

ACCOUNTS OF CHEMICAL RESEARCH®

AUGUST 1991

Registered in U.S. Patent and Trademark Office; Copyright 1991 by the American Chemical Society

Copper-Containing Group IV and Group V Chalcogenides

PATRICIA M. KEANE, YING-JIE LU, and JAMES A. IBERS*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received March 26, 1991 (Revised Manuscript Received July 1, 1991)

The synthesis of new compounds is the essential first step in establishing relationships among the stoichiometry, structure, and physical properties of solid-state materials. The well-known problems of solid-state synthesis have recently been summarized:¹ we lack general methods of synthesis, and we cannot predict eventual stoichiometry, let alone structure and physical properties. As a consequence, solid-state synthesis is arguably the most challenging area of synthetic chemistry.

Solid-state transition-metal chalcogenides became a very active area of research about 3 decades ago²⁻⁶ and have remained so since.⁷ This interest is stimulated largely by the discoveries of the physical properties,^{3,8-11} unusual structural features, and applications^{10,12,13} of the new materials. Among their interesting physical properties are superconductivity^{8,9} (of the old-fashioned variety!) and charge-density waves.^{3,11} In addition to their use as high-temperature lubricants, the materials have been used as hydrodesulfurization catalysts^{12,13} and their intercalates as energy storage systems;¹⁰ indeed these compounds show an extensive intercalation chemistry¹⁰ that will be discussed only very briefly here. Rather, the focus of this Account is on synthesis and structural chemistry. We have recently discovered that the nonstandard reactive flux method¹⁴ has broad application to the synthesis of certain classes of new

solid-state chalcogenides. In this Account, we describe the application of this technique to an area of rich new structural chemistry in ternary (Cu/group IV/Te) and quaternary (K/Cu/Nb/S,Se) systems. The structures we have found and describe here are very different from the classic ones known previously in these systems.

Previously Known Compounds

The word chalcogen, which pertains to the elements S, Se, and Te, is derived from the Greek words *chalkos* meaning copper or brass and *genes* meaning born. The name is fitting, owing to the tendency of the chalcogens to occur in nature as ores with Cu. This is particularly true of Se and Te whose main sources are Cu₂Se and Cu₂Te produced from the refinement and production of elemental Cu from ores. Therefore, it is not surprising that there is an abundance of binary, ternary, and even quaternary Cu-containing chalcogenides.

Within the Cu/group IV or group V/Q system alone, where we use the general symbol "Q" for S, Se, or Te, there are numerous solid-state compounds. The great majority have classic structures: these include inter-

Patricia M. Keane received her B.S. degree from the University of Missouri-Rolla in 1985. She then worked at General Motors on the development of rare-earth iron boron supermagnets through 1988 when she joined the Ph.D. program at Northwestern University.

Ying-Jie Lu received his undergraduate education and M.S. degree from Northeastern Normal University, People's Republic of China, in 1982. He became a Lecturer at Dalian University of Technology in 1983 and joined the Ph.D. program at Northwestern University in 1989.

James A. Ibers received his B.S. and Ph.D. degrees from Caltech. He joined Northwestern University in 1965, where he is currently Charles E. & Emma H. Morrison Professor of Chemistry. He is a member of the U.S. National Academy of Sciences. His research interests are in solid-state and coordination chemistry.

- (1) DiSalvo, F. J. *Science* **1990**, *247*, 649-655.
- (2) Goodenough, J. B. *Prop. Phys. Struct. Dériv. Semi-Métal.* **1967**, *263* (Paris: CNRS).
- (3) Wilson, J. A. *Phys. Rev. B: Condens. Matter* **1979**, *19*, 6456-6468.
- (4) Hulliger, F. *Struct. Bonding (Berlin)* **1968**, *4*, 83-229.
- (5) Jellinek, F. *Ark. Kemi* **1962**, *20*, 447-480.
- (6) Kadijk, F.; Huisman, R.; Jellinek, F. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 768-775.
- (7) Jobic, S.; Deniard, P.; Breck, R.; Rouxel, J.; Drew, M. G. B.; David, W. I. F. *J. Solid State Chem.* **1990**, *89*, 315-327.
- (8) Matthias, B. T.; Marezio, M.; Corenzwit, E.; Cooper, A. S.; Barz, H. E. *Science* **1972**, *175*, 1465-1466.
- (9) Fisher, Ø; Odermatt, R.; Bongli, G.; Jones, H.; Chevrel, R.; Sergent, M. *Phys. Lett.* **1973**, *45A*, 87-88.
- (10) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41-99.
- (11) DiSalvo, F. J. *Surf. Sci.* **1976**, *58*, 297-311.
- (12) Müller, A. *Polyhedron* **1986**, *5*, 323-340.
- (13) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430-445.
- (14) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202-6204.

calation complexes (Cu_nMQ_2), spinels (CuM_2Q_4), and those related to sulvanite (Cu_3VS_4). The primary methods for their preparation and crystal growth are the standard ones of halogen transport, direct elemental reactions, and electrolytic methods.

Intercalation compounds of the type Cu_nMQ_2 ($0 < n < 1$) comprise strongly bonded covalent layers of MQ_2 . For these transition-metal dichalcogenides, the coordination of the transition metal by the chalcogen is trigonal prismatic or octahedral. Between these layers is a van der Waals' gap where bonding is weak enough to allow intercalation of foreign atoms or molecules in an ordered arrangement. Methods for the preparation of the Cu_nMQ_2 materials include halogen transport ($\text{Cu}_{0.53}\text{NbS}_2^{16}$ and $\text{Cu}_{0.70}\text{TiS}_2^{16}$), reaction of the intercalate with the host binary compound ($\text{Cu}_{0.65}\text{NbS}_2^{17}$), direct reaction of the elements ($\text{Cu}_{0.75}\text{VS}_2^{18}$, $\text{Cu}_{0.67}\text{TaS}_2^{19}$ and $\text{Cu}_{0.67}\text{NbSe}_2^{20}$), and electrolytic methods ($\text{Cu}_{0.17}\text{NbSe}_2^{21}$). Some intercalated compounds show metallic conductivity. Some are superconductors, as are many of the MQ_2 binary compounds, such as NbS_2^{22} , $\text{Nb}_{1-x}\text{Se}_2^{23}$, NbSe_2^{24} , NbTe_2^{25} , $\text{Nb}_{1+x}\text{Te}_2^{25}$, TaS_2^{25} and TaSe_2^{25} .

