Synthesis of $CsCuS_6$ and $Cs_6Cu_2(TeS_3)_2(S_6)_2$ in Molten $Cs_2S_xTe_y$ Salts. Novel Compounds Containing Polychalcogenide Ligands

Timothy J. McCarthy, Xiang Zhang, and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

Received November 13, 1992

The reaction of Cu with excess Cs_2S_x and $Cs_2S_xTe_y$ produced two new copper/polychalcogenides $CsCuS_6$ (**1**) and $Cs_6Cu_2(S_6)_2(TeS_3)_2$ (**2**). Orange-red **1** was synthesized by the reaction of copper powder with Cs_2S_{11} in the 1.25:1 molar ratio at 270 °C for 4 days. Red **2** was synthesized by the reaction of copper powder with $Cs_2S_6Te_{0.7}$ in the 2:3 molar ratio at 230 °C for 96 h or by the reaction of CuTe with Cs_2S_6 in a 2:3 molar ratio at 250 °C for 96 h. Crystal data for **1**: triclinic $P\bar{1}$, $Z = 2$, $a = 10.664(2)$ Å, $b = 11.223(1)$ Å, $c = 7.1599(8)$ Å, $\alpha = 94.64(1)°$, $\beta = 101.32(1)°$, $\gamma = 74.04(1)°$, $V = 807.5(4)$ Å^3, $2\theta_{max} = 60°$. Number of data measured: 4709. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 2800. Final $R/R_w = 0.036/0.044$. Crystal data for **2**: $a = 21.072(4)$ Å, $b = 13.173(3)$ Å, $c = 11.948(2)$ Å, $V = 3317(1)$ Å^3 at 20 °C, $2\theta_{max} = 55°$, space group *Cmca*, Mo Kα radiation. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 1437. Final $R/R_w = 0.031/0.026$. The structure of $CsCuS_6$ is assembled from one-dimensional $[Cu(S_6)]_n^{n-}$ centrosymmetric chains (running parallel to the crystallographic [011] direction) separated by Cs^+ atoms. $Cs_6Cu_2(S_6)_2(TeS_3)_2$ contains a dimeric anion assembled from two tetrahedral Cu^+ atoms joined by two trigonal pyramidal TeS_3^{2-} ligands and two chelating S_6^{2-} ligands. The infrared and UV/vis/near-IR spectra of these compounds are reported.

Introduction

Solid-state compounds with polychalcogenide units in the lattice are still rare despite recent discoveries.[1,2] The use of molten alkali metal/polychalcogenide fluxes as both reactants and solvent media affords a wide variety of new alkali metal/transition metal/polychalcogenide compounds, especially when the reaction temperature is held within the range of 200–400 °C.[1] Copper reacts with various alkali metal/polychalcogenide fluxes and forms, among many, α-$ACuQ_4$ (A=K, Rb, Cs; Q=S, Se) and β-$KCuS_4$.[1,3] These compounds have one-dimensional structures and contain S_4^{2-} ligands. Further experimentation with Cs_2S_x fluxes as well as *mixed* $Cs_2S_xTe_y$ fluxes revealed two new solid-state copper/polychalcogenide compounds $CsCuS_6$ and $Cs_6Cu_2(S_6)_2(TeS_3)_2$, which also feature long polysulfide ligands. The mixed fluxes were used on the basis of the premise that the large size difference between S and Te would result in mixed S-/Te-containing compounds in which these elements would occupy well-defined ordered sites and not be positionally disordered. Furthermore, Te can play a dual role in such fluxes, one as a chalcogenide ion and one as a metalloid in which it can be oxidized by the polysulfide flux and form high oxidation state ions in the same way other metals do. The role will be influenced by the x/y ratio in the $A_2S_xTe_y$ flux. $CsCuS_6$ possesses a novel, one-dimensional structure containing exclusively $(S_6)^{2-}$ units, while $Cs_6Cu_2(S_6)_2(TeS_3)_2$ contains a discrete molecular complex anion with a remarkable butterfly-type structure containing both $(S_6)^{2-}$ units and the novel TeS_3^{2-} ligand. The latter has been known for some time as an alkali or alkaline earth salt,[4-6] but on the basis of the results reported in this paper, it promises to be a new multidentate ligand for new coordination chemistry involving transition metals, either in the molecular or the solid-state regime. It is noteworthy that $Cs_6Cu_2(S_6)_2(TeS_3)_2$ can also be prepared by the reaction of CuTe with Cs_2S_x flux.

Experimental Section

Reagents. Chemicals in this work were used as obtained: (i) copper electrolytic dust, Fisher Scientific Co., FairLawn, NJ; (ii) sulfur powder, sublimed, J. T. Baker Chemical Co., Phillipsburg, NJ; (iii) tellurium powder, 200 mesh, cesium metal, analytical reagent, Johnson Matthey/AESAR Group, Seabrook, NH: (iv) methanol, anhydrous, Mallinckrodt Inc., Paris, KY: DMF, analytical reagent, diethyl ether, ACS anhydrous, EM Science, Inc., Gibbstown, NJ.

