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Hydrothermal Synthesis of Copper Selenides $CsCu_4Se_3$ and $CsCuSe_4$

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Synthetic investigations of the Cs–Cu–Se system were carried out in evacuated sealed fused silica ampoules at temperatures below 200°C. Reactions between CsCl, A_2Se_x (A = Na, K; x = 2, 4, 5), and Cu under hydrothermal conditions were examined. Two phases have been isolated: a layered $CsCu_4Se_3$ phase ($P4/mmm$, $Z = 1$, $a = 4.090$ (2) Å, $c = 10.089$ (2) Å, $R = 3.83$, $R_w = 4.39\%$) and a linear chain $CsCuSe_4$ phase ($P2_12_12_1$, $Z = 4$, $a = 5.574$ (2) Å, $b = 9.020$ (2) Å, $c = 13.931$ (3) Å, $R = 2.44$, $R_w = 3.21\%$). The structures have isostructural parents KCu_4S_3 and $(NH_4)CuS_4$, respectively. This report illustrates, for the first time, the propensity of polychalcogenide salts to act as reagents in hydrothermal copper chemistry. © 1994 Academic Press, Inc.

1. INTRODUCTION

Several years ago, Berger recounted the wealth of chemistry observed in the Tl–Cu–Q(Q = S, Se) phase diagram (1), wherein greater than 14 compounds were isolated in at least seven distinct structure types. Since then, at least three new structures have been elucidated (2–4). Other investigators, including Bronger *et al.* (5–7), Burschka (8–10), Klepp *et al.* (11), and recently Kanatzidis *et al.* (12–17), have prepared alkali-metal copper chalcogenides from either the molten elements (i.e., molten Q) or the binaries (i.e., K_2Q_x, $1 \le x \le 6$) at temperatures ranging from 210 (12) to over 700°C (i.e., (11)). The solution chemistry of copper sulfides in particular has yielded a host of elegant cluster compounds. Müller's work accounts for a large portion of the "inorganic ring systems" (18–21) comprising such anions as $[Cu_3(S_4)_3]^{3-}$. Despite the rich polychalcogenide chemistry observed in solution (22–29), we have found that aqueous media, in particular hydrothermal conditions, have not been extensively used for the synthesis of transition-metal polychalcogenides.

Recently, both Sheldrick *et al.* (30–34) and Kanatzidis *et al.* (29, 35, 36) illustrated the utility of hydrothermal and methanothermal reactions in the preparation of tin, indium, and molybdenum chalcogenides. Earlier reports by Cambi and Elli (37, 38), Flamini and Grubessi (39), Rustembekov *et al.* (40), and Popolitov (41) described hydrothermal reactions of metals and chalcogenides yielding several simple late-transition-metal binaries. None of these reactions showed the formation of more complex copper chalcogenide structures, and in particular the formation of polychalcogenide copper complexes. We report here the first synthesis of two copper selenides prepared under mild hydrothermal conditions, α-$CsCuSe_4$ and the mixed-valence compound $CsCu_4Se_3$.

To the best of our knowledge, the structures of both of the title compounds have not been reported, but their parent compounds are known. The parent structure type for α-$CsCuSe_4$, $(NH_4)CuS_4$ (10), consists of chains of tetrahedrally coordinated copper(I) bound via S_4^{2-} polysulfide chains. Kanatzidis recently reported the structure of α-$KCuS_4$ (12) and provided lattice constants for the α-$CsCuSe_4$ (13) prepared from the alkali-metal polychalcogenide melts below 310°C. The structure determination of our compound is consistent with the reported structure type.

Since it was first reported (42), the layered KCu_4S_3 "mixed-valence" compound has commanded attention. Klepp and Boller reproted six compounds having the KCu_4S_3 layered structure type (11), one of which was $CsCu_4Se_3$, prepared from the Cs_2CO_3 melt. They reported the structure of the isotypic Tl^+ salt (11), as well as lattice parameters from powder X-ray diffraction of other alkali-metal sulfide and selenide derivatives.