A number of spinels of the type CuM_2Q_4 have been prepared by allowing the elements to react with chalcogen ($\text{CuNb}_2\text{S}_4^{26}$, $\text{CuTi}_2\text{S}_4^{27}$ and $\text{CuV}_2\text{S}_4^{27}$), by reaction of the binary chalcogenides ($\text{CuTi}_2\text{S}_4^{28}$), through use of TeCl_4 as a transport agent²⁹ (CuV_2S_4 , CuVTi_2S_4 , and CuCrZrS_4), or by allowing the oxides to react with H_2S ($\text{CuV}_2\text{S}_4^{27}$ and $\text{CuTi}_2\text{S}_4^{27}$). These layered compounds contain chalcogen atoms in a cubic closest packed array with Cu occupying one-eighth of the tetrahedral sites and M occupying the octahedral sites. The effects of cation size and charge on the electrical, magnetic, and optical properties have been extensively studied.

There are several derivative compounds of the mineral sulvanite, Cu_3VS_4 .³⁰ These include the S, Se, and Te compounds of the V triad.^{31,32} In the sulvanite structure, the Cu and V atoms are tetrahedrally coordinated by S atoms, and these tetrahedra share edges. Derivatives of this structural type with alkali metals³³⁻³⁵

or Ti^{36} in place of Cu have also been synthesized.

Use of Reactive Fluxes

Molten salts or fluxes have been extensively studied and widely used as high-temperature solvents in the temperature range 300–1800 °C to promote crystal growth.³⁷ These fluxes play a crucial role for the crystallization of numerous solid-state compounds. Crystallization of a solid-state compound from a flux parallels the more familiar crystallization of a coordination or organometallic compound from a suitable solvent; the major difference is that the flux is typically a higher temperature liquid. While solid-state synthesis often involves highly refractory powders that diffuse together very slowly, even at high temperatures, the use of a liquid flux enhances the rate of diffusion and increases particle mobility. Hence, the flux promotes reaction of the starting materials and crystallization of the final product. In some cases, the use of a flux allows for crystallization at a lower temperature, which may be necessary for incongruently melting or refractory materials as well as for materials that undergo high-temperature phase transitions. Although the majority of the compounds crystallized from these high-temperature solvents have been elements, binaries, or ternary oxides, binary or ternary chalcogenides have been crystallized from molten salts of the type A_2S_n (A = alkali metal).^{38,39} In general, these A_2S_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 method⁴⁰ for the synthesis of new compounds. But as we first described for the $\text{K}_2\text{S}/\text{S}$ system,¹⁴ the use of a reactive flux takes advantage of low-melting A/Q systems (A = alkali metal; Q = S, Se, Te) and exploits the reactive polychalcogenides A_2Q_n not only as classic fluxes but also as reactants to offer the alkali metal and chalcogen and even the polychalcogen to the final product. Indeed, this appears to be a general solid-state route to preparing new compounds containing polychalcogenide species.¹⁴

The compositions of the starting binary polychalcogenide materials can be obtained through variation of the A/Q ratio in reactions either in the solid state^{14,41} or in liquid ammonia.⁴²⁻⁴⁴ 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 $\text{K}_4\text{Ti}_3\text{S}_{14}^{14}$ (S_2^{2-}), $\text{Na}_2\text{Ti}_2\text{Se}_8^{41}$ (Se_2^{2-}), KCuS_4^{45} (S_4^{2-}), KAuSe_5^{46} (Se_5^{2-}),

(15) Nitsche, R.; Wild, P. *J. Cryst. Growth* 1968, 4, 153-158.

(16) Nagard, N. L.; Gorochov, O.; Collin, G. *Mater. Res. Bull.* 1975, 10, 1287-1295.

(17) Koerts, K. *Acta Crystallogr.* 1963, 16, 432-433.

(18) Nagard, N. L.; Collin, G.; Gorochov, O. *Mater. Res. Bull.* 1977, 12, 975-982.

(19) DiSalvo, F. J.; Hull, G. W., Jr.; Schwartz, L. H.; Voorhoeve, J. M.; Waszczak, J. V. *J. Chem. Phys.* 1973, 59, 1922-1929.

(20) Voorhoeve-van den Berg, J. M. *J. Less-Common Metals* 1972, 26, 399-402.

(21) Beal, A. R.; Liang, W. Y.; Pethica, J. B. *Phil. Mag.* 1976, 33, 591-602.

(22) Van Maaren, M. H.; Schaeffer, G. M. *Phys. Lett.* 1966, 20, 131.

(23) Selte, K.; Kjekshus, A. *Acta Chem. Scand.* 1965, 19, 258-260.

(24) Revolinsky, E.; Spiering, G. A.; Beerntsen, D. J. *J. Phys. Chem. Solids* 1965, 26, 1029-1034.

(25) Van Maaren, M. H.; Schaeffer, G. M. *Phys. Lett.* 1967, 24A, 645-646.

(26) Eibichütz, M.; Hermon, E.; Shtrikman, S. *Acta Crystallogr.* 1967, 22, 944-945.

(27) Bouchard, R. J.; Russo, P. A.; Wold, A. *Inorg. Chem.* 1965, 4, 685-688.

(28) Hahn, V. H.; Harder, B. Z. *Anorg. Allg. Chem.* 1956, 288, 257-259.

(29) Mähl, V. D.; Pickardt, J.; Reuter, B. Z. *Anorg. Allg. Chem.* 1982, 491, 203-207.

(30) Pauling, L.; Hultgren, R. Z. *Kristallogr.* 1933, 84, 204-212.

