CuClCu₂TeS₃: Synthesis, Structure Determination, and Raman Spectroscopic Characterization of a New Zincblende Derivative[†]

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Pure black CuClCu₂TeS₃ was prepared by reaction of stoichiometric amounts of CuCl, Cu, Te, and S in evacuated silica ampules. The crystal structure was determined from single crystals at room temperature. The compound crystallizes in the rhombohedral system, space group $R3m$ with $a = 7.361(1)$ Å and $c = 10.401(1)$ Å (hexagonal setting), and $Z = 3$. Structural considerations and group-subgroup relationships show that CuClCu₂TeS₃ can be regarded as a new ordered zincblende derivative. In this material copper and sulfur are four-coordinate. By contrast tellurium has a trigonal pyramidal coordination and chlorine is located in a trigonal planar surrounding. Raman spectra are dominated by stretching modes of thiometalate ions [TeS₃]²⁻ at $\nu_{asym} = 359$ cm⁻¹ and $\nu_{sym} = 336$ cm⁻¹, respectively. DTA measurements reveal a peritectic decomposition of CuClCu₂TeS₃ at 448 °C.

Introduction

The preparation of new materials containing thiometalate groups made a large progress in the past decade by extension of the well-known use of supercritical mineral acids[1] to organic solvents[2,3] and so-called reactive-flux techniques.[4−6] Following a new preparative route, that is the use of copper(I) halides as solid solvents, a number of neutral or low-charged molecular arrangements of group 15 and group 16 elements could recently be obtained in the solid state. Various examples for novel phosphorus polymers, e.g. $^1_\infty[P_{12}^{\pm 0}]$ (two different types) in $(CuI)_8P_{12}$[7] and $(CuI)_3P_{12}$,[8] $^1_\infty[P_{14}^{\pm 0}]$ in $(CuI)_2P_{14}$,[9] and $^1_\infty[P_{20}^{2-}]$ in $(CuBr)_{10}Cu_2P_{20}$[10] were prepared and characterized. Ordered heteroatomic chalcogen chains $^1_\infty[SeTe]$ and $^1_\infty[STe]$ were observed in CuXSeTe (X = Cl, Br, I)[11] and in CuXSTe (X = Cl, Br),[12] respectively. Contrary to these almost completely ordered heteroatomic chalcogen chains, the first examples for tellurium-rich six-membered rings $Se_{6-x}Te_x$ ($x \leq 3$) suffer from structural disorder of the chalcogen molecules.[13] All of these compounds have in common that copper ions are four-coordinate by halide ions and the group 15 or group 16 elements, respectively. Bond distances and angles within these polymers are not significantly influenced by the coordination to the copper ions. Nevertheless quantum chemical calculations show a certain degree of stabilization at least of the phosphorus strands.[14] Besides these copper(I) halide adducts to neutral molecules first examples of a new class of mixed copper(I) halide thiometalates ("composite materials") which can be rationalized by the general formula $(CuX)_nCu_mM^{(6-m)+}S_3$, namely $(CuI)_3Cu_2TeS_3$[15] and $(CuI)_2Cu_3SbS_3$,[16] were described recently. $CuBrCu_{1.2}TeS_2$[17] is the first proof that also polychalcogenide ions, at least the novel 19 electron radical anion TeS₂•⁻ and the dianion TeS₂²⁻, can be obtained in such composite materials. The pronounced ionic conductivity of these materials can be explained by either weak bonding interactions of the copper ions and the neutral polymers[18] or the local environment of the copper ions.[16] Here the synthesis and characterization of CuClCu₂TeS₃ are reported. By comparison with the crystal structures of $(CuI)_3Cu_2TeS_3$[15] and $CuBrCu_{1.2}TeS_2$[17] the structural flexibility of copper(I) halides in such composite materials becomes evident. Compounds crystallizing in an acentric structure and consisting of highly polarizable building units, e.g. complex [TeS₃]²⁻ anions and halide ions, may exhibit interesting physical properties for e.g. the application in storage media.

