because in the transition state the dominant 2e-3c bond of the Cu-S-Cu unit and Cu-C-Cu unit remains intact, while only the contribution of the π-bonding to the Cu-S bond is lost.

Conclusion

The use of the novel monoanionic, bidentate amine-thiolate ligands $SC_6H_3(CH(R')NMe_2)$-2-R″-3 (R′ = H, R″ = H, Cl; R′ = Me, R″ = H) resulted in the synthesis and characterization of trinuclear copper arenethiolates $[CuSC_6H_3(CH(R')NMe_2)$-2-R″-3$]_3$. These copper arenethiolates are soluble, and this has allowed a detailed study of their fluxional behavior in solution. The structural features of these copper arenethiolates indicate that in copper thiolates with acute Cu-S-Cu angles the likely bonding description of the Cu_2S unit is an sp^2-hybridized sulfur atom bridging two copper atoms in an electron-deficient three-center two-electron interaction. In copper thiolates this type of bonding allows the organic group and the sulfur lone pair to exchange positions and thus provides "sulfur inversion" with a low-energy barrier.

Acknowledgment. This work was supported in part (A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Tables S1-S6, listing fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal parameters, ^1H NMR spectra at 223 and 353 K of **4a-d** (Figure S1a-d), and a COSY 2D spectrum of **4b** (Figure S2) (8 pages); a listing of observed and calculated structure factor amplitudes for **4b** (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the New Quaternary One-Dimensional Chain Materials $K_2CuNbSe_4$ and $K_3CuNb_2Se_{12}$

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Received November 9, 1990

The one-dimensional chain materials $K_2CuNbSe_4$ and $K_3CuNb_2Se_{12}$ have been synthesized at 800 and 870 °C, respectively, through the use of molten alkali-metal selenides as reactive fluxes. $K_2CuNbSe_4$ crystallizes in space group D_{2h}^{24}-*Fddd* of the orthorhombic system with eight formula units in a cell of dimensions $a = 5.745$ (1), $b = 13.444$ (1), and $c = 23.907$ (3) Å. The structure consists of infinite linear chains separated from the K^+ ions. These chains, which are along the c axis, consist of edge sharing of alternating $NbSe_4$ and $CuSe_4$ tetrahedra. The structural motif thus represents an elaboration of that in $KFeS_2$. There are no short Se⋯Se interactions and so formal oxidation states of K(I), Cu(I), Nb(V), and Se(−II) are assigned. The compound is a poor conductor, having a resistance greater than 10 MΩ cm at room temperature. $K_3CuNb_2Se_{12}$ crystallizes in space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four formula units in a cell with dimensions $a = 9.510$ (6), $b = 13.390$ (9), and $c = 15.334$ (10) Å and $\beta = 96.09$ (4)°. The structure consists of an infinite Cu/Nb/Se chain separated from K^+ cations. The infinite chain can be formulated as $^1_\infty[CuNb_2(Se)_2(Se_2)_3(Se_4)^{3-}]$ or alternatively as $^1_\infty[CuNb_2(Se)_3(Se_2)_3(Se_3)^{3-}]$ depending upon the choice of a cutoff for the length of an Se-Se bond. In the former instance the chain contains Cu(I) and Nb(IV) centers while in the latter instance it contains Cu(I) and Nb(V) centers. The two crystallographically distinct Nb atoms are seven-coordinate and the Cu atom is tetrahedral.

Introduction

Molten salts and high-temperature solvents have been extensively used as fluxes in the temperature range 300-1800 °C to promote crystal growth.[1] The majority of the compounds crystallized from these high-temperature solvents have been elements, binaries, or ternary oxides; however, binary and ternary chalcogenides have been crystallized from molten salts of the type A_2Q_n (A = alkali metal, Q = S, Se).[2,3] In general, these A_2Q_n fluxes are unreactive, and A is not incorporated into the final product. The use of a *reactive* flux does not appear to be a standard preparative method[4] for the synthesis of new compounds. But, as we first described for the K_2S/S system,[5] the use of a reactive flux takes advantage of low-melting A/Q systems (A = alkali metal; Q = S, Se, Te) and uses the reactive polychalcogenides A_2Q_n not only as classic fluxes but also as reactants so that the alkali metal and chalcogen and often the polychalcogen are incorporated into the final product. This reactive flux method appears to be a general solid-state route to preparing new compounds containing polychalcogenide species.[5]