(31) van Arkel, A. E.; Crevecoeur, C. *J. Less-Common Metals* 1963, 5, 177-180.

(32) Hulliger, F. *Helv. Phys. Acta* 1961, 34, 379-382.

(33) van den Berg, J. M.; de Vries, R. *Proc. K. Ned. Akad. Wet., Ser. B* 1964, 67, 178-180.

(34) Lacroche, M.; Ibers, J. A. *Inorg. Chem.* 1990, 29, 1503-1505.

(35) Yun, H.; Randall, C. R.; Ibers, J. A. *J. Solid State Chem.* 1988, 76, 109-114.

(36) Crevecoeur, C. *Acta Crystallogr.* 1964, 17, 757.

(37) Elwell, D.; Scheel, H. J. *Crystal Growth from High-Temperature Solutions*; Academic Press: London, 1975.

(38) Scheel, H. J. *J. Cryst. Growth* 1974, 24, 669-673.

(39) Garner, R. W.; White, W. B. *J. Cryst. Growth* 1970, 7, 343-347.

(40) Hagemuller, P. *Preparative Methods in Solid State Chemistry*; Academic Press: New York, 1972.

(41) Kang, D.; Ibers, J. A. *Inorg. Chem.* 1988, 27, 549-551.

(42) Lu, Y.-J.; Ibers, J. A. *Inorg. Chem.*, in press.

(43) Lu, Y.-J.; Ibers, J. A. *J. Solid State Chem.*, in press.

(44) Lu, Y.-J.; Ibers, J. A. Manuscript in preparation.

(45) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* 1989, 111, 3767-3769.

(46) Park, Y.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 914-915.

one-dimensional chains,^{14,41,45-47} three-dimensional structures,⁴⁷ and molecular species.⁴⁸ Recently, we have demonstrated that the reactive flux method can be extended to the ternary polytellurides⁴⁹ and even to quaternary sulfides^{43,44} and selenides.⁴²⁻⁴⁴ These systems similarly display fascinating structural features, such as Se_n^{2-} ($n = 2-4$) and Te_n^{2-} ($n = 2-3$) ligands and alternating mixed-metal chains. 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 are more prevalent among the low-temperature syntheses. The method is not restricted to A_2Q_n fluxes; indeed Cu_nTe_m solutions may be used as reactive fluxes. The Cu_nTe_m phases, similar to the A_nTe_m phases, exhibit a low-melting region between ~50 and 100% Te.

We now demonstrate that there is unequivocally an abundance of rich novel structural chemistry to be explored in the Cu-containing group IV and group V chalcogenides. The unusual structural features of these new compounds, synthesized from reactive fluxes (A_2Q_n , A = alkali metal or Cu, Q = S, Se, Te) at high temperatures, will be reviewed.

Preparative Methods

K/Cu/Nb/Q (Q = S, Se) System. In the quaternary system K/Cu/Nb/Q (Q = S, Se), six new solid-state compounds have been synthesized through the use of K_2Q_5 (Q = S, Se) as a reactive low-melting flux: $\text{K}_2\text{CuNbSe}_4$,⁴² $\text{KCu}_2\text{NbSe}_4$,⁴³ KCu_2NbS_4 ,⁴³ $\text{K}_3\text{CuNb}_2\text{Se}_{12}$,⁴² $\text{K}_3\text{Cu}_3\text{Nb}_2\text{S}_8$,⁴⁴ and $\text{K}_3\text{Cu}_3\text{Nb}_2\text{Se}_8$.⁴⁴ These materials all exhibit low-dimensional structures. The K_2Q_5 starting materials were synthesized by the stoichiometric reaction of K and S or Se powder in liquid ammonia.⁴²⁻⁴⁴ The reactants (elemental Cu, Nb, and S or Se) and K_2Q_5 were loaded into a quartz tube under argon, the tube was evacuated and sealed, and it was then heated for 4 days at 800–880 °C, depending upon the compound. Although single crystals of $\text{KCu}_2\text{NbSe}_4$ and $\text{K}_3\text{CuNb}_2\text{Se}_{12}$ form in the presence of a melt at 800 °C from nonstoichiometric mixtures, stoichiometric reactions at 870 °C amazingly afford yields of 100% crystalline $\text{KCu}_2\text{NbSe}_4$ or $\text{K}_3\text{CuNb}_2\text{Se}_{12}$. In general, a slow cooling rate of 4 °C/h provides the optimum condition for crystal growth. Single crystals as long as 2.0 mm have been grown.

Cu/M/Te (M = Ti, Zr, Hf) System. In the ternary system Cu/M/Te (M = Ti, Zr, Hf), four new compounds have been synthesized and characterized: Cu_2MTe_3 ⁵⁰ (M = Ti, Zr, Hf) and $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$.⁵¹ These compounds display two new structural motifs: one is closest packed; the other is three-dimensional. The synthesis proceeded by direct reaction of the elemental powders. These were heated at 650 °C in an evacuated quartz tube to allow formation of the Cu_nTe_m melt; the tube was then kept at 900 °C for 4 days and was then slowly cooled at a rate of 3 °C/h. The choice of the Cu:Te ratio is crucial, as the low-melting flux region

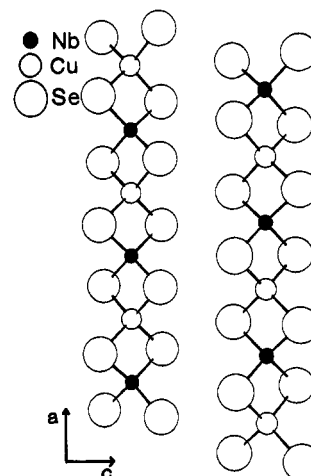


Figure 1. Infinite anionic chains in $\text{K}_2\text{CuNbSe}_4$.

