

Synthesis and Characterization of Two New Copper Tellurites, $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ and $\text{BaCu}_2\text{Te}_2\text{O}_6\text{Cl}_2$, in Supercritical H_2O

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Received October 10, 1997

Two new compounds containing tellurite building blocks coordinated to copper and barium atoms have been isolated from hydrothermal solvents. A new layered compound, $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ (**I**), has been obtained by reacting $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, CuO , and $\text{Te}(\text{OH})_6$ in NH_4Cl solution at 375°C for 4 days. Green, platelike crystals of **I** crystallize in the centrosymmetric space group, $P\bar{1}$, with $a = 9.275(2) \text{ \AA}$, $b = 12.135(2) \text{ \AA}$, $c = 9.263(2) \text{ \AA}$, $\alpha = 98.23(3)^\circ$, $\beta = 108.35(3)^\circ$, $\gamma = 110.90(3)^\circ$, and $Z = 2$. The compound contains two types of layers, one based on copper oxides linked by Te_4O_{11} groups, and the other based on Cu_2Cl_4 units. The tellurium atoms adopt the common TeO_{3+1} units or TeO_3 pyramids, and the oxygen-coordinated copper atoms adopt a square planar CuO_4 arrangement. Dark green, prismatic crystals of $\text{BaCu}_2\text{Te}_2\text{O}_6\text{Cl}_2$ (**II**) were obtained by reacting $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Cu_2O , and $\text{Te}(\text{OH})_6$ in NH_4Cl solution at 375°C for 18 h. Compound **II** was refined in the acentric monoclinic space group, $P2_1$ ($a = 7.434(2) \text{ \AA}$, $b = 7.448(2) \text{ \AA}$, $c = 8.271(2) \text{ \AA}$, $\beta = 97.42(3)^\circ$, $Z = 2$), and is based on Te_2O_6 units connected by copper atoms or copper chloride groups. As in **I**, tellurium atoms are contained within TeO_{3+1} or TeO_3 units and the connecting copper atoms are nearly square planar. The chloride-coordinated copper atoms group adopt a square pyramidal CuO_3Cl_2 geometry with a chlorine atom occupying the apical position. The formal oxidation states of the copper atoms in compound **I** are distributed such that the connecting atoms in an oxide environment are $2+$ and atoms within a chloride environment are $1+$, whereas in compound **II**, all copper atoms are $2+$. Bond valence sums for both compounds and magnetic susceptibility data for **I** support these assignments. The optical band gap for **I** was determined by diffuse reflectance spectroscopy and indicate that it is a wide band gap material ($E_g = 3.00 \text{ eV}$).

Introduction

Recent research efforts in our group have focused on the synthesis of new materials in supercritical fluids, based on the techniques reported by Rabenau.¹ Supercritical fluids provide a number of advantages over conventional solid state systems. Chemical manipulation is often easier and the relatively low temperatures lead to the isolation of numerous kinetically stabilized phases. A large number of chalcogenide compounds, such as $\text{Cs}_3\text{Ag}_2\text{Sb}_3\text{S}_8$,² Cs_2AgMS_4 ($M = \text{As}, \text{Sb}$),² $\text{CsCu}_2\text{SbS}_3$,³ and $\text{Cs}_5\text{Sb}_8\text{S}_{18}(\text{HCO}_3)_4$,⁴ have been isolated from supercritical amines in our labs. Recently, we have shown that divalent transition metal group 15–16 phases such as MnSb_2S_4 can also be obtained hydrothermally.⁵

In an attempt to illustrate the breadth of this technique, we recently became interested in the use of tellurates and tellurites as building blocks in extended solid systems.^{6,7} The tellurites are especially appealing because they adopt a number of very

unusual coordination environments. In addition to the usual pyramidal TeO_3^{2-} fragments^{8,9} like sulfites and selenites, tellurites also form four-coordinated TeO_4^{4-} fragments^{10,11} with C_{2v} symmetry. In fact they are one of the few sources of a main group building block with this symmetry. Finally tellurites also adopt a unique TeO_{3+1}^{4-} geometry,^{6,11–12} whereby one of the axial sites of the pseudotrigonal bipyramid is much longer than the other. Thus their coordination chemistry is of interest since they should be a source of new and interesting solid state phases. This unusually rich chemistry has recently led us to investigate the synthesis and chemistry of a series of isostructural metal tellurites $\text{M}_2\text{Te}_3\text{O}_8$ ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$).⁶

We are attempting to expand this chemistry by introducing alkaline-earth ions to the metal tellurites. Due to its unusual coordination chemistry, copper was our initial target. Indeed we were successful in forming a series of novel barium copper tellurites, but we also found that chloride ions from the mineralizer became incorporated in the lattice, forming barium copper tellurium oxyhalides. In this paper we report on two new phases which contain copper(II) in unusual square planar coordination environments created by tellurium(IV) oxyanion ligands.

