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Crystal Structure of $NaCu_5S_3$

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The hexagonal compound $NaCu_5S_3$ [$a = 6.978(5)$, $c = 7.209(6)$ Å, space group $P6_322\text{-}D_6^6$, $Z = 2$] was synthesized under hydrothermal conditions. The crystal structure was solved by direct methods from 140 single crystal X-ray data. The refinement yielded an R value of 2.3%. The Na atom has an octahedral coordination of S atoms [Na—S = 2.89 Å, 6 ×]. The atom Cu(1) is bound to two S atoms at 2.19 Å and the atom Cu(2) to three atoms at 2.36 Å. In addition the Cu(1) atom is coordinated to four Cu(2) atoms, and the Cu(2) atom to six Cu(1) atoms with Cu—Cu distances of 2.70 Å and 2.72 Å. The S atom has an irregular coordination figure built up by two Na and four Cu atom neighbours. The connection of the different coordination polyhedra results in a framework structure.

(Keywords: $NaCu_5S_3$; *Hydrothermal synthesis; Crystal structure; Crystal chemistry)*

Die Kristallstruktur von $NaCu_5S_3$

Die hexagonale Verbindung $NaCu_5S_3$ [$a = 6.978(5)$, $c = 7.209(6)$ Å, Raumgruppe $P6_322\text{-}D_6^6$, $Z = 2$] wurde unter Hydrothermalbedingungen synthetisiert. Die Kristallstruktur wurde mittels direkter Methoden anhand von 140 Einkristall-Röntgendaten gelöst; die Verfeinerung ergab einen R-Wert von 2.3%. Das Na-Atom hat eine oktaedrische Koordination von S-Atomen [Na—S = 2.89 Å, 6 ×]. Das Atom Cu(1) ist an zwei S-Atome mit 2.19 Å und das Atom Cu(2) an drei S-Atome mit 2.36 Å gebunden. Weiters wird das Atom Cu(1) von vier Cu(2)-Atomen und das Atom Cu(2) von sechs Cu(1)-Atomen umgeben, wobei die Cu—Cu-Abstände 2.70 Å und 2.72 Å betragen. Das S-Atom hat ein unregelmäßiges Koordinationspolyeder, das aus zwei Na- und vier Cu-Atomen aufgebaut wird. Die Verknüpfung dieser unterschiedlichen Koordinationspolyeder ergibt eine Gerüststruktur.

Introduction

Within the last decade several alcali metal-copper/silver-chalcogenides were synthesized. This class of substances was obtained by melting mixtures of the following three products in different ratios: copper or silver, chalcogene (S, Se, or Te) and an alcali metal or an alcali carbonate. The crystal structure of two sodium-copper-sulfides, synthesized from melts, are well known: $Na_2Cu_4S_3$[1] and $Na_3Cu_4S_4$[2] (for further literature on this class of compounds cf. these two articles). Contrary to the two sodium-copper-sulfides mentioned above, $NaCu_5S_3$ was synthesized under hydrothermal conditions. For specification of the crystal chemistry a crystal structure determination of the title compound was performed.

Experimental

The compound $NaCu_5S_3$ was synthesized as follows: 0.5 g native Cu (powder) was put into a "teflon" vessel ($\sim 6\,cm^3$), 2 g $Na_2S \cdot 9\,H_2O$ was added, and the volume of the vessel was filled up with H_2O to about 80%. The closed vessel was heated for 5 days at 413 (5) K. The results were black coloured prismatic crystals of $NaCu_5S_3$ (diameter max. 0.3 mm). As crystal forms {10.0} and {10.1} were observed. The crystals of the title compound are stable under athmospheric conditions for some weeks only, then they get coated with white rims; a decomposition to an amorphous compound was observed. The chemical composition was determined by a single crystal structure determination. A combination of a classic semiquantitative chemical analysis and an EMS analysis (Edax) of $NaCu_5S_3$ confirmed the chemical formula.

The collected X-ray intensities (cf. Table 1) were corrected for absorption (emperical ψ scans of three reflections) as well as for *Lorentz*- and polarization effects. Afterwards the data were merged and the result was a set of 140 unique structure amplitudes, which were used for the solution of the crystal structure. The positions of the Cu atoms were located by direct methods. A subsequent *Fourier* summation revealed the positions of the Na and S atoms. The atomic coordinates and the anisotropic temperature factors were refined by full-matrix least-squares techniques. Complex scattering functions for neutral atoms were taken from the "International Tables for X-ray Crystallography" (1974)[3]. The secondary isotropic extinction was corrected according to *Zachariasen*[4]. Table 1 gives a survey

Table 1. *Summary of crystal data, Intensity measurements, and crystal structure refinement for* $NaCu_5S_3$