Until recently the new compounds synthesized with this preparative method were ternary sulfides and selenides, often with unusual structural features. These typically include chalcogen-chalcogen bonding, as in $K_4Ti_3S_{14}$[5] (S_2^{2-}), $Na_2Ti_2Se_8$[6] (Se_2^{2-}), $KCuS_4$[7] (S_4^{2-}), and $KAuSe_5$[8] (Se_5^{2-}), one-dimensional chains,[5-9] three-dimensional structures,[9] and molecular species.[10] While many of these reactions have been carried out at low temperatures (200-500 °C), some have been carried out at temperatures as high as 900 °C. Compounds containing polychalcogenide ligands have been made over the entire temperature range, although they may be more prevalent among the low-temperature syntheses.

In an attempt to delineate the applicability of the reactive flux method, we continue to investigate a number of potential new systems. In so doing, we have recently demonstrated that the

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Table I. Crystal Data and Experimental Details

formula	$K_2CuNbSe_4$	$K_3CuNb_2Se_{12}$
fw	550.5	1314
space group	D_{2h}^{24}-*Fddd*	C_{2h}^{5}-$P2_1/n$
a, Å	5.745 (1)	9.510 (6)
b, Å	13.444 (1)	13.390 (9)
c, Å	23.907 (3)	15.334 (10)
β, deg	90	96.09 (4)
V, Å^3	1847	1942
Z	8	4
t, °C	−120[a]	−120[a]
d(calcd), g cm^{-3} (−120 °C)	3.959	4.494
λ(Cu Kα_1), Å	1.540 56	1.540 56
μ, cm^{-1}	395	434
transm factors[b]	0.028–0.274	0.060–0.246
$R(F^2)$	0.143	0.132
$R_w(F^2)$	0.206	0.183
R [on F for $F_o^2 > 3\sigma(F_o^2)$]	0.080	0.075

[a] The low temperature system is based on a design by J. J. Bonnet and S. Askenazy. [b] The analytical method was used for the absorption correction, ref 14.

method can be applied readily to the synthesis of materials containing polytellurides.[11] Here we show that it may be used in the synthesis of new *quaternary* materials. We chose to react Nb and Cu metals with a K/Se flux. The choice of Nb was dictated by our interest in the group V metals. Cu was chosen because we have found that it has a propensity to assume an oxidation state of I and hence act as a pseudo alkali metal but with a very different coordination preference. We describe two new quaternaries in the K/Cu/Nb/Se system prepared in this manner. Each contains a one-dimensional mixed-metal chain.

Experimental Section

Syntheses. $K_2CuNbSe_4$ was prepared from a reaction of K_2Se_5 (99 mg, 0.21 mmol) with elemental Nb (39 mg, 0.42 mmol), Cu (27 mg, 0.42 mmol), and Se (50 mg, 0.63 mmol) powders (Nb, 99.8%, AESAR; Cu, 99.5%, ALFA; Se, 99.5%, Aldrich). K_2Se_5 was made from the stoichiometric reaction of elemental K (98%, AESAR) with Se in liquid ammonia under an atmosphere of dry, oxygen-free argon. In a drybox 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 from room temperature to 800 °C in 12 h, kept at 800 °C for 4 days, and then slowly cooled to room temperature at a rate of 4 °C/h. Red single crystals found on the surface of the melt were suitable for X-ray diffraction analysis. A chemical analysis of four crystals selected at random was performed with the electron microprobe of an EDAX-equipped Hitachi S-570 LB scanning electron microscope, and afforded the composition K:Cu:Nb:Se = 2.1:1.0:1.0:4.2, in excellent agreement with the composition $K_2CuNbSe_4$ deduced from the X-ray crystal structure determination. The yield of crystalline material approaches 50%, the other major component being KCu_2NbSe_4.[12] The two materials could be distinguished visually and separated by hand.

$K_3CuNb_2Se_{12}$ was synthesized from a reaction of K_2Se_5 (199 mg, 0.42 mmol) with elemental Nb (52 mg, 0.56 mmol), Cu (17.8 mg, 0.28 mmol), and Se (99.5 mg, 1.26 mmol). The sealed tube was heated to 870 °C for 12 h and held at 870 °C for 4 days before it was slowly cooled to room temperature at a rate of 4 °C/h. EDAX analysis of the black needlelike crystals so obtained led to the composition K:Cu:Nb:Se = 2.1:1.0:2.0:12.5, in good agreement with that of $K_3CuNb_2Se_{12}$ established from the X-ray structure determination. The yield of crystalline material is close to 100%.

