4612 *Inorg. Chem.* **1999,** *38,* 4612−4614

Synthesis and Crystal Structure of the New Quaternary Polysulfide $Na_8Cu_4Nb_2S_{21}$ Containing S^{2-}, S_3^{2-}, and S_5^{2-} Anions in Different Bridging Modes

Christian Rumpf, Christian Näther, and Wolfgang Bensch*

Institut für Anorganische Chemie, Universität Kiel,
Olshausenstrasse 40 , D-24098 Kiel, Germany

Received January 6, 1999

Introduction

The so-called reactive flux method is a well-established synthetical route to synthesize multinary chalcogenides showing all levels of dimensionality with fascinating structural features as well as interesting physical properties.[1−3] During our investigations of the quaternary systems $A_2M^IM^VQ_4$ (one-dimensional chain compounds) and $AM^I_2M^VQ_4$ (two-dimensional layer compounds) with A = Na, K, Rb, and Cs, M^I = Cu and Ag, M^V = V and Nb, and Q = S and Se with respect to their structural and physical properties,[4−9] we synthesized $NaCu_2NbS_4$, the first sodium compound crystallizing in the $AM^I_2M^VQ_4$ type structure. A systematical variation of the synthetic conditions results in the formation of single crystals of a new quaternary sodium polysulfide compound with composition $Na_8Cu_4Nb_2S_{21}$ exhibiting an unusual structure without any precedent in the literature.

Experimental Section

Preparation. $Na_8Cu_4Nb_2S_{21}$ was prepared from a reaction of Na_2S_3 (152 mg, 1.07 mmol), Cu (45 mg, 0.71 mmol), Nb (33 mg, 0.36 mmol), and S (69 mg, 2.15 mmol) in a 3:2:1:6 ratio (Cu 99.5%, Alfa; Nb 99.8%, Alfa; S 99.99%, Heraeus). The binary sulfide Na_2S_3 was synthesized from a reaction of stoichiometric amounts of elemental Na (99.5%, Alfa) and S in liquid ammonia under an argon atmosphere. The starting materials were mixed in a glovebox and then loaded into a glass ampule, which was evacuated (1×10^{-5} mbar) and sealed. The ampule was placed in a computer-controlled furnace and heated to 500 °C within 6 h. It was held at this temperature for 6 days and then slowly cooled to room temperature with a cooling rate of 3°/h. To remove unreacted Na_2S_x the resultant melt was washed with DMF and ether. The product consists of two phases: yellow cubes of Cu_3NbS_4 as the major component and red plates of $Na_8Cu_4Nb_2S_{21}$ as the minor.

Structure Determination. Single-crystal X-ray work was performed on a CAD 4 diffractometer at 220 K using monochromated Mo Kα radiation ($\lambda = 0.7109$ Å). Technical details of the data acquisition as well as some refinement results are summarized in Table 1. Selected interatomic distances are given in Table 2. Lists of observed and calculated structure factors and anisotropic displacement parameters can be obtained from the authors on request. Structure solution was performed using SHELXS-94. Refinement was done against F^2 using SHELXL-93. A face-indexed absorption correction was applied. All atoms were refined using anisotropic displacement parameters. The determination of the absolute structure yielded a value for the Flack *x* parameter of 0.37(3), indicating a slightly racemic twinning. Refinement of the inverted structure did not lead to any significant differences of the *R* values and of the geometrical parameters. The same problem was observed for a second data set measured for a second crystal. However, from the observed extinction rules several space groups are possible. The structure was solved and refined in all of these space groups, resulting in no improvement of the structure. The data sets contained some weak reflections excluding the presence of an additional *n* glide plane. Ignoring these violations the centrosymmetric space group *Pmmn* or the non-centrosymmetric space group $Pmn2_1$ is also possible. But refinements in both space groups lead to significantly poorer reliability factors and disorder of the S_5^{2-} ligand as well as of some Na^+ cations introduced by additional symmetry elements. In addition, in space group $Pmn2_1$ the absolute structure also cannot be determined. Therefore, the problems in determining the absolute structure may originate from the pseudo-centrosymmetry of the crystal. To exclude the formation of a superstructure a complete data set was measured using a STOE imaging plate diffraction system with an area detector. The inspection of the reciprocal space using the programs “recipe” and “space” gives no hints for the formation of a superstructure.