$a = 6.978\,(5)$ Å
$c = 7.209\,(6)$ Å
$Z = 2\,\{NaCu_5S_3\}$
Laue symmetry: 6/m 2/m 2/m
space group: $P6_322\text{-}D_6^6$
temperature: 295 K
$d_{calc} = 4.78\,g\,cm^{-3}$
$\mu(MoK\alpha) = 177\,cm^{-1}$
No. of variables: 18
$R = 0.023$
$R_w = 0.017$
$w = 1.277/[\sigma(F_0)]^2$

STOE four-circle diffractometer and
program system STRUCSI on an ECLIPSE S/140
crystal dimensions: $0.15 \times 0.15 \times 0.30\,mm^3$
graphite monochromatized $MoK\alpha$ radiation
ω-scan mode with a step width of 0.05°
steps/reflection: $40 + (\alpha_1, \alpha_2)$ splitting
time/step: 0.5 to 1.5 s
3 standard reflections
measured each 60 min
range of data: $3° \leqslant 2\theta \leqslant 45°$
measured reflections: 821 ($\pm h$—$k \pm l$)
unique reflections: 140

Table 2. *Atomic coordinates and anisotropic temperature factors* for* $NaCu_5S_3$ *with e.s.d.'s in parentheses; origin at* 6_321

Atom	*Wyckoff* notation	x/a	y/b	z/c
Na	$2b$	0	0	1/4
Cu(1)	$6h$	0.48631 (8)	$= -x/a$	1/4
Cu(2)	$4f$	2/3	1/3	0.02363 (16)
S	$6g$	0.67576 (27)	$= x/a$	1/2

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.027 (2)	$= U_{11}$	0.026 (4)	$= 1/2\, U_{11}$	0	0
Cu(1)	0.0375 (5)	$= U_{11}$	0.0234 (7)	0.0187 (5)	—0.0096 (5)	$= U_{13}$
Cu(2)	0.0240 (5)	$= U_{11}$	0.0308 (6)	$= 1/2\, U_{11}$	0	0
S	0.0155 (7)	$= U_{11}$	0.0176 (9)	0.0061 (8)	—0.0003 (4)	$= -U_{13}$

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* $ATF = \exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j]$.

Table 3. *Interatomic distances (Å) for* $NaCu_5S_3$ *with e.s.d.'s in parentheses*

Na—S = 2.893 (1) 6 ×

S—Na = 2.893 (1) 2 ×
S—Cu(1) = 2.186 (1) 2 ×
S—Cu(2) = 2.364 (1) 2 ×

Cu(1)—S = 2.186 (1) 2 ×
Cu(1)—Cu(2) = 2.704 (1) 2 ×
Cu(1)—Cu(2′) = 2.723 (1) 2 ×

Cu(2)—S = 2.364 (1) 3 ×
Cu(2)—Cu(1) = 2.704 (1) 3 ×
Cu(2)—Cu(1′) = 2.723 (1) 3 ×

about crystal data, intensity measurements, and reliability values for $NaCu_5S_3$. Table 2 gives the parameters for the crystal structure, Table 3 all the interatomic distances $\leqslant 3.20$ Å.

Discussion

In $NaCu_5S_3$ the Na atom has an octahedral coordination with six equal Na—S distances of 2.893 (1) Å. The NaS_6 octahedron is slightly elongated parallel to [001], with six S—Na—S angles of 85.29 (6)° and six angles of 94.71 (6)°. The NaS_6 octahedra are connected to each other via two common faces building up rods parallel to [001]. The Na—S distances of the title compound are in good agreement with those given for $Na_2Cu_4S_3$[1]

[Na—S = 2.97(2) Å to 3.04(2) Å] and $Na_3Cu_4S_4$[2] [Na—S = 2.846(2) Å to 3.109(2) Å].

The atom Cu(1) has only two S atom neighbours with equal Cu(1)—S bond lengths of 2.186(1) Å and an angle S—Cu(1)—S of 171.3(4)°. A formally monovalent Cu atom in a more or less linear [2] coordination