Experimental Section

Synthesis and Characterization. Pure CuClCu₂TeS₃ was prepared by reaction of CuCl (99%, Fluka), Cu (shot, m5N, Johnson Matthey), Te (99.999%, Heraeus), and S (pieces, 99.999%, Fluka) with the molar ratio CuCl/Cu/Te/S = 1:2:1:3. Prior to use CuCl was purified by recrystallization from concentrated aqueous hydrochloric acid. The white microcrystalline powder was filtered from the solution, subsequently washed with demineralized water and ethanol, and then dried in a vacuum for several days. Copper was freshly reduced in a stream of H₂/Ar at 650 °C. The starting materials were sealed in evacuated silica ampules and homogenized for 6 h at 600 °C. After cooling to room temperature the samples were ground and then tempered at 400 °C for 2 weeks. A mixture of black single crystals and microcrystalline

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Table 1. Crystallographic Data for CuClCu₂TeS₃

empirical formula	CuClCu₂TeS₃	fw [g mol⁻¹]	449.87
a^a	7.361(1)	space group	$R3m$ (No. 160)
c^a	10.401(1)	T [°C]	20
V [Å³]	488.05(4)	λ [Å]	0.71073
Z	3	ρ_{calc} [g cm⁻³]	4.590
μ(Mo Kα) [cm⁻¹]	154.4	R (all reflcns)^b	0.0164
		R_w (all reflcns)^b	0.0435

^{a} Powder data (20 °C). ^{b} $R = [\sum||F_{obs}| - |F_{calc}||]/\sum|F_{obs}|$; $R_w = [\sum w(|F_{obs}|^2 - |F_{calc}|^2)^2/\sum w|F_{obs}|^4]^{1/2}$; and $w = \{[\sigma^2(|F_{obs}|^2) + (0.015|F_{obs}|^2)^2]\}$.

Table 2. Fractional Atomic Coordinates and Displacement Parameters U_{eq}^a [Å²] for CuClCu₂TeS₃

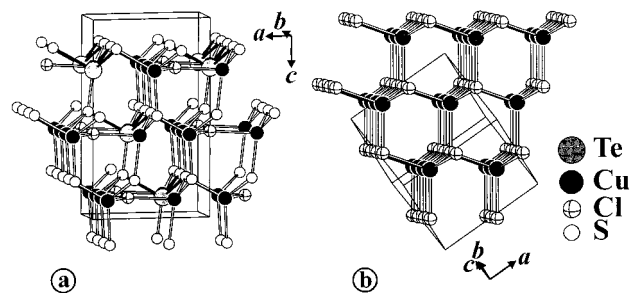| atom	Wyckoff position	x	y	z	U_{eq}
Cu	9b	0.523 91(5)	$1-x$	0.245 93(4)	0.024 9(1)
Te	3a	0.0	0.0	¼	0.013 54(8)
S	9b	0.502 92(5)	$1-x$	0.471 46(7)	0.013 8(2)
Cl	3a	0.0	0.0	0.570 5(1)	0.017 2(2)

^{a} U_{eq} is defined as one-third of the trace of the anisotropic $\mathbf{U}_{ij}$ tensor.

powder was obtained. X-ray powder techniques (SIEMENS D5000, Cu Kα₁ (λ = 1.540 51 Å), Si as an external standard) and DTA measurements (LINSEIS L62, Al₂O₃ as reference material) were employed for characterization. CuClCu₂TeS₃ shows peritectical decomposition at 448 °C. Raman spectra of microcrystalline black CuClCu₂TeS₃ were recorded in a backscattering mode with a Bruker RFS 100/S spectrometer equipped with a Nd:YAG laser providing an excitation wavelength of 1064 nm.