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Table 1. X-ray Crystallographic Data

empirical formula	Ba ₂ Cu ₄ Te ₄ O ₁₁ Cl ₄ (I)	BaCu ₂ Te ₂ O ₆ Cl ₂ (II)
space group	<i>P</i> 1 (No. 2)	<i>P</i> 2 ₁ (No. 4)
<i>a</i> (Å)	9.275(2)	7.434(2)
<i>b</i> (Å)	12.135(2)	7.448(2)
<i>c</i> (Å)	9.263(2)	8.271(2)
α (deg)	98.23(3)	90
β (deg)	108.35(3)	97.42(3)
γ (deg)	110.90(3)	90
<i>V</i> (Å ³)	885.2(3)	454.1(2)
<i>Z</i>	2	2
ρ _{calcd} (g cm ⁻³)	5.091	5.021
μ (cm ⁻¹)	162.06	158.02
fw (g mol ⁻¹)	1357.05	686.52
<i>T</i> (°C)	room temp	room temp
λ (Å)	0.71073	0.71073
R ^a (<i>F</i> _o > 6σ(<i>F</i> _o))	0.0458	0.0388
R _w ^b (<i>F</i> _o > 6σ(<i>F</i> _o))	0.0678	0.0491

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; \\ w = 1/[\sigma^2(|F_o|) + 0.0025(|F_o|)^2].$$

Experimental Details

Synthesis. The compounds obtained in this study were prepared using modifications on techniques reported by Rabenau.¹ Compound **I**, Ba₂Cu₄Te₄O₁₁Cl₄, was originally prepared by loading BaCl₂·2H₂O (73 mg, 0.30 mmol, Strem, 99+%), CuO (48 mg, 0.60 mmol, Strem, 99.9%), and Te(OH)₆ (138 mg, 0.603 mmol, Strem, 99.9%) into fused silica tubes (5 mm i.d., 7 mm o.d., ~1.6 cm³ sealed volume). A 0.7 mL amount (45% fill) of a 2 M NH₄Cl solution was added, and the tubes were flame-sealed after the solvent was frozen in liquid nitrogen. The tubes were placed in a high-pressure autoclave with 2500 psi of argon counter-pressure to prevent bursting of the tubes during reaction. The autoclave was placed in a furnace and heated at 375 °C for 5 days, after which the autoclave was removed directly from the furnace. After cooling, **I** was obtained in ~30% yield as green plates, with the remainder of the products being the highly crystalline phases, Cu₂Te₃O₈ (yellow plates)⁶ and TeO₂ (clear prisms). The products were filtered, washed with distilled water and acetone, and physically separated by color. Compound **I** is indefinitely stable in air. It was subsequently determined that yields of **I** approaching 50% could be achieved by reacting BaCl₂·2H₂O, CuO, and TeO₂ (Strem, 99.9%) in a 1:2:2 ratio in 5 M NH₄Cl at 375 °C for 4 days.

Large, green prismatic crystals of BaCu₂Te₂O₆Cl₂ (**II**) were obtained by heating a mixture of BaCl₂·2H₂O (74 mg, 0.30 mmol), Cu₂O (43 mg, 0.30 mmol, Strem, 99.9%), and Te(OH)₆ (139 mg, 0.605 mmol) in 1 M NH₄Cl solution at 375 °C for 18 h. This material was obtained at <10% yield with CuTeO₄ as the major phase in the form of a yellow polycrystalline powder. Longer reaction times with similar amounts of starting materials yielded varying mixtures of **I**, Cu₂Te₃O₈, and CuTeO₄.¹³ Compound **II** proved to be somewhat air or moisture sensitive, as the material degraded after several days in air, but showed no visible indications of decomposition after several weeks in mineral oil.

Qualitative SEM/EDS analyses on crystals of both compounds verified the presence of Ba, Cu, Te, Cl, and O and the absence of any impurity elements heavier than F.

Crystallography. Crystals of both phases were mounted onto the ends of glass fibers using quick-drying epoxy and were studied using a Rigaku AFC7R four-circle diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. An ω-2θ scan mode was utilized for room-temperature data collection for both compounds. Three standard reflections measured after every 97 reflections indicated that the crystals were stable (<2% decay) for both compounds, and 2θ limits of 52° for **I** and 55° for **II** were employed. The intensity data were corrected for both Lorentz and polarization effects. Additional data are included in Table 1.

The centrosymmetric space group, *P*1̄, was chosen for **I** on the basis of lattice parameters and statistical tests. The systematic absence *0k0*, *k* = 2*n* + 1, indicated that **II** could be either *P*2₁ or *P*2₁/*m*. The acentric

space group, *P*2₁, was chosen after a refinement in *P*2₁/*m* failed to yield a satisfactory model for the structure. Both structures were solved by direct methods (TEXSAN)¹⁴ and refined on |*F*| by full-matrix least-squares techniques in SHELXTL-PLUS.¹⁵ Absorption effects were compensated for by the use of empirical ψ-scan data.¹⁶ All atomic parameters in **I** were refined anisotropically, except for O(11), which was refined isotropically. Due to the enlarged thermal parameters associated with Cu(3) and Cu(4), a number of alternative refinements were attempted. In one model, Cu(3) and Cu(4) were each separated into two sites with half-occupancy 0.2 Å apart. Upon refinement, this model diverged and the separate sites coalesced to their original single positions. Alternatively, attempts at refining site occupancies of Cu(3) and Cu(4) failed to yield improvements in the structural model, residual peak densities, and refinement parameters. Further details are included in Results and Discussion. All atomic parameters in **II** were refined anisotropically, and a refinement in the opposite chirality was performed to determine the best fit. The refinement with the lowest R and R_w was used as the final structural solution. No higher symmetry was detected for either compound with the MISSYM algorithm within the PLATON program suite.^{17,18} Crystallographic details are given in Table 1. The final positional parameters, relevant interatomic distances, and relevant bond angles for both compounds are given in Tables 2, 3, and 4, respectively. The anisotropic thermal parameters can be obtained in the Supporting Information.