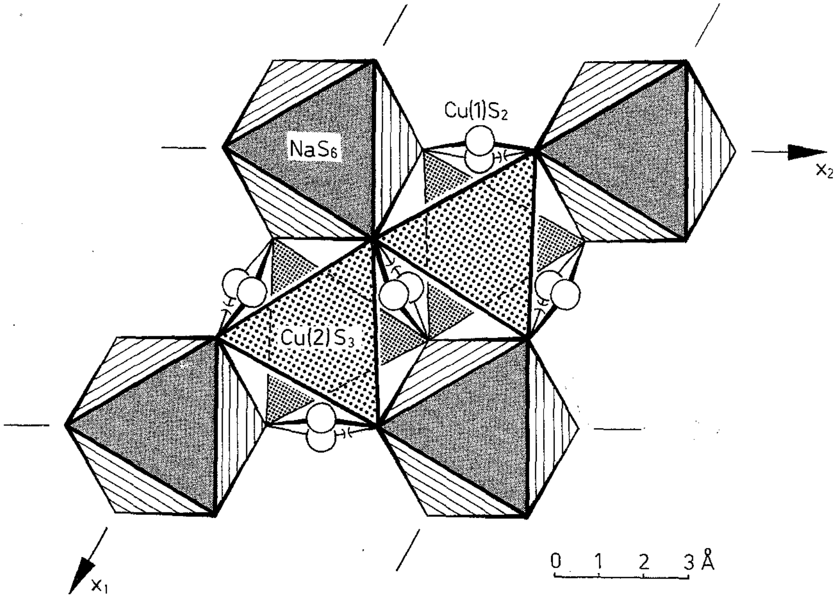

Fig. 1. The crystal structure of $NaCu_5S_3$ in a projection parallel to [001]. In a mixed technique the face sharing NaS_6 octahedra [Na atoms at $z/c = 1/4$ and 3/4], the "linear" $Cu(1)S_2$ coordinations [Cu(1) atoms at $z/c = 1/4$ and 3/4)], and the $Cu(2)S_3$ pyramids [Cu(2) atoms at $z/c \sim 0$ and 1/2] are drawn

against S atoms is rather the exception than the rule. A further compound with Cu atoms in a comparable [2] coordination is djurleite[5], $Cu_{31}S_{16}$. This crystal structure contains 62 crystallographic different Cu atoms of which one Cu atom shows a "linear" [2] coordination (Cu—S = 2.19 Å and 2.20 Å, S—Cu—S = 172.2°). Another example is the disordered crystal structure of high chalcocite[6], Cu_2S, in which $Cu^{[2]}$—S bond lengths of 2.06 Å are presumed for a part of the Cu atoms (the percentages are not given). In contrary, such a [2] coordination of monovalent Cu atoms is well known against oxygen atoms (cf. Cu_2O, cuprite[7]). The coordination number [2] of the Cu(1) atom helps to explain the short Cu(1)—S distances compared with those of the $Cu(2)^{[3S]}$ atom in $NaCu_5S_3$ [Cu(2)—

S = 2.364(1) Å, 3 ×]. Comparable [3] coordinations of Cu atoms with three S atoms have been reported for $Na_2Cu_4S_3$[1] [Cu—S ranges from 2.23 (1) Å to 2.50 (1) Å] and $Na_3Cu_4S_4$[2] [Cu—S ranges from 2.251 (1) Å to 2.312 (1) Å]. In all these cases the Cu atoms form with the three S atoms flat trigonal pyramids with the Cu atom at the apex. The elevation of the Cu(2) atom from the plane defined by the three S atoms is 0.170 (1) Å, a value which is comparable to the values in the two other sodium-copper-sulfides (range of 0.177 Å to 0.645 Å).

In addition the two Cu atoms are coordinating each other. The atom Cu(1) has four Cu(2) atom neighbours whereas the atom Cu(2) has six Cu(1) atom neighbours. The Cu—Cu distances are 2.704(1) Å and 2.723 (1) Å. These distances are significant longer than the shortest Cu—Cu distance in native copper with 2.556 Å[8]. But nevertheless one can consider weak "metallic" interactions between the Cu atoms in $NaCu_5S_3$. From both Cu atoms the distances to further neighbours are longer than 3.20 Å.

The crystal structure of $NaCu_5S_3$ is based on a hexagonal close-packed arrangement of S atoms. Each S atom is unilateral coordinated by four Cu atoms building a tetragonal pyramide with the S atom at the apex. The Cu—S—Cu angles are 72.79 (8)° and 73.40 (7)°. The coordination figure of the S atom is completed by two Na atoms at the side beeing withdrawn from the Cu atoms [Na—S—Na = 77.06 (8)°].

Fig. 1 shows the crystal structure of $NaCu_5S_3$ in a projection parallel to [001]. The three-dimensional network of the crystal structure is built up by the Cu coordination figures which are connected over common S atom corners. Thereby the "linear" coordinated Cu(1) atoms are combined to each other by S atoms [Cu(1)—S—Cu(1) = 111.78 (9)°] resulting in a zigzag chain parallel to [001]. The sodium atoms are located within channels running parallel to [001]. Together with their coordinating S atoms they build up the rods of the NaS_6 octahedra as discussed above. The connection of the three different coordination polyhedra indicates that the title compound has no pronounced cleavage and helps to explain qualitatively the short prismatic habitus of the crystals of $NaCu_5S_3$.

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