X-ray Studies. The crystal structure of CuClCu₂TeS₃ at room temperature was determined from a single crystal of suitable size, i.e., $0.25 \times 0.25 \times 0.20$ mm³. The crystal was glued on a glass capillary and mounted on a CAD4 (NONIUS) single-crystal diffractometer providing monochromatic Mo Kα (λ = 0.710 73 Å) radiation. The orientation matrix and lattice constants were determined from 25 well-centered reflections, see Table 1. A total of 2932 reflections with $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, and $-16 \leq l \leq 16$ up to $2\theta_{max} = 70°$ were collected. Absorption was corrected empirically by the use of ψ-scans. The reflections were merged to give 561 symmetry independent reflections ($R_{int} = 0.050$). A starting model for the structure refinement was obtained by direct methods (NRCVAX[19]). Structural data were refined against F^2 by full-matrix least-squares methods using the JANA98 program package[20] and scattering factors therein. During the refinement no hints for twinning were detected. After introduction of anisotropic displacement parameters for all atoms and an isotropic extinction coefficient the refinement of 19 parameters converged to R = 0.0164 and R_w = 0.0435 for all reflections. The largest peak in the final difference Fourier calculation was 1.47 e Å⁻³, 0.661 Å apart from tellurium. To provide a good comparability to the structure of γ-CuCl the z parameter of tellurium (which was used to define the origin in space group $R3m$) was fixed to ¼. Table 2 contains the refined atomic coordinates and the displacement parameters. Selected interatomic distances and angles are summarized in Table 3.

Results and Discussion

Crystal Structure. CuClCu₂TeS₃ represents a new derivative of the sphalerite type structure. Figure 1 shows a section of the crystal structure of CuClCu₂TeS₃ and for comparison that of γ-CuCl, which crystallizes in the sphalerite type.[21] The structural similarities but also the differences become immediately obvious. As expected for a sphalerite type compound Cu⁺ is four-coordinate, that is, a coordination [CuS₃Cl] is found. Interatomic distances are about $\bar{d}$(Cu–S) = 2.323 Å and d(Cu–

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Figure 1. Crystal structures of (a) CuClCu₂TeS₃ and of (b) γ-CuCl (sphalerite type) to show the close structural relationship and also the deviations caused by the 3:1 ordering of both cations and anions.
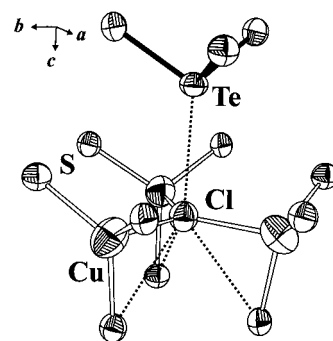
Figure 2. Section of the crystal structure and labeling scheme for CuClCu₂TeS₃. Ellipsoids represent a probability of 95%. The dashed lines correspond to distances d(Te–Cl) = 3.325 Å and d(Cl–S) = 3.258 Å, respectively.

Table 3. Selected Interatomic Distances [Å] and Angles [deg] for CuClCu₂TeS₃

Cu–Cl		2.4249(4)	S–Cu–S	2×	121.33(2)
Cu–S	2×	2.2981(5)	S–Cu–S		108.70(3)
Cu–S		2.3548(8)	S–Cu–Cl	2×	107.59(2)
			S–Cu–Cl		85.65(3)
Te–S	3×	2.3837(5)	S–Te–S	3×	98.30(2)
Te–Cl		3.325(1)	S–Te–Cl	3×	119.14(2)
			Cu–Cl–Cu	3×	119.86(1)
Cl–Cu	3×	2.4249(4)	Cu–Cl–Te	3×	92.16(3)
S–Cu	2×	2.2981(5)	Cu–S–Cu		86.32(2)
S–Cu		2.3548(8)	Cu–S–Cu	2×	123.03(2)
S–Te		2.3837(5)	Te–S–Cu	2×	103.75(3)
			Te–S–Cu		112.63(2)