Physical Characterization. The magnetic susceptibility data were determined using a Quantum Design SQUID magnetometer. A sample (~20 mg) of ground crystals of **I** was placed in a gelatin pill capsule which was subsequently held in a standard plastic drinking straw. Readings of the sample holder showed negligible diamagnetic effects on the bulk sample. Room-temperature diffuse reflectance measurements from 800 to 200 nm on compound **I** were made using a Shimadzu UV3100 spectrophotometer equipped with an integrating sphere attachment. Barium sulfate was used as the reflectance standard. The reflectance data were converted to absorbance data using the Kubelka-Monk function.¹⁹

Results and Discussion

Structure. Compound **I**, Ba₂Cu₄Te₄O₁₁Cl₄, is a two-dimensional compound with two types of layers situated in the *ac* plane as shown in Figure 1. The structure is made up of two copper tellurite layers separated by a copper chloride layer. This arrangement of three layers is separated by a layer of barium atoms. The copper tellurite layer consists of nearly square planar CuO₄ units, TeO₃ pyramids, and TeO₃₊₁ polyhedra. The copper chloride layer is made up of CuCl₄ tetrahedra and a CuCl₂O unit, which is in essentially a distorted trigonal planar arrangement.

The copper tellurite layer, shown in Figure 2 as a projection in the *ac* plane, can be viewed as having Te₄O₁₁ subunits alternating throughout the layer. These subunits are made by joining two TeO₃₊₁ polyhedra through an apical oxygen atom and then adding TeO₃ pyramids to the opposite apical atom of each TeO₃₊₁ polyhedra. These Te₄O₁₁ subunits are linked to one another through copper atoms, which are connected to the ends of two separate subunits and the center of a third.

All of the coordination polyhedra for copper and tellurium in this layer are fairly regular and have been observed in other compounds. The TeO₃₊₁ polyhedra have equatorial Te—O

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Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2)

	X	Y	Z	U_{eq}^a
Ba₂Cu₄Te₄O₁₁Cl₄ (I)				
Ba1	0.28067(8)	0.5513(6)	0.01879(7)	0.0098(3)
Ba2	0.78471(8)	0.55869(6)	0.52130(7)	0.0098(3)
Te1	-0.02330(8)	0.24221(7)	0.02612(8)	0.0085(4)
Te2	0.22106(9)	0.24132(7)	-0.21702(8)	0.0084(3)
Te3	0.47654(9)	0.26492(7)	0.55264(8)	0.0090(3)
Te4	0.74715(9)	0.26235(7)	0.27196(8)	0.0095(3)
Cu1	0.4002(2)	0.3282(1)	0.1872(2)	0.0090(5)
Cu2	0.8985(2)	0.3280(1)	0.6853(2)	0.0092(5)
Cu3	0.0982(3)	0.0160(2)	0.2371(3)	0.054(1)
Cu4	0.4448(3)	-0.0178(2)	0.3042(2)	0.048(1)
Cl1	0.0384(5)	0.1443(3)	0.3727(4)	0.028(2)
Cl2	0.3155(4)	0.0882(3)	0.1548(4)	0.024(1)
Cl3	0.4606(4)	-0.1553(3)	0.1260(4)	0.024(1)
Cl4	0.7102(4)	0.0884(3)	0.5377(4)	0.024(1)
O1	-0.0905(9)	0.3495(7)	0.1945(8)	0.009(3)
O2	-0.0558(10)	0.3524(8)	-0.0876(8)	0.013(3)
O3	0.0532(10)	0.1655(8)	-0.1249(9)	0.017(4)
O4	0.1289(9)	0.3502(8)	-0.2769(9)	0.013(3)
O5	0.1964(10)	0.3496(8)	0.1666(8)	0.012(3)
O6	0.3814(10)	0.3523(7)	-0.0216(8)	0.011(3)
O7	0.4117(10)	0.3484(8)	-0.3075(8)	0.011(3)
O8	0.4540(10)	0.3622(8)	0.4171(8)	0.011(3)
O9	0.6348(10)	0.3621(8)	0.2297(9)	0.014(4)
O10	0.7057(10)	0.3657(8)	0.6703(9)	0.013(3)
O11	0.8840(9)	0.3596(7)	0.4802(8)	0.009(2)
BaCu₂Te₂O₆Cl₂ (II)				
Ba1	0.13612(8)	0.84350	0.07030(7)	0.0113(2)
Te1	0.13133(9)	0.4694(2)	0.39125(8)	0.0089(2)
Te2	0.3446(1)	0.1920(2)	0.76730(8)	0.0083(2)
Cu1	0.6901(2)	0.3144(2)	0.4038(2)	0.0119(4)
Cu2	0.3617(2)	0.3410(2)	0.0878(2)	0.0104(4)
Cl1	-0.1203(5)	0.0845(5)	0.2347(4)	0.0211(9)
Cl2	-0.5532(5)	0.1081(5)	0.3742(4)	0.0196(8)
O1	0.2012(11)	0.1812(13)	-0.0619(9)	0.011(2)
O2	0.1551(12)	0.4518(14)	0.1683(9)	0.013(2)
O3	0.5512(12)	0.4563(16)	0.2346(10)	0.018(2)
O4	-0.1212(12)	0.5000(14)	0.3719(10)	0.014(2)
O5	0.1909(13)	0.7142(14)	0.3994(9)	0.012(2)
O6	0.4743(11)	0.7748(17)	0.0672(10)	0.016(3)

