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Synthesis of the Quaternary One-Dimensional Triple-Chain Materials $K_3Cu_3M_2Q_8$ (M = Nb, Ta; Q = S, Se): The Structure of $K_3Cu_3Nb_2S_8$

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The one-dimensional triple-chain materials $K_3Cu_3Nb_2S_8$, $K_3Cu_3Nb_2Se_8$, $K_3Cu_3Ta_2Se_8$, and $K_3Cu_3Ta_2S_8$ have been prepared by the reactive flux method in which Cu and Nb or Ta were reacted with K_2Q_5/Q (Q = S, Se) at 850°C. $K_3Cu_3Nb_2S_8$ has been characterized by single-crystal X-ray diffraction techniques. It crystallizes with four formula units in space group C^6_{2h}–$C2/c$ of the monoclinic system in a cell of dimensions $a = 23.446(3)$, $b = 5.545(3)$, $c = 14.204(3)$ Å, $\beta = 120.87(3)°$ at −120°C. It is composed of one-dimensional $^1_\infty[Cu_3Nb_2S_8^{3-}]$ chains isolated from one another by K^- cations. These chains are triple in nature, and consist of successive corner-sharing CuS_4–CuS_4 tetrahedra and edge-sharing CuS_4–NbS_4 tetrahedra. This edge-sharing results in Nb–Cu distances of 2.772(2)–2.781(1) Å. $K_3Cu_3Nb_2Se_8$ with cell dimensions $a = 23.453(4)$, $b = 5.592(12)$, $c = 14.223(3)$ Å, $\beta = 120.7(3)°$ at −120°C ($\lambda(CuK\alpha_1) = 1.54056$ Å); $K_3Cu_3Ta_2Se_8$ with cell dimensions $a = 23.493(9)$, $b = 5.538(7)$, $c = 14.204(12)$ Å, $\beta = 120.5(9)°$ at −165°C ($\lambda(MoK\alpha_1) = 0.70930$ Å); and $K_3Cu_3Ta_2S_8$ with cell dimensions $a = 23.450(6)$, $b = 5.541(3)$, $c = 14.110(6)$ Å, $\beta = 120.47(3)°$ at −165°C ($\lambda(MoK\alpha_1) = 0.70930$ Å) appear to be isostructural with $K_3Cu_3Nb_2S_8$. $K_3Cu_3Nb_2S_8$ has a resistivity greater than 10^5 mΩ cm at room temperature.

Introduction

Many new quaternary/K/Cu/Nb or Ta/S or Se/solid-state compounds, most with unusual structures, have been synthesized by use of the reactive flux method (*1*). These include the one-dimensional chain compounds K_2CuMSe_4 (M = Nb (*2*), Ta (*3*)) and $K_3CuNb_2Se_{12}$ (*2*). These structures exhibit one-dimensional mixed-metal chains formed by successive edge-sharing of tetrahedra (K_2CuMSe_4) or by alternation of face-sharing and edge-sharing of mixed polyhedra and tetrahedra ($K_3CuNb_2Se_{12}$). With the addition of $CuSe_4$ tetrahedra in a corner-sharing arrangement, the two-dimensional layer compounds KCu_2MSe_4 (M = Nb (*4*), Ta (*3*)) and KCu_2NbS_4 (*4*) are formed. The conceptual addition of corner-sharing CuQ_4 (Q = S, Se) tetrahedra to the $^1_\infty[CuMQ_4^{2-}]$ structure would produce a one-dimensional triple-chain structure. Here we report the synthesis and characterization of the $K_3Cu_3M_2Q_8$ series, a series that exhibits this structure.

Experimental

Synthesis. $K_3Cu_3Nb_2S_8$ was prepared from a stoichiometric reaction of K_2S_5 (142.8 mg, 0.6 mmol) with powders of elemental Nb (74 mg, 0.8 mmol), Cu (76 mg, 1.2 mmol), and S (6.4 mg, 0.2 mmol) (Nb, 99.8%, AESAR; Cu, 99.5%, Alfa; K, 99%,

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AESAR; S, 100.0%, Mallinckrodt). K_2S_5 was prepared by the stoichiometric reaction of elemental K and S in liquid ammonia under an atmosphere of Ar. In a glove box the starting materials were loaded into a quartz tube that was subsequently evacuated to 10^{-4} Torr and sealed. It was then placed in a furnace that was heated to 500°C, held there for 24 hr, then ramped to 850°C, kept there for four days, and then cooled to 25°C at a rate of 4°C/hr. Yellow, plate-like single crystals extracted from the surface of the melt were suitable for X-ray diffraction analysis. Chemical analysis of three crystals selected at random was performed with the electron microprobe of an EDAX-equipped Hitachi S-570 LB scanning electron microscope; the composition found was K : Cu : Nb : S = 1.5 : 1.5 : 1 : 4.2, in good agreement with that of 3 : 3 : 2 : 8 established from the X-ray structure determination.

