



Incorporation of hydrogen into the strongly bound double-metal layers in the monohalide can be accomplished at low enough temperatures (150–450 °C) that more stable alternatives are not accessible. The fact that the hydrogen dissociation pressure over the two ZrXH phases is about 700 times that above ZrH₂ (at 400 °C⁴) would suggest that decomposition would ensue if bonding of the halide and the remaining zirconium in the halide product were anything like that in the reactant. Evidently Zr₆X₁₂ clusters fulfill this role better than the alternate, layered ZrX₂ structure at temperatures necessary for decomposition. The layered ZrCl₂ is known to be a filled-band semiconductor, each metal having six neighbors at 3.39 Å compared with four at about 3.20 Å in the cluster. The total Zr–Zr bond order per metal is then greater in the cluster, but the number of Zr–Cl interactions is less, and the layered ZrCl₂ appears to be the more stable form below about 650 °C. (Actually most of the earlier synthetic experiments with layered dihalides which were pertinent to this transformation involved the more common, substoichiometric Zr_{1+x}X₂ phase¹¹ for which disproportionation is also involved in the (unfavorable) conversion to Zr₆X₁₂.) The cluster becomes more stable at higher temperatures, consistent with an X-ray density which is 11% lower (for the chloride) principally because of the vacancy in the middle of the cluster.

The evident simplicity of the cluster syntheses via ZrXH appears to depend at least in part on the predetermined stoichiometry therein. Another advantage is that the equilibrium is reached through states with lower partial pressures of ZrX₄, which makes it possible to heat the system at higher temperature from the beginning and avoid the formation of other phases stable only at lower temperatures. In contrast, ZrX–ZrX₄ reactions, which must be heated slowly to avoid excessive ZrX₄ pressures, tend to produce mixtures

of phases which are not at equilibrium, particularly in the region ZrX–Zr_{1+x}X₂,^{3,11} while the more oxidized systems ZrX₂–ZrX₃ generate unusual pressures at the necessary temperatures, e.g., about 27 atm at 600 °C for X = Cl.³¹ Ordinarily the zirconium monohalides are stable to disproportionation to temperatures³ well in excess of the stability region for the cluster compounds. However, the introduction of hydrogen into the system drastically alters the free energy balance by stabilizing the metal through the formation of zirconium hydrides. At 1 atm of H₂ the free energy of formation of ZrH_{2-x} is estimated to be –46, –33, and –22 kJ/mol at 600, 700, and 800 °C, respectively, from integration of the area between the isotherm and P = 1 atm in the published dissociation pressure data.³²

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Registry No. Zr₆Cl₁₂, 66908-76-7; Zr₆Br₁₂, 75444-52-9; K₂Zr₂Cl₁₈, 75716-17-5; Na₂Zr₇Cl₁₈, 75716-16-4; Cs₂Zr₇Cl₁₈, 75716-18-6; K₂ZrCl₆, 18346-99-1; Na₂ZrCl₆, 18346-98-0; Zr₆Cl₁₅, 65762-00-7; H₂, 1333-74-0; ZrCl, 14989-34-5; ZrBr, 31483-18-8; KCl, 7447-40-7; NaCl, 7647-14-5; CsCl, 7647-17-8; ZrCl₄, 10026-11-6; ZrCl₃, 10241-03-9; ZrBr₃, 24621-18-9; ZrH₂, 7704-99-6.

Supplementary Material Available: Structure factor data for K₂Zr₆Cl₁₈ (2 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Properties of Bis(2,5-dithiahexane)copper(I) and -copper(II) and Mixed-Valence Complexes. Comparison of Tetrahedral and Distorted Octahedral Geometries of Thioether-Coordinated Copper(II)

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X-ray diffraction results are reported for the series of complexes Cu^I(2,5-DTH)₂ClO₄, Cu^I₂Cu^{II}(2,5-DTH)₆(ClO₄)₄, and Cu^{II}(2,5-DTH)₂(ClO₄)₂ (2,5-DTH = 2,5-dithiahexane). The copper(I) and mixed-valence salts are isomorphous and crystallize in the cubic space group *I*43*d* with *a* = 17.214 (1) and 17.273 (2) Å, respectively. The mixed-valence salt contains crystallographically equivalent copper(I) and copper(II) and is more correctly formulated as Cu(2,5-DTH)₂(ClO₄)_{4/3}. Both the copper(I) and mixed-valence salts have 12 copper atoms per unit cell but differ in the number of perchlorates: 12 for the copper(I) salt and 16 for the mixed-valence salt. The copper atom is tetrahedrally surrounded by a thioether S₄ donor set. The copper(II) salt crystallizes in the space group *P*2₁/*n*, with *a* = 8.249 (3) Å, *b* = 10.185 (4) Å, *c* = 11.169 (3) Å, β = 108.26 (2)°, and *Z* = 2. The geometry of the copper(II) complex is distorted octahedral, involving a square-planar S₄ donor set and semicoordination to axial perchlorate groups. This series of complexes allows comparisons to be made between the two common geometries of copper without adjusting for a change in ligands. Interestingly, the Cu–S distance is observed to lengthen as copper(I) oxidizes: Cu(2,5-DTH)₂ClO₄, 2.263 (6); Cu(2,5-DTH)₂(ClO₄)_{4/3}, 2.27 (2); Cu(2,5-DTH)₂(ClO₄)₂, 2.320 (1), 2.354 (1) Å. As the geometry changes from distorted octahedral to tetrahedral, the position of the S(σ) → Cu^{II} charge transfer is red shifted only ca. 400 cm⁻¹.