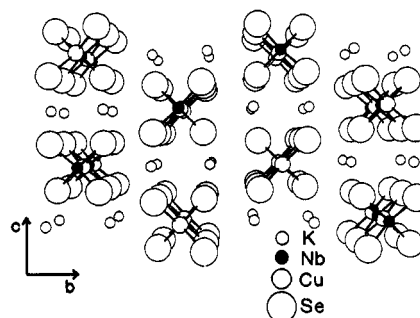


Figure 2. Projection of the $\text{K}_2\text{CuNbSe}_4$ structure down [100].

exists between approximately 50 and 100% Te. Single crystals of a given ternary were manually extracted from the Cu/Te melt.

Descriptions of the Structures

$\text{K}_2\text{CuNbSe}_4$. The structure of $\text{K}_2\text{CuNbSe}_4$ comprises one-dimensional infinite chains that consist of edge sharing of successive CuSe_4 and NbSe_4 tetrahedra [$-\text{Cu}-\text{Nb}-\text{Cu}-$] (Figure 1). These linear chains extend parallel to [100] and are well separated from one another by K^+ cations (Figure 2). As there are no Se–Se bonds, the formal oxidation states are K(I), Cu(I), Nb(V), and Se(–II). The chains are an elaboration of those in SiS_2 ⁵² and KFeS_2 ,^{53,54} in that apparently there is an ordered alternation of Cu(I) and Nb(V) centers, presumably as a result of charge separation. A similar chain, though described as disordered, has been found in the structure of $[\text{NH}_4][\text{CuMoS}_4]$.⁵⁵ In the present structure, consistent with the assigned oxidation states, the Cu–Se distance is 2.457 (1) Å, the Nb–Se distance is 2.413 (1) Å, and the MSe_4 tetrahedra are fairly regular. The edge sharing of the tetrahedra leads to a Nb–Cu bond length of 2.873 (1) Å, which is slightly longer than that in Cu_nNbSe_2 ²⁰ (Nb–Cu, 2.81 Å). The metal–metal distances in elemental hexagonally closest packed Cu and Nb are 2.556⁵⁶ and 2.858 Å,⁵⁷ respec-

(52) Peters, J.; Krebs, B. *Acta Crystallogr.* 1962, B38, 1270–1272.

(53) Boon, J. W.; MacGillavry, C. H. *Recl. Trav. Chim. Pays-Bas* 1942, 61, 910–920.

(54) Bronger, W.; Müller, P. *J. Less-Common Metals* 1984, 100, 241–247.

(55) Bensch, W.; Stauber-Reichmuth, G.; Reller, A.; Oswald, H. R. *Recl. Chim. Min.* 1987, 24, 503–508.

(56) Krull, W. E.; Newman, R. W. *J. Appl. Crystallogr.* 1970, 3, 519–521.

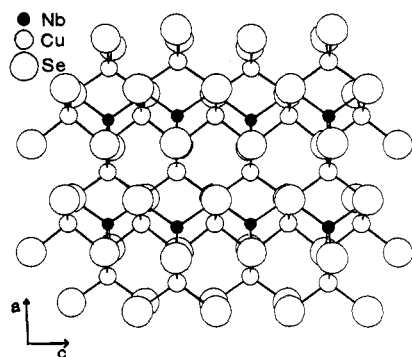
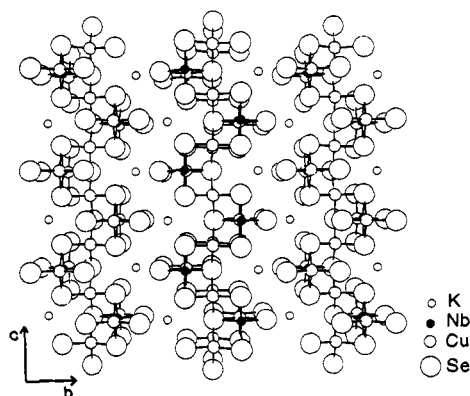
(47) Kanatzidis, M. G. *Chem. Mater.* 1990, 2, 353–363.

(48) Schreiner, S.; Aleandri, L. E.; Kang, D.; Ibers, J. A. *Inorg. Chem.* 1989, 28, 392–398.

(49) Keane, P. M.; Ibers, J. A. *Inorg. Chem.* 1991, 30, 1327–1329.

(50) Keane, P. M.; Ibers, J. A. *J. Solid State Chem.*, in press.

(51) Keane, P. M.; Ibers, J. A. *Inorg. Chem.*, in press.

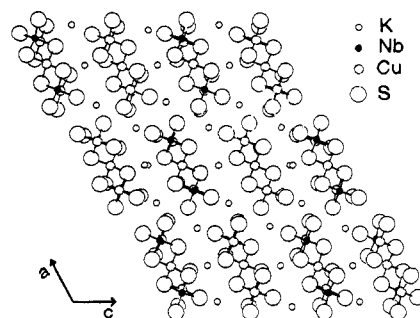
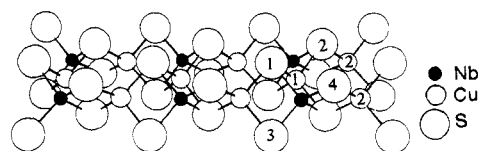
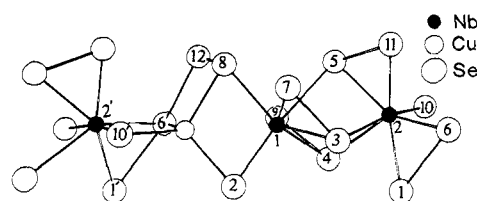
Figure 3. Anionic net in $\text{KCu}_2\text{NbSe}_4$.Figure 4. Structure of $\text{KCu}_2\text{NbSe}_4$ viewed along [100].

tively. Consistent again with the formal oxidation states, $\text{K}_2\text{CuNbSe}_4$ is a poor conductor, having a resistance greater than $10 \text{ M}\Omega\text{-cm}$ at room temperature.