$$^a U_{\text{eq}} = \sum_i \sum_j (U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j).$$

distances of ranging from 1.865(6) to 1.871(11) Å and axial distances of 2.009(10) and 2.264(10) Å. This coordination environment is highly similar to those in $\text{M}_2\text{Te}_3\text{O}_8$ ⁶ or CuTe_2O_5 .¹² The TeO_3 pyramid has Te–O distances ranging from 1.857(9) to 1.914(9) Å and has been seen in several other tellurite materials as well. The square planar arrangement of oxygen atoms around Cu(1) and Cu(2) are both fairly regular with bond distances ranging from 1.953(10) to 1.971(8) Å, which is similar to those in CuTe_2O_5 ¹² or CuTeO_3 .²⁰ However, the copper atom in both crystallographically distinct square planar arrangements is slightly out of plane (0.31–0.32 Å) with respect to the oxygen atoms. This arises due to the linkage with the copper chloride layer. There are long contacts of 2.676(4) and 2.666(3) Å for Cu(1)–Cl(2) and Cu(2)–Cl(4), respectively, which contribute to the binding of the tellurite layer with the chloride layer.

Both crystallographically distinct barium atoms are contained within virtually identical eleven-membered coordination environments, consisting of ten oxygen atoms and one chlorine atom. The oxygen atoms are grouped in planes, one containing four oxygen atoms and sitting above the barium atom, and the other containing the remaining six oxygen atoms and sitting below. The chlorine atom is a longer contact (3.182(4) Å for Ba(1)–Cl(3A) and 3.225(4) Å for Ba(2)–Cl(1A)) that lies below the

Table 3. Relevant Interatomic Distances with ESD's (in Å)

Ba₂Cu₄Te₄O₁₁Cl₄ (I)			
Te(1)–O(1)	2.264(10)	Cu(4)–Cl(2)	2.360(5)
–O(2)	1.865(10)	–Cl(3)	2.251(5)
–O(3)	2.013(11)	–Cl(4)	2.398(5)
–O(5)	1.869(6)	–Cl(4)	2.446(3)
Te(2)–O(3)	2.009(10)	Ba(1)–Cl(3)	3.182(4)
–O(4)	1.871(11)	–O(1)	2.905(9)
–O(6)	1.865(6)	–O(2)	2.910(11)
–O(7)	2.263(9)	–O(2)	2.926(7)
Te(3)–O(7)	1.901(10)	–O(4)	2.944(8)
–O(8)	1.857(9)	–O(5)	2.961(9)
–O(10)	1.872(7)	–O(6)	2.906(10)
Te(4)–O(1)	1.914(9)	–O(6)	2.919(9)
–O(9)	1.867(11)	–O(7)	2.926(7)
–O(11)	1.861(6)	–O(9)	2.871(10)
Cu(1)–Cl(2)	2.676(4)	–O(10)	2.858(9)
–O(5)	1.953(10)	Ba(2)–Cl(1)	3.225(4)
–O(6)	1.960(8)	–O(1)	2.902(7)
–O(8)	1.971(8)	–O(4)	2.866(9)
–O(9)	1.958(9)	–O(5)	2.872(8)
Cu(2)–Cl(4)	2.666(3)	–O(7)	2.889(9)
–O(2)	1.965(8)	–O(8)	2.882(11)
–O(4)	1.963(9)	–O(8)	2.878(7)
–O(10)	1.968(11)	–O(9)	2.889(8)
–O(11)	1.964(9)	–O(10)	2.875(10)
Cu(3)–Cl(1)	2.192(6)	–O(11)	2.878(9)
–Cl(2)	2.305(5)	–O(11)	2.893(10)
–O(3)	2.030(8)		
BaCu₂Te₂O₆Cl₂ (II)			
Te(1)–O(2)	1.879(7)	Cu(2)–O(1)	1.998(9)
–O(4)	1.877(9)	–O(2)	1.936(9)
–O(5)	1.876(10)	–O(3)	1.937(9)
Te(2)–O(1)	1.878(8)	–O(6)	1.944(9)
–O(3)	1.920(12)	Ba(1)–Cl(1)	3.062(4)
–O(4)	2.374(9)	–Cl(1)	3.166(4)
–O(6)	1.895(8)	–O(1)	2.810(10)
Cu(1)–O(3)	1.941(10)	–O(1)	2.777(9)
–Cl(1)	2.717(4)	–O(2)	2.851(8)
–Cl(2)	2.362(4)	–O(2)	3.026(10)
–O(4)	2.011(10)	–O(5)	2.867(8)
–O(5)	1.902(8)	–O(6)	2.569(9)

six-membered oxygen plane. The Ba–O distances (2.858(9)–2.961(9) Å) tend to be slightly shorter than the calculated value (2.95 Å) using the sum of the Ba and O crystal radii.²¹

