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Expanding crystal chemistry of anhydrous copper oxysulfates: synthesis and crystal structure of $K_{1.5}(Pb, Na, \square)_{0.5}[Cu_5O_2](SO_4)_4$

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Abstract: A new anhydrous sulfate $K_{1.5}(Pb, Na, \square)_{0.5}[Cu_5O_2](SO_4)_4$ (**1**) was synthesized in an evacuated silica ampoule. **1** is triclinic, $P\bar{1}$, $a = 8.7357(2)$, $b = 9.4633(3)$, $c = 10.0243(3)$ Å, $\alpha = 107.080(2)$, $\beta = 97.326(2)$, $\gamma = 105.831(2)^\circ$, $V = 742.42(4)$ Å³ and $R_1 = 0.027$. The crystal structure represents a new structure type based on strongly corrugated $[Cu_5O_2]^{6+}$ chains. This feature can be attributed to the flexibility of the $[Cu_5O_2]^{6+}$ chain in accommodating ‘lone-pair’ Pb^{2+} cations at one of the *A* sites. The crystal chemistry of known fumarolic minerals and synthetic compounds structurally based on $[M_5O_2]^{n+}$ chains is discussed.

Keywords: anhydrous sulfates; copper; oxocentered complexes; fumarolic sulfate minerals

1 Introduction

Anhydrous sulfates of alkali and divalent transition metals are of essential interest due to the richness of their crystal chemistry, which underpins a variety of attractive properties, such as electrochemical^{1,2} or magnetic.^{3–5} This large class of inorganic compounds hosts two relatively large groups. The main families of the first group are: i) itelmenite $A_2^{+}M_2^{2+}(SO_4)_4$ ($A = Na, K, Rb, Cs, Tl, Ca$; $M = Cu, Mg, Zn, Co, Ni, Cd, Mn, Fe$),^{6–8} ii) saranchinaite $A_2^{+}Cu(SO_4)_2$ ($A = Na, K, Rb, Cs$),^{9–11} iii) langbeinite $A_2^{+}M_2^{2+}(SO_4)_3$ ($A = Na, K, Rb, Cs, Tl$; $M = Mn, Fe, Co, Ni, Cu, Zn$).^{1,11} Their structures commonly exhibit morphotropism, i.e. structural and sometimes slight compositional variations dependent on the size of the alkali cation. The structures within the

second group contain “additional” O^{2-} anions not incorporated into oxyanions. The largest family therein is formed by the analogs of puninite with the general formula $A_2^{+}[Cu_3O](SO_4)_3$ ($A = Na, K, Rb, Cs$).^{12–14} Several smaller families, comprising only a few representatives each, include cryptochalcite/cesiodymite $A_2^{+}[Cu_5O](SO_4)_5$ ($A = K, Rb, Cs$),^{10,15} piypite $A_4^{+}Cu_4O_2(SO_4)_4 \cdot (A^{+}, Cu)Cl$ ($A = Na, K, Rb$),^{10,16} etc.

The hitherto largest natural source of anhydrous sulfates has been minerals from fumarolic sublimates of Mt. Tolbachik (Kamchatka, Russia), Mt. Vulcano and Mt. Vesuvius (Italy). Illustrative examples are koryakite $NaKMg_2Al_2(SO_4)_6$,¹⁷ structurally related NASICON-type materials; hermannjahnite $CuZn(SO_4)_2$ ¹⁸ and dravertite $CuMg(SO_4)_2$,¹⁹ as well as wulfite $K_3Na[Cu_4O_2](SO_4)_4$ and parawulfite $K_5Na_3[Cu_8O_4](SO_4)_8$.²⁰ To date, no synthetic analogues have been reported for any of these minerals. The temperature in the Tolbachik fumaroles varies between 250 and 650 °C. The situation is additionally complicated by the extremely high hygroscopicity of most of these mineral species. Under “ambient” humidity, some of them completely decay within hours.

A typical crystal-chemical feature of many anhydrous fumarolic minerals, not only of sulfates, is the occurrence of oxocentered tetrahedra, as found e.g. in the structures of georgbokiite $[Cu_5O_2](SeO_3)_2Cl_2$,²¹ antipovite $[Cu_5O_2](PO_4)_2$,²² klyuchevskite $K_3[Cu_3(Fe^{3+}, Al)O_2](SO_4)_4$,²³ as well as in the previously noted wulfite, parawulfite, cryptochalcite, etc. Akin to the “classical” cation-centered polyhedra, these species can also share vertices and edges, forming architectures of varied nuclearity and dimensionality, which have been systematically treated in Ref. 24.

Most synthetic compounds of this family have been prepared by vapor transport in a temperature gradient, mimicking the physicochemical processes in fumaroles.^{25,26} The starting reagents are taken in the desired ratios, carefully dehydrated at elevated temperatures, ground, and vacuum-sealed into silica tubes. The tubes are then placed in a vertical or horizontal furnace and annealed according to a desired protocol (temperature gradient and annealing time). The small amount of water absorbed during grinding is essential, as it serves as a transport agent. In other cases, crystals can be grown by melting (congruent or peritectic) and subsequent cooling of the sample. It should be noted that

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these approaches do not always yield targeted stoichiometries, particularly when attempting to prepare synthetic analogs of minerals whose natural formation mechanisms may differ substantially from synthetically available protocols. Herein, we report a new representative of this attractive family, $K_{1.5}(Pb,Na,\square)_{0.5}[Cu_5O_2](SO_4)_4$ (**1**), which belongs to a new structure type.