KCu_2NbQ_4 ($\text{Q} = \text{Se}, \text{S}$). $\text{KCu}_2\text{NbSe}_4$ is a new two-dimensional layered material that consists of $[\text{Cu}_2\text{NbSe}_4]$ anionic layers that are orthogonal to [010] (Figure 3) and are separated by K^+ cations (Figure 4). As in $\text{K}_2\text{CuNbSe}_4$, there are no Se-Se bonds, so formal oxidation states of K(I) , Cu(I) , Nb(V) , and Se(-II) may be assigned. The presence of CuSe_4 and NbSe_4 tetrahedra is consistent with these oxidation states, as is the observed diamagnetism for the compound. Similar to the one-dimensional alternating metal chain in $\text{K}_2\text{CuNbSe}_4$, the NbSe_4 tetrahedra and one type of CuSe_4 tetrahedra share edges in an alternating pattern along [100], while the NbSe_4 tetrahedra and the other type of CuSe_4 tetrahedra share edges along [001]. The corner sharing of the two types of CuSe_4 tetrahedra along [100] and [001] completes this two-dimensional network. This unusual structure can be described in terms of double chains that are interconnected in a zigzag arrangement along [001] and are separated by K^+ cations (Figure 4).

The Nb-Se distances, which vary from 2.392 (3) to 2.452 (3) Å, are comparable to those found in K_3NbSe_4 ³⁴ (Nb-Se, 2.387 (1)–2.403 (1) Å) and $\text{K}_2\text{CuNbSe}_4$ (Nb-Se, 2.413 (1) Å). The Cu-Se bond distances are in the narrow range of 2.427 (2)–2.440 (4) Å, slightly shorter than those in $\text{K}_2\text{CuNbSe}_4$ (2.457 (1) Å). One of the CuSe_4 tetrahedra is somewhat distorted with Se-Cu-Se angles ranging from 103.3 (1) to 115.6 (1)°.

As seen in $\text{KCu}_2\text{NbSe}_4$, the edge and corner sharing among the tetrahedra lead to a Nb-Cu bond 2.831 (4) Å in length. This distance is even shorter than the Nb-Cu distance in $\text{K}_2\text{CuNbSe}_4$ (Nb-Cu, 2.873 (1) Å)

Figure 5. View of the $\text{K}_3\text{Cu}_3\text{Nb}_2\text{S}_8$ structure along [010].Figure 6. View of the anionic triple chain in $\text{K}_3\text{Cu}_3\text{Nb}_2\text{S}_8$.Figure 7. Part of the infinite one-dimensional anionic chain in $\text{K}_3\text{CuNb}_2\text{Se}_{12}$.

and only slightly longer than that in Cu_nNbSe_2 ²⁰ (2.81 Å).

On the basis of a unit-cell determination, KCu_2NbS_4 is isostructural with $\text{KCu}_2\text{NbSe}_4$.

$\text{K}_3\text{Cu}_3\text{Nb}_2\text{Q}_8$ ($\text{Q} = \text{S}, \text{Se}$). The structure of $\text{K}_3\text{Cu}_3\text{Nb}_2\text{Q}_8$ consists of a new infinite one-dimensional anionic chain separated by K^+ cations. The projection down [010] of this anionic chain of the $\text{Q} = \text{S}$ material is shown in Figure 5. Once again there are no Q-Q bonds, so for this and stereochemical reasons, the formal charge assignment of K(I) , Cu(I) , Nb(V) , and Q(-II) is reasonable. The triple chain, which runs parallel to [010] (Figure 6), consists of successive CuS_4 and NbS_4 edge-sharing tetrahedra and CuS_4 - CuS_4 corner-sharing tetrahedra. This arrangement creates eight-membered rings along the infinite alternating-metal chains. The Cu-S-Cu angles in this eight-membered ring are 109.72 (9) and 110.76 (9)°. The ring is saddle shaped. Part of this triple chain is reminiscent of the alternating-metal chain structure found in $\text{K}_2\text{CuNbSe}_4$, where the CuSe_4 and NbSe_4 tetrahedra are edge sharing. To our knowledge, the present one-dimensional mixed-metal triple chain consisting of successive corner-sharing and edge-sharing tetrahedra is unique. There are two crystallographically distinct Cu atoms in the structure, and both CuS_4 tetrahedra show S-Cu-S angles that deviate up to about 6° from the tetrahedral value. The Cu-S distances are normal, ranging from 2.333 (2) to 2.360 (2) Å. The NbS_4 tetrahedron is slightly distorted, with S-Nb-S angles deviating by less than 3° from the tetrahedral value. The Nb-S distances range from 2.264 (2) to 2.307 (2) Å.

On the basis of a unit-cell determination, $\text{K}_3\text{Cu}_3\text{Nb}_2\text{Se}_8$ is isostructural with $\text{K}_3\text{Cu}_3\text{Nb}_2\text{S}_8$.

$\text{K}_3\text{CuNb}_2\text{Se}_{12}$. As opposed to the three structures just described, $\text{K}_3\text{CuNb}_2\text{Se}_{12}$ is an infinite one-dimen-

(57) Straumanis, M. E.; Zysczynski, S. *J. Appl. Crystallogr.* 1970, 3, 1-6.

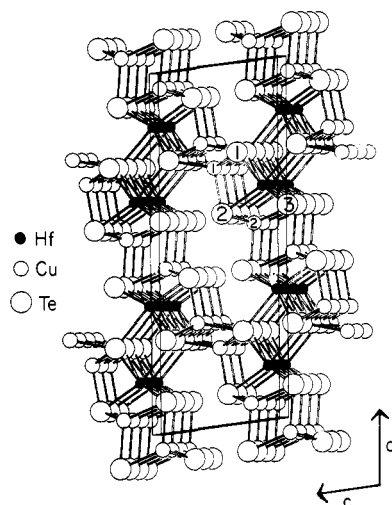


Figure 8. Perspective view of the Cu_2HfTe_3 structure along [010].

sional mixed-metal chain structure that exhibits a wide range of Se_n^{2-} ligands ($n = 2-4$), some of which bind to multiple metal centers (Figure 7). These anionic chains are well separated by K^+ cations. The Cu atom is in a distorted tetrahedral coordination and the two crystallographically independent Nb atoms are seven coordinate. The Cu-centered tetrahedra edge share with the Nb-centered polyhedra. The Nb(1)- and Nb(2)-centered polyhedra in turn share faces to create an infinite mixed-metal alternating chain in the pattern $[-\text{Cu}-\text{Nb}(1)-\text{Nb}(2)-]$.