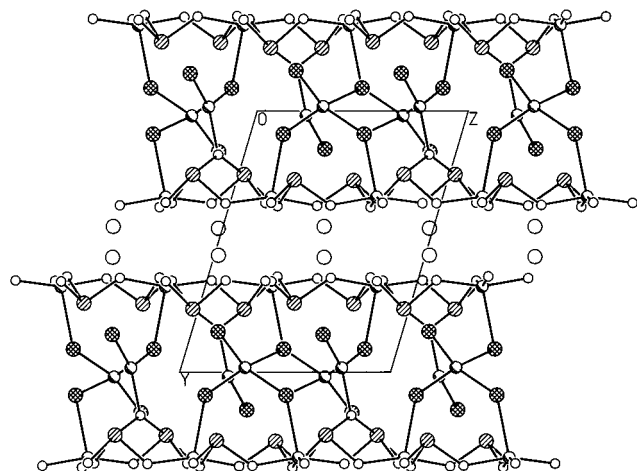
The copper chloride layer can be broken down into $[\text{Cu}_2\text{OCl}_4]_2$ units which are shown in Figure 3. Each unit is made up of two distorted CuCl_4 tetrahedra, related by the inversion operator, which are then connected to a trigonal planar CuOCl_2 unit. The tetrahedral arrangement of chlorine atoms around Cu(4) is highly distorted with Cu–Cl distances ranging from 2.251(5) to 2.446(3) Å and Cl–Cu–Cl angles ranging from 92.2(1) to 122.7(2)°. The trigonal planar arrangement around Cu(3) is relatively close to ideal, with the copper atom only 0.16 Å out of plane with respect to the oxygen and chlorine atoms. The L–Cu(3)–L (L = O, Cl) angles range from 111.7(3) to 125.9(4)° which also indicates a fairly regular trigonal planar geometry. The oxygen atom in this environment is actually contained within the copper tellurite layer, and the Cu(3)–O(3) bond seems to be necessary to stabilize the binding of the copper chloride layer to the tellurite layer.

In addition, both Cu(3) and Cu(4) are typified by significantly larger thermal parameters than the copper atoms in the tellurite layer. A number of alternative refinements (vide supra) suggest that these atoms are each a single site but have larger thermal motion. This appears to be the result of the irregular coordination environments of these atoms. These atoms are coordinated

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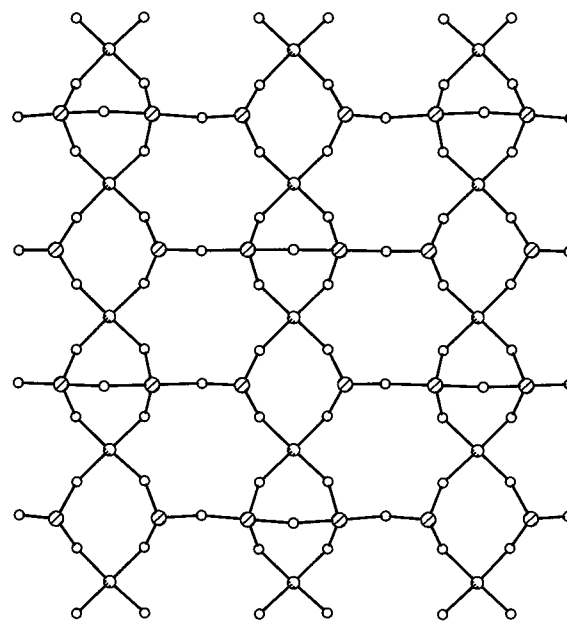
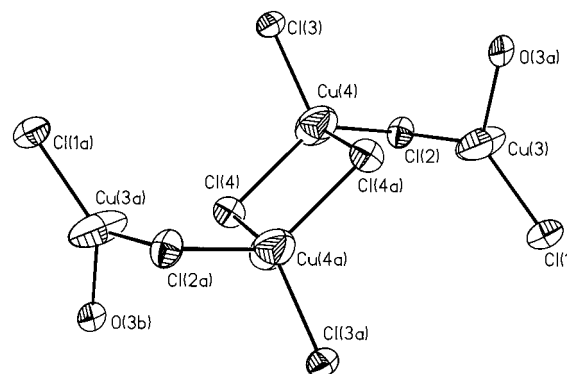
Table 4. Relevant Angles with ESDs (deg)