2 Experimental

2.1 Synthesis

Initially, we aimed to prepare the synthetic analog of elemelanite $(K_2Pb)[Cu_4O_2](SO_4)_4$.²⁷ Lead oxide (massicot), potassium sulfate, copper oxide, and copper sulfate (prepared from the pentahydrate by annealing at 450 °C overnight) were mixed in a 1:1:2:2 molar ratio, carefully ground, and placed in a silica ampoule. The mixture was preheated in dynamic vacuum until the residual pressure dropped to ~50 mTorr (~7–8 Pa), whereupon the sample was flame-sealed and annealed at 450 °C for one week. The initially pinkish powder turned pale green but did not attain the dark green color characteristic of the natural mineral. The sample was re-ground and annealed repeatedly at 550–575 °C until it developed an intense green color and single crystals suitable for X-ray diffraction analysis appeared.

Chemical data for **1** were obtained using: a Hitachi TM3000 scanning electron microscope equipped with a built-in silicon drift detector. The crystal of **1** was coated with a carbon film to prevent charge buildup. Unfortunately, the crystals were unstable under the electron beam to perform quantitative analysis. The analysis revealed no other elements, except K, Cu, S, Pb and Na.

2.2 Single-crystal X-ray studies

A crystal for structural studies was selected under a binocular microscope, mounted with an epoxy glue onto a glass fiber, and mounted on a Rigaku Synergy-S X-ray diffractometer equipped with a micro-focus X-ray tube operating with MoK α radiation at 50 kV and 1 mA. Empirical absorption correction was applied using spherical harmonics as implemented in the SCALE3 ABSPACK scaling algorithm within CrysAlis PRO 1.171.42.102a. The structure was solved by direct methods and refined using the SHELX software package.²⁸ The results are summarized in Tables 1–3. Bond-valence sum (BVS) calculations were performed using the parameters from Ref. 29.

Table 1: Experimental data for **1**.

Crystal data	
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	8.7357(2)
<i>b</i> (Å)	9.4633(3)
<i>c</i> (Å)	10.0243(3)
α (°)	107.080(2)
β (°)	97.326(2)
γ (°)	105.831(2)
<i>V</i> (Å ³)	742.42(4)
Calculated density (g/cm ³)	3.691
Absorption coefficient (mm ^{−1})	9.607
Absorption correction	Multi-scan
<i>T</i> _{min} , <i>T</i> _{max}	0.705, 1.000
Data collection	
Radiation type, wavelength (Å)	MoK α (λ = 0.71073)
Temperature (K)	293
θ range (°)	3.410–27.998
<i>h</i> , <i>k</i> , <i>l</i> ranges	−11 → 11, −11 → 12, −13 → 13
Total number of reflections	12,232
Observed reflections, <i>R</i> _{int}	3,585, 0.028
Number of parameters/restrictions	272, 0
Weighting scheme, <i>a</i> , <i>b</i>	0.0277, 1.9720
Structure refinement	
<i>R</i> ₁ [<i>F</i> > 4 σ <i>F</i>], <i>wR</i> ₁ [<i>F</i> > 4 σ <i>F</i>]	0.027, 0.063
<i>R</i> _{all} , <i>wR</i> _{all}	0.033, 0.065
GoF	1.063
$\Delta\rho_{\max/\min}$ (e/Å ³)	2.858, −1.385
CCDC no.	2531067

3 Results and discussion

3.1 Crystal structure of **1**

3.1.1 Coordination of atoms

The alkali and lead cations are distributed over three symmetry independent positions (A1–A3); there are also five fully occupied copper (Cu1–Cu5), four sulfur (S1–S4), and eighteen oxygen sites (O1–O18) (Figure 1). Most of these correspond to the general 2i Wyckoff site, while A1 adopts the special 1*d* site.

Both A1 and A2 are fully occupied by K⁺ cations. The former has eight oxygen neighbors 8 with a mean A1–O distance of 2.89 Å. The A2 coordination number is ten, and the mean A2–O distance is 2.96 Å. Both modes are common for the potassium cations.³⁰ Calculated bond valence sums for these sites are 0.99 and 1.09 v.u., respectively, considering the bonds with contributions of 0.03 v.u. and above.

Table 2: Atomic coordinates and displacement parameters ($\text{\AA}^2$) for 1.