For each of the compounds listed above, isolation of good single crystals from the melt proved to be difficult, and often only powders were isolated. In our reactions, nearly quantitative yields with respect to Cu (based on powder X-ray diffraction patterns) of high-quality crystals were obtained. We are reporting here the single crystal structures of two of the phases isolated from our hydrothermal reactions: α-$CsCuSe_4$ and $CsCu_4Se_3$.

2. EXPERIMENTAL

Synthesis

Elemental copper (99.9%, Aesar), selenium (99.999%, Johnson Matthey), potassium and sodium (Mallinkrodt),

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and CsCl (Mallinckrodt) were used as received (potassium and sodium were washed with dried hexanes before use) and stored in an inert atmosphere (N_2) glove box. The compounds A_2Se_x (A = Na, K; x = 2, 4, 5) were prepared by combining the elements in liquid ammonia as previously described (43). All reactants, except for deionized water, were loaded into fused silica ampoules in the glove box. Typical reaction scales were on the order of 250 mg with millimolar ratios of 1–5 : 0.5–1 : 1, A_2Se_x : Cu : CsCl.

Deionized water (500 μl) was introduced into the ampoules, and the ampoules were then cooled in liquid N_2, evacuated to $\sim 10^{-4}$ Torr, and flame sealed. The ampoules were then loaded into tube furnaces and heated to 120–170°C for 120 hr, followed by a slow cooling (10°/hr) in the furnace after the power had been turned off. The ampoules were then opened in air and the contents filtered and washed with deionized water. Powder X-ray diffraction patterns were collected on an Enraf-Nonius Guinier camera using a silicon internal standard.

Crystals for single-crystal X-ray diffraction analysis were choosen from two reactions. One reaction (1.0 : 0.59 : 1.0 mmol, K_2Se_4 : Cu : CsCl, heated to 120°C for 120 hr) yielded black needles of the α-$CsCuSe_4$ phase, quantitative with respect to Cu metal. No evidence of simple binary compounds such as $CuSe_2$, CuSe, or Cu_2Se was observed (44, 45). A second reaction (1.0 : 0.68 : 1.0 mmol, K_2Se_2 : Cu : CsCl, heated to 120°C for 120 hr) yielded a mixture of α-$CsCuSe_4$ needles and $CsCu_4Se_3$ black plates. This reaction was repeated at 170°C and yielded polycrystalline $CsCu_4Se_3$ (80%) and a mixture of CuSe and Cu_2Se (20%).

Structure Determination

Single crystals from two reactions were examined for single-crystal X-ray diffraction. Crystals were mounted on the four-circle goniometer of a Siemens *P*4 diffractometer. At least 20 reflections from the rotation photographs were chosen for centering of the crystals. Axial photographs of the crystals confirmed the Laue classes of the unit cells. Redundant data sets were collected at 2–3°/min in ω. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction (Psi-scans) was applied to the data. Both structures were solved by direct methods and refined by least-squares analysis (46). For both data sets, F_o was consistently smaller than F_c for the intense reflections, and so consequently a secondary extinction coefficient was refined by the method of Rogers (47). This led to better $F_o : F_c$ and lower R, R_w values. For $CsCuSe_4$, after running an enantimorph check on our first model (47), the structure was refined in the alternate enantimorph which yielded lower residuals.