Crystallography. Cell constants, orthorhombic symmetry, and the space group *Fddd* of $K_2CuNbSe_4$ were determined from a preliminary data collection on an Enraf-Nonius CAD-4 diffractometer at -120 °C. Six standard reflections measured every 2 h during the data collection showed no significant variation in intensity. The data were collected by the ω–2θ technique in the range $3° \leq \theta(\text{Cu K}\alpha_1) \leq 75°$. Some crystallographic details are given in Table I. Further details may be found in Table IS. The structure was solved by direct methods. All calculations were carried out on a Stellar GS2000 computer with the use of programs standard in this laboratory.[13] An analytical absorption correction was applied.[14] Upon correction for absorption, 2215 reflections were reduced to a set of 481 unique reflections after averaging. The structure was refined on F_o^2 by full-matrix least-squares methods, and involved 481 observations and 10 variables. Thermal motion was restricted to isotropic; we felt that there was little justification for anisotropic refinement of these low-temperature data collected on a highly absorbing crystal whose shape was somewhat difficult to define. The resultant isotropic thermal parameters do not suggest much, if any, disorder of the Nb and Cu sites, and for that reason the ordered model has been retained. The conventional R index $R(F)$ for those 300 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.080. Final positional and thermal parameters are given in Table II. Table IIS[15] presents a list of structure amplitudes.

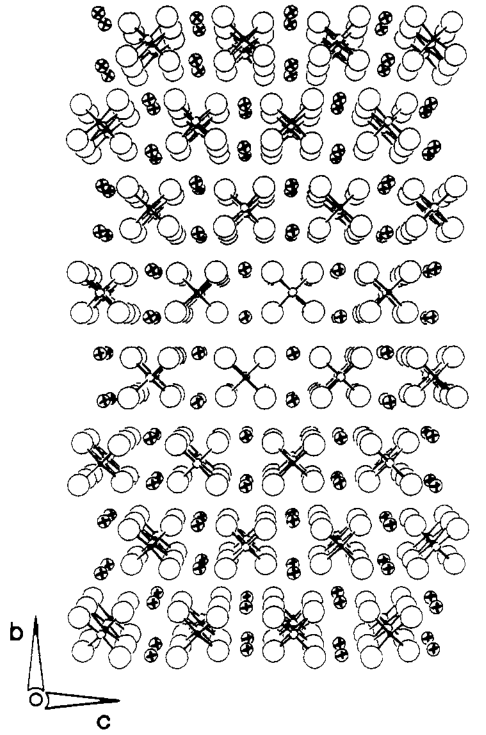

Figure 1. Projection of the structure of $K_2CuNbSe_4$ down [100]. Here and in Figure 2, Cu atoms are small filled circles, Nb atoms are small open circles, and Se atoms are large open circles. The K atoms are cross-hatched circles.

The crystal structure determination of $K_3CuNb_2Se_{12}$ proceeded in a similar manner except that the symmetry and space group were first established by precession methods and the final model involved anisotropic motion of the atoms (3925 observations, 164 variables). The value of $R(F_o)$ for those 2407 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.075. The final positional and equivalent isotropic thermal parameters are given in Table III. Anisotropic thermal parameters and structure amplitudes are given in Tables IIIS and IVS.[15] Again, the reasonableness of the thermal parameters suggests the absence of nonstoichiometry and of substitutional disorder.

Results and Discussion

$K_2CuNbSe_4$. A projection of the structure of $K_2CuNbSe_4$ down [100] is shown in Figure 1. The K^+ cations, which are eight-coordinate, are well separated from the chains of anions. Table IV presents selected distances and angles. As there are no short Se···Se interactions we can assign formal oxidation states of K(I), Se(-II), Cu(I), and Nb(V). Consistent with these formal oxidation states the compound is a poor conductor, having a resistance greater than 10 MΩ cm at room temperature. The one-dimensional linear chains are infinite and consist of the sharing of tetrahedral edges by successive MSe_4 tetrahedra (M = metal) (Figure 2). The X-ray scattering factors of Cu and Nb differ only modestly, and so the possibility of disorder between the Cu and Nb sites cannot be eliminated. The thermal parameters of Table I, as derived in the ordered model, are certainly reasonable. If there were significant mixing of Cu and Nb over the two sites,