$K_3Cu_3Nb_2Se_8$ was synthesized from a similar reaction of K_2Se_5 (284 mg, 0.6 mmol) with elemental Nb (74 mg, 0.8 mmol), Cu (76 mg, 1.2 mmol), and Se (16 mg, 0.2 mmol). K_2Se_5 was prepared by the stoichiometric reaction of K with Se in liquid ammonia. The heating regime was the same as above, but the cooling rate was 2°C/hr. Deep yellow and yellow-orange crystals extracted from the surface of the melt were suitable for X-ray diffraction analysis. Chemical analysis by EDAX gave K : Cu : Nb : Se = 1.8 : 1.6 : 1 : 4.6.

$K_3Cu_3Ta_2S_8$ was synthesized from a reaction of K_2S_5 (100 mg, 0.42 mmol) with elemental Ta (101 mg, 0.56 mmol), Cu (53 mg, 0.84 mmol), and S (4.5 mg, 0.14 mmol) in the same heating regime used for $K_3Cu_3Nb_2Se_8$. Bright yellow and orange plate-like crystals that formed in the tube were suitable for X-ray analysis. Chemical analysis by EDAX gave K : Cu : Ta : S = 1.4 : 1.5 : 1 : 4.1.

$K_3Cu_3Ta_2Se_8$ was synthesized from a reaction of K_2Se_5 (284 mg, 0.6 mmol) with elemental Ta (145 mg, 0.8 mmol), Cu (76 mg, 1.2 mmol), and Se (16 mg, 0.2 mmol). In the same heating regime used for $K_3Cu_3Nb_2Se_8$, yellow-orange plate-like crystals formed in the tube that were suitable for X-ray analysis. Chemical analysis by EDAX gave K : Cu : Ta : Se = 1.6 : 1.7 : 1 : 4.4.

X-ray crystallography. Weissenberg photography indicated that $K_3Cu_3Nb_2S_8$ belongs to the monoclinic system and displays systematic absences consistent with the space groups C_s^4–Cc, and C_{2h}^6–$C2/c$. The unit cell dimensions, a = 23.446(3), b = 5.545(3), c = 14.204(3) Å, β = 120.87(3)° at −120°C, were obtained by a least-squares analysis of the setting angles of 25 reflections automatically centered in the range of $43° \leq 2\theta$ ($\mathrm{Cu}K\alpha_1$) $\leq 46°$ on an Enraf–Nonius CAD4 diffractometer. $K_3Cu_3Nb_2Se_8$ with cell dimensions a = 23.453(4), b = 5.592(12), c = 14.223(3) Å, β = 120.7(3)° at −120°C ($\lambda(\mathrm{Cu}K\alpha_1)$ = 1.54056 Å); $K_3Cu_3Ta_2Se_8$ with cell dimensions a = 23.493(9), b = 5.538(7), c = 14.204(12) Å, β = 120.5(9)° at −165°C ($\lambda(\mathrm{Mo}K\alpha_1)$ = 0.70930 Å); and $K_3Cu_3Ta_2S_8$ with cell dimensions a = 23.450(6), b = 5.541(3), c = 14.110(6) Å, β = 120.47(3)° at −165°C ($\lambda(\mathrm{Mo}K\alpha_1)$ = 0.70930 Å) appear to be isostructural. Intensity data for $K_3Cu_3Nb_2S_8$ were collected by methods standard in this laboratory (*5*) with use of the θ–2θ technique in the range $2° \leq \theta(\mathrm{Cu}K\alpha_1) \leq 75°$. Six standard reflections, chosen from diverse regions of reciprocal space and monitored every 3 hr during data collection, showed no significant change. In the solution and refinement of the structure all calculations were carried out on a Stellar GS2000 computer. The centrosymmetric space group C_{2h}^6–$C2/c$ was chosen, since averaging hkl and $h\bar{k}l$ reflections, after correction for absorption, led to a satisfactory residual of 0.069. The structure was solved by direct methods (*6*). An analytical absorption correction was applied (*7*). The structure was refined on F_o^2 by full-matrix least-squares methods. The final anisotropic re-