TABLE 1
Crystal Data for $CsCuSe_4$ and $CsCu_4Se_3$

	$CsCuSe_4$	$CsCu_4Se_3$
Space group (No.), Z	$P2_12_12_1$ (19), 4	$P4/mmm$ (123), 1
a (Å)	5.574 (2)	4.094 (2)
b (Å)	9.020 (2)	—
c (Å)	13.931 (3)	10.089 (2)
V (Å^3)	700.4 (3)	169.09 (12)
Crystal dimensions (mm)	0.08 × 0.44 × 0.06	0.03 × 0.16 × 0.36
Crystal habit	Black needle	Black plate
Calculated density (g/cm^3)	4.858	6.172
Instrument	Siemens P4	Siemens P4
Radiation	Mo$K\alpha$	Mo$K\alpha$
2θ range	4.0–50.0	4.0–50.0
Scan mode	2θ–θ	2θ–θ
Octants	$-h$, $-k$, $\pm l$	h, $-k$, $\pm l$
Reflections		
Collected	1452	346
Independent	1242 (R_{int} = 1.56%)	121 (R_{int} = 6.4%)
Observed	1165 ($F > 4.0\ \sigma F$)	118 ($F > 2.5\ \sigma F$)
Variables	56	13
Absorption coefficient (mm^{-1})	28.90	33.73
Range of transmission	0.107–0.177	0.133–0.447
R^a	2.44	3.83
$R_w{}^b$	3.21^c	4.39^d
Largest residuals (e/Å^3)	1.40, −1.24	2.33, −2.15
Secondary external coefficient^e (×10^3)	1.01 (8)	17 (2)
GOF^f	0.82	0.91

[a] $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.
[b] $R_w = [\Sigma\,w(|F_o| - |F_c|)^2/\Sigma\,w(|F_o|)^2]^{1/2}$.
[c] $w^{-1} = [\sigma^2(F) + 0.0010\,F^2]$.
[d] $w^{-1} = [\sigma^2(F) + 0.0019\,F^2]$.
[e] $F^* = F[1 + 0.002\,\chi F^2/\sin(2\theta)]^{-1/4}$.
[f] $\mathrm{GOF} = [\Sigma\,(w(|F_o| - |F_c|))^2/M - N]^{1/2}$.

Table 1 compiles the collection and refinement data. The atomic parameters and important bond distances and angles are given in Tables 2–4. Tables of anisotropic thermal parameters and F_0/F_c are deposited with NAPS.[2]

3. RESULTS AND DISCUSSION

$CsCuSe_4$

As was reported for the parent structure type $(NH_4)CuS_4$, α-$CsCuSe_4$ comprises infinite one-dimen-

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[2] See NAPS document No. 05153 for 7 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. 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, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2)[a]

Atom	Wyckoff	*x*	*y*	*z*	*U* (eq)
			$CsCu_4Se_3$		
Cs	1*b*	0	0	0.5	0.021(1)
Cu	4*i*	0	0.5	0.1519(2)	0.027(1)
Se1	1*a*	0	0	0	0.017(1)
Se2	2*h*	0.5	0.5	0.2802(2)	0.017(1)
			$CsCuSe_4$		
Cs	4*a*	0.8334(1)	0.0604(1)	0.6690(1)	0.029(1)
Cu	4*a*	0.9587(2)	0.1364(1)	−0.0588(1)	0.026(1)
Se1	4*a*	0.8459(2)	0.3615(1)	0.1620(1)	0.021(1)
Se2	4*a*	0.6717(2)	0.1150(1)	0.4080(1)	0.023(1)
Se3	4*a*	0.1350(2)	0.1966(1)	0.0966(1)	0.020(1)
Se4	4*a*	0.9143(2)	0.5797(1)	0.0699(1)	0.024(1)

[a] Calculated ESDs are in parentheses.

sional chains of $[CuSe_4]_n^{n-}$ that run along [100], separated by the cesium cations (Fig. 1). A view along [011] (Fig. 2) illustrates the chelating nature of the polychalcogenide in a single chain of $[CuSe_4]_n^{n-}$. Se(2) is bound to a single copper atom and Se(4); Se(4) is bound only to two selenium atoms (Se(2) and Se(1)); Se(1) is bound to two selenium atoms and a copper atom; and Se(3) is bound to one selenium and two different copper atoms to create $[CuSe_4]$ five-membered heteroatomic rings as links along the chain. The cesium atoms are located in a distorted nine-fold-coordinated capped square prism of selenium with Cs–Se distances ranging from 3.617 to 3.768 Å.