The coordination polyhedra are rather distorted, owing to the presence of Se-Se bonds. The Cu-Se bond distances range from 2.388 (4) to 2.509 (4) Å with Se-Cu-Se angles between 92.4 (1) and 116.3 (1)°. The Nb-Se distances range from 2.407 (3) to 2.928 (3) Å for Nb(1) and 2.426 (3) to 2.847 (3) Å for Nb(2).

If a maximum Se-Se bond length is considered to be less than 2.75 Å, then the anionic chain may be represented as $\frac{1}{2}[\text{CuNb}_2(\text{Se})_2(\text{Se}_2)_3(\text{Se}_4)^{3-}]$, with the Se_4^{2-} ligand bonded to three metal centers. This formulation leads to formal oxidation states of Cu(I) and Nb(IV). There is an arbitrariness in what can be considered a single Se-Se bond; while the Se-Se single bond is generally around 2.34 Å, Se-Se bonds as long as 2.663 Å have been described in Nb_2Se_9 .⁵⁸ With a cutoff of 2.55 Å for an Se-Se bond, we can alternatively describe the chain as $\frac{1}{2}[\text{CuNb}_2(\text{Se})_3(\text{Se}_2)_3(\text{Se}_3)^{3-}]$. The formal oxidation states are then Cu(I) and Nb(V).

Note that the Se_n^{2-} ($n = 3, 4$) species can exist at temperatures $> 800^\circ\text{C}$. This is not surprising, since Nb_2Se_9 , prepared above 900°C , contains the Se_5^{2-} species.⁵⁸ The Se_3^{2-} species is also found in $\text{K}_2\text{AuSe}_{13}$,⁴⁶ and the Se_4^{7-} species is found in $\alpha\text{-KCuSe}_4$.⁴⁷ Both of these compounds are synthesized by the reactive flux technique in the temperature range $250-340^\circ\text{C}$.

Cu_2MTe_3 ($\text{M} = \text{Ti, Zr, Hf}$). Cu_2HfTe_3 is a new two-dimensional structure type that consists of hexagonally closest packed layers of Te atoms extending orthogonal to [100], in which the distorted octahedral and tetrahedral voids are filled in an unusual manner. The atom labeling is given in the perspective view of Figure 8. One-half the octahedral sites are occupied

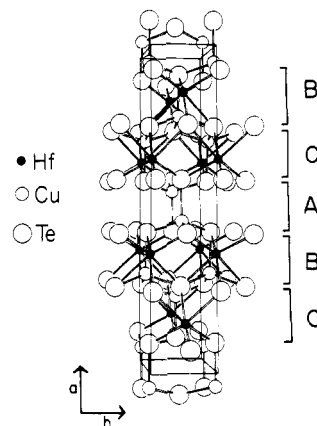


Figure 9. Basic subunits in the Cu_2HfTe_3 structure.

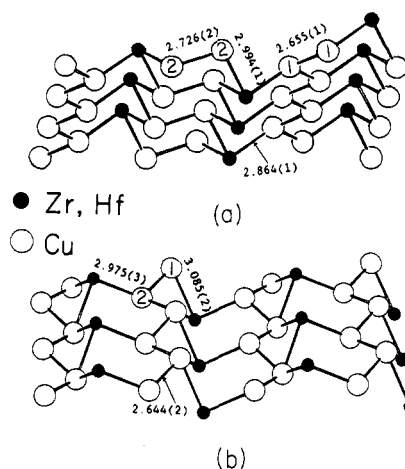


Figure 10. Layers of metal-metal bonded atoms in (a) Cu_2HfTe_3 and (b) $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$.

by Hf atoms in two-thirds of the layers. In these same layers, one-quarter of the tetrahedral sites are filled by Cu(1) atoms, and in the remaining layer, one-half the tetrahedral sites are occupied by Cu(2) atoms.

There are three basic subunits in Cu_2HfTe_3 (Figure 9). Slab A comprises four close-packed and tightly bound layers of Te-Cu(2)-Cu(2)-Te. These Cu(2)-centered tetrahedra are edge sharing, which leads to a Cu(2)-Cu(2) bond length of 2.726 (2) Å.

Within the symmetry-related layers B and C, the octahedra of the Hf atoms and the tetrahedra of the Cu(1) atoms are face sharing. This uncommon connectivity results in a Cu(1)-Hf bond length of 2.864 (1) Å. (Metal-metal distances in hexagonally closest packed Cu and Hf metals are 2.556⁵⁸ and 3.195 Å,⁵⁹ respectively.)

Between layers A and B as well as A and C, the Hf-centered octahedra share edges with the Cu(2)-centered tetrahedra, resulting in another short metal-metal interaction of 2.994 (1) Å between Hf and Cu(2) atoms. As this distance is slightly longer than that of Cu(1)-Hf, the Cu-Hf interactions within the same layer are stronger than between layers.

These four metal-metal bonds interconnect to create graphite-like buckled layers that extend parallel to (201). This arrangement is shown in Figure 10a and is contrasted with a related arrangement (Figure 10b) in the structure of $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$ (vide infra). Alternatively,

(58) (a) Meerschaut, A.; Guémas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* 1979, B35, 1747-1750. (b) Sunshine, S. A.; Ibers, J. A. *Acta Crystallogr.* 1987, C43, 1019-1022.

(59) Russell, R. B. *J. Appl. Phys.* 1953, 24, 232-233.

