Refinement of the Crystal Structures of $CuTe_2Br$ and $CuTe_2I$

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The crystal structures of $CuTe_2Br$ and $CuTe_2I$ have been refined on the basis of single crystal data. Both compounds crystallize monoclinically in space group $P2_1/c$. The structures are isotypic with that of $CuTe_2Cl$. The lattice parameters of $CuTe_2Br$ are a = 834.5(8) pm, b = 492.8(4) pm, c = 1573.3(5) pm and β = 135.3(2)°. The unit cell dimensions of $CuTe_2I$ are a = 866.5(8) pm, b = 491.4(4) pm, c = 1649.6(3) pm and β = 135.1(2)°.

Introduction

The copper chalcogen halides with the general formula CuY_nX (Y = Se, Te; X = Cl, Br, I; n = 1, 2, 3) [1] contain chalcogen fragments in a formal oxidation state of zero. They can be divided into two groups: There are six-membered rings of Se in $CuSe_3Br$ [2] and $CuSe_3I$ [3] and infinite chalcogen screws in $CuSe_2Cl$ [4] and in the homologous series CuTeX [5–7] and $CuTe_2X$ [8] (X = Cl, Br, I). $CuTe_2Br$ and $CuTe_2I$ are the only copper chalcogen halides, of which single crystal data have not been reported so far. Thus, the structure refinement and description of these compounds are presented.

Experimental

$CuTe_2Br$ and $CuTe_2I$ were synthesized from CuBr (CuI, resp.) and elemental Te in the corresponding hydrogen halide solution under hydrothermal conditions [1]. Both compounds crystallize in form of black needles with metallic lustre. The reflection intensities up to 2θ = 60° were measured on a Philips fourcircle diffractometer PW 1100 (graphite monochromator, MoKα-radiation). Measuring time for the background was half of the time for the peak intensity. The stability of the primary beam intensity was controlled by three reference reflections measured at fixed time intervals during the data collection. Data pertaining to the structure refinement are summarized in Tables I and II. The reflection intensities of both compounds were corrected for absorption by the program DIFABS [9]. The atomic positions of the isotypic $CuTe_2Cl$ [8] were taken as starting values for the refinement. Applying anisotropic temperature factors the procedure converged at R_w = 0.049 for $CuTe_2Br$ and R_w = 0.054 for $CuTe_2I$.

Structure Description

The crystal structure of $CuTe_2X$ (X = Br, I) (Fig. 1) is built up of infinite, pseudo-fourfold Te spirals along the b-axis. These screws are connected by –Cu–X–Cu-links forming layers parallel to the a–b-plane. The copper atoms are tetrahedrally coordinated by two Te and two halogen atoms. The Te–Te bond lengths in the screws alternate at 273.1 pm and 278.4 pm in $CuTe_2Br$ and at 275.0 pm and 278.7 pm in $CuTe_2I$. With 381.9 pm in $CuTe_2Br$ and 405.3 pm in $CuTe_2I$, the distances between different Te spirals are clearly smaller than the sum of the van-der-Waals radii of tellurium (440 pm) [12] (Table III).

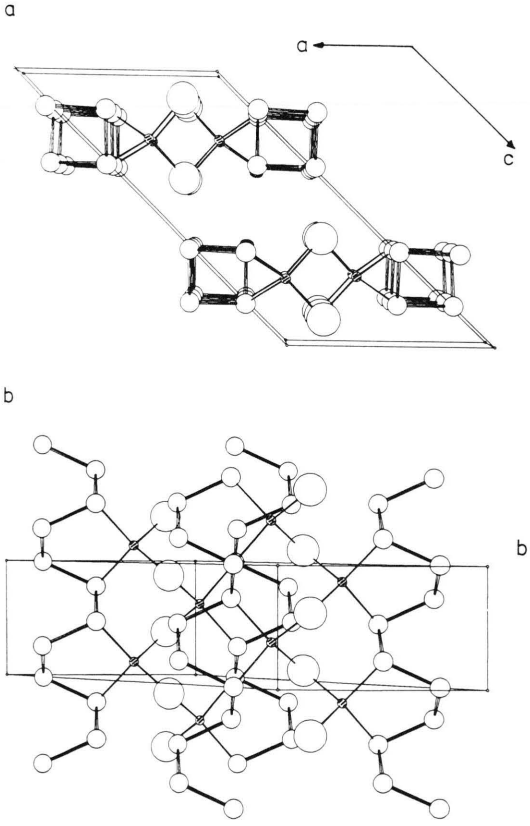

Fig. 1. Crystal structure of $CuTe_2X$ (X = Br, I), hatched circles: Cu; small open circles: Te; big open circles: halogen; a) Perspective view along b; b) Perspective view perpendicular to b.

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Table I. Crystal structure data for $CuTe_2Br$ and $CuTe_2I$.