Atom	B.V.S.	Wyck. site	x	y	z	U_{10}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	2.00	2i	0.19872(5)	0.25709(5)	0.42261(4)	0.00977(11)	0.0087(2)	0.0089(2)	0.00925(19)	0.00328(15)	0.00017(16)	-0.00029(16)
Cu2	2.02	2i	-0.11327(5)	0.08188(5)	0.52833(4)	0.00884(10)	0.0106(2)	0.0092(2)	0.00910(19)	0.00448(15)	0.00326(16)	0.00497(17)
Cu3	1.97	2i	0.55088(5)	0.41658(5)	0.37892(4)	0.00843(11)	0.0061(2)	0.0100(2)	0.00689(19)	-0.00015(15)	0.00009(15)	0.00304(16)
Cu4	2.04	2i	-0.08737(5)	-0.01915(5)	0.20886(4)	0.00952(11)	0.0116(2)	0.0083(2)	0.00708(19)	0.00050(15)	-0.00137(16)	0.00474(17)
Cu5	1.90	2i	0.24127(6)	0.54284(5)	0.31771(5)	0.01269(11)	0.0141(2)	0.0107(2)	0.0134(2)	0.00457(17)	-0.00121(17)	0.00579(18)
S1	5.98	2i	-0.26748(10)	-0.22742(10)	-0.12145(8)	0.00825(17)	0.0089(4)	0.0085(4)	0.0061(3)	0.0009(3)	0.0002(3)	0.00033(3)
S2	5.95	2i	0.85654(10)	0.29647(9)	0.35121(8)	0.00734(16)	0.0071(4)	0.0075(4)	0.0080(3)	0.0027(3)	0.0013(3)	0.00034(3)
S3	5.96	2i	0.15262(12)	0.78247(10)	0.18989(9)	0.01236(18)	0.0188(5)	0.0132(4)	0.0093(4)	0.0044(3)	0.0035(3)	0.0111(4)
S4	6.01	2i	0.41110(12)	0.25259(11)	0.68821(11)	0.0167(2)	0.0122(4)	0.0116(4)	0.0265(5)	0.0102(4)	0.0003(4)	0.00020(4)
Al ^a	0.99	1d	-1/2	0	0	0.0370(4)	0.0233(7)	0.0297(8)	0.0510(9)	-0.0020(7)	0.0053(7)	0.0164(6)
Al ^b	1.08	2i	0.25236(13)	0.51175(11)	-0.08054(9)	0.0239(2)	0.0350(5)	0.0216(4)	0.0181(4)	0.0081(3)	0.0079(4)	0.0119(4)
Al ^b	1.26	2i	0.48343(17)	-0.04032(16)	0.55782(19)	0.0463(4)	0.0279(7)	0.0290(7)	0.0773(11)	0.0107(7)	0.0070(7)	0.0125(6)
O1	2.03	2i	0.0341(3)	0.0674(3)	0.4050(2)	0.0079(5)	0.0087(11)	0.0076(11)	0.0069(10)	0.0021(9)	0.0014(9)	0.0023(9)
O2	2.04	2i	0.3508(3)	0.4482(3)	0.4257(2)	0.0089(5)	0.0080(11)	0.0092(12)	0.0092(11)	0.0029(9)	0.0007(9)	0.0031(10)
O3	1.92	2i	0.8300(3)	0.2622(3)	0.4839(3)	0.0131(5)	0.0209(14)	0.0127(12)	0.0111(11)	0.0076(10)	0.0068(10)	0.0088(11)
O4	1.91	2i	1.0291(3)	0.3842(3)	0.3697(3)	0.0131(5)	0.0072(12)	0.0129(12)	0.0193(13)	0.0053(10)	0.0025(10)	0.0037(10)
O5	2.04	2i	-0.4453(3)	-0.2711(3)	-0.1843(3)	0.0172(6)	0.0097(13)	0.0236(15)	0.0111(12)	-0.0039(10)	-0.0013(10)	0.0069(11)
O6	1.98	2i	0.8083(3)	0.1490(3)	0.2284(3)	0.0134(5)	0.0161(13)	0.0111(13)	0.0106(11)	0.0005(10)	-0.0017(10)	0.0065(11)
O7	1.99	2i	0.2871(3)	0.3161(3)	0.6344(3)	0.0159(5)	0.0193(14)	0.0188(14)	0.0131(12)	0.0059(10)	0.0029(10)	0.0117(11)
O8	2.07	2i	0.7555(3)	0.3908(3)	0.3244(3)	0.0110(5)	0.0092(12)	0.0127(12)	0.0136(12)	0.0054(10)	0.0033(10)	0.0063(10)
O9	2.09	2i	0.2490(3)	0.9010(3)	0.3319(3)	0.0130(5)	0.0125(13)	0.0150(13)	0.0126(12)	0.0046(10)	0.0039(10)	0.0056(10)
O10	2.15	2i	-0.2402(3)	-0.1155(3)	0.0235(3)	0.0141(5)	0.0165(13)	0.0156(13)	0.0077(11)	-0.0016(10)	-0.0013(10)	0.0092(11)
O11	2.01	2i	-0.2253(4)	-0.3659(3)	-0.1209(3)	0.0165(6)	0.0276(15)	0.0118(13)	0.0127(12)	0.0043(10)	0.0029(11)	0.0111(11)
O12	1.97	2i	-0.1731(3)	-0.1488(3)	-0.2065(3)	0.0149(5)	0.0201(14)	0.0111(13)	0.0121(12)	0.0037(10)	0.0058(11)	0.0022(11)
O13	2.05	2i	-0.0128(3)	0.7972(3)	0.1659(3)	0.0197(6)	0.0206(15)	0.0135(14)	0.0204(14)	-0.0016(11)	-0.0038(11)	0.0104(12)
O14	2.04	2i	0.1221(4)	0.6216(3)	0.1967(3)	0.0182(6)	0.0275(16)	0.0122(13)	0.0165(13)	0.0050(10)	-0.0014(11)	0.0115(12)
O15	1.98	2i	0.3350(4)	0.0864(3)	0.6636(3)	0.0254(7)	0.0294(17)	0.0115(14)	0.0273(15)	0.0089(12)	-0.0055(13)	-0.0026(12)
O16	1.94	2i	0.2363(4)	0.8012(4)	0.0793(3)	0.0270(7)	0.0417(19)	0.0293(17)	0.0188(14)	0.0111(12)	0.0190(14)	0.0167(15)
O17	2.01	2i	0.5397(4)	0.2676(4)	0.6068(4)	0.0341(8)	0.0257(17)	0.040(2)	0.051(2)	0.0266(17)	0.0194(16)	0.0155(15)
O18	1.79	2i	0.4752(4)	0.3428(4)	0.8408(3)	0.0341(8)	0.037(2)	0.0304(18)	0.0245(16)	0.0047(13)	-0.0087(14)	0.0067(15)

^aS.O.F. = $K_{1.00}$, ^bS.O.F. = $Na_{0.24}, Pb_{0.13}, \square_{0.13}$.

Table 3: Selected interatomic distances (Å) in the structure of **1**.