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Table II. Final Positional and Isotropic Thermal Parameters for $K_2CuNbSe_4$

atom	Wyckoff notation	symmetry	x	y	z	B, Å^2
Nb	8b	222	$^1/_8$	$^1/_8$	$^5/_8$	1.62 (5)
Cu	8a	222	$^1/_8$	$^1/_8$	$^1/_8$	2.20 (8)
Se	32h	1	0.36840 (17)	0.72919 (10)	0.182711 (53)	2.01 (5)
K	16g	2	$^1/_8$	$^1/_8$	0.44573 (17)	2.44 (8)

Table III. Final Positional Parameters and Equivalent Isotropic Thermal Parameters for $K_3CuNb_2Se_{12}$

atom	x	y	z	B, Å^2
Nb(1)	0.16538 (19)	0.27801 (14)	0.07663 (12)	1.54 (4)
Nb(2)	−0.01476 (19)	0.22252 (14)	0.27389 (11)	1.48 (4)
Se(1)	−0.24878 (25)	0.29236 (18)	0.20069 (15)	1.87 (5)
Se(2)	0.06759 (25)	0.33975 (18)	−0.06436 (15)	1.89 (5)
Se(3)	0.02758 (25)	0.39475 (17)	0.17103 (15)	1.71 (5)
Se(4)	−0.04949 (26)	0.15837 (18)	0.10295 (15)	1.86 (5)
Se(5)	0.24306 (26)	0.18256 (18)	0.24669 (16)	1.83 (5)
Se(6)	−0.13847 (26)	0.35819 (19)	0.36177 (16)	1.89 (5)
Se(7)	0.26892 (26)	0.43395 (18)	0.16059 (15)	1.88 (5)
Se(8)	0.43881 (25)	0.27123 (19)	0.06611 (15)	1.86 (5)
Se(9)	0.16596 (29)	0.08724 (18)	0.05965 (16)	2.14 (6)
Se(10)	−0.08187 (27)	0.06580 (18)	0.33722 (16)	1.87 (5)
Se(11)	0.20424 (26)	0.28157 (20)	0.37112 (15)	1.97 (5)
Se(12)	0.00822 (28)	0.38481 (20)	0.50839 (16)	2.19 (6)
Cu	0.31216 (37)	0.31098 (26)	−0.07807 (22)	2.05 (8)
K(1)	0.00653 (59)	0.10252 (43)	−0.16032 (38)	2.7 (1)
K(2)	0.26129 (65)	0.58519 (45)	−0.00862 (36)	2.7 (1)
K(3)	−0.42128 (58)	0.08607 (38)	0.22473 (33)	2.3 (1)

Table IV. Selected Bond Distances (Å) and Angles (deg) for $K_2CuNbSe_4$

Nb–4Se	2.413 (1)	K–2Se	3.460 (1)
Nb–Cu	2.873 (1)		3.516 (4)
Se–Se	3.921 (3)		3.523 (2)
	3.929 (2)		3.643 (4)
	3.932 (3)	Cu–4Se	2.457 (1)
	3.958 (3)		
Se–Cu–Se	106.27 (5)	Se–Nb–Se	109.02 (6)
	110.50 (6)		109.16 (5)
	111.69 (6)		110.24 (6)