All manipulations were carried out in a glovebox under a nitrogen atmosphere. Cs_2S was prepared by dissolving the stoichiometric amount of the elements in liquid ammonia.

Preparation of $CsCuS_6$. A 0.032-g amount (0.50 mmol) of Cu, 0.119 g (0.40 mmol) of Cs_2S, and 0.128 g (4.00 mmol) of S were mixed together with a spatula in a glass vial. The mixture was transferred to a 6-mL Pyrex tube and was subsequently flame-sealed in vacuum (~10^{-3} Torr). The mixture was heated to 270 °C over a 12-h period in a computer-controlled furnace and then isothermed at 270 °C for 96 h, followed by cooling to 130 °C at a rate of 2 °C/h and then to 50 °C in 1 h. The excess Cs_2S_x was dissolved in 150 mL of degassed methanol to give a yellow solution. The insoluble product was washed with methanol repeatedly until the washings were colorless and then with ether. The product was then washed with ethylenediamine followed by ether to remove a small amount of orange powder giving 0.115 g (59% yield) of transparent, red rectangular platelike crystals. Quantitative microprobe analysis on the red single crystals gave $Cs_{1.0}Cu_{1.2}S_{5.9}$ (average of three data acquisitions).

Preparation of $Cs_6Cu_2(S_6)_2(TeS_3)_2$. Method A. A 0.032-g amount (0.50 mmol) of Cu, 0.224 g (0.75 mmol) of Cs_2S, 0.064 g (0.50 mmol) of Te, and 0.128 g (4.0 mmol) of S were mixed and loaded into a Pyrex tube, which was subsequently flame-sealed under vacuum. The mixture was heated to 230 °C in 12 h, kept constant for an additional 96 h, followed by cooling to 100 °C at a rate of 2 °C/h and then to 50 °C at 5 °C/h. The product mixture was washed with DMF overnight to remove excess flux. Red crystals obtained slowly dissolve in DMF upon further washing. The solid product was further washed with ethanol and ether giving 0.304 g (69% yield) of dark red chunky crystals. Quantitative microprobe analysis on the single crystals gave a composition of $Cs_{2.7}Cu_{1.0}Te_{1.1}S_{8.2}$.

Method B. A 0.096-g amount (0.50 mmol) of CuTe (made by combination of elements at 400 °C), 0.224 g (0.50 mmol) of Cs_2S, and

---

[1] (a) Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 353–363. (b) Kanatzidis, M. G.; Park, Y. *Chem. Mater.* **1990**, *2*, 99–101. (c) Park, Y.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 914–915. (d) Park, Y. Ph.D. Dissertation, Michigan State University, 1992.

[2] (a) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202–6204. (b) Kang, D.; Ibers, J. A. *Inorg. Chem.* **1989**, *27*, 549–551.

[3] Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767–3769.

[4] Jumas, J.-C.; Bibes, M.; Maurin, M.; Philippot, E. *Acta Crystallogr.* **1976**, *32B*, 444–448.

[5] Dittmar, G.; Schafer, H. *Z. Anorg. Allg. Chem.* **1978**, *439*, 212–218.

[6] Gerl, H.; Eisenmann, B.; Roth, P.; Schafer, H. *Z. Anorg. All. Chem.* **1974**, *407*, 135–143.

0020-1669/93/1332-2944$04.00/0

Table I. Crystallographic Data for $CsCuS_6$ and $Cs_6Cu_2(TeS_3)_2(S_6)_2$

	$CsCuS_6$	$Cs_6Cu_2(TeS_3)_2(S_6)_2$
formula	$CsCuS_6$	$Cs_6Cu_2Te_2S_{18}$
fw	388.82	1756.82
a, Å	10.664(2)	21.072(4)
b, Å	11.223(1)	13.173(3)
c, Å	7.1599(8)	11.948(2)
α, deg	94.64(1)	90.0
β, deg	101.32(1)	90.0
γ, deg	74.04(1)	90.0
V, Å^3	807.5(4)	3317(1)
Z	2	4
space group	$P\bar{1}$ (No. 2)	*Cmca* (No. 64)
T, °C	20	20
λ, Å (Mo Kα)	0.710 73	0.710 73
ρ_{calcd}, g·cm^{-3}	3.198	3.518
μ, cm^{-1}	85.224	105.59
$R(F_o)^a$	0.036	0.031
$R_w(F_o)^a$	0.044	0.026

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

0.128 g (4.0 mmol) of S were used. The procedure was the same as in method A, except that the reaction was held at 250 °C. Yield: 72%.