TABLE 3
Relevant Bond Distances[a]

Atom 1	Atom 2	Distance (Å)
	$CsCu_4Se_3$	
Cu	Se1	2.557(1)
Cu	Se2	2.422(1)
Cs	Se2	3.647(1)
Cu	Cu	2.895(1)
Se2	Se2	4.094(2)
	$CsCuSe_4$	
Cs	Se1	3.768(1)
Cs	Se2	3.686(1)
Cs	Se3	3.635(1)
Cs	Se4	3.617(1)
Cu	Se1	2.594(1)
Cu	Se2	2.427(1)
Cu	Se3	2.408(1)
Cu	Se3′	2.438(1)
Se1	Se3	2.375(1)
Se1	Se4	2.380(1)
Se2	Se4	2.350(1)

[a] Calculated ESDs are in parentheses.

TABLE 4
Relevant Bond Angles[a]

Atoms	Angle (°)
$CsCu_4Se_3$	
Se1–Cu–Cu	55.5(1)
Se1–Cu–Cu	124.5(1)
Se2–Cu–Cu	126.7(1)
Se2–Cu–Cu	53.3(1)
Se1–Cu–Se1	106.4(1)
Se1–Cu–Se2	108.7(1)
Se2–Cu–Se2	115.4(1)
Cu–Se1–Cu	180.0(1)
Cu–Se1–Cu	69.0(1)
Cu–Se1–Cu	73.6(1)
Cu–Se1–Cu	111.0(1)
Cu–Se1–Cu	106.4(1)
Cu–Se2–Cu	73.4(1)
Cu–Se2–Cu	115.4(1)
$CsCuSe_4$	
Se1–Cu–Se2	98.6(1)
Se1–Cu–Se3	119.8(1)
Se3–Cu–Se1	98.9(1)
Se2–Cu–Se3	108.6(1)
Se3–Cu–Se2	119.9(1)
Se3–Cu–Se3	110.9(1)
Se4–Se2–Cu	98.2(1)
Se3–Se1–Se4	101.7(1)
Se3–Se1–Cu	110.9(1)
Se4–Se1–Cu	80.1(1)
Se1–Se3–Cu	101.9(1)
Se1–Se3–Cu	101.6(1)
Se1–Se4–Se2	101.5(1)
Cu–Se3–Cu	104.3(1)

[a] Calculated ESDs are in parentheses.

It is important to note that no phase isotypic with the previously known β-$KCuS_4$ chain phase (12) was observed as a product from our syntheses, this being the thermodynamically favored product in the K/Cu/S system studied in molten K_2S_x salts at temperatures greater than 250°C.

Until recently (35, 36) only Q^{2-} ligands were observed in the products of hydrothermal syntheses (30–34). Kanatzidis and Liao reported the first "$[Se_7]^{8-}$" unit in their $[Mo_{12}Se_{56}]^{12-}$ cluster compound (35). This unit comprises three Se_2^{2-} units capped by a single Se^{2-} to form an end-capped trigonal prism of selenium atoms. Kanatzidis has also reported the hydrothermal synthesis of $[In_2$

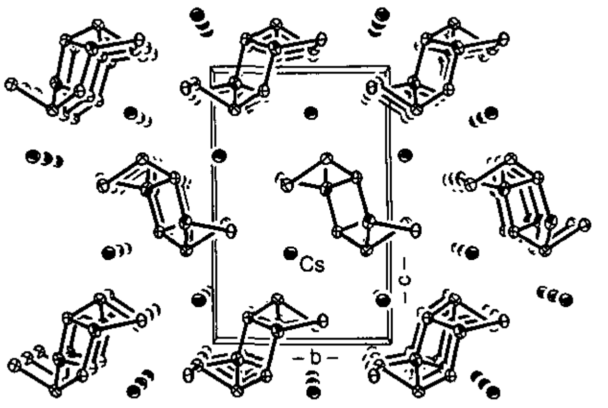

FIG. 1. *A view of* $CsCuSe_4$ *along [100] highlighting the relationship* of the cesium atoms to the $[CuSe_4]_n^{n-}$ chains that run along the [100] direction. Thermal ellipsoids are a 90% probability.