Cu1–O1	1.914(2)	Cu4–O1	1.926(2)	A1–O10	2.787(3)	S1–O11	1.456(3)
Cu1–O2	1.919(2)	Cu4–O10	1.943(2)	A1–O10	2.787(3)	S1–O10	1.469(2)
Cu1–O7	2.016(3)	Cu4–O13	1.970(3)	A1–O5	2.886(3)	S1–O12	1.476(3)
Cu1–O12	2.059(2)	Cu4–O6	2.014(3)	A1–O5	2.886(3)	S1–O5	1.493(3)
<Cu1–O _{eq} >	1.98	<Cu4–O _{eq} >	1.96	A1–O16	2.908(3)	<S1–O>	1.474(1)
Cu1–O4	2.251(3)	Cu4–O12	2.401(3)	A1–O16	2.908(3)		
<Cu1–O>	2.03	Cu4–O15	2.674(3)	A1–O6	2.990(2)	S2–O4	1.467(3)
		<Cu4–O _{ap} >	2.54	A1–O6	2.990(2)	S2–O8	1.470(3)
Cu2–O1	1.899(2)	<Cu4–O>	2.155(1)	<A1–O>	2.89	S2–O6	1.476(2)
Cu2–O9	1.947(3)					S2–O3	1.489(2)
Cu2–O1	1.972(2)	Cu5–O2	1.914(2)	A2–O11	2.760(3)	<S2–O>	1.476(1)
Cu2–O3	2.052(3)	Cu5–O14	1.935(3)	A2–O16	2.789(3)		
<Cu2–O _{eq} >	1.97	Cu5–O17	2.100(4)	A2–O18	2.854(3)	S3–O16	1.430(3)
Cu2–O15	2.357(3)	Cu5–O11	2.139(3)	A2–O8	2.854(3)	S3–O13	1.485(3)
Cu2–O13	2.882(3)	<Cu5–O _{eq} >	2.02	A2–O18	2.884(4)	S3–O9	1.495(3)
<Cu2–O _{ap} >	2.62	Cu5–O4	2.269(3)	A2–O13	2.898(3)	S3–O14	1.496(3)
<Cu2–O>	2.185(1)	Cu5–O3	2.556(3)	A2–O7	3.018(3)	<S3–O>	1.476(1)
		<Cu5–O _{ap} >	2.41	A2–O14	3.093(3)		
Cu3–O2	1.926(2)	<Cu5–O>	2.152(1)	A2–O14	3.139(3)	S4–O15	1.461(3)
Cu3–O2	1.943(2)			A2–O5	3.358(3)	S4–O18	1.462(3)
Cu3–O5	1.955(2)			<A2–O>	2.97	S4–O17	1.471(3)
Cu3–O8	1.990(3)					S4–O7	1.491(3)
<Cu3–O _{eq} >	1.95			A3 ... A3	1.579(5)	<S4–O>	1.471(1)
Cu3–O7	2.591(3)			A3–O15	2.167(4)		
Cu3–O17	3.015(3)			A3–O17	2.232(4)		
<Cu3–O _{ap} >	2.80			A3–O9	2.286(3)		
<Cu3–O>	2.237(1)			A3–O9	2.662(3)		
				A3–O17	2.700(4)		
				A3–O3	2.852(3)		
				A3–O15	2.888(4)		
				<A3–O>	2.54		

The A3 site is split and partially occupied by Pb^{2+} , Na^+ and also contains a vacancy. Such joint occupation by the lead and alkali cations is uncommon but has been observed in certain minerals, including philoxenite $(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$, found in fumarolic deposits of Tolbachik³¹ and acmonidesite $(NH_4,K,Pb^{2+},Na)_9Fe_4^{2+}(SO_4)_5Cl_8$, from Vulcano.³² The coordination number for this site is seven and its environment is one-sided which is common for the Pb^{2+} cations. The average A3–O bond distance is 2.54 Å. Among these, short A3–O bonds (with O15, O17 and O9) with an average length of 2.23 Å and long A3–O bonds (with O9, O17, O3, O15) with an average length of 2.78 Å stand out.

The coordination of the copper cations is discussed hereafter according to Ref. 33. Cu1 forms a distorted tetragonal pyramid with mean equatorial bond length of 1.98 Å and a longer apical Cu1–O4 of 2.251(3) Å. Cu2 resides in a distorted [4 + 1 + 1]-type octahedron with a mean equatorial bond length of 1.97 Å. The apical Cu2–O13 bond of 2.882(3) Å makes a very small contribution to the BVS (0.034 v.u.). The second apical bond of 2.357(3) Å is significantly shorter. This

coordination can be considered as intermediate between an octahedron [4 + 2] and a square pyramid. Cu3, similar to Cu1, forms a distorted square antiprism with a mean <Cu3–O_{eq}> distance of 1.95 Å (O_{eq} denotes equatorial bonds). The apical Cu3–O7 bond of 2.591(3) Å is long. The sixth Cu3–O17 contact of 3.015(3) Å has a very low contribution of 0.023 v.u.; even when considered, the coordination polyhedron of Cu3 can be described as a strongly distorted [4 + 1 + 1]-type, since the relative difference in the apical bond lengths exceeds the 12.5 % threshold.³³ Cu4 forms a distorted octahedron with a mean <Cu4–O_{eq}> distance of 1.96 Å. As in the previous case, there are two longer apical (O_{ap}) bonds, Cu4–O15 = 2.674(3) Å and Cu4–O12 = 2.401(3) Å. Their relative difference is below the 12.5 % threshold and the octahedron can be considered as a [4 + 2] type. A boundary situation is observed for Cu5 with Cu5–O_{eq} = 2.02 Å. The relative difference between the apical Cu5–O4 = 2.269(3) Å and Cu5–O3 = 2.556(3) Å is only 12.6 %; thus both [4 + 2] and [4 + 1 + 1] descriptions are possible. Across all five sites, the mean <Cu–O> bond length is 2.12 Å,