Physical Measurements. Infrared Spectroscopy. FT-IR spectra of the two compounds were recorded as solids in a CsI matrix. The sample was ground with dry CsI into a fine powder, and a pressure of about 7 metric tons was applied to the mixture to make a translucent pellet. The spectra were recorded in the far-IR region (600-100 cm^{-1}, 4-cm^{-1} resolution) with the use of a Nicolet 740 FT-IR spectrometer equipped with a TGS/PE detector and silicon beam splitter.

Electron Microscopy. Quantitative microprobe analysis of the compounds was performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 1-min accumulation time. A 1.2 correction factor was applied to the Te atomic percent in this system as a result of examination of several other Te containing crystals.

UV/Vis/Near-IR Spectroscopy. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The measurement of diffuse reflectivity can be used to obtain values for the band gap which agree rather well with values obtained by absorption measurements from single crystals of the same material. The digitized spectra were processed using the Kaleidagraph software program. $BaSO_4$ powder was used as reference at all energies (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka-Munk function:[7]

$$\alpha/S = \frac{(1-R)^2}{2R}$$

R is the reflectance at a given wavelength, a is the absorption coefficient, and S is the scattering coefficient. The scattering coefficient has been shown to be practically wavelength independent for particles larger than 5 mm, which is smaller than the particle size of the samples used here.[7a,b] The band gap was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a $(\alpha/S)^2$ vs E plot.

Crystallographic Studies. Both compounds were examined by X-ray powder diffraction for the purpose of phase purity and identification. Accurate d_{hkl} spacings (Å) were obtained from the powder patterns recorded on a calibrated (with FeOCl as internal standard) Phillips XRG-3000 computer-controlled powder diffractometer with Ni-filtered Cu Kα radiation operating at 35 kV and 35 mA. The data were collected at a rate of 0.002°/s.

Table II. Fractional Atomic Coordinates and B_{eq} Values for $CsCuS_6$ with Estimated Standard Deviations (Esd's) in Parentheses

atom	x	y	z	$B_{eq}{}^a$
Cs(1)	0.69760(5)	0.57849(5)	0.17031(7)	2.51(2)
Cs(2)	0.30248(6)	0.92783(5)	0.31970(8)	2.94(3)
Cu(1)	0.4928(1)	0.3874(1)	0.3999(1)	2.87(5)
Cu(2)	0.4972(1)	0.8706(1)	−0.1540(2)	2.88(5)
S(1)	0.6210(2)	0.7634(2)	0.6191(3)	2.11(8)
S(2)	0.8007(2)	0.7303(2)	−0.1927(3)	2.48(9)
S(3)	0.9331(2)	0.5973(2)	0.6809(3)	2.7(1)
S(4)	0.9344(2)	0.4299(2)	0.7843(3)	2.8(1)
S(5)	0.8013(2)	0.3606(2)	0.5913(3)	2.61(9)
S(6)	0.3751(2)	0.5872(2)	0.3049(3)	2.27(8)
S(7)	0.3926(2)	0.7178(2)	−0.1530(3)	2.45(9)
S(8)	0.2004(2)	0.7592(2)	−0.1020(3)	2.26(8)
S(9)	0.0803(2)	0.8886(2)	−0.2925(3)	2.8(1)
S(10)	0.0809(2)	1.0616(2)	−0.1641(3)	2.8(1)
S(11)	0.8021(2)	0.8671(2)	0.2965(3)	2.33(8)
S(12)	0.6082(2)	0.9233(2)	0.1562(3)	2.28(8)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Fractional Atomic Coordinates and B_{eq} Values for $Cs_6Cu_2(S_6)_2(TeS_3)_2$ with Estimated Standard Deviations (Esd's) in Parentheses

atom	x	y	z	$B_{eq}{}^a$
Cs(1)	0	0.04069(6)	0.16866(7)	1.95(3)
Cs(2)	0.15414(3)	0.29650(4)	0.17837(5)	2.29(2)
Te	0	−0.23313(6)	0.57785(7)	1.24(3)
Cu	0.07044(7)	0	1/2	2.21(7)
S(1)	0	−0.1255(2)	0.4163(3)	1.5(1)
S(2)	−0.0863(1)	−0.3397(2)	0.5471(2)	1.81(9)
S(3)	0.1275(1)	0.0623(2)	0.3517(2)	1.89(9)
S(4)	0.2095(1)	0.1320(2)	0.4038(2)	2.3(1)
S(5)	0.2792(1)	0.0232(2)	0.4167(2)	2.8(1)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Experimental details of both compounds are given in Table I. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6 diffractometer for $CsCuS_6$ and a four-circle Nicolet (Siemens) automated diffractometer for $Cs_6Cu_2(S_6)_2(TeS_3)_2$, respectively. All data were corrected for Lorentz and polarization effects. None of the crystals showed any significant intensity decay upon monitoring check reflections periodically throughout data collection. The space groups were determined from systematic absences and intensity statistics. The structures were solved by direct methods of SHELXS-86[8a] and refined with the TEXSAN package of crystallographic programs.[8c] Empirical absorption correction based on ψ-scans were applied to each data set, followed by a DIFABS[8b] correction to the isotropically refined structure. All atoms were eventually refined anisotropically. All calculations were performed on a VAXstation 3100 Model 76 computer. The coordinates and average temperature factors (B_{eq}) of all atoms and their estimated standard deviations for both compounds are given in Tables II and III.