$Se_2(Se_4)_2]^{2-}$ and $[In_3Se_3(Se_4)_3]^{3-}$ molecular ions that contain Se_4^{2-} units (29).

It is also not too surprising to find the intact Se_4^{2-} unit in α-$CsCuSe_4$ prepared from our hydrothermal reactions based on the spectroscopic and electrochemical evidence of polyselenides in aqueous solutions by Lyons and Young (23). Lyons and Young observed that the average Se_x^{2-} species found in an equilibrium between K_2Se and Se in basic solutions was a species with $x = 3.8$. The solution-phase ^{77}Se NMR indicated a net oxidation state lying between Se^{2-} and Se^{4+} in a rapid equilibrium.

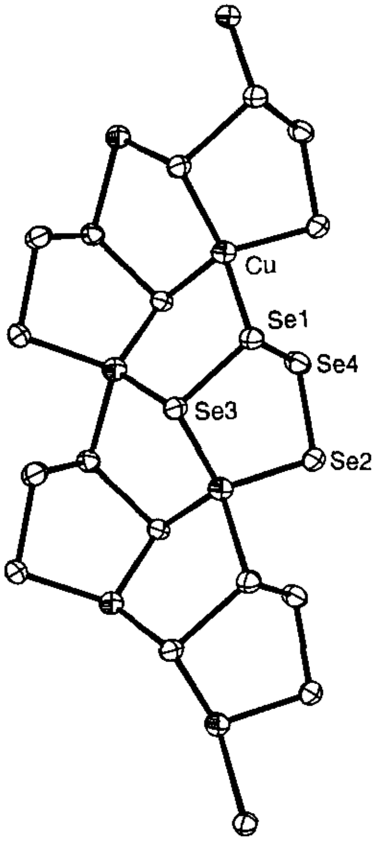

FIG. 2. A side view of the truncated $[CuSe_4]_n^{n-}$ chains that run along the [100] direction. The cesium atoms have been eliminated for clarity. Thermal ellipsoids are a 90% probability.

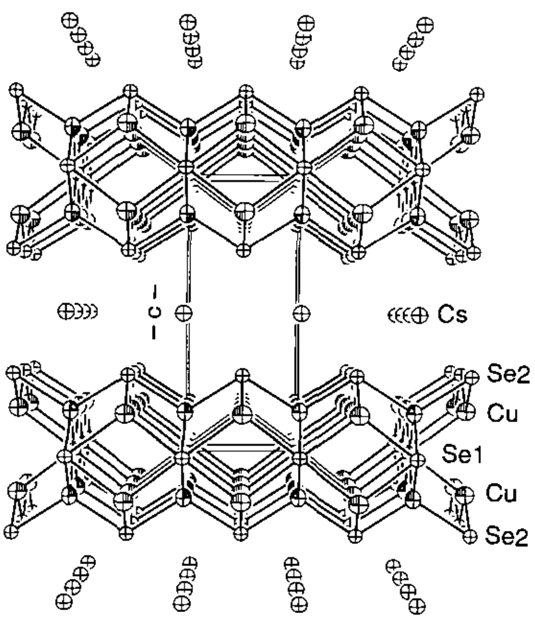

FIG. 3. A view along [100] of the layered $CsCu_4Se_3$. The unit cell is highlighted. Thermal ellipsoids are a 90% probability.