Table 1. Crystallographic Data

empirical formula	$Na_8Cu_4Nb_2S_{21}$
a (Å)	7.7899(5)
b (Å)	29.856(2)
c (Å)	6.6961(6)
V (Å^3)	1557.3
Z	2
fw (g/mol)	1297.16
space group	$P2_12_12$
T (K)	220
λ (Å)	0.7109
D_c (g/cm^3)	2.766
μ (mm^{-1})	4.92
R1 for all $F_o \geq 4\sigma(F_o)^a$	0.0226
wR2^b for all reflections	0.0565

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 1.10P]$; $P = (\text{Max}\,(F_o^2,0) + 2F_c^2)/3$.

Table 2. Selected Distances (Å) and Angles (deg) with Estimated Standard Deviations Given in Parentheses

Nb−S(1)	2.312(1)	Cu(2)−S(5)	2.286(2)
Nb−S(2)	2.282(2)	Cu(2)−S(7)	2.382(2)
Nb−S(3)	2.285(2)	Nb−Cu(1)	2.768(1)
Nb−S(4)	2.275(1)	Nb−Cu(2)	2.784(1)
Cu(1)−S(1)	2.352(2)	S(5)−S(6)	2.066(1)
Cu(1)−S(2)	2.323(2)	S(7)−S(8)	2.083(1)
Cu(1)−S(5)	2.288(2)	S(8)−S(9)	2.058(2)
Cu(1)−S(7)	2.356(2)	S(9)−S(10)	2.067(2)
Cu(2)−S(1)	2.343(2)	S(10)−S(11)	2.077(2)
Cu(2)−S(3)	2.314(2)		

S(4)−Nb−S(2)	110.30(5)	S(1)−Cu(1)−S(7)	111.92(4)
S(4)−Nb−S(3)	110.82(5)	S(5)−Cu(2)−S(3)	115.54(4)
S(2)−Nb−S(3)	107.95(3)	S(5)−Cu(2)−S(1)	112.94(4)
S(4)−Nb−S(1)	112.65(3)	S(3)−Cu(2)−S(1)	104.93(4)
S(2)−Nb−S(1)	107.99(5)	S(5)−Cu(2)−S(7)	102.79(3)
S(3)−Nb−S(1)	106.94(5)	S(3)−Cu(2)−S(7)	109.95(5)
S(5)−Cu(1)−S(2)	117.22(4)	S(1)−Cu(2)−S(7)	110.79(4)
S(5)−Cu(1)−S(1)	111.66(4)	S(5)−S(6)−S(5)	110.71(6)
S(2)−Cu(1)−S(1)	105.30(4)	S(9)−S(8)−S(7)	105.49(6)
S(5)−Cu(1)−S(7)	102.37(3)	S(8)−S(9)−S(10)	107.17(6)
S(2)−Cu(1)−S(7)	108.48(5)	S(9)−S(10)−S(11)	103.93(5)

---

(1) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202.
(2) Kanatzidis, M. G.; Sutorik, A. C. *Prog. Inorg. Chem.* **1995**, *43*, 151.
(3) Pell, M. A.; Ibers, J. A. *Chem. Ber.* **1997**, *130*, 1.
(4) Rumpf, C.; Näther, C.; Jess, I.; Bensch, W. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 1165.
(5) Rumpf, C.; Tillinski, R.; Näther, C.; Dürichen, P.; Jess, I.; Bensch, W. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 1187.
(6) Tillinski, R.; Rumpf, C.; Näther, C.; Dürichen, P.; Jess, I.; Schunk, S. A.; Bensch, W. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1285.
(7) Lu, Y.-J.; Ibers, J. A. *J. Solid State Chem.* **1991**, *94*, 381.
(8) Lu, Y.-J.; Ibers, J. A. *J. Solid State Chem.* **1993**, *107*, 58.
(9) Bensch, W.; Dürichen, P.; Weidlich, C. *Z. Kristallogr.* **1996**, *211*, 931.