Results and Discussion

The synthesis of $CsCuS_6$ was accomplished by the reaction of copper powder with Cs_2S_{11} in the 1.25:1 molar ratio at 270 °C for 4 days and cooling at 2°/h. The orange-red rectangular platelike crystals obtained are stable in air and water. The window of stability for this compound is relatively narrow and its upper temperature is ~300 °C.

Mixed S/Te compounds are very rare. A handful of examples exist in the mineral world such as $Bi_8Te_7S_5$ and $Bi_6(TeS_3)$.[9] The synthesis of orange-red $Cs_6Cu_2(S_6)_2(TeS_3)_2$ was accomplished by the reaction of copper powder with $Cs_2S_6Te_{0.7}$ in the 1:1.5 molar ratio at 230 °C for 96 h. The formal oxidation state of

---

(7) (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Kotüm, G. *Reflectance Spectroscopy*; Springer Verlag: New York, 1969. (c) Tandon, S. P.; Gupta, J. P. *Phys. Stat. Solidi* **1970**, *38*, 363-367.

(8) (a) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C. C., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175-189. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *39A*, 158. (c) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, 1991, Molecular Structure Corp., The Woodlands, TX 77381.

(9) Beglaryan, M. L.; Abrikasov, H. K. *Dokl. Akad. Nauk. SSSR* **1959**, *129*, 135.

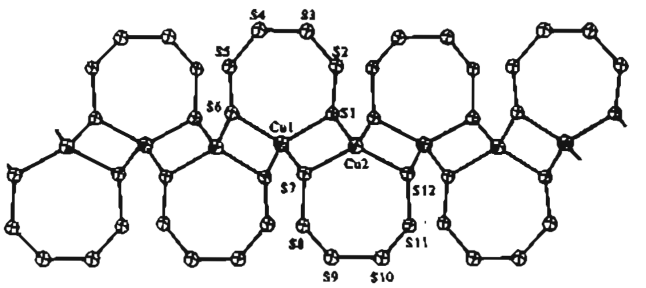
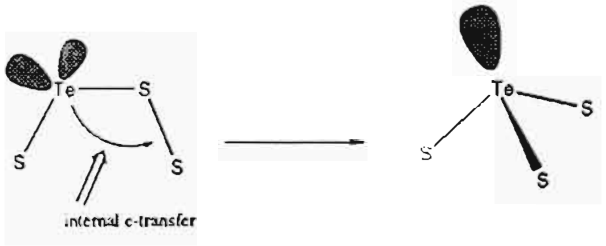


Figure 1. View of the $[Cu(S_6)]_n^{n-}$ infinite chain with labeling scheme.

Scheme I



Te in this compound is +4. The upper limit for formation of this new compound lies near 260 °C. Interestingly, $Cs_6Cu_2(S_6)_2(TeS_2)_2$ can also be prepared by the reaction of CuTe with Cs_2S_6 flux in a 1:1.5 molar ratio at 250 °C for 96 h. This observation implies that binary and ternary metal tellurides may be good starting materials for reactions with A_2S_x fluxes to yield new mixed multinary S/Te compounds. In both methods, the Te is found in a S-rich environment and acts as a metalloid being oxidized and then coordinated by sulfide ions. Thus, instead of forming a mixed S/Te polychalcogenide chain, a pyramidal isomeric structure occurs which places the Te at a apex surrounded by three sulfide ions; see Scheme I. This structure results from internal redox chemistry between Te and S–S bonds. This redox behavior is a consequence of the electronegativity differences between S and Te.

The solid-state far-IR spectrum of $CsCuS_6$ in a CsI matrix shows a broad overlapping collection of absorbences associated with S–S and Cu–S stretching vibrations at 470, 462, 453, and 441 cm^{-1}. The corresponding far-IR spectrum of $Cs_6Cu_2(S_6)_2(TeS_3)_2$ also shows a rich collection of absorbances associated with S–S, Te–S, and Cu–S stretching vibrations. These are at 485, 449, and 437 cm^{-1}, which are attributed to S–S vibrations, at 371 and 327 cm^{-1}, which are attributed to Te–S vibrations, and at 257, 237, 197, and 182 cm^{-1}, for low-energy absorptions, which may be bending modes in the molecule.