Table I.
Three-Dimensional Polyhedral Connectivity in $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$ ^a

[100]	[010]	[001]
face sp_y /oct	edge oct/oct	face bctp/oct
edge sp_y /tet	edge sp_y / sp_y	vertex bctp/ sp_y
edge oct/tet	vertex tet/tet	vertex bctp/tet
face bctp/bctp	face bctp/bctp	

^a sp_y = square pyramid; bctp = bicapped trigonal prism; oct = octahedron; tet = tetrahedron.

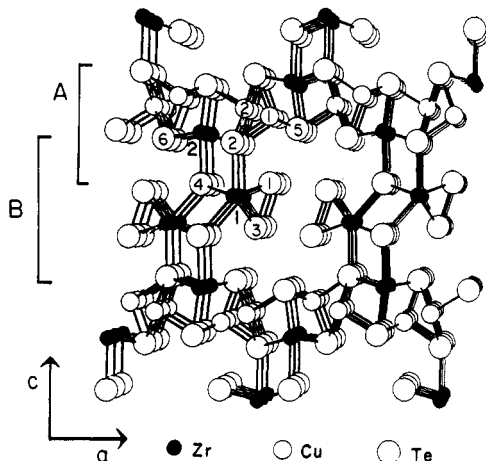


Figure 11. Perspective view of $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$.

the sheets in Cu_2HfTe_3 can be considered as the interlinking of six-membered rings of chair conformation.

As there are no Te–Te bonds, the formal oxidation states can be assigned as Cu(I), Hf(IV), and Te(–II). Resistivity measurements indicate that along [010] Cu_2HfTe_3 and Cu_2ZrTe_3 are metallic, exhibiting nearly linear temperature dependence with $\rho_{298\text{K}} = 3.8 \times 10^{-4}$ and $2.0 \times 10^{-3} \Omega\text{-cm}$ and $\rho_{5\text{K}} = 2.3 \times 10^{-4}$ and $1.8 \times 10^{-3} \Omega\text{-cm}$, respectively. Temperature-dependent magnetic susceptibility measurements indicate Pauli paramagnetic behavior.

On the basis of unit-cell determinations, the Ti and Zr analogues are isostructural with the Hf compound.

$\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$. This compound exhibits a remarkably complex three-dimensional structure in which the coordination polyhedra vertex, edge, and face share in all three crystallographic directions (Table I). This new structure contains two crystallographically independent Zr atoms: atom Zr(1) has bicapped trigonal prismatic coordination, while atom Zr(2) has octahedral coordination by Te atoms. Similarly, there are two crystallographically independent Cu atoms: atom Cu(1) with tetrahedral and atom Cu(2) with square-pyramidal coordination by Te atoms.

The structure can be viewed as layers that extend orthogonal to [001]; layer A at approximately $1/4$ and $3/4$ in z and B at 0 and $1/2$ in z (Figure 11). In the [010] direction, the octahedra and square pyramids edge share while the tetrahedra vertex share with themselves. The bicapped trigonal prisms face share as in ZrTe_5 ,⁶⁰ ZrTe_3 ,⁶¹ and $\text{K}_4\text{Hf}_3\text{Te}_{17}$.⁴⁹

The tetrahedra edge share with both the square pyramids and octahedra. In addition, these square pyramids face share with the adjacent octahedra in the

(60) Furuseth, S.; Brattås, L.; Kjekshus, A. *Acta Chem. Scand.* 1973, 27, 2367–2374.

(61) Furuseth, S.; Brattås, L.; Kjekshus, A. *Acta Chem. Scand.* 1975, A29, 623–631.

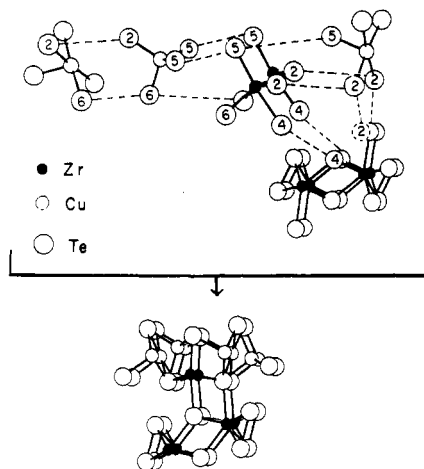


Figure 12. Basic repeat unit in $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$.

same A layer. The overall structure can be viewed as layers of A linked together by bicapped trigonal prismatic dimers, $1/2[\text{Zr}_2\text{Te}_8]$.

To clarify the atomic arrangement in the basic repeat unit, an exploded view is provided (Figure 12). The atomic patterns within layers A and B are the result of condensing the infinite polyhedral chains to form layers that extend orthogonal to their direction of propagation ([010]). Within layer A, the Cu(2) atom shares atom Te(5) and two Te(2) atoms with the Zr(2) atom, which in turn shares the Te(6) atom with the Cu(1) atom. The Cu(1) atom shares this same Te(6) atom as well as Te(2) atoms with the Cu(2) atom, and this sequence then repeats. This ultimate configuration is the basic building unit of the structure. $\text{Cu}_{1.85}\text{Zr}_2\text{Te}_6$ contains one single-bond interaction between atoms Te(1) and Te(3) at 2.735 (2) Å along the edge of the trigonal prisms. This Te–Te single-bond distance is comparable to those found in ZrTe_3 ⁶¹ (2.761 (3) Å) and HfTe_5 ⁶⁰ (2.763 (4) Å).

Most interesting is the metal–metal bonding within layer A as a result of the dense packing of the coordination polyhedra. The Zr(2), Cu(1), and Cu(2) atoms are bonded to one another, with Zr(2)–Cu(1) = 3.085 (2) Å, Zr(2)–Cu(2) = 2.975 (3) Å, and Cu(1)–Cu(2) = 2.644 (2) Å. (The Zr–Zr distance in hexagonally closest packed Zr is 3.234 Å.⁶²) These metal–metal bonds interconnect to create interfused buckled four- and six-membered rings that extend orthogonal to [001] at $z = 1/4$ and $3/4$ (Figure 10b).