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR $K_3Cu_3Nb_2S_8$

Formula	$K_3Cu_3Nb_2S_8$
Formula weight	750.27
Space group	C^6_{2h}–$C2/c$
a, Å	23.446(3)
b, Å	5.545(3)
c, Å	14.204(3)
β, deg.	120.87(3)
Vol. Å^3	1583
Z	4
Temperature, °C	-120^a
ρ(calc), g cm^{-3} (-120°C)	3.147
λ(Cu$K\alpha_1$), Å	1.54056
μ, cm^{-1}	330
Crystal shape	Plate bounded by $\{20\bar{1}\}$, $\{010\}$, $\{101\}$
Transmission factors	0.070–0.279
Crystal vol., mm^3	1.3×10^{-3}
Take-off angle, deg.	3.5
Scan type	θ–2θ
Scan range, θ deg.	± 1.0
Data collected	$2 \leq \theta \leq 75°$; $\pm h$, $\pm k$, l
p factor	0.04
No. of data collected	3372
No. of unique data	1727
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1403
R [on F for $F_o^2 > 3\sigma(F_o^2)$]	0.069
$R(F_o^2)$	0.152
$R_w(F_o^2)$	0.159
Error in observation of unit weight (e^2)	2.54

[a] The low temperature system for the Nonius CAD4 diffractometer is from a design by Professor J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. de Vic, 31320 Castanet-Tolosan, France.

finement of 1728 observations and 76 variables converged to values of $R(F_o^2)$ of 0.152 and $R_w(F_o^2)$ of 0.159. The conventional R index $R(F)$ for those 1403 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.069. Some crystallographic details are given in Table I. The final positional and equivalent isotropic thermal parameters are given in Table II. Anisotropic thermal parameters and structure amplitudes are given in Table IS.[1]

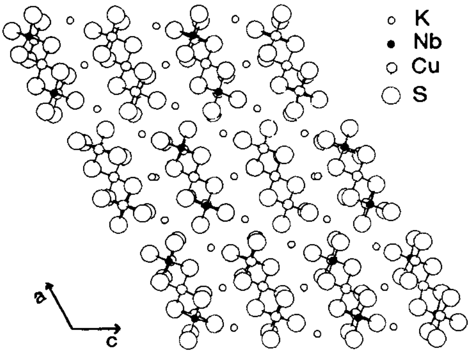

FIG. 1. Projection of the $K_3Cu_3Nb_2S_8$ structure down [010].

Results and Discussion

The crystal structure of $K_3Cu_3Nb_2S_8$ consists of well-separated cations and anions (Fig. 1). The anion is the new one-dimensional chain $^1_\infty[Cu_3Nb_2S_8^{3-}]$. Figure 2 shows this anionic chain with the labeling scheme. This triple-metal chain, which runs along [010], comprises successive CuS_4–NbS_4 edge-sharing tetrahedra and CuS_4–CuS_4 corner-sharing tetrahedra. It may be thought of as the addition of CuQ_4–CuQ_4 corner-sharing tetrahedra to the successive CuQ_4–NbQ_4 chains in $K_2CuNbSe_4$ (*2*). In the present structure there are two crystallographically distinct Cu atoms. The NbS_4 and Cu(2)S_4 tetrahedra edge share along b, while

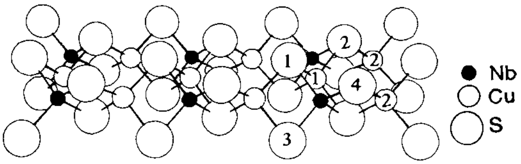

FIG. 2. The one-dimensional triple chain $^1_\infty[Cu_3Nb_2S_8^{3-}]$ in $K_3Cu_3Nb_2S_8$.

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[1] See NAPS document No. 04922 for 10 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling. $1.75 for postage of any microfiche orders.

TABLE II

POSITIONAL AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR $K_3Cu_3Nb_2S_8$

Atom	Wyckoff Notation	x	y	z	B_{eq}[a]
Nb(1)	8f	0.127063(29)	0.28240(13)	0.280696(47)	0.73(2)
Cu(1)	4e	0	0.27823(37)	$\frac{1}{4}$	1.13(5)
Cu(2)	8f	0.376968(65)	0.28201(26)	0.21811(10)	1.14(4)
K(1)	8f	0.30991(10)	0.03699(42)	0.40645(16)	1.76(6)
K(2)	4a	0	0	0	1.43(8)
S(1)	8f	0.092236(96)	0.04895(40)	0.37627(15)	0.99(6)
S(2)	8f	0.038720(98)	0.51802(39)	0.15839(16)	1.01(6)
S(3)	8f	0.15757(10)	0.03092(40)	0.18658(16)	1.11(6)
S(4)	8f	0.287670(99)	0.02891(40)	0.10776(16)	1.11(6)