Structure of $CsCuS_6$. The structure of $CsCuS_6$ is assembled from one-dimensional $[Cu(S_6)]_n^{n-}$ centrosymmetric chains (running parallel to the crystallographic [011] direction) separated by Cs^+ atoms. This compound represents a rare example of a solid-state compound containing a long polychalcogenide. The chain structure is shown in Figure 1, and it features a new binding mode for a S_6^{2-} ligand which chelates a copper atom via its terminal sulfur atoms. This mode of ligation for S_6^{2-} is similar to that of the S_4^{2-} ligand in β-$KCuS_4$. The S_6^{2-} ligands also act as bridges to other copper atoms forming a zigzag array (Cu–Cu–Cu angle is 174°), which is comparable to the linear Cu–Cu–Cu spine observed in β-$KCuS_4$. The $[Cu(S_6)]_n^{n-}$ chains can be viewed as being composed of fused seven-membered CuS_6 rings and Cu_2S_2 rhombi. The center of symmetry lies at the center of the Cu_2S_2 rhombi. The formally monovalent copper atoms are tetrahedrally coordinated by sulfur atoms. The Cu–S distances range from 2.277(2) to 2.414(2) Å with an average of 2.34(5) Å. The Cu–Cu distances, ranging from 2.830(2) to 3.509(2) Å, are much longer than the 2.66 Å observed in β-$KCuS_4$.[3] The average S–S distance in the S_6^{2-} ligand is 2.06(1) Å, and it ranges from 2.041(3) to 2.081(3) Å. Selected distances and angles are given in Table IV. The $[Cu(S_6)]_n^{n-}$ chains run parallel to each other and alternate with rows of Cs^+ atoms forming a single layer. These layers stack directly on top of each other separated only by van der Waals contacts. This is best shown in the packing diagrams of Figures 2 and 3. This compound can be thought of as pseudo-two-dimensional in the sense that the two most important types of bonding are found in the crystallographic *bc* plane. That is, along the [011] direction bonding is mostly covalent (within the $[Cu(S_6)]_n^{n-}$ chains) while perpendicular to it bonding is ionic (between Cs^+ and $[Cu(S_6)]_n^{n-}$ chains). Along the *a*-axis only van der Waals contacts are found. The Cs^+ ions are 12-coordinate with Cs–S distances ranging from 3.645(2) to 3.867(2) Å with an average of 3.75(8) Å.

Table IV. Selected Distances (Å) and Angles (deg) in the $[CuS_6]_n^{n-}$ Chains with Standard Deviations in Parentheses[a]

Cu(1)–S(1)	2.320(2)	S(4)–S(5)	2.048(3)
Cu(1)–S(6)	2.331(2)	S(5)–S(6)	2.076(3)
Cu(1)–S(6)′	2.342(2)	S(7)–S(8)	2.071(3)
Cu(1)–S(7)	2.394(2)	S(8)–S(9)	2.055(3)
Cu(2)–S(1)	2.341(2)	S(9)–S(10)	2.081(3)
Cu(2)–S(7)	2.289(2)	S(10)–S(11)	2.057(3)
Cu(2)–S(12)	2.414(2)	S(11)–S(12)	2.063(3)
Cu(2)–S(12)′	2.277(2)	S–S(mean)	2.06(1)
Cu–S(mean)	2.34(5)	Cu(2)–Cu(2)′	3.509(2)
S(1)–S(2)	2.074(3)	Cu(2)–Cu(1)′	3.252(2)
S(2)–S(3)	2.041(3)	Cu(1)–Cu(1)″	2.830(2)
S(3)–S(4)	2.070(3)	Cu–Cu(mean)	
Cu(1)–S(1)–S(2)	115.8(1)	Cu(1)′–Cu(1)–Cu(2)	174.24(7)
Cu(1)–S(6)–S(5)	109.8(1)	Cu(1)–Cu(2)–Cu(2)′	173.86(6)
Cu(1)–S(7)–S(8)	136.1(1)	S(1)–S(2)–S(3)	106.6(1)
Cu(2)–S(1)–S(2)	94.3(1)	S(2)–S(3)–S(4)	106.0(1)
Cu(2)–S(7)–S(8)	121.1(7)	S(3)–S(4)–S(5)	106.4(1)
Cu(2)–S(12)–S(11)	132.6(1)	S(4)–S(5)–S(6)	106.0(1)
S(1)–Cu(1)–S(6)	118.83(8)	S(7)–S(8)–S(9)	108.8(1)
S(1)–Cu(1)–S(7)	90.64(8)	S(8)–S(9)–S(10)	106.5(1)
S(1)–Cu(2)–S(7)	92.75(8)	S(9)–S(10)–S(11)	106.6(1)
S(7)–Cu(2)–S(12)′	123.79(9)	S–S–S(mean)	107(1)
Cu(1)–S(1)–Cu(2)	88.48(8)		

[a] The estimated standard deviations in the mean bond lengths and the mean bond angles are calculated by the equations $\sigma l = \{\sum_n (l_n - l)^2/n(n-1)\}^{1/2}$, where l_n is the length (or angle) of the *n*th bond, *l* the mean length (or angle), and *n* the number of bonds.