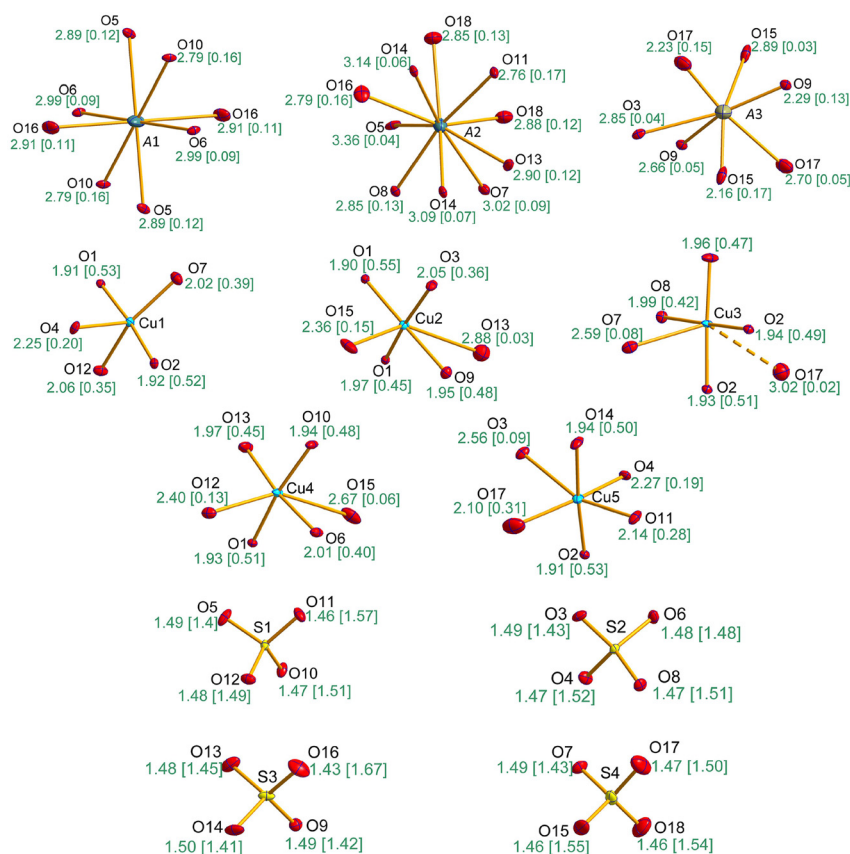


Figure 1: Coordination of the A, Cu, and S sites in the structure of **1**. The respective bond lengths and valences (in brackets) are also indicated. The dotted line indicates weak bonds with a valence contribution of less than 0.03 v.u. Thermal ellipsoids are shown at 50 % probability level.

the mean equatorial bond length is 1.98 Å, and the mean apical bond length is 2.50 Å. The bond valence sums for Cu1, Cu2, Cu, Cu4 and Cu5 are 1.99, 2.02, 1.97, 2.04, and 1.90 v.u., considering contributions of 0.03 v.u. or above.

All sulfur sites correspond to the sulfate tetrahedra with mean S–O bond lengths of 1.47 Å, 1.48 Å, 1.48 Å, and 1.47 Å for S1–O, S2–O, S3–O and S4–O, respectively, which agrees to the averaged values given in Ref. 34. The bond-valence sums are 5.98, 5.95, 5.96, and 6.02 v.u.

The O1 and O2 sites correspond to the centers of $[OCu_4]^{6+}$ tetrahedra. The mean O1–Cu and O2–Cu distances are 1.93 Å and 1.92 Å, respectively. The bond-valence sums are 2.03 v.u. for O1 and 2.04 v.u. for O2.

3.1.2 Structure description

3.1.2.1 Cation-centered approach

The CuO_n ($n = 5, 6$) and SO_4 polyhedra share edges and vertices to form complex layers parallel to the *ab* plane. These layers are pierced by wide channels running along the *c* axis (Figure 2). The interlayer space accommodates the A1 and A2 cations, while the A3 site is located within the layers.

3.1.2.2 Anion-centered approach

Due to the variability of coordination polyhedra around Cu^{2+} cations, the copper-oxide substructure of **1** can be conveniently described in terms of oxocentered OCu_4 tetrahedra (Figure 3a). Two $O1Cu_4$ tetrahedra share a common Cu3...Cu3 edge, thereby forming $[Cu_6O_2]^{8+}$ dimers. An identical situation is observed for the $O2Cu_4$ tetrahedra which also share a common Cu2...Cu2 edge and consequently produce $[Cu_6O_2]^{8+}$ dimers. Hence, the connectivity diagram (Figure 3b) is the same for both oxocentered tetrahedra in the structure of **1**. The resulting $[Cu_6O_2]^{8+}$ dimers share a common Cu1 vertex, producing strongly corrugated $[Cu_5O_2]^{6+}$ chain, as depicted in Figure 3c. These chains are aligned in the *ab* plane (Figure 4). The resulting structural architecture based on oxocentered units contains the interlayer space and a system of channels running along the *c* axis. Interlayer space is filled partly by isolated sulfate tetrahedra and partly by A1 site occupied by K. Channels are filled by A2 and A3 sites occupied by K, Na, Pb. Compositionally identical $[Cu_5O_2]^{6+}$ chains, but with a different topology, were first described in the structure of georgbokiite²¹ and will be discussed below.