Cl) = 2.4315 Å. The bond angle ∠(S–Cu–S) varies from 108.71 to 121.32°, and ∠(Cl–Cu–S), from 85.65 to 107.59°, and thus indicate the large deviations from an ideal tetrahedral surrounding of the Cu⁺ ion. Taking these distortions into account the coordination of copper is better represented by an almost trigonal planar coordination [CuS₃] with one additional chlorine atom above the plane. Sulfur is coordinated by copper and tellurium as expressed by the formulation [SCu₃Te]. The deviations from an ideal tetrahedral environment are comparable to those found for copper, and the angles ∠(Cu–S–Cu) and ∠(Te–S–Cu) are in the range from 86.32 to 123.03°. Tellurium formally takes the oxidation state +4 and three bonds exclusively to sulfur with d(Te–S) = 2.3901 Å and ∠(S–Te–S) = 98.31° are observed. Trigonal pyramidal thiotellurate ions [TeS₃]²⁻ result. Chlorine is bonded to three copper atoms only with d(Cl–Cu) = 2.4315 Å and ∠(Cu–Cl–Cu) = 119.86°, that is, chlorine has an almost ideal trigonal planar coordination by copper atoms, see Figure 2. A similar surrounding for chlorine by copper(I) has not yet been reported. Different reasons might be discussed for this finding. Although the coordination number is three for chlorine, the distances d(Cl–Cu) are comparably large for copper(I) compounds. In γ-CuCl

F$\bar{4}$3m

Cu: 4c	Cl: 4b
$\bar{4}$3m	$\bar{4}$3m
0.25	0.5
0.25	0.5
0.25	0.5

γ-CuCl (sphalerite type)

t4
-a/2+b/2, -b/2+c/2, a+b+c

R3m

Bi: 3a	O: 3a
3m	3m
0.	0.
0.	0.
0.25	0.525

BiO

i4
-2a, -2b, c

R3m

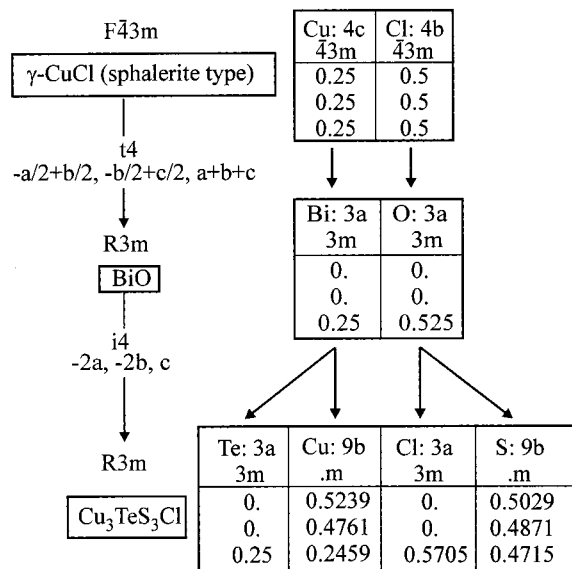| Te: 3a	Cu: 9b	Cl: 3a	S: 9b
3m	.m	3m	.m
0.	0.5239	0.	0.5029
0.	0.4761	0.	0.4871
0.25	0.2459	0.5705	0.4715

Cu$_3$TeS$_3$Cl

Figure 3. Group−subgroup relationship between CuClCu$_2$TeS$_3$ and the sphalerite type structure. By means of this "Bärnighausen tree" the symmetry reduction becomes evident in an effective way.

Figure 4. Raman spectra of a) CuClCu$_2$TeS$_3$ and of b) (CuI)$_3$Cu$_2$-TeS$_3$. Both spectra show ν(Te−S) stretching modes for the [TeS$_3$]$^{2-}$ group at about 350 cm^{-1}.

