4$O$_{10}$, with <$^{[4]}$Cu-O> 1.93 Å (Bensch and Schur 1995) is blue, as are its Ba and Sr analogues, effenbergerite and wesselsite, respectively (Giester and Rieck 1994, 1996). A search for further violet compounds containing Cu and O revealed about 35 examples. Among these are BaCuSi$_2$O$_6$, Ba$_3$Cu$_2$Si$_6$O$_{17}$, anthonyite [Cu(OH,Cl)$_2$·3H$_2$O], Cu$_{0.6}$NbO$_{2.6}$F$_{0.4}$, Cu$_3$V$_2$O$_8$, and many organometallic compounds. Crystal structure data are only available for BaCuSi$_2$O$_6$, Cu$_3$V$_2$O$_8$, and Cu$_{0.6}$NbO$_{2.6}$F$_{0.4}$. The first compound has fourfold-coordinated Cu^{2+} (<Cu-O> 1.93 Å; Finger et al. 1989; Janczak and Kubiak 1992), whereas the two Cu^{2+} ions in the violet-red compound Cu$_3$V$_2$O$_8$ show a distinct [4+2]- and an irregular [2+2+2]-coordination, with Cu-O distances of 2 × 1.912, 2 × 1.977, 2 × 2.595 Å, and 1.931 – 2.632 Å, respectively (Shannon and Calvo 1972). Cu$_3$V$_2$O$_8$ was synthesized at higher pressures (30 kbar), i.e., conditions which usually lead to an increase in coordination numbers. In the violet-red compound Cu$_{0.6}$NbO$_{2.6}$F$_{0.4}$, Cu is monovalent and coordinated to two O and two F, with similar bond lengths (≈ 1.94 Å; Lundberg and Ndalamba a lunga 1981).

Hydrogen bonding

Bond-valence calculations demonstrate that two O atoms, OW1 and OW2, are part of H$_2$O molecules, as their bond-valence sums are both 0.19 v.u. (valence units), respectively (Table 3). OW1 and OW2 are bonded to H9 and H10, respectively, at

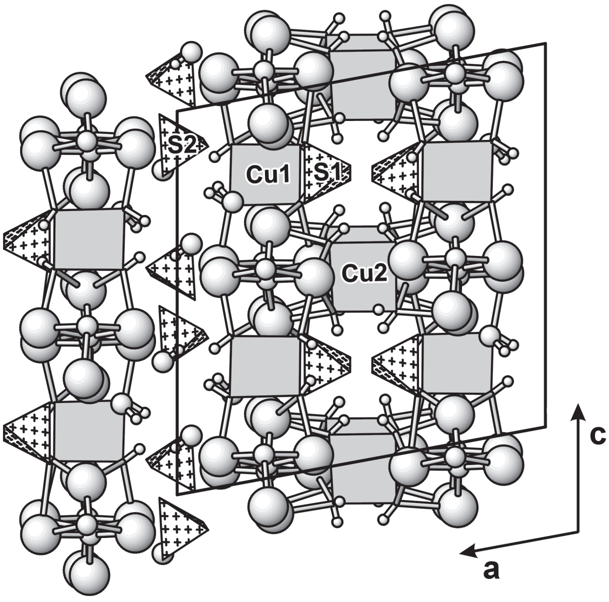

FIGURE 1. The structure framework in elyite projected down [010], parallel to the direction of the "rods" formed by the Pb atoms (large balls). SO_4 tetrahedra are shown with crosses, planar CuO_4 squares are shaded, O atoms are represented by small balls and H atoms by very small balls. O atoms belonging to SO_4 and CuO_4 are not drawn, and, for improved clarity, only those Pb-O bonds within 2.8 Å are shown. The unit cell is outlined. All drawings were done with ATOMS (version 5.0; Shape Software, 1999).

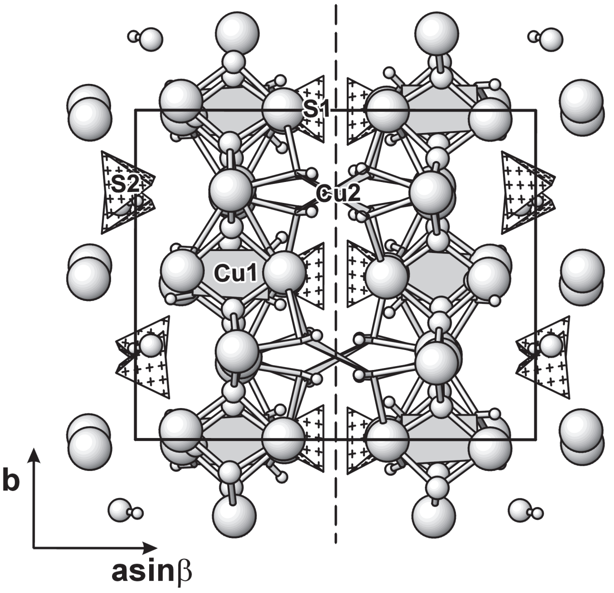

FIGURE 2. View of the elyite structure down [001]. The pseudo-mirror plane parallel to {100} (dashed line) explains the non-merohedral twinning reported in other samples (see text). Symbols are as in Figure 1.