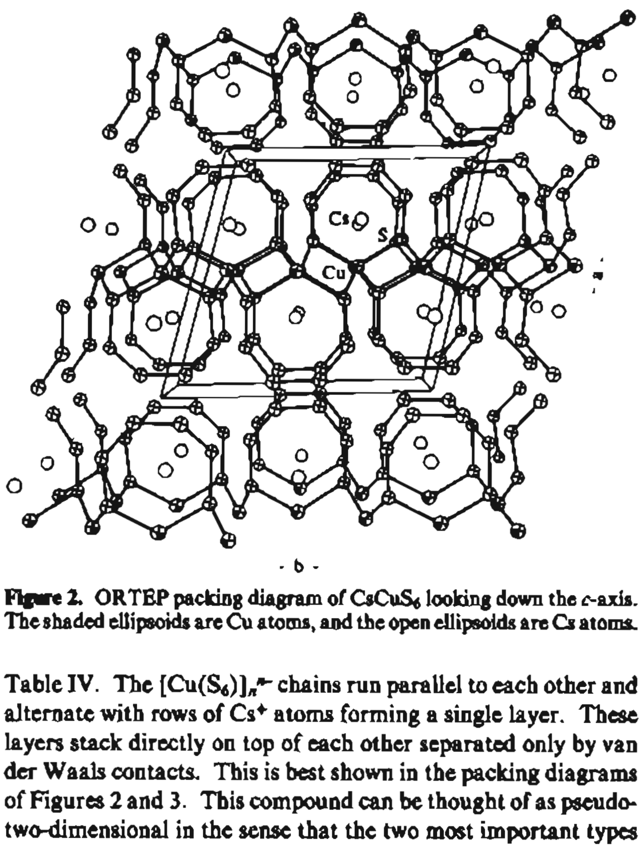


Figure 2. ORTEP packing diagram of $CsCuS_6$ looking down the *c*-axis. The shaded ellipsoids are Cu atoms, and the open ellipsoids are Cs atoms.

Extended solid-state structures containing long polychalcogenides (e.g. S_x^{2-}, $x \geq 4$) are rare and include $KAuQ_5$,[1c] K_3AuSe_{13},[1c] $(Ph_4P)AgSe_4$,[10] $(Me_4N)AgQ_5$,[10,11] α- and β-$KCuQ_4$,[3]

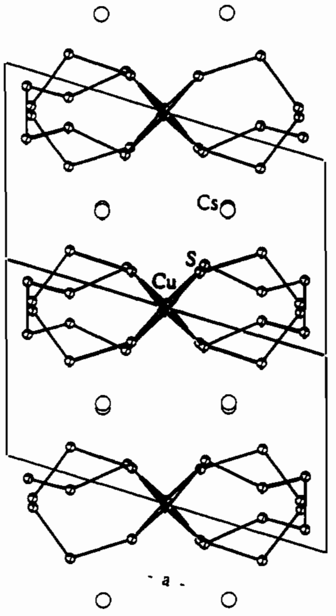


Figure 3. ORTEP packing diagram of $CsCuS_6$ along the [011] direction.

$K_2Sn_2S_2(S_4)_2$,[12] K_2PdSe_{10}[13] and $(H_3NCH_2CH_2NH_3)Cu_2S_{10}$,[14] and $(NH_4)_2PdS_{11}$.[15] Such compounds are only recent additions to the literature and are expected to have interesting reactivity in the solid state by virtue of their Q–Q bonds. Available evidence, to date, suggests that such structures are most likely to be stabilized from polychalcogenide-rich environments and at intermediate to low temperatures (e.g. $T < 300$ °C), the exact maximum temperature depending on the particular system.

Structure of $Cs_6Cu_2(S_6)_2(TeS_3)_2$. $Cs_6Cu_2(S_6)_2(TeS_3)_2$ contains an unusual dimeric anion which is shown in Figure 4. The complex, which is situated on a crystallographic mirror plane and an inversion center, is assembled from two tetrahedral Cu^+ atoms joined by two trigonal pyramidal TeS_3^{2-} ligands. The latter are monodentate utilizing only one of the three sulfur atoms potentially available for bonding. This creates a Cu_2S_2 rhombic unit which is then ligated at each of the Cu sites by two S_6^{2-} ligands. The Cu–Cu distance is 2.969(3) Å precluding any significant Cu–Cu interaction. The Cu–S distances are normal and range from 2.293(2) to 2.437(3) Å (average 2.36(8) Å). The Te–S distances range from 2.327(2) to 2.395(3) Å (average 2.35(4) Å). The S–S distances range from 2.053(3) to 2.083(5) Å (average 2.06(1) Å). Selected distances and angles are given in Table V.