[a] $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

the NbS_4 and $Cu(1)S_4$ tetrahedra edge share along a (Fig. 3). This sharing alternates Nb and Cu atoms, as was found in $K_2CuNbSe_4$ (*2*). As a result of this edge-sharing, the $Cu(1)S_4$ and $Cu(2)S_4$ tetrahedra corner-share. The Cu(1), Cu(2), S(1), and S(2) atoms thus form eight-member rings, with Cu(1)–S–Cu(2) angles ranging from 109.73(8)° to 110.76(9)°. Figure 3b shows a polyhedral representation of the anionic chains.

Table III lists selected distances and angles in $K_3Cu_3Nb_2S_8$, while Table IV compares metrical data among related structures. The Cu–S distances in the present structure range narrowly from 2.333(2) to 2.360(2) Å, comparing well with those in α- and β-$[CuS_4]_n^{n-}$ (Cu–S, 2.298(4)–2.432(4) Å (*8*)) and that in Cu_3VS_4 (2.285(14) Å (*9*)). The Nb–Cu distances of 2.772(2), 2.777(2), and 2.781(1) Å are shorter than the corresponding distances in $K_2CuNbSe_4$ (2.873(1) Å (*2*)) and in KCu_2NbSe_4 (2.831(1)–2.833(4) Å (*4*)), because of the substitution of S for Se. The Nb–S distances range from 2.264(2) to 2.307(2) Å and are comparable to those in K_3NbS_4 (2.241(8)–2.257(8) Å (*10*)). In transition-metal sulfides or selenides Nb atoms are most often found in trigonal prismatic coordination, as in NbS_2 (*11*), most binary chalcogenides (*12*), the incommensurate double-layer structures $(MS)_nTS_2$, n = 1.08–1.19 (M = Sn, Pb, Bi, rare earth elements; T = Nb, Ta) (*13–15*), and $Nb_2Pd_3Se_8$ (*16*), or in polyhedral coordination, as in $Nb_4Se_{22}^{6-}$ (*17*) and $K_3CuNb_2Se_{12}$ (*2*). While Nb is found in tetrahedral coordination in the MQ_4^{3-} anions (M = Nb, Ta; Q = S, Se) (*10*, *18*) as well as in $Ba_6(NbS_4)(NbS_3O)_3$ (*19*), tetrahedral coordination of Nb seems unusually prevalent in the K/Cu/Nb/Q systems (*2–4*, *20*). The two crystallographi-

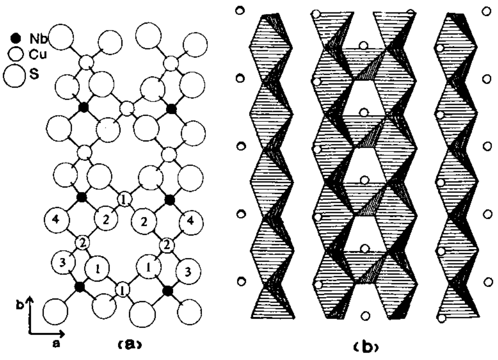

FIG. 3. (a) View of the anionic chain $^1_\infty[Cu_3Nb_2S_8^{3-}]$ down [001]. (b) Polyhedral representation of the structure of $K_3Cu_3Nb_2S_8$ down [001].