with a coordination number of four for cations and anions the distance d(Cl−Cu) is about 2.347 Å if the tendency to leave the central tetrahedral position of copper is neglected.[21,22] Thus the preference of Cu$^+$ for a trigonal planar coordination by sulfur results in the unusual long distance d(Cu−Cl). Another explanation for the deviations of the crystal structure of CuClCu$_2$TeS$_3$ from the ordinary sphalerite type is the electron count for this compound. For the formation of a regular tetrahedral structure an average of four valence electrons per atom is needed.[23] In the case of the title compound 34 valence electrons are available for eight atoms, that is, there is a surplus of two electrons. As a consequence one bond is broken and two lone electron pairs are formed. These two lone electron pairs are located on Te^{4+} and on Cl$^-$.[24] Thus the repulsion of the lone electron pairs on these two atoms can be regarded as the reason for the long distance of d(Cl−Te) = 3.325 Å as compared to d(Cl−S) = 3.258 Å, see Figure 2.

The relations of CuClCu$_2$TeS$_3$ to the aristotype sphalerite can be rationalized by means of a "Bärnighausen tree," [25] which is shown in Figure 3. It is evident that the symmetry of the cubic cell of the sphalerite structure type is reduced in two steps in order to give the structure of CuClCu$_2$TeS$_3$. First the cubic symmetry is reduced to rhombohedral symmetry. A representative of the resulting structure type is rhombohedral BiO[26] with only slight deviations of the atomic sites from the ideal positions that were 0, 0, $^1/_4$ for Bi and 0, 0, $^1/_2$ for O. In a second step the unit cell volume is increased four times and the resulting four positions of the cations and of the anions are both ordered in a 3:1 manner. In an ideal, undistorted cell the atomic positions were Te, 0, 0, $^1/_2$; Cu: $^1/_2$, $^1/_2$, $^1/_4$; Cl: 0, 0, $^1/_2$; and S: $^1/_2$, $^1/_2$, $^1/_2$. The largest deviation from the ideal data is found for the z parameter of chlorine, which is 0.5705 instead of $^1/_2$.

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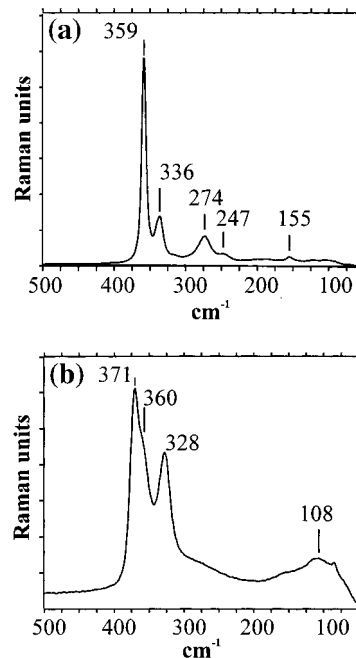(26) Zavyalova, A. A.; Imamov, R. M.; Pinsker, Z. G. *Kristallografiya* **1965**, *10*, 480.

The resulting 3-fold coordination of chlorine by copper atoms has already been discussed, vide supra. From a crystallographic viewpoint the title compound should be named Cu$_3$TeS$_3$Cl but this formula does not fit the chemical approach for the description of this composite material, namely a mixture of CuCl and hypothetic Cu$_2$TeS$_3$. The composition of Cu$_2$TeS$_3$ is close to that of Cu$_{17.6}$Te$_8$S$_{26}$[4] ($\approx$8Cu$_2$TeS$_3$) with a crystal structure related to the tetrahedrite type Cu$_{12}$Sb$_4$S$_{13}$.[27]