Ba ₂ Cu ₄ Te ₄ O ₁₁ Cl ₄ (I)			
O(1)–Te(1)–O(2)	82.3(4)	O(6)–Cu(1)–O(8)	161.6(4)
O(1)–Te(1)–O(3)	173.5(3)	O(6)–Cu(1)–O(9)	86.7(4)
O(1)–Te(1)–O(5)	82.9(4)	O(8)–Cu(1)–O(9)	89.5(4)
O(2)–Te(1)–O(3)	92.9(4)	O(2)–Cu(2)–O(4)	91.5(4)
O(2)–Te(1)–O(5)	95.4(4)	O(2)–Cu(2)–O(10)	85.9(4)
O(3)–Te(1)–O(5)	93.0(4)	O(2)–Cu(2)–O(11)	162.2(4)
O(3)–Te(2)–O(4)	92.8(4)	O(4)–Cu(2)–O(10)	161.0(4)
O(3)–Te(2)–O(6)	93.2(3)	O(4)–Cu(2)–O(11)	86.8(4)
O(3)–Te(2)–O(7)	173.2(4)	O(10)–Cu(2)–O(11)	89.9(4)
O(4)–Te(2)–O(6)	94.5(4)	Cl(1)–Cu(3)–Cl(2)	120.7(2)
O(4)–Te(2)–O(7)	82.2(4)	Cl(1)–Cu(3)–O(3)	125.9(4)
O(6)–Te(2)–O(7)	82.8(3)	Cl(2)–Cu(3)–O(3)	111.7(3)
O(7)–Te(3)–O(8)	92.7(4)	Cl(2)–Cu(4)–Cl(3)	105.3(2)
O(7)–Te(3)–O(10)	92.9(4)	Cl(2)–Cu(4)–Cl(4)	106.7(2)
O(8)–Te(3)–O(10)	93.7(4)	Cl(2)–Cu(4)–Cl(4)	122.7(2)
O(1)–Te(4)–O(9)	92.1(4)	Cl(3)–Cu(4)–Cl(4)	110.9(2)
O(1)–Te(4)–O(11)	92.2(3)	Cl(3)–Cu(4)–Cl(4)	119.7(2)
O(9)–Te(4)–O(11)	93.9(4)	Cl(4)–Cu(4)–Cl(4)	92.2(1)
O(5)–Cu(1)–O(6)	91.4(4)		
O(5)–Cu(1)–O(8)	86.8(4)		
O(5)–Cu(1)–O(9)	162.3(4)		
BaCu ₂ Te ₂ O ₆ Cl ₂ (II)			
O(2)–Te(1)–O(4)	98.3(4)	Cl(2)–Cu(1)–O(3)	87.2(3)
O(2)–Te(1)–O(5)	92.9(4)	Cl(2)–Cu(1)–O(4)	166.3(2)
O(4)–Te(1)–O(5)	96.5(4)	Cl(2)–Cu(1)–O(5)	95.7(3)
O(1)–Te(2)–O(3)	103.7(4)	O(3)–Cu(1)–O(4)	81.2(4)
O(1)–Te(2)–O(4)	84.8(3)	O(3)–Cu(1)–O(5)	167.4(4)
O(1)–Te(2)–O(6)	83.7(4)	O(4)–Cu(1)–O(5)	97.3(4)
O(3)–Te(2)–O(4)	72.7(3)	O(1)–Cu(2)–O(2)	91.7(4)
O(3)–Te(2)–O(6)	93.1(4)	O(1)–Cu(2)–O(3)	168.5(4)
O(4)–Te(2)–O(6)	159.0(4)	O(1)–Cu(2)–O(6)	79.4(4)
Cl(1)–Cu(1)–Cl(2)	88.7(1)	O(2)–Cu(2)–O(3)	98.1(4)
Cl(1)–Cu(1)–O(3)	103.6(3)	O(2)–Cu(2)–O(6)	158.1(4)
Cl(1)–Cu(1)–O(4)	87.2(3)	O(3)–Cu(2)–O(6)	93.3(4)
Cl(1)–Cu(1)–O(5)	88.8(3)		

**Figure 1.** Unit cell view of Ba₂Cu₄Te₄O₁₁Cl₄ (I) parallel to the *a* axis. Barium atoms are large open spheres, copper atoms are shaded spheres, tellurium atoms are striped spheres, chlorine atoms are crosshatched spheres, and oxygen atoms are small, open spheres.

nearly exclusively by low-coordinate chlorine atoms which also have somewhat larger thermal ellipsoids due to their low coordination numbers. This unusual behavior of chlorine atoms has been observed in other tellurium oxyhalides such as Te₆O₁₁Cl₂²² and H₃Fe₂(TeO₃)₄Cl.²³

The structure of compound II, BaCu₂Te₂O₆Cl₂, differs greatly from compound I, notwithstanding the addition of an oxygen

**Figure 2.** View of the copper tellurite layer in compound I in the *ac* plane. Copper atoms are shaded spheres, tellurium atoms are striped spheres, and oxygen atoms are small, open spheres.**Figure 3.** [Cu₂OCl₄]₂ unit in Ba₂Cu₄Te₄O₁₁Cl₄ (I). All ellipsoids are at the 70% probability level.

atom to the general formula. Whereas compound I is highly ordered, with tetrahedral or trigonal planar copper atoms largely coordinated to chlorine atoms separated from square planar copper atoms associated with oxygen atoms, compound II (Figure 4) appears to contain a considerably lower degree of organization. The structure of II is best described as being based on Te₂O₆ units joined together by copper atoms. These Te₂O₆ units consist of a TeO₃₊₁ unit joined through an oxygen atom to a TeO₃ pyramid. The Te–O bond distances are fairly typical for their environments with the TeO₃₊₁ unit having three bonds at 1.878(8)–1.920(12) Å and a fourth bond at 2.374(9) Å and the TeO₃ unit having bond distances of 1.876(10)–1.879(7) Å. These units are linked to one another through a copper atom and, when built up around the 2₁ screw axis, form an infinite spiral channel running along the *b* axis. This channel contains the barium atoms. The coordination sphere of the copper atom within the spiral chain is nearly square planar, with the oxygen atoms having a small distortion of ~0.2 Å out-of-plane and Cu–O distances of 1.936(9)–1.998(9) Å. The spiral chains are held together by the remaining copper atom, which is contained within a square pyramidal arrangement of three oxygen atoms and two chlorine atoms. All three oxygen atoms (Cu–O distance: 1.902(8)–2.011(10) Å) and one of the chlorine atoms (Cu–Cl distance: 2.362(4) Å) make up the