Concluding Remarks

The assignments of formal oxidation states made here suggest that during the reactions in the fluxes Cu is oxidized to Cu(I), while the group IV and group V atoms are oxidized to their highest possible levels. In view of the propensity of Cu(I) to disproportionate to Cu(0) and Cu(II) in solution in the presence of chalcogen, this is an interesting result. Of course, the assignment of formal oxidation states in solid-state compounds is an oversimplification that is often useful. The assignment of formal oxidation states of Cu(I), Hf(IV), and Te(–II) in Cu_2HfTe_3 is certainly an oversimplification, as the compound is an excellent metallic conductor and displays Pauli paramagnetism. Indeed, the measurement of transport properties of new materials, such as those described here, is essential to our ultimate under-

(62) Evans, D. S.; Raynor, G. V. *J. Nuc. Mater.* 1961, 4, 66–69.

standing of bonding in these and other solid-state systems. But if compounds have not been prepared, their physical properties cannot be measured! The present eclectic compilation of novel and interesting structure types underscores the enormous potential of the reactive flux method for the synthesis of new sol-

id-state materials.

The research described here was supported by the U.S. National Science Foundation (Grant DMR88-13623). Use was made of Central Facilities supported by the U.S. National Science Foundation through the Northwestern University Materials Research Center (Grant DMR88-21571).

Cytochalasan Synthesis: Macrocyclic Formation via Intramolecular Diels–Alder Reactions

ERIC J. THOMAS

Department of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.

Received April 8, 1991 (Revised Manuscript Received July 1, 1991)

The cytochalasans are fungal metabolites of considerable importance because of their potent biological activities, including effects on transport across mammalian cell membranes and cell morphology.^{1,2} Structurally they are characterized by the presence of a reduced isoindolone nucleus fused to a macrocyclic ring, which can be either a lactone, as in cytochalasin B (1),² a carbonate, as in cytochalasin E (2),³ or a carbocycle, as in cytochalasins D,² H,⁴ and K (3–5).⁵ The biosynthesis of the cytochalasans has been studied⁶ and the N(2)–C(4) fragment shown to be derived from an amino acid, usually phenylalanine,⁷ although other amino acids can be incorporated, e.g., tryptophan into cytochalasin G (6)⁸ and leucine into the aspochalasans, e.g., aspochalasin C (7)⁹ (Scheme I).

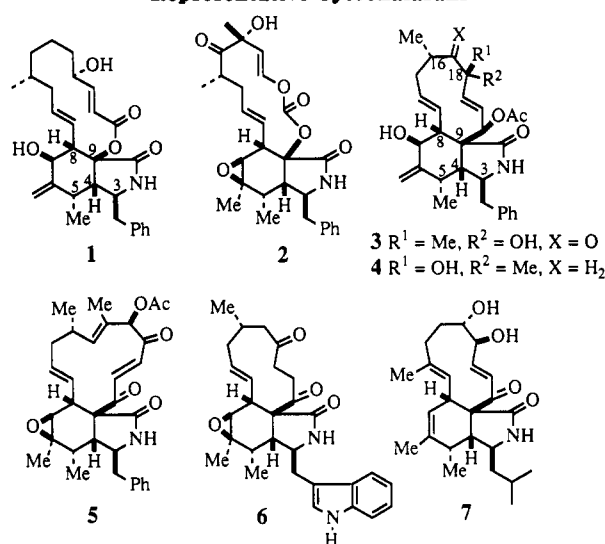
In developing a synthesis of the cytochalasans, two problems that have to be overcome are the control of stereochemistry, particularly around the heavily functionalized isoindolone nucleus, and the efficient formation of the macrocyclic ring. Most approaches to the isoindolone have used Diels–Alder reactions. However, the efficient formation of macrocyclic rings is still a major problem in organic synthesis because of competing intermolecular processes, and several approaches have been developed for the introduction of the macrocyclic ring into cytochalasan precursors including ring-expansion and fragmentation processes, together with direct ring formation. The *simultaneous* formation of the isoindolone and the large ring via an intramolecular Diels–Alder reaction is the focus of the present Account, although relevant intermolecular Diels–Alder reactions will be discussed first to introduce the chemistry that is involved.

Hydroisoindolone Synthesis via Intermolecular Diels–Alder Reactions

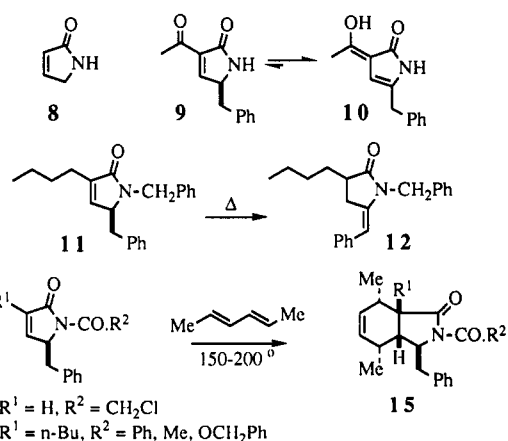
Synthesis of the isoindolone fragment of the cytochalasans via Diels–Alder reactions of pyrrol-2(5*H*)-ones

E. J. Thomas was born in 1946 in Stockport, England. He earned B.A. (1968), M.A., and Ph.D. (1971) degrees at Cambridge University and has held the following appointments: Postdoctoral Assistant, Dyson Perrins Laboratory, Oxford, 1971–1973; University Lecturer, University of London, King's College, 1973–1979; University Lecturer, University of Oxford, and Fellow of Exeter College, 1979–1988; Professor of Organic Chemistry, University of Manchester, 1988–present. His research interests include aspects of β -lactam chemistry, total synthesis of natural products, and the development of new synthetic methods with particular reference to organotin chemistry.

Scheme I Representative Cytochalasans



Scheme II Pyrrol-2(5*H*)-ones as Dienophiles



has been widely investigated, with the nature of the N-substituent being found to be particularly important.

(1) Pendse, G. S. *Recent Advances in Cytochalasans*; Chapman and Hall: London, 1986.

(2) Binder, M.; Tamm, C. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 370–380.