The formal +4 oxidation state for Te makes the TeS_3^{2-} ion isoelectronic to SO_3^{2-}. Since this is the first transition metal complex to contain this new TeS_3^{2-} ligand, this bonding mode is one of potentially many others which are possible. This result forecasts a new direction in the synthesis of new complexes prepared by exploiting the coordination chemistry of the TeS_3^{2-} ligand. To the best of our knowledge, the only other Te/S mixed-chalcogenide compounds known in the literature include $BaTeS_3$,[4] $K_3(SH)TeS_3$,[5] K_2TeS_3,[6] and $(NH_4)_2TeS_3$.[6]

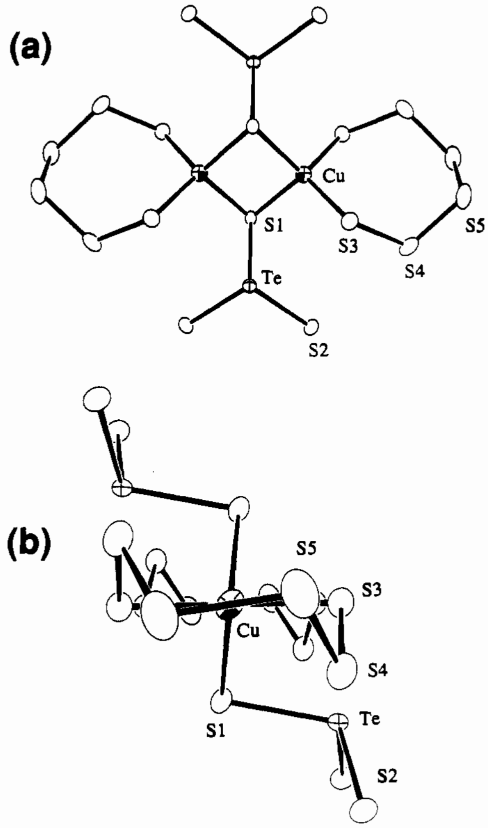


Figure 4. ORTEP representation and labeling scheme of the dimeric anion $[Cu_2(S_6)_2(TeS_3)_2]^{6-}$.

Table V. Selected Distances (Å) and Angles (deg) in the $[Cu_2(S_6)_2(TeS_3)_2]^{6-}$ Anion with Standard Deviations in Parentheses[a]

Cu–S(1)	2.437(3)	Cu- - -Cu	2.969(3)
Cu–S(3)	2.293(2)	S(3)–S(4)	2.053(3)
Te–S(1)	2.395(3)	S(4)–S(5)	2.057(3)
Te–S(2)	2.327(2)	S(5)–S(5)′	2.083(5)
S(1)–Cu–S(1)′	104.9(1)	S(2)–Te–S(2)′	102.8(1)
S(1)–Cu–S(3)	104.18(9)	Cu–S(3)–S(4)	111.5(1)
S(1)–Cu–S(3)′	113.17(9)	S(4)–S(5)–S(5)′	106.0(2)
S(3)–Cu–S(3)′	116.8(1)	S(4)–S(5)–S(5)′	106.0(2)
S(1)–Te–S(2)	103.29(8)	Cu–S(1)–Cu	106.0(2)

Conformation of the S_6^{2-} Ligands. The occurrence of S_6^{2-} ligands is rather rare. Examples of polysulfide complexes with S_6^{2-} ligands include $[Mn(S_6)(S_5)]^{2-}$,[16] $[Hg(S_6)_2]^{2-}$,[17] $[Bi_2(S_7)S_6]^{4-}$,[18] and $[Sn(S_6)(S_4)_2]^{2-}$.[12] The observed S–S bonds are in the normal range of single S–S bond distances reported for other metal–polysulfide compounds.[19] It is interesting to note that in the seven-membered CuS_6 ring the Cu(1), S(1), S(3), S(4), and S(6) atoms lie very close to a plane with S(2) and S(5) positioned respectively 1.12 and 1.09 Å above and below it. In $Cs_6Cu_2(S_6)_2(TeS_3)_2$, Cu, S(3), S(5), S(5′), and S(3)′ define an excellent least-squares plane with S(4) and S(4)′ disposed respectively 1.13 Å above and below it. The same conformation has also been observed in the seven-membered InS_6 and HgS_6 rings in the $[In(S_4)(S_6)_2Br]^{2-}$ [20] and $[Hg(S_6)_2]^{2-}$ [17] complexes and appears to be the most stable stereochemical conformation.

The optical properties of $CsCuS_6$ and $Cs_6Cu_2(S_6)_2(TeS_3)_2$ were assessed by studying the UV/visible/near-IR reflectance spectra of the materials, which are found to be wide band-gap semiconductors. The spectra, shown in Figures 5 and 6, exhibit intense,

---

(10) (a) Kanatzidis, M. G.; Huang, S.-P. *J. Am. Chem. Soc.* **1989**, *111*, 760–761. (b) Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1991**, *30*, 1455–1466.