a distance of 0.78(7) and 0.93(8) Å. Both OW atoms are only weakly bonded to Pb atoms, with Pb-OW distances between 2.90 and 3.26 Å. Weak hydrogen bonds from the two H_2O molecules are accepted by at least two O atoms, O8 and O6 (Table 4). All eight ligands of the two planar CuO_4 squares are OH groups, as shown by their bond-valence sums, which range between 1.12 and 1.23 v.u. (Table 3). Bond-valence sums for O1, O2, and O3, all of which belong to the S1O_4 tetrahedron, are low (1.51, 1.65, and, 1.48 v.u., respectively). They indicate that these O atoms are acceptors of hydrogen bonds from several OH and OW atoms at suitable O···O distances and O-H···O angles (Table 4). The sites O5, O6, and O8, with bond valences between 1.71 and 1.84 v.u., may also be acceptor atoms (Table 4). The hydrogen bond donated by the OH6-H6 group is bifurcated, involving both O1 and OH7. Although the sites O9, O10, O11, and O12, which all form bonds solely with Pb atoms, appear to be very overbonded (with ~2.4 v.u.), experience indicates that the high calculated bond-valence sums are due to insufficiently flexible bond-valence parameters applied to short Pb-O bonds.

Formula for elyite

The structure determination of elyite suggests that its formula is $Pb_4Cu(SO_4)O_2(OH)_4{\cdot}H_2O$, which has one oxygen atom less than the formula given by Williams (1972), and two water molecules in the asymmetric unit. The formula reported by Miyawaki et al. (1997), $Pb_{4.00}Cu_{0.94}(SO_4)_{1.07}[O_{0.73}(OH)_{6.28}]_{\Sigma 7.01}$, with 11 O atoms, is in accord with the present results. A powder pattern calculated from the crystal structure data shows good agreement with the improved X-ray powder data given by Miyawaki et al. (1997).

Relation to other species

Elyite is chemically closely related to chenite $Pb_4Cu(OH)_6(SO_4)_2$ (Paar et al. 1986), which is further enriched in sulfate by comparison and has a sky-blue color. The triclinic ($P\overline{1}$) crystal structure of chenite consists of SO_4 tetrahedra and $Cu(OH)_4O_2$, $Pb(OH)_3O_5$, and $Pb(OH)_4O_4$ polyhedra which are linked through vertices and edges into a three-dimensional network (Hess et al. 1988). The presence of an additional sulfate group in chenite (when compared to elyite) is reflected by the fact that the Cu atom has [4+2]-coordination, being linked to a SO_4 tetrahedron via its apical O atoms. Hess et al. (1988) noted that one of the S-O bonds is unrealistically short, with a distance of only 1.38 Å. As this seemed unlikely, we reinvestigated the crystal structure of chenite and found that all four S-O bonds are in the expected range (1.469 to 1.484 Å), and that the symmetry of the SO_4 tetrahedron is close to ideality (the detailed results of the refinement will be published elsewhere). Linarite, $PbCu(OH)_2(SO_4)$, and the closely related selenite-selenate schmiederite, $Pb_2Cu_2(OH)_4(SeO_3)(SeO_4)$ (Effenberger 1987), both have a higher Cu:Pb ratio than elyite. Their Cu atoms have [4+2]-coordination, and their Cu-O polyhedra share edges to form chains. No natural or synthetic Pb-Cu-selenates are known. Therefore, it would seem interesting to synthesize possible selenate analogues of elyite and chenite and observe their colors.

ACKNOWLEDGMENTS

The authors thank R. Bayerl of Stuttgart, Germany, for kindly furnishing the investigated specimens. We are grateful to R. Miyawaki for providing us with a reprint of his paper and additional information. H. Effenberger is thanked for comments on the manuscript. A. Pring provided further comments and improved the language. The manuscript was further improved by careful reviews and critical suggestions by two anonymous referees and Associate Editor R. Oberti.

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MANUSCRIPT RECEIVED FEBRUARY 2, 2000
MANUSCRIPT ACCEPTED AUGUST 3, 2000
PAPER HANDLED BY ROBERTA OBERTI