This treatment of selenium polyanions is perhaps an oversimplification of a very complex set of reactions, especially in light of the fact that the Se_4^{2-} ligand is not simply a bidentate, four-membered chain. In the structure of α-$CsCuSe_4$, both terminal Se atoms (Se2 and Se3) are bound to copper, but Se3 is bound to a second copper (Fig. 2), and Se1, not "terminal" in the Se_4^{2-} chain, is bound to a third copper atom. Despite this simplification, our reactions proceed to generate a metal–polyselenide chain structure, and although the α-$CsCuSe_4$ parent structure type is known, our experiments provide further evidence for the formation of transition-metal polychalcogenides from hydrothermal syntheses.

$CsCu_4Se_3$

The structure of $CsCu_4Se_3$ comprises $CuSe_4$ tetrahedra that share five of their six sides to generate layers of $[Cu_4Se_3]_n^{n-}$. These layers, shown in Fig. 3, are alternating Se–Cu–Se–Cu–Se square networks and are separated by a layer of cesium cations, the average interlayer Cu–Cu distance being 3.071 Å and the nearest Cu–Cu distance being 2.895 Å. The average Se–Se distance of 4.090 Å illustrates the Se^{2-} nature of the chalcogenide that has been observed in previous hydrothermal chalcogenide syntheses (30–34). Cesium ions are found in a square prismatic geometry surrounded by eight selenium atoms at 3.647 Å.

The metal-rich $CsCu_4Se_3$ compound was one major product of reactions involving K_2Se_2, the other being α-$CsCuSe_4$. For these reactions, the reduction of Se_2^{2-} by Cu can be postulated as

$$Se_2^{2-} + 2e^- \rightarrow 2\,Se^{2-}. \quad [1]$$

It is also believed that the selenide species in solution can undergo association (23) to yield higher order selenides. These higher order selenides provide the Se_4^{2-} unit necessary to build the $CsCuSe_4$ chain structure, while the remaining Se^{2-} is incorporated into the $CsCu_4Se_3$ layered structure; one can thus account for the generation of both $CsCu_4Se_3$ and $CsCuSe_4$ from these reactions. This reaction scheme is consistent with our observations that both phases are produced from reactions with K_2Se_2. At higher reaction temperatures, the majority phase observed (80%) was $CsCu_4Se_3$, along with a limited amount of CuSe and Cu_2Se. As this mixture was quite intimate, yield estimates were based on powder X-ray diffraction intensity measurements.

Reactions run in the absence of any polyselenide in solution (i.e., Cu + K_2Se + CsCl) yielded neither $CsCu_4Se_3$ nor α-$CsCuSe_4$, but rather only CuSe and Cu_2Se. Without selenide association, oxidation of copper by Se^{2-} would not be possible (23). As a consequence, polyselenides must play a role in the oxidation of copper even in these reactions. It is unclear, however, what that mechanism might be (37–41). There is also no clear evidence for the role of the solvent in any of these reactions since we did not observe formation of residual gases after the reactions were opened, a sign of solvent reduction or oxidation by the reactants. These remaining questions are the impetus for our continued studies into polyselenides in hydrothermal reactions.

We have illustrated the utility of alkali-metal polyselenide hydrothermal reactions as a method for preparing several copper selenide compounds. Unlike previous hydrothermal and methanothermal reactions, the polyselenide Se_4^{2-} is observed in the structure intact after reaction with the copper metal to yield α-$CsCuSe_4$. This is the first occasion where this compound has been prepared using hydrothermal reactions. Using K_2Se_2, the thermodynamically stable $CsCu_4Se_3$ is formed in conjunction with α-$CsCuSe_4$ or with copper selenide binaries. We are currently examining these and other hydrothermal chalcogenide systems so as to better understand the chemistry therein. Polychalcogenides have shown a propensity to react with Co, Ni, and Pb in aqueous solutions (27, 38), and we will be investigating the chemistry of these elements under hydrothermal conditions in future work.

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