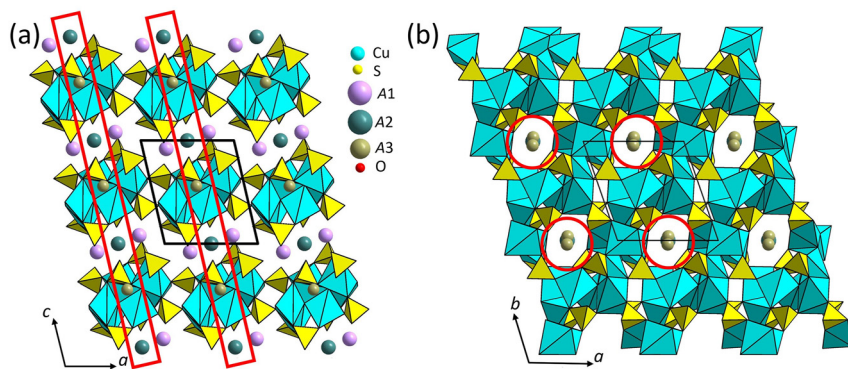


Figure 2: Cation-centered polyhedral (CuO_n = blue, SO_4 = yellow) representation of the structure of **1**, projected onto the ac (a) and the ab (b) planes. The channels running parallel to c and occupied by the large A cations are highlighted in red.

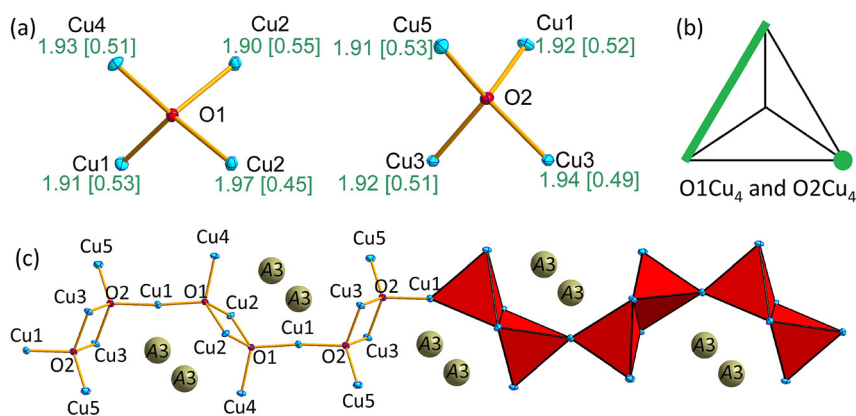


Figure 3: Tetrahedral coordination of O1 and O2 atoms (bond lengths and valence contributions in v.u. are given) (a). Connectivity diagram for the $O1Cu_4$ and $O2Cu_4$ tetrahedra: a solid green line denotes a shared edge, and a green dot denotes a shared vertex (b). Ball-and-stick and polyhedral representation of the $[Cu_5O_2]^{6+}$ chain and location of $A3$ sites with Pb^{2+} and Na^+ cations (c).

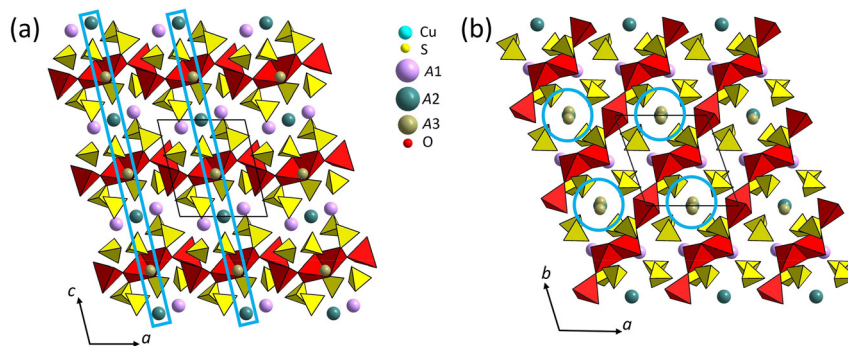


Figure 4: The structure of **1** represented in oxocentered OCu_4 (red) and SO_4 tetrahedra (yellow) and projected onto ac (a) and ab (b) planes. The channels parallel to c are highlighted in blue.

3.2 Relationship to structures of other copper oxysulfates

The new compound **1** represents a novel structure type. However, both cation- and anion-centered descriptions classify it as a “pierced-layered” structure. The oxocentered perspective allows for a detailed comparison with fumarolic copper–alkali sulfate minerals.

Many fumarolic anhydrous sulfate minerals contain oxocentered complexes, as illustrated in Figure 5. Euchlorine, $KNa[Cu_3O](SO_4)_3$,³⁵ is one of the most widespread copper oxysulfates in fumarolic environments. Its structure contains $[Cu_6O_2]^{8+}$ dimers (Figure 5a), which are identical to

those that form the chain in the structure of **1**. In the euchlorine structure, the $[Cu_6O_2]^{8+}$ complexes are linked via sulfate tetrahedra into layers parallel to the bc plane, with K^+ and Na^+ cations residing in the interlayer space. In cryptochalcite, $K_2Cu_5O(SO_4)_5$, and its isostructural counterpart cesiodymite, $CsKCu_5O(SO_4)_5$,¹⁵ analogous $[Cu_6O_2]^{8+}$ dimers are also formed (Figure 5b). However, in the structure of cryptochalcite, cation-centered copper complexes are additionally present. Thus, the framework is built from both CuO_n polyhedra and oxocentered OCu_4 tetrahedra. A two-dimensional system of channels hosts the K^+ cations. An isostructural rubidium analogue, $Rb_2Cu_5O(SO_4)_5$, was reported in Ref. 10.