Compound	$CuTe_2Br$	$CuTe_2I$
Synthesis method	Hydrothermal from CuBr and Te in HBr [1]	Hydrothermal from CuI and Te in HI [1]
Crystal system, space group	Monoclinic $P2_1/c$ (No. 14)	Monoclinic $P2_1/c$ (No. 14)
Lattice parameters	a = 834.5(8) pm b = 492.8(4) pm c = 1573.3(5) pm β = 135.3(2)°	a = 866.5(8) pm b = 491.4(4) pm c = 1649.6(3) pm β = 135.1(2)°
Cell volume	$454.8 \cdot 10^6$ pm^3	$496.2 \cdot 10^6$ pm^3
Formula weight	398.6 g mol^{-1}	445.6 g mol^{-1}
Z	4	4
Calculated density ϱ	5.84 g cm^{-3}	5.99 g cm^{-3}
Temperature	20 °C	20 °C
Absorption coefficient	248.7 cm^{-1}	207.2 cm^{-1}
Diffractometer	Philips PW 1100/15	
Radiation	MoKα, λ = 71.069 pm (graphite-monochromator)	
Scan mode, scan width	ω-scan, 1.2°	ω-scan, 1.6°
scan speed	0.08° sec^{-1}	0.08° sec^{-1}
Theta range	$3° \leq \theta \leq 30°$	$2° \leq \theta \leq 30°$
Measured sections of reciprocal space	whole sphere	whole sphere
Number of measured reflections	3528	4114
Unique reflections	585	1084
Observed reflections ($\geq 3\sigma(F^2)$)	549	1070
Structure solution	Starting parameters taken from $CuTe_2Cl$ [8]	
Absorption correction	Program DIFABS [9]	
Refinement procedure	Least-squares methods, SHELX [10]	
$R_w(R)$-value	0.049 (0.055)	0.054 (0.059)
Number of refined parameters	38	38
Max./min. residual electron density ($e^-/Å^3$)	2.67/−1.66	2.04/−3.35

Table II. Atomic positions and temperature factors of $CuTe_2Br$ and $CuTe_2I$.

$CuTe_2Br$				
	Cu	Te 1	Te 2	Br
x	.6761(5)	.9954(3)	.2933(2)	.6822(4)
y	.1431(6)	.4997(3)	.2836(3)	.8936(5)
z	.2492(3)	.3603(2)	.3573(1)	.3872(2)
U_{eq}	373(24)	278(10)	285(11)	318(18)
$CuTe_2I$				
	Cu	Te 1	Te 2	I
x	.6857(3)	.9913(2)	.2842(2)	.6896(2)
y	.1341(5)	.4971(2)	.2776(2)	.8887(2)
z	.2489(2)	.3535(1)	.3543(1)	.3929(9)
U_{eq}	350(14)	267(7)	277(7)	283(7)

The temperature factors U_{eq} are given in pm^2.

Table III. Distances and angles of $CuTe_2Br$ and $CuTe_2I$; comparison with data of trigonal tellurium.

	$CuTe_2Br$	$CuTe_2I$	Te [11]
Cu−Te 1	257.4(3) pm	258.9(2) pm	
Cu−Te 2	257.3(5) pm	258.0(4) pm	
Cu−X	243.9(4) pm 246.4(6) pm	261.6(2) pm 264.3(4) pm	
Te−Te	273.4(4) pm 278.5(2) pm	274.9(2) pm 278.7(2) pm	283.5(2) pm
Te···Te	381.9(3) pm	405.3(2) pm	349.5 pm
Bond angle β (Te−Te−Te)	100.2(1)° 102.4(1)°	100.6(6)° 101.8(5)°	103.2(1)°
Dihedral angle γ	40.1° 56.3°	40.7° 55.4°	100.7°

Discussion

$CuTe_2Br$ and $CuTe_2I$ complete the series $CuTe_2Cl$ [8] – $CuTe_2Br$ – $CuTe_2I$ within the well-investigated copper chalcogen halides [1]. The Te–Te bond lengths in the characteristic building units – the Te screws – are considerably smaller than those in the trigonal element structure [11] (Table III). This observation is reasonable taking into account Pauling's description of partial bonds [12]. Accordingly an increasing number of nonbonding, homonuclear contacts between fragments of covalently bonded atoms enlarges the bond length. Assuming no nonbonding distances it is possible to calculate a single bond length d_1 which should be realized in the case of isolated fragments. For elemental trigonal Te d_1 is 277.0 pm, which is in good agreement with the Te–Te bond lengths in the $CuTe_2X$ compounds (Table III).

Therefore the Te screws in the copper tellurium halides can be seen as almost isolated element fragments with real Te–Te single bonds.

As mentioned by Fenner [8], the structures of this type can be interpreted as defect tetrahedral polyanionic arrangements according to the nomenclature of Parthé [13]. The complete notation of these compounds is $Cu^{[2+2;0]}\underline{Te}_2{}^{[1;2]}\underline{\underline{X}}^{[2;0]}$.

Additional crystal structure data have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Inquiries should be accompanied by the depository number CSD 53662, the names of the authors, and the literature citation.

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