10.1021/ic9900206 CCC: $18.00

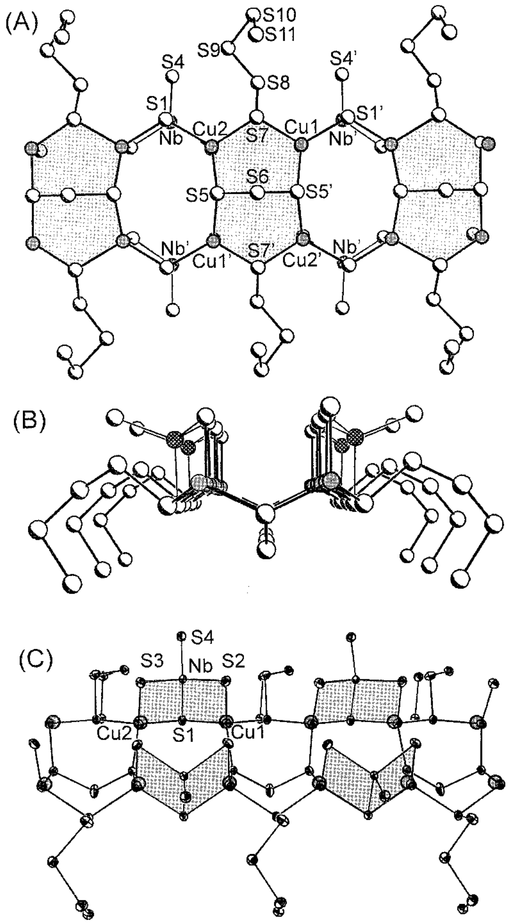

Figure 1. View of the anionic chains in $Na_8Cu_4Nb_2S_{21}$: (A) view on (001), (B) view on (100), and (C) side view of the polycyclic ring system with displacement ellipsoids drawn at the 50% probability level (the prime symbol (′) designates symmetry-equivalent atoms).

Results and Discussion

The quaternary polysulfide $Na_8Cu_4Nb_2S_{21}$ crystallizes in the orthorhombic space group $P2_12_12$ with $Z = 4$. The two crystallographically independent Cu centers are in a tetrahedral environment of four S atoms. Alternating $Cu(1)S_4$ and $Cu(2)S_4$ tetrahedra are connected by common corners leading to the formation of single chains running parallel to the *a* axis. One bridging atom in this chain is a S^{2-} anion (S2), and the other bridge is realized by the terminal atom of a S_5^{2-} polysulfide anion (S7−S11). These single chains are connected into double chains by the two terminal S atoms of a S_3^{2-} anion (S5−S6−S5′). Hence, every CuS_4 tetrahedron is joined to three other CuS_4 tetrahedra, two of the same chain and one of the neighboring chain (see Figure 1A). This connection of the CuS_4 tetrahedra leads to the formation of different voids, of which some are occupied by Nb atoms in an ordered way, and the Nb centers are tetrahedrally coordinated by four S atoms. The CuS_4 and NbS_4 tetrahedra share common edges (Figure 1B).

A view onto the double chains leads to an alternative description of the anionic part of the structure. Two six-membered Cu_2S_4 rings (Cu1−S7−Cu2−S5−S6−S5′) each in a boat conformation are connected via the common S_3^{2-} anion, thus forming a condensed metallabicycle (Figure 1A), which can be derived from bicyclo[3.3.1]nonane. Each Cu(1) and Cu(2) cation of the bicyclic ring system is joined via S^{2-} anions to the copper cations of the neighboring bicycle forming an eight-membered Cu_4S_4 ring in a crown conformation built up of alternating copper cations and S^{2-} anions. These rings show a slightly ellipsoidal shape; their dimensions are 6.3 Å × 4.4 Å (Figure 1C). The connection of the different ring systems leads to a fascinating infinite polycyclic ring system of alternating bicyclic and monocyclic rings. The $Cu(1)S_4$ and $Cu(2)S_4$ tetrahedra of neighboring rings are connected via common corners share common edges with the NbS_4 tetrahedra. Again a bicyclic ring system is formed which can be derived from bicyclo[2.2.0]hexane (Figure 1C). These bicyclic rings are built up of one niobium, two copper, and three sulfur atoms in a "butterfly"-like conformation.

The S_5^{2-} and S_3^{2-} polyanions found in the title compound behave in a rather unusual manner. One terminal atom of the S_5^{2-} unit connects two Cu cations, a bonding mode observed in $[Ag(S_5)](Me_4N)$[10] and in $[enH_2][Cu(S_5)]_2\cdot 4H_2O$.[11] The average S−S distance within the S_5^{2-} polyanion is 2.071 Å with a bonding pattern "long−short−medium−medium" (see Table 2). Depending on the actual bonding mode, other sequences were reported.[10−13]