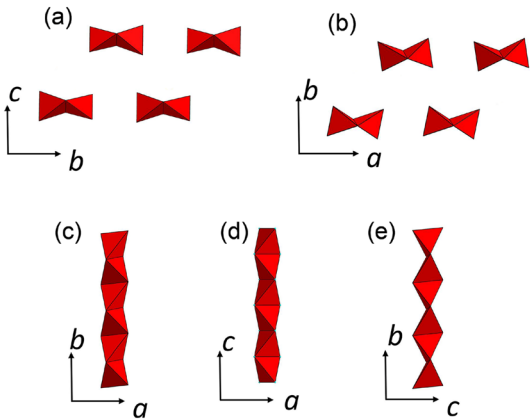


Figure 5: $[Cu_nO_m]^{2+}$ units in the crystal structures of alkali-copper oxysulfate minerals: euchlorine (a), cryptochalcite (b), eleomelanite (c), piypite (d) and wulfite (e). See the text for details.

In the structure of eleomelanite, $(K_2Pb)[Cu_4O_2](SO_4)_4$,²⁷ the $[Cu_6O_2]^{8+}$ dimers condense via edge-sharing into simple one-dimensional chains, as shown in Figure 5c. The chains are decorated by sulfate tetrahedra, resulting in rod-like copper–sulfate clusters, surrounded by K sites and mixed (K, Pb) sites.

Very similar one-dimensional rod-like copper–sulfate complexes are found in wulfite, $K_3Na[Cu_4O_2](SO_4)_4$, parawulfite, $K_5Na_3Cu_8O_4(SO_4)_8$, and piypite, $K_4[Cu_4O_2](SO_4)_4 \cdot (Na,Cu)Cl$ (Figure 5d and e). Their structures are differing primarily in the ordering of the alkali cations surrounding the chains; in piypite, additional Cl^- anions occupy some of the interchain positions.

Thus, among anhydrous copper–alkali sulfates, only three topologies of oxocentered complexes have been identified so far, and the synthetic compound **1** adds a new member to this family. The fundamental building block in all these structures is the $[Cu_6O_2]^{8+}$ dimer, which can either remain as an isolated unit or polymerize through shared vertices and edges into chains of different topologies.

3.3 Comparison of the $[M_5O_2]^{n+}$ chains in oxysalt structures

The oxocentered $[Cu_5O_2]^{6+}$ chains were previously described in the structure of the oxyselenite mineral georgbokiite²¹ and several other species (Table 4). The $[Cu_5O_2]^{6+}$ complex but with

Table 4: Known minerals and synthetic compounds containing $[M_5O_2]^{n+}$ chains.

Mineral, formula	Space group	$[M_5O_2]^{n+}$ chain conformation	O–O–O angle value (°)	Reference
$K_{1.5}(Pb,Na,\square)_{0.5}[Cu_5O_2](SO_4)_4$ (1)	$P\bar{1}$		123.7 and 133.2	This work
Georgbokiite $[Cu_5O_2](SeO_3)_2Cl_2$	$P2_1/c$		114.2	21
Parageorgbokiite $[Cu_5O_2](SeO_3)_2Cl_2$	$P2_1/c$		109.8	39
Antipovite $[Cu_5O_2](PO_4)_2$	$P\bar{1}$		109.6	22
Popovite $[Cu_5O_2](AsO_4)_2$	$P\bar{1}$		150.8	40
$[Hg_5O_2]Re_2O_8$	$P2_1/c$		127.3	41
$[PbGa_3GeO_2]Pb_2Ga_7O_{18}$ ($A^{2+}_3X^{3+}_{10}Y^{4+}_{20}O_{20}$ family)	$C2/m$		100.3–104.8	42–44

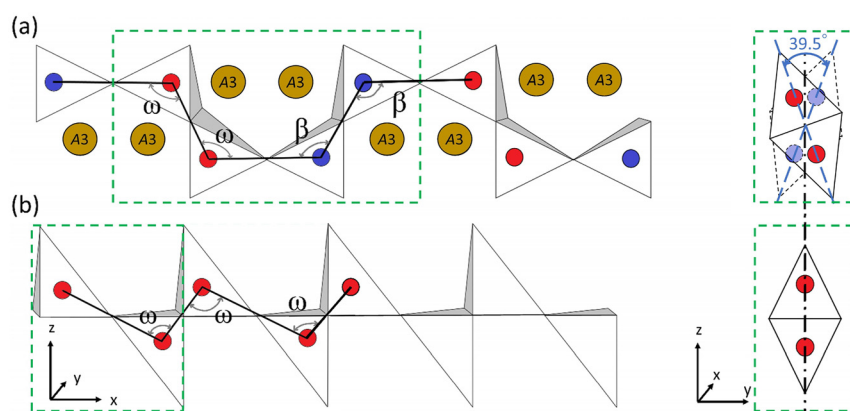


Figure 6: Comparison of the distorted $[Cu_5O_2]^{6+}$ chain in the structure of **1** with the previously reported $[M_5O_2]^{6+}$ chain in minerals and inorganic compounds. Schematic representation of the $[Cu_5O_2]^{6+}$ chain in the structure of **1** (a). Red and blue spheres denote the two symmetry-independent oxygen sites at the centres of the $O1Cu_4$ and $O2Cu_4$ tetrahedra, respectively; neighbouring A3 sites are shown in yellow. The O–O–O angles at O1 and O2 are unequal ($\beta \neq \omega$), and the axes of adjacent dimers are tilted by 39.5° relative to each other. $[M_5O_2]^{6+}$ chain previously reported in several minerals and synthetic compounds (listed in Table 4) (b). In these chains, all O–O–O angles are equal (ω).

layered and band topology is observed in the averievite family $[Cu_5O_2](T^{6+}O_4)_2 \cdot (MX)$ ($T = P, V$; $M = K, Rb, Cs, Cu$; $X = Cl, Br, I$)^{36,37} and aleutite $[Cu_5O_2](AsO_4)(VO_4) \cdot (Cu_{0.5}\square_{0.5})Cl$, respectively.³⁸