Raman Spectra. To date only a few compounds containing the thiotellurate ions [TeS$_3$]$^{2-}$ are known, e.g. (CuI)$_3$Cu$_2$TeS$_3$,[15] RbCuTeS$_3$,[28] BaTeS$_3$,[29] and (NH$_4$)$_2$TeS$_3$.[30] Accordingly, there exist almost no vibrational spectroscopic data for the [TeS$_3$]$^{2-}$ units in the literature. The only data available are some IR frequencies obtained for ACuTeS$_3$, AAgTeS$_3$ (A = alkali metal),[28] and (CuI)$_3$Cu$_2$TeS$_3$. Here the first Raman spectra of thiotellurate(IV) ions either with an ideal C_{3v} symmetry in CuClCu$_2$TeS$_3$ or (for comparison) with C_1 symmetry in (CuI)$_3$-Cu$_2$TeS$_3$ are reported, see Figure 4. In contrast to the IR spectra the bands obtained by Raman spectroscopy are much sharper. The spectra reveal bands at about 350 cm^{-1} which are assigned to tellurium−sulfur stretching modes. A second group of bands in the range from 245 to 290 cm^{-1} (not resolved for (CuI)$_3$-Cu$_2$TeS$_3$) has probably to be assigned to copper−sulfur stretching modes, and the bands at 155 cm^{-1} (CuClCu$_2$TeS$_3$) and at 108 cm^{-1} ((CuI)$_3$Cu$_2$TeS$_3$), are due to the corresponding copper−halide modes. The [TeS$_3$]$^{2-}$ unit in CuClCu$_2$TeS$_3$ has an ideal C_{3v} symmetry, and in accordance with this crystallographic finding only two bands are found in the corresponding Raman spectrum. One band is assigned to the ν_{asym} mode at 359 cm^{-1} and the other band is assigned to the ν_{sym} mode at 336 cm^{-1}, see Figure 4a. In the case of (CuI)$_3$Cu$_2$TeS$_3$ the [TeS$_3$]$^{2-}$ units have C$_1$ symmetry and the ν_{asym} modes are no

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longer degenerated. As a consequence a shoulder at about 360 cm^{-1} is found for the high energy mode. The splitting of the symmetrical and the asymmetrical modes for (CuI)$_3$Cu$_2$TeS$_3$ is stronger than for CuClCu$_2$TeS$_3$, which is due to the different degree of distortion of the [TeS$_3$]$^{2-}$ units in the solid state. However, the mean value of the Te−S stretching frequencies is about $\bar{\nu} = 350$ cm^{-1} for both compounds. This mean frequency is in good accord with the IR data published for the above-mentioned compounds. The somewhat higher variations observed for ACuTeS$_3$ and AAgTeS$_3$ are probably caused by additional bonding interactions of tellurium with sulfur atoms in a so-called nonbonding distance with d(Te−S) $\leq$ 4 Å. If these additional interactions are present a red-shift of the stretching modes is to be expected as compared to [TeS$_3$]$^{2-}$ units, which are isolated from each other. A similar behavior was observed for (CuI)$_2$Cu$_3$SbS$_3$ and β-Cu$_3$SbS$_3$.[16] In the composite material (CuI)$_2$Cu$_3$SbS$_3$ the [SbS$_3$]$^{3-}$ units are well separated from each other whereas in Cu$_3$SbS$_3$[31−33] in addition to three sulfur atoms belonging to the thioantimonate(III) group five more sulfur atoms are within a distance d(Sb−S) < 4 Å. Thus some important information about the bonding situation in these materials can be obtained by Raman spectroscopic investigations.

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Conclusion

Extension of the use of copper(I) halides as solid solvent for the synthesis of new composite materials based thiometalate ions provided CuClCu$_2$TeS$_3$. This compound is a derivative of the sphalerite type structure revealing a new 3:1 ordering scheme for cations and anions. Raman spectroscopic data for the thiotellurate(IV) ions clearly show, that these units are well separated from each other, that is, besides three covalent bonds Te−S no additional sulfur atoms with d(Te−S) < 4 Å are observed about tellurium. From preliminary conductivity measurements it can be concluded that the title compound exhibits predominantly electronic conductivity whereas ionic conduction is negligible. Since this compound crystallizes in an acentric structure and consists of highly polarizable building units, interesting physical properties, e.g. for the application in storage media, are to be expected.

Supporting Information Available: X-ray crystallographic files, in CIF format, providing more details regarding data collection and structure refinement for CuClCu$_2$TeS$_3$. Access information is given on any current masthead page.