Table V. Selected Distances (Å) and Angles (deg) for $K_3CuNb_2Se_{12}$

Nb(1)–Nb(2)	3.706 (3)	K(1)–Se(1)	3.604 (7)
Nb(1)–Cu	2.911 (5)	K(1)–Se(2)	3.523 (7)
Nb(2)–Cu	2.976 (5)	K(1)–Se(4)	3.615 (7)
Nb(1)–Se(2)	2.407 (3)	K(1)–Se(5)	3.979 (6)
Nb(1)–Se(3)	2.580 (3)	K(1)–Se(6)	3.398 (6)
Nb(1)–Se(4)	2.661 (3)	K(1)–Se(7)	3.401 (6)
Nb(1)–Se(5)	2.928 (3)	K(1)–Se(9)	3.474 (7)
Nb(1)–Se(7)	2.592 (3)	K(1)–Se(9)	3.554 (6)
Nb(1)–Se(8)	2.624 (4)	K(1)–Se(10)	3.656 (7)
Nb(1)–Se(9)	2.568 (4)	K(1)–Se(11)	3.347 (7)
Nb(2)–Se(1)	2.561 (3)	K(2)–Se(1)	3.362 (6)
Nb(2)–Se(3)	2.847 (3)	K(2)–Se(2)	3.576 (7)
Nb(2)–Se(4)	2.745 (3)	K(2)–Se(2)	3.820 (7)
Nb(2)–Se(5)	2.586 (4)	K(2)–Se(3)	3.517 (6)
Nb(2)–Se(6)	2.615 (3)	K(2)–Se(7)	3.286 (6)
Nb(2)–Se(10)	2.426 (3)	K(2)–Se(8)	3.625 (7)
Nb(2)–Se(11)	2.555 (3)	K(2)–Se(10)	3.817 (6)
Cu–Se(2)	2.389 (5)	K(2)–Se(10)	3.556 (7)
Cu–Se(6)	2.509 (5)	K(2)–Se(11)	3.365 (7)
Cu–Se(8)	2.461 (4)	K(3)–Se(1)	3.253 (6)
Cu–Se(10)	2.388 (4)	K(3)–Se(2)	3.396 (6)
Se(1)–Se(6)	2.726 (3)	K(3)–Se(3)	3.238 (6)
Se(3)–Se(7)	2.376 (4)	K(3)–Se(5)	3.493 (6)
Se(4)–Se(9)	2.416 (4)	K(3)–Se(6)	3.399 (6)
Se(5)–Se(11)	2.384 (4)	K(3)–Se(8)	3.626 (6)
Se(6)–Se(12)	2.542 (3)	K(3)–Se(10)	3.505 (6)
Se(8)–Se(12)	2.389 (4)	K(3)–Se(12)	3.337 (6)
Se(2)–Cu–Se(6)	113.6 (2)	Se(1)–Nb(2)–Se(6)	63.5 (1)
Se(2)–Cu–Se(8)	110.1 (2)	Se(4)–Nb(2)–Se(3)	74.6 (1)
Se(6)–Cu–Se(8)	92.4 (1)	Se(5)–Nb(2)–Se(3)	83.5 (1)
Se(10)–Cu–Se(2)	114.0 (2)	Se(5)–Nb(2)–Se(4)	78.5 (1)
Se(10)–Cu–Se(6)	108.5 (2)	Se(5)–Nb(2)–Se(6)	135.5 (1)
Se(10)–Cu–Se(8)	116.3 (2)	Se(6)–Nb(2)–Se(3)	79.7 (1)
Se(2)–Nb(1)–Se(3)	97.2 (1)	Se(6)–Nb(2)–Se(4)	134.0 (1)
Se(2)–Nb(1)–Se(4)	96.5 (1)	Se(10)–Nb(2)–Se(1)	103.8 (1)
Se(2)–Nb(1)–Se(5)	170.7 (1)	Se(10)–Nb(2)–Se(3)	168.9 (1)
Se(2)–Nb(1)–Se(7)	105.1 (1)	Se(10)–Nb(2)–Se(4)	95.8 (1)
Se(2)–Nb(1)–Se(8)	104.3 (1)	Se(10)–Nb(2)–Se(5)	100.4 (1)
Se(2)–Nb(1)–Se(9)	104.8 (1)	Se(10)–Nb(2)–Se(6)	104.0 (1)
Se(3)–Nb(1)–Se(4)	80.5 (1)	Se(10)–Nb(2)–Se(11)	105.5 (1)
Se(3)–Nb(1)–Se(5)	82.0 (1)	Se(11)–Nb(2)–Se(1)	139.4 (1)
Se(3)–Nb(1)–Se(7)	54.7 (1)	Se(11)–Nb(2)–Se(3)	85.3 (1)
Se(3)–Nb(1)–Se(8)	128.4 (1)	Se(11)–Nb(2)–Se(4)	131.5 (1)
Se(4)–Nb(1)–Se(5)	74.2 (1)	Se(11)–Nb(2)–Se(5)	55.3 (1)
Se(7)–Nb(1)–Se(4)	131.8 (1)	Se(11)–Nb(2)–Se(6)	82.4 (1)
Se(7)–Nb(1)–Se(5)	82.1 (1)	Cu–Se(6)–Nb(2)′	71.0 (1)
Se(7)–Nb(1)–Se(8)	74.4 (1)	Cu–Se(10)–Nb(2)′	76.4 (1)
Se(8)–Nb(1)–Se(4)	140.4 (1)	Cu–Se(2)–Nb(1)	74.7 (1)
Se(8)–Nb(1)–Se(5)	83.2 (1)	Cu–Se(8)–Nb(1)	69.8 (1)
Se(9)–Nb(1)–Se(3)	131.8 (1)	Nb(1)–Se(3)–Nb(2)	86.0 (1)
Se(9)–Nb(1)–Se(4)	55.0 (1)	Nb(1)–Se(4)–Nb(2)	86.6 (1)
Se(9)–Nb(1)–Se(5)	69.7 (1)	Nb(1)–Se(5)–Nb(2)	84.2 (1)
Se(9)–Nb(1)–Se(7)	147.9 (1)	Nb(1)–Nb(2)–Cu′	173.6 (1)
Se(9)–Nb(1)–Se(8)	86.9 (1)	Nb(1)–Cu–Nb(2)′	161.9 (1)
Se(1)–Nb(2)–Se(3)	68.2 (1)	Nb(2)–Nb(1)–Cu	177.0 (1)
Se(1)–Nb(2)–Se(4)	71.6 (1)	Se(6)–Se(12)–Se(8)	93.3 (1)
Se(1)–Nb(2)–Se(5)	143.1 (1)	Se(12)–Se(6)–Se(1)	165.7 (1)