A specific feature of **1** is the presence of two symmetry-independent oxygen sites, which makes the chain structure somewhat more complex compared to that in georgbokiite. Two adjacent “binuclear” fragments are inclined at an angle of 39.5° to each other. The O–O–O angles at the two symmetry-independent oxygen atoms differ (123.7° and 133.2°) (Figure 6a), in contrast to the known $[M_5O_2]^{6+}$ chains in other minerals and synthetic compounds (Table 4). This distortion is likely induced by the stereochemically active lone pair of Pb^{2+} , which partially occupies the A3 site adjacent to the chains. A classic example of the influence of Pb^{2+} on chain conformation is alamosite $PbSiO_3$, where the

pyroxene-type chain adopts a 12-fold periodicity instead of the usual 2-fold repeat (as in enstatite $MgSiO_3$).⁴⁵

The ω angle shown in Figure 6b ranges from 100.3° to 150.7° (Table 4). The smallest values are found in compounds of the $A^{2+}_3X^{3+}_{10}Y^{4+}O_{20}$ -type, in which the angle increases with the size of the constituent cations. Despite having the same composition, georgbokiite and parageorgbokiite differ substantially in their structural arrangement, particularly with regard to the chloride anions surrounding the chains of oxocentered tetrahedra; this influences the O–O–O angle discussed here. The largest ω value occurs in popovite $[Cu_5O_2](AsO_4)_2$, which may be attributed to the larger size of the arsenate group compared to sulfate or selenite.

As shown in Figure 7, two principal types of chain packing can be distinguished. The parallel arrangement is adopted by

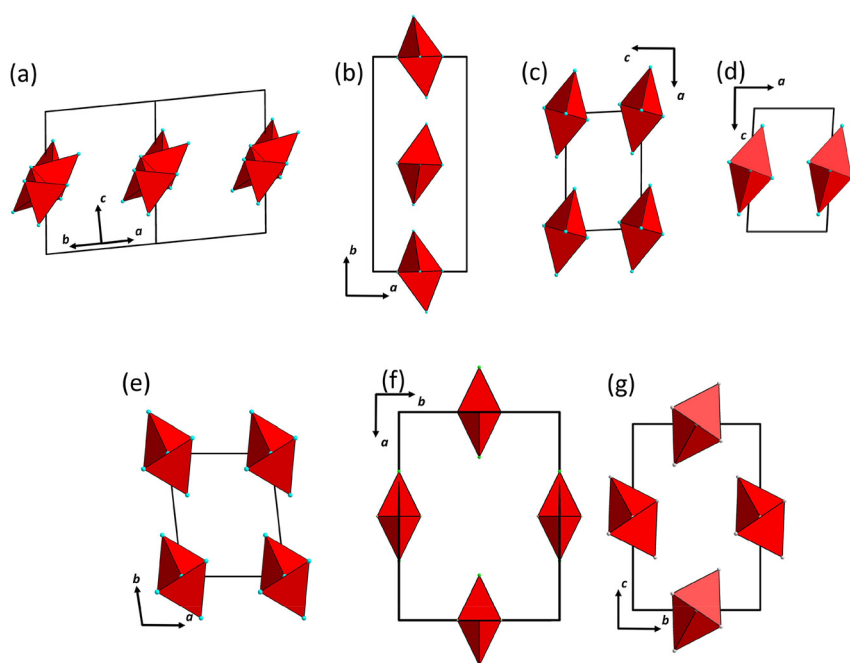


Figure 7: Mutual arrangements of the $[M_5O_2]^{n+}$ chains in **1** (a), georgbokiite (b), parageorgbokiite (c), antipovite (d), popovite (e), compounds of the $A^{2+}_3X^{3+}_{10}Y^{4+}O_{20}$ family (f), and $[Hg_5O_2]Re_2O_8$ (g). Unit cells are outlined.

the majority of structures, including **1**, antipovite, popovite, parageorgebokiite and the $A^{2+}_3X^{3+}_{10}Y^{4+}O_{20}$ family which means that vertices of oxocentered tetrahedra are co-directed. “Zigzag” packing, which is characterized by not co-directed vertices of tetrahedrons. is observed in georgbokiite, and synthetic $[Hg_5O_2]Re_2O_8$.

4 Conclusions

The new anhydrous copper oxysulfate $K_{1.5}(Pb,Na,\square)_{0.5}[Cu_5O_2](SO_4)_4$ adopts a unique structure type characterized by a previously unobserved, strongly corrugated $[Cu_5O_2]^{6+}$ chain topology. Moreover, the mixed occupancy of the A3 site by cations of substantially different radii underscores the flexibility of this position and suggests that such a compound could also crystallize as a mineral under the high-temperature conditions typical of volcanic fumaroles. The structural analysis demonstrates that the stereochemically active lone pair of Pb^{2+} , which occupies the A3 site adjacent to the chains, induces a significant distortion reflected in two distinct O–O–O angles and in the relative tilt of adjacent dimers in the structure of **1**. Comparison with other $[Cu_5O_2]^{6+}$ -bearing minerals and synthetic compounds reveals that the primary building block, the $[Cu_6O_2]^{8+}$ dimer, is remarkably conserved, while the chain packing and conformation vary with cation size. These findings suggest that the purposeful incorporation of lone-pair cations (e.g. Tl^+ , Bi^{3+}) could be exploited to engineer specific chain geometries and, by extension, to modulate the magnetic dimensionality and overall framework topology of copper oxysulfates.^{5,46} The present work thus provides a crystal-chemical foundation for the rational design of novel anhydrous sulfate architectures with potentially tunable physical properties.

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Use of Large Language Models, AI and Machine Learning

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