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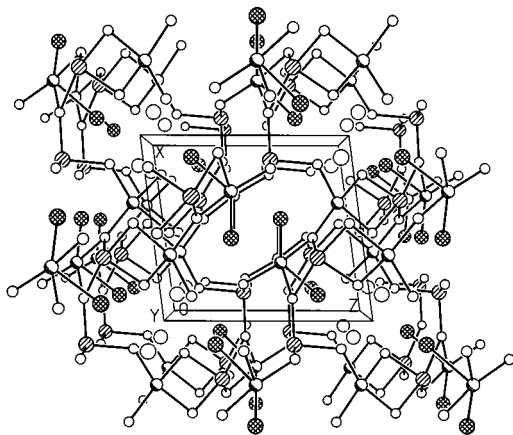


Figure 4. Unit cell view of $\text{BaCu}_2\text{Te}_2\text{O}_6\text{Cl}_2$ (**II**) parallel to the b axis. Barium atoms are large open spheres, copper atoms are shaded spheres, tellurium atoms are striped spheres, chlorine atoms are crosshatched spheres, and oxygen atoms are small, open spheres.

square plane, with a long copper–chlorine contact (2.717(4) Å) completing the coordination environment.

The barium atom in this structure sits within a highly irregular coordination sphere, consisting of six oxygen atoms and two chlorine atoms. To best describe the coordination environment, a distorted square planar arrangement of three oxygen atoms and one chlorine atom is defined around the central barium atom. There are two oxygen and one chlorine atoms below this plane and a lone oxygen atom above the plane. All of the Ba–O distances except for Ba(1)–O(6) correspond reasonably well (2.777(9)–3.026(10) Å) to the calculated value of 2.78 Å.²¹ The Ba(1)–O(6) distance (2.569(9) Å) is considerably shorter than the expected value, but it is situated in an otherwise empty region of the barium coordination sphere and is also locked in as a member of the TeO_{3+1} unit and the CuO_4 square plane.

Valence Bond Sums. Due to the potentially ambiguous nature of the oxidation states of the copper atoms in compound **I**, the well-known correspondence between bond distance and bond valence²⁴ was used to help in the determination of the possible oxidation states of the copper atoms in both structures. Utilizing the common assignments of +2 for barium, –1 for chlorine, and –2 for oxygen, and assigning a +4 oxidation state for all tellurium atoms, which is indicated by the obvious steric effects of a lone pair in either the TeO_{3+1} or the TeO_3 environment, in compound **I**, there remain six positive charges which must be distributed between four copper atoms. By using the assumption that the copper atoms in an oxide environment were +2 and that those in a chloride environment were +1, the valence bond sums were calculated accordingly. The bond sums (Table 5) confirmed all these assignments and suggest that the simplest formulation for compound **I** is correct.

Using similar common assignments for compound **II** suggested that this material is entirely Cu(II). Valence bond sums also indicated that these assignments are correct, although the bond sum for Cl(2) is somewhat low, due to the fact that it only has a significant contact with Cu(1), and the distant contacts with Cu(1), Cu(2), and Te(2) (3.111, 2.938, and 3.490 Å, respectively) have no appreciable effect on the overall bond sum. Although this low coordination number for Cl(2) seems somewhat unusual, there are other examples of low-coordinate to uncoordinated chlorine atoms in tellurium oxyhalides, specifically in $\text{Te}_6\text{O}_{11}\text{Cl}_2$ ²² and $\text{H}_3\text{Fe}_2(\text{TeO}_3)_4\text{Cl}$.²³

Table 5. Valence Bond Sums for $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ and $\text{BaCu}_2\text{Te}_2\text{O}_6\text{Cl}_2$ ^a

	Ba	Cu	Te	O	Cl
$\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ (I)					
atom 1	2.08(1)	2.02(2)	4.06(5)	2.02(3)	0.582(6)
atom 2	2.21(2)	2.00(2)	4.06(5)	2.18(4)	0.653(5)
atom 3		0.882(9)	3.94(5)	2.07(4)	0.555(5)
atom 4		0.936(6)	3.90(5)	2.17(4)	0.548(3)
atom 5				2.18(3)	
atom 6				2.19(3)	
atom 7				2.06(4)	
atom 8				2.24(4)	
atom 9				2.22(4)	
atom 10				2.20(3)	
atom 11				2.23(3)	
$\text{BaCu}_2\text{Te}_2\text{O}_6\text{Cl}_2$ (II)					
atom 1	2.12(2)	1.94(2)	3.93(5)	2.14(3)	0.728(5)
atom 2		1.91(2)	4.06(6)	2.15(3)	0.355(4)
atom 3				2.16(4)	
atom 4				2.06(4)	
atom 5				2.07(4)	
atom 6				2.20(3)	

^a $\sum s(\text{M}-\text{L}) = \sum \exp[(r_0 - r)/0.37]$; s = individual bond valences, r = bond distance in structure, and r_0 = empirically derived M–L single-bond distance (Ba–O = 2.285, Ba–Cl = 2.660, Cu^I–O = 1.515, Cu^{II}–O = 1.679, Cu^I–Cl = 1.819, Cu^{II}–Cl = 1.979, Te–O = 1.977 Å). All distances are either from table or calculated from the formula found in reference 24.