For S_5^{2-} anions several bridging modes were reported. In $KAuS_5$ the two terminal S atoms connect two Au centers leading to the formation of 1D chains.[14] In $[Me_4N]_3[MoS_4Cu_3(S_5)_2]$ the two S_5^{2-} anions bridge across a pair of Cu atoms to form a S_5Cu_2S metallacycle.[12] A bidentate behavior was reported for $(PPh_4)_2[Te(S_5)_2]$.[13] In $[Ag(S_5)](Me_4N)$ one terminal S bridges two Ag(I) ions, while the other end is bonded to a third silver atom. A third type of bonding is realized by a β-S atom of the S_5^{2-} chain.[10] This mode is also found in $[enH_2][Cu(S_5)]_2\cdot 4H_2O$.[11]

The angles around the S7 atom bonded to the two Cu centers are between 98.8° and 110.5°, clearly demonstrating the strong distortion from tetrahedral geometry, while angles around the other S atoms of the S_5 chain are in normal range (103.1−107.7°). The two torsion angles in the S_5^{2-} unit amount to 89.33(7)° and −81.05(8)° and are comparable to those in α-Na_2S_5 (2 × 88.6°).[15]

Unusual bonding properties are observed for the S_3^{2-} anion. The two terminal S atoms connect the two neighboring CuS_4 tetrahedron chains. Due to the bonding requirements, the angles around the S5 atom are strongly distorted, ranging from 127.3° for Cu(2)−S(5)−Cu(1) to 109.1° for S(6)−S(5)−Cu(2).

The Cu(1)−S distances scatter between 2.288 and 2.356 Å (average, 2.330 Å), and for Cu(2)−S the bond lengths are between 2.286 and 2.382 Å (average, 2.331 Å).

The distortion of the CuS_4 tetrahedra is evidenced by the S−Cu−S angles, which are between 102.37(3)° and 117.22(4)° for Cu(1) and between 102.79(3)° and 115.54(4)° for Cu(2). The S−Nb−S angles show a less strong deviation from the ideal value (106.94(5)−112.65(3)°). The Nb−S distances range from 2.275 to 2.312 Å (average, 2.289 Å). The connection of the CuS_4 and NbS_4 tetrahedra via common edges results in short Nb−Cu distances of 2.7677(7) and 2.7842(7) Å. Using the tabulated radii for Cu(I) and Nb(V) in a tetrahedral environment, the distances are too large for appreciable interactions.

The five crystallographically independent Na cations separating the double chains are all in an irregular environment with

---

(10) Banda, R. M. H.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *Polyhedron* **1989**, *8*, 2379.

(11) Kiel, G.; Gattow, G.; Dingeldein, T. *Z. Anorg. Allg. Chem.* **1991**, *596*, 111.

(12) Guo, G.-C.; Kwok, R. W. M., Mak, T. C. W. *Inorg. Chem.* **1997**, *36*, 2475.

(13) Bubenheim, W.; Frenzen, G.; Müller, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1046.

(14) Park, Y., Kanatzidis, M. G. *J. Alloys. Compd.* **1997**, *257*, 137.

(15) Böttcher, P.; Keller, R. *Z. Naturforsch.* **1984**, *39b*, 577.

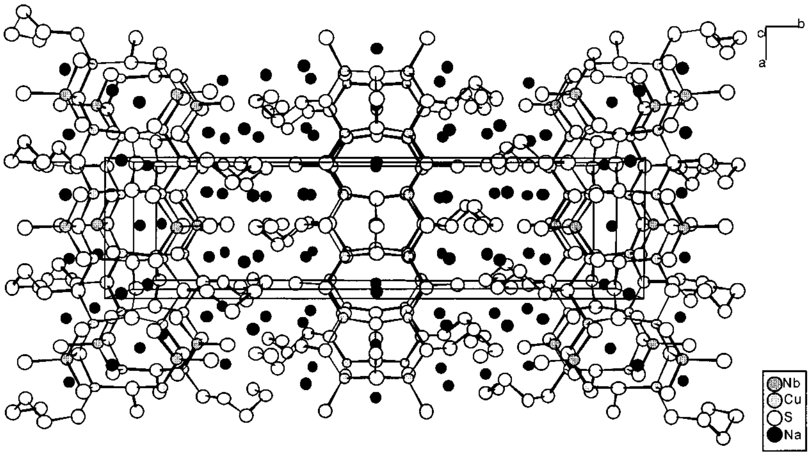

Figure 2. Crystal structure of $Na_8Cu_4Nb_2S_{21}$ viewed along [001].