then one would expect a large thermal parameter for Nb and a small one for Cu when the ordered model was refined. Such is not the case. Moreover, the metal–metal distance is very short (2.873(1) Å), and hence the drive toward maximum charge separation would favor the ordered model. An analogous Cu/Mo chain[16] is found in $[NH_4][CuMoS_4]$.[17,18] The question of Cu/Mo disorder in these chains is complicated by the need to establish the direction of the polar crystallographic axis. The disordered model was chosen, but the statistical evidence in its favor is minimal. Of course, order–disorder in these systems may depend upon subtle preparative differences. Such differences are not subtle in this instance, as the present compound was grown from a high-temperature melt whereas $[NH_4][CuMoS_4]$ was prepared at room temperature by solution methods. If we accept the ordered model, then the chains in $K_2CuNbSe_4$ are an elaboration of those in SiS_2[19] and in $KFeS_2$[20,21] where there are infinite edge-shared SiS_4 and FeS_4 tetrahedra, respectively.

Both the Cu and Nb atoms have crystallographically imposed 222 symmetry. Consequently each must have a single M–Se distance and each has three independent Se–M–Se angles. The Cu–Se distance is 2.457 (1) Å, and the Se–Cu–Se angles are 106.27 (5), 110.50 (6), and 111.69 (6)°. The Nb–Se distance is 2.413 (1) Å, matching well with that of K_3NbSe_4[22] (Nb–Se, 2.387 (1)–2.403 (1) Å), and the Se–Nb–Se angles are 109.02 (6), 109.16 (5), and 110.24 (6)°. Interestingly, the edge sharing of the tetrahedra leads to a Nb–Cu distance of only 2.873 (1) Å, slightly longer than that in Cu_xNbSe_2[23] (Nb–Cu, 2.81 Å).

$K_3CuNb_2Se_{12}$. The structure consists of an infinite Cu/Nb/Se chain separated from K^+ cations. Figure 3 shows part of an

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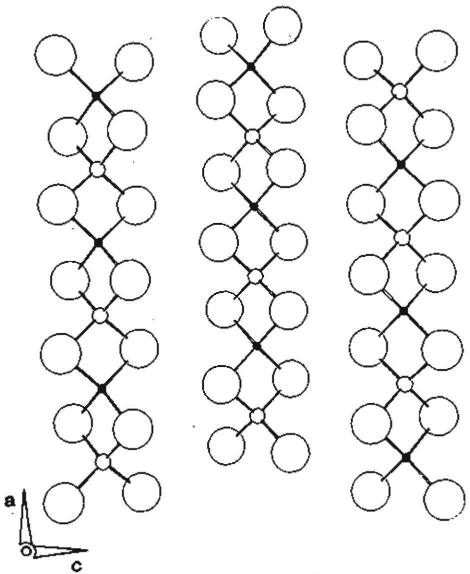

Figure 2. Anionic chains in $K_2CuNbSe_4$.