TABLE III

Selected Distances (Å) and Angles (deg) for $K_3Cu_3Nb_2S_8$

Nb–Cu(1)	2.781(1)	K(1)–S(1)	3.577(3)
Nb–Cu(2)	2.777(2)	K(1)–S(3)′	3.296(3)
Nb–Cu(2)′	2.772(2)	K(1)–S(3)	3.326(3)
Cu(1)–Cu(2)	3.871(2)	K(1)–S(3)	3.352(3)
Cu(1)–Cu(2)′	3.841(2)	K(1)–S(4)	3.499(3)
Nb–S(1)	2.307(2)	K(1)–S(4)	3.569(3)
Nb–S(2)	2.307(2)	K(1)–S(4)	3.180(3)
Nb–S(3)	2.286(2)	K(2)–2S(1)	3.426(2)
Nb–S(4)	2.264(2)	K(2)–2S(2)	3.306(2)
Cu(1)–2S(1)	2.351(2)	K(2)–2S(2)	3.470(2)
Cu(1)–2S(2)	2.345(2)	K(2)–2S(3)	3.264(2)
Cu(2)–S(1)	2.346(2)	S(1)–Nb–S(2)	107.98(7)
Cu(2)–S(2)	2.360(2)	S(3)–Nb–S(1)	108.26(8)
Cu(2)–S(3)	2.349(2)	S(3)–Nb–S(2)	109.55(7)
Cu(2)–S(4)	2.333(2)	S(4)–Nb–S(1)	112.27(7)
S(1)···S(1)	3.956(4)	S(4)–Nb–S(2)	108.32(8)
S(1)···S(2)	3.732(3)	S(4)–Nb–S(3)	110.40(8)
S(1)···S(2)	3.858(3)	S(1)–Cu(1)–S(1)	114.54(13)
S(1)···S(2)	3.979(3)	2S(1)–Cu(1)–S(2)	105.27(7)
S(1)···S(3)	3.722(3)	2S(1)–Cu(1)–S(2)	110.47(7)
S(1)···S(3)	3.878(3)	S(2)–Cu(1)–S(2)	110.91(13)
S(1)···S(4)	3.796(3)	S(1)–Cu(2)–S(2)	115.47(9)
S(1)···S(4)	3.955(3)	S(1)–Cu(2)–S(3)	104.89(9)
S(2)···S(2)	3.862(4)	S(3)–Cu(2)–S(2)	109.94(9)
S(2)···S(2)	3.899(4)	S(4)–Cu(2)–S(1)	115.40(9)
S(2)···S(3)	3.752(3)	S(4)–Cu(2)–S(2)	104.30(9)
S(2)···S(3)	3.856(3)	S(4)–Cu(2)–S(3)	106.54(9)
S(2)···S(4)	3.705(3)	Cu(2)–Nb–Cu(1)	88.40(5)
S(3)···S(4)	3.736(3)	Cu(2)–S(1)–Cu(1)	109.73(8)
S(3)···S(4)	3.750(3)	Cu(2)–S(2)–Cu(1)	110.76(9)
S(3)···S(4)	3.752(3)		
S(4)···S(4)	3.599(4)		

cally distinct Cu atoms show similar distortions from tetrahedral symmetry with S–Cu(1)–S angles ranging from 105.27(7)° to 114.54(13)° and S–Cu(2)–S angles ranging from 104.30(9)° to 115.47(9)°, while the NbS_4 tetrahedra are somewhat more regular (⟨S–Nb–S = 107.98(7)°–112.27(7)°).

There are four crystallographically distinct S atoms. Atoms S(3) and S(4) are connected to the Nb and Cu(2) atoms; atoms S(1) and S(2) are connected to all three metals. There are two crystallographically distinct K atoms. If we choose 4.0 Å as an upper limit for K–S interactions then atom K(1) is seven coordinate while atom K(2) is eight coordinate.

Since there are no close S···S interactions formal oxidation states of K(I), Cu(I), Nb(V), and S(−II) may be assigned. This assignment is consistent with the fact that the resistivity of $K_3Cu_3Nb_2S_8$ is greater than 10^5 mΩ cm at room temperature.

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TABLE IV

COMPARATIVE DISTANCES (Å) IN RELATED MQ_4 TETRAHEDRA (M = Cu, Nb; Q = S, Se)

Compound	Cu–Q	Nb–Q	Nb–Cu	Ref.
α- and β-$KCuS_4$	2.298(4)–2.432(4)			(*8*)
Cu_3VS_4	2.285(14)			(*9*)
K_3NbS_4		2.241(8)–2.257(8)		(*10*)
$Ba_6(NbS_4)(NbS_3O)_3$		2.238(5)–2.284(5)		(*19*)
KCu_3S_2	2.24–2.86			(*21*)
KCu_4S_3	2.312(2)–2.451(1)			(*22*)
$[NH_4][CuMoS_4]$	2.283(4)			(*23*)
CuAsS	2.30(1)–2.34(1)			(*24*)
$TlCu_7Se_4$	2.377(5)–2.658(3)			(*25*)
$TlCu_5Se_3$	2.389(2)–2.629(3)			(*26*)
$K_2CuNbSe_4$	2.457(1)	2.413(1)	2.873(1)	(*2*)
KCu_2NbSe_4	2.427(2)–2.440(4)	2.392(3)–2.452(3)	2.831(1)–2.833(4)	(*4*)
$K_3Cu_3Nb_2S_8$	2.333(2)–2.360(2)	2.264(2)–2.307(2)	2.772(2)–2.781(1)	This work

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