coordination numbers CN = 5 for Na(1) (Na(1)−S average, 2.894 Å), CN = 7 for Na(2), Na(3), and Na(4) (Na(2)−S average, 3.019 Å; Na(3)−S average, 3.058 Å; Na(4)−S average, 2.961 Å), and CN = 6 for Na(5) (Na(5)−S average, 2.924 Å), using a cutoff of 3.2 Å. The average Na−S distances correspond well to the sum of their ionic radii ($r(Na^+)$ 1.24 Å + $r(S^{2-})$ 1.84 Å = 3.08 Å) and are comparable to those in other sodium compounds.[16−20] Interesting features of the different environments are found for Na(1) and Na(2). The Na(1) cation is "chelated" by the S_5^{2-} polysulfide anion, forming a six-membered NaS_5 ring. The Na(2) cation is bidentate coordinated to the terminal S atoms of the S_3^{2-} anion, yielding a four-membered NaS_3 ring. The arrangement of the anionic chains and the Na^+ cations is displayed in Figure 2.

There are two short interchain nonbonding S−S contacts of 3.261 and 3.374 Å, both being significantly shorter than the sum of the van der Waals radii. The latter S···S weak interaction (S(9)−S(10′)) leads to 2D corrugated sheets in the 001 plane. The former contact (S(11)−S(8″)) results in the formation of a 3D network. The origin of these weak interactions is not clear but is probably associated with the well-known catenation capacity of sulfur. As pointed out in the Introduction, the crystal structure of the title compound is completely different from those known for quaternary group(V) group(I) chalcogenides. Up to now only the compounds with the $A_2M^IM^VQ_4$, $AM^I_2M^VQ_4$, or sulvanite-type structure as well as the two quaternary compounds $K_3CuNb_2Se_{12}$ and $K_3Cu_3Nb_2S_8$ are known.[21,22] The structure of $K_3CuNb_2Se_{12}$ consists of infinite Cu/Nb/Se chains separated by K^+ cations. These chains can be formulated as ${}^{1}_{\infty}[CuNb_2(Se)_3(Se_2)_3(Se_3)^{3-}]$ (cutoff of 2.55 Å for Se−Se bonds). $K_3Cu_3Nb_2S_8$ is composed of one-dimensional triple chains isolated by K^+ cations. The chains consist of successive corner-sharing CuS_4 tetrahedra and edge-sharing between CuS_4 and NbS_4 tetrahedra. The sulfides are present as S^{2-} anions. Hence, the title compound which can be formulated as $Na_8Cu_4Nb_2S_8(S_3)(S_5)_2$ represents the first example for a quaternary copper niobium polychalcogenide with a S_5^{2-} and a S_3^{2-} anion, both exhibiting interesting and unusual bonding modes. The occurrence of the S_5^{2-} unit in the title compound may be due to the special conditions used in the molten-flux synthesis. Due to the relatively low reaction temperature, larger polychalcogenide fragments are retained and are stable under these conditions. When the low-temperature approach was applied, the S_5^{2-} anion was also found in compounds like $K_6Nb_4S_{25}$ and $(t\text{-}BuC_5H_4)_4Nb_2S_9$.[23,24] It can be assumed that many more compounds with novel and interesting structures are accessible using this synthetic route.

Acknowledgment. This work has been supported by the state of Schleswig-Holstein and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and full bond lengths and angles including details of the structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9900206

---

(16) Mansuetto, M. F.; Keane, P. M.; Ibers, J. A. *J. Solid State Chem.* **1993**, *105*, 580.

(17) Klepp, K. O.; Sing, M.; Boller, H. *J. Alloys Compd.* **1993**, *198*, 25.

(18) Klepp, K. O.; Sing, M.; Boller, H. *J. Alloys Compd.* **1992**, *184*, 265.

(19) Bensch, W.; Näther, C.; Dürichen, P. *Angew. Chem.* **1998**, *110*, 140.

(20) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(21) Lu, Y.-J.; Ibers, J. A. *J. Solid State Chem.* **1992**, *98*, 312.

(22) Lu, Y.-J.; Ibers, J. A. *Inorg. Chem.* **1990**, *30*, 3317.

(23) Bensch, W.; Dürichen, P. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1233.

(24) Brunner, H.; Klement, U.; Wachter, J.; Tsunoda, M; Leblanc, J.-C.; Moise, C. *Inorg. Chem.* **1990**, *29*, 585.