(11) Banda, R. M. H.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *Polyhedron* **1989**, *8*, 2379–2383.

(12) Liao, H.-J.; Varotsis, K.; Kanatzidis, M. G. Submitted for publication.

(13) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878–4883.

(14) Kiel, G.; Gattow, G.; Dingeldein, T. *Z. Anorg. Allg. Chem.* **1991**, *596*, 111–119.

(15) (a) Haradem, P. S.; Cronin, J. L.; Krause, R. L.; Katz, L. *Inorg. Chim. Acta* **1977**, *25*, 173–179 and references therein. (b) Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1969**, *8*, 779–783.

(16) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24–31.

(17) Müller, A.; Zimmermann, M.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 273–274.

(18) Müller, A.; Schimanski, J.; Schimanski, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 159–160.

(19) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742–757.

(20) Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1991**, *10*, 1069–1073.

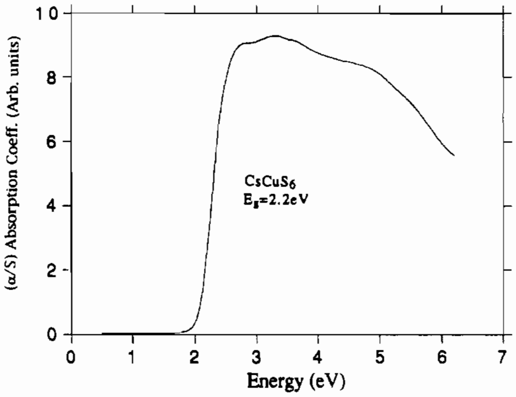


Figure 5. Optical absorption spectrum of $CsCuS_6$.

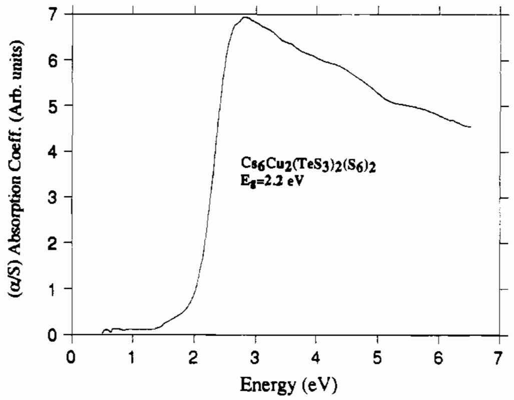


Figure 6. Optical absorption spectrum of $Cs_6Cu_2(S_6)_2(TeS_3)_2$.

steep absorption edges with the same onset at ~2.2 eV. In the case of the polymeric $CsCuS_6$ 2.2 eV can be taken to represent its band gap while in $Cs_6Cu_2(S_6)_2(TeS_3)_2$ the 2.2-eV value represents the HOMO–LUMO gap in the molecular ion $[Cu_2(S_6)_2(TeS_3)_2]^{6-}$. The origin of these electronic transitions is most likely S → Cu charge transfer in character.

The isolation of $Cs_6Cu_2(S_6)_2(TeS_3)_2$ and occurrence of the $[TeS_3]^{2-}$ ligand point to the possible excellent utility of this ligand for coordination to a large number of metal ions in a conceptually similar fashion as $[MoS_4]^{2-}$,[21] dithiocarbamates,[22] dithiophosphates,[23] $[VS_4]^{3-}$,[24] etc. Work exploring this idea is in progress.[25]

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-9202428) and the Beckman Foundation is gratefully acknowledged. M.G.K. is an A. P. Sloan Foundation Fellow (1991–1993).

Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, and bond angles, and anisotropic thermal parameters (43 pages). Ordering information is given on any current masthead page.

---

(21) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955. (b) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201–209. (c) Müller, A. *Polyhedron* **1986**, *5*, 323–340. (d) Müller, A.; Bögge, H.; Schimanski, U.; Penk, M.; Nieradzik, K.; Dartmann, M.; Krickemeyer, E.; Schimanski, J.; Römer, C.; Römer, M.; Dornfeld, H.; Wienböker, U.; Hellmann, W.; Zimmermann, M. *Monatsh. Chem.* **1989**, *120*, 367–391.

(22) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233–371. (b) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301–469.

(23) (a) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65–129. (b) Mehrotra, R. C.; Svrivastava, G.; Chauhan, B. P. S. *Coord. Chem. Rev.* **1984**, *55*, 207–259.

(24) Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731–6732.

(25) (a) Zhang, X.; Kanatzidis, M. G. *Abstracts of Papers*, 204th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1992; INOR 277. (b) Huang, S.-P.; Kanatzidis, M. G. *Abstracts of Papers*, 204th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1992; INOR 281. (c) Zhang, X.; Kanatzidis, M. G. Manuscript in preparation.