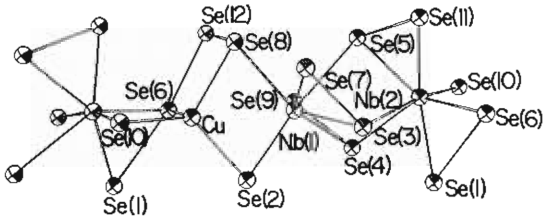

Figure 3. Infinite chain in $K_3CuNb_2Se_{12}$ with labeling scheme.

anionic chain, along with the labeling scheme. The compound is a new infinite, mixed-metal chain structure. This complex one-dimensional chain –[–Cu–Nb–Nb–]– extends parallel to [101]. The Cu atom has distorted tetrahedral coordination with Cu–Se distances ranging from 2.388 (4) to 2.509 (5) Å and Se–Cu–Se angles varying from 92.4 (1) to 116.3 (1)° (Table V). Both crystallographically independent Nb atoms are seven-coordinate with Nb–Se distances ranging from 2.407 (3) to 2.928 (3) Å for atom Nb(1) and 2.426 (3) to 2.847 (3) Å for atom Nb(2). These are comparable with those in Nb_8PtSe_{20}[24] (Nb–Se, 2.58 (1)–2.77 (1) Å).

In Figure 3, we have drawn as bonds all Se⋯Se interactions less than 2.75 Å. Consequently, the chain, as drawn, is $^{1}_{\infty}[CuNb_2(Se)_2(Se_2)_3(Se_4)^{3-}]$ with atoms Se(1), Se(6), Se(12), and Se(8) making up the Se_4^{2-} ligand that has five metal–selenium bonds. This formulation leads to formal oxidation states of Cu(I) and Nb(IV). The Se_4^{2-} ligand, though common in molecular species,[25] is uncommon in solid-state structures, although with a different metal–selenium bonding scheme it is found in $KCuSe_4$[7] and in $[Ag(Se_4)]_n^{n-}$.[26] Of the Se–Se interactions drawn in Figure 3, that of 2.726 (3) Å between atoms Se(1) and Se(6) is the longest. If one chooses to limit Se–Se interactions to distances less than 2.55 Å (Se(6)–Se(12) = 2.542 (3) Å), then the chain may be described as $^{1}_{\infty}[CuNb_2(Se)_3(Se_2)_3(Se_3)^{3-}]$ with atoms Se(6), Se(8), and Se(12) making up the Se_3^{2-} ligand. This formulation leads to formal oxidation states of Cu(I) and Nb(V). Such an Se_3^{2-} species is rare in solid-state structures but is found in K_3AuSe_{13}[8] and in a number of molecular species.[25] Se–Se interactions as long as 2.663 Å have been described as bonds, e.g. in Nb_2Se_9.[27] There is thus arbitrariness to the assignment of formal oxidation states in the present chain. Nevertheless, it appears that in the synthesis of both $K_3CuNb_2Se_{12}$ and $K_2CuNbSe_4$ Cu has not been oxidized to its highest oxidation state and that the Se_n^{2-} ($n = 3, 4$) species can exist at temperatures above 800 °C.

The present study demonstrates that new materials, in this instance new quaternaries, can be made with the use of the reactive flux method. This, along with its extension to tellurides,[11] greatly increases the utility of the method in the synthesis of new materials. The present quaternaries, though both members of the relatively small class of one-dimensional materials, show drastically different structural features. Interestingly, a common feature is the presence of Cu(I) in both systems.

Acknowledgment. Use was made of the X-ray and scanning electron microscope facilities of the Northwestern University Materials Research Center supported under the NSF-MRL program (Grant DMR-88-21571). This research was supported by the National Science Foundation (Grant DMR-88-13623).

Registry No. $K_2CuNbSe_4$, 134756-49-3; $K_3CuNb_2Se_{12}$, 135041-37-1; K_2Se_5, 134629-64-4; K, 7440-09-7; Se, 7782-49-2; Nb, 7440-03-1; Cu, 7440-50-8.

Supplementary Material Available: Complete crystallographic details for both compounds (Table IS) and anisotropic thermal parameters for $K_3CuNb_2Se_{12}$ (Table IIIS) (3 pages); structure amplitudes for both compounds (Table IIS and IVS) (18 pages). Ordering information is given on any current masthead page.

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