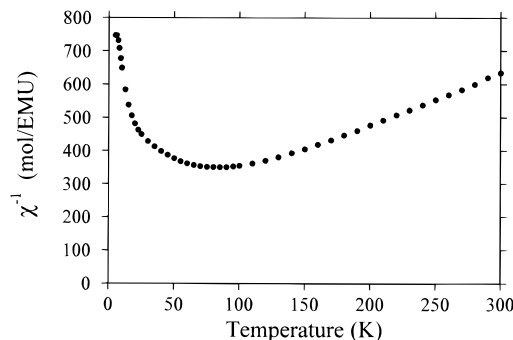


Figure 5. Temperature-dependent plot of the inverse of magnetic susceptibility (χ^{-1}) vs temperature (T) for $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ (**I**). The material displays a broad antiferromagnetic transition that begins at 90 K.

Physical Properties of $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$. A temperature-dependent plot of the magnetic susceptibility (Figure 5) was obtained for compound **I** and shows that it has a broad antiferromagnetic transition with $T_N \cong 90$ K. The plot of χ^{-1} vs T for the data above T_N shows that the material exhibits Curie–Weiss behavior with constants of $C = 0.708$ emu K/mol and $\theta = -142$ K. The valence assignments indicate that only the two Cu(II) atoms have any significant paramagnetic contribution, with each atom having one unpaired electron. Using the Curie constant the magnetization is $1.68 \mu_B/\text{Cu(II)}$ center, which is in good agreement with the theoretical spin-only value of $1.73 \mu_B$. This suggests that the valence assignments are correct. Furthermore, the presence of an antiferromagnetic transition suggests the presence of superexchange, possibly through the square planar copper atoms.

Diffuse reflectance spectroscopy was used to determine the optical band gap of **I**. The plot of absorbance vs energy is shown in Figure 6. The plot of (absorbance)^{1/2} vs energy at the absorption edge (2.50–3.20 eV, correlation coefficient 0.995) has a better linear dependence than does the plot of (absorbance)² vs energy (correlation coefficient 0.974), which suggests that the material has an indirect band gap.²⁵ Therefore,

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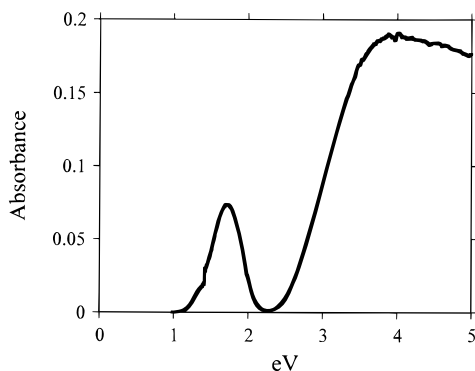


Figure 6. Plot of diffuse reflectance spectrum of $\text{Ba}_2\text{Cu}_4\text{Te}_4\text{O}_{11}\text{Cl}_4$ (**I**) in units of absorbance vs eV.

the band gap was obtained by determining the inflection point of the first-derivative curve of reflectance vs energy. This results in a band gap of 3.00 eV, indicative of an essentially insulating material. There is also a peak at 1.7 eV, which is indicative of a spin-allowed transition at the Cu(II) centers. For Cu(II) in a square planar D_{4h} environment, three spin-allowed transitions are possible, which normally occur between 10 000 and 14 000 cm^{-1} .²⁶ The fact that we observe only one broad transition in the region of 13 600 cm^{-1} is probably due to the poor resolution of this broad band. Our inability to obtain compound **II** in any reasonable quantity or purity precluded any reliable physical characterization of this compound.

Conclusion

Only compound **I** was obtained in sufficient yield for full physical characterization. It is a wide band gap, antiferromag-

netic material with tetrahedral or trigonal planar Cu(I) and square planar Cu(II) sites located in separate chloride and oxide layers, respectively. The magnetic susceptibility data and valence bond sums also indicate that the assigned distribution of copper oxidation states is probably correct. The tellurium atoms in both compounds are exclusively coordinated by oxygen atoms and are contained within common TeO_{3+1} or TeO_3 units. Valence bond sums of **II** are used to suggest that the structural model is correct.

Since all attempts to obtain compound **II** in greater quantity were unsuccessful, it is theorized that compound **II** is an intermediate in the formation of compound **I**. Any prolonged heating led to the complete disappearance of **II** in favor of increased quantities of **I**. The relative low yields, lack of stability, and difficulty in producing large quantities of this material seem to lend credence to the hypothesis that **II** is an intermediate en route to the formation of **I**. Attempts at the synthesis of calcium and strontium analogues of either phase failed to yield the desired products. The presence of NH_4Cl is essential to the formation and crystallization of the title phases. Reactions that contain only BaCl_2 as a mineralizer did not produce the desired products.

Acknowledgment. C.R.F. thanks George L. Schimek for many valuable discussions. The authors thank Thomas P. Thrash at Rice University for the SQUID measurements. This work was supported by the National Science Foundation.

Supporting Information Available: Tables of crystallographic and refinement details, tables of anisotropic thermal parameters and bond angles, supplemental figures, and descriptions (14 pages). Ordering information is given on any current masthead page.

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