Introduction

Crystal structures of copper(I) and copper(II) complexes with the metal coordinated to the same ligands or groups of ligands have received considerable attention for what they may reveal about structural changes accompanying oxidation and reduction of copper in metalloenzymes.¹⁻³ In none of the

structures reported to date is the environment around copper kept as fixed upon loss or gain of an electron as it is likely to

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be in a protein. This is largely due to the propensity of copper(II) to attain a distorted octahedral and copper(I) to attain a tetrahedral coordination geometry. It was for this reason that we felt the results of our structural investigation of a mixed-valence compound containing both copper(I) and copper(II) in identical tetrahedral environments⁴ were especially pertinent to this issue. This compound is also unique in that it contains *cationic* tetrahedral copper(II) as well as thioether sulfur coordination. We now wish to report the structures of the all copper(I) and all copper(II) salts of the same ligand 2,5-dithiahexane so that a more complete comparison of structural details can be made. The solution of these structures marks the end of 10 years of effort in sorting out the chemistry of these complexes. Whenever a ligand is capable of coordinating to both oxidation states of copper and of reducing copper(II), a very complicated chemistry can result, as was noted quite recently in the case of the ligand hydrazine.⁵ Subtle changes in solvent, temperature, or concentration or change in counterion can influence the course of the reaction. In dilute methanol solutions, mixing 2,5-dithiahexane (2,5-DTH) and copper perchlorate hydrate in ratios greater than 4 to 1 results in complete reduction to pale green $\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$. In fairly concentrated solutions, or in dilute solutions containing a 2 to 1 ratio of ligand to copper perchlorate, the red-brown copper(II) complex $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$ precipitates. A similarly dilute solution containing a 3 to 1 ratio of ligand to copper perchlorate produces the dark green mixed-valence complex $\text{Cu}^{\text{I}}_2\text{Cu}^{\text{II}}(2,5\text{-DTH})_6(\text{ClO}_4)_4$. Confusion to the laboratory workers arose in part because both the red-brown and dark-green *crystals* appear black and both are isolated from olive green solutions. Initially, the mixed-valence complex was incorrectly assumed to be $\text{Cu}(2,5\text{-DTH})_3(\text{ClO}_4)_2$ on the basis of the carbon and hydrogen analyses. However, once the crystal structure revealed the correct mixed-valence formulation, we discovered that the complex could be easily prepared by mixing methanolic solutions of $\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$ and $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$ in a 2 to 1 ratio. The optimal conditions for its production will be seen to be quite reasonable in light of the X-ray diffraction results.

Experimental Section

Preparation of Compounds. Reagents. The following materials were obtained from the indicated sources: 2,5-dithiahexane (2,5-DTH), Aldrich Chemical Co., Milwaukee, Wis.; $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, G. Frederick Smith Chemical Co., Columbus, Ohio; methanol, anhydrous, Mallinckrodt Inc., Paris, Ky.

$\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$. A solution of 1.86 g (5 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol (50 mL) was added to a solution of 1.84 g (15 mmol) of 2,5-dithiahexane in methanol (108 mL). The solution turned dark olive with a very dark precipitate visible after 10 min. The solution was refrigerated for 24 h. The very dark, red-brown crystals were filtered, washed with cold methanol, and air-dried. The crystals were recrystallized from boiling methanol; yield 2.0 g (3.9 mmol). Anal. Calcd for $\text{Cu}_2\text{S}_4\text{C}_8\text{H}_{20}\text{Cl}_2\text{O}_8$: Cu, 12.53; C, 18.95; H, 3.98. Found: Cu, 12.49; C, 19.48; H, 3.96. *Caution:* explodes when subjected to heat or shock.

$\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$. A total of 0.49 g (4.0 mmol) of 2,5-dithiahexane was added dropwise to a refluxing solution of 0.25 g (0.49 mmol) of $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$ in methanol (25 mL). The initially dark olive solution turned clear in 15 min, and the solution was refrigerated for 24 h. The white crystals were filtered, washed with

cold methanol, and air-dried. They were recrystallized from hot methanol. The yield was 0.18 g (0.44 mmol).

$\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_{4/3}$. Method 1. A solution of 0.37 g (1.0 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol (50 mL) was added to a solution of 0.37 g (3.0 mmol) of 2,5-dithiahexane in methanol (50 mL). The solution turned light olive, and no precipitate was visible after 1 h. The solution was placed at -15°C for 48 h. The very dark, green crystals were filtered, washed with cold methanol, and air-dried. They were recrystallized from boiling methanol. The yield was 0.40 g (0.91 mmol).

Method 2. A total of 0.41 g (1.0 mmol) of $\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$ and 0.25 g (0.5 mmol) of $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$ was dissolved in hot methanol (20 mL). The solution was refrigerated for 24 h. The very dark, green crystals were recovered as in method 1. The yield was 0.60 g (1.4 mmol). Anal. Calcd for $\text{Cu}_3\text{S}_6\text{C}_{24}\text{H}_{60}\text{Cl}_4\text{O}_{16}$: Cu, 14.42; Cl, 10.73; C, 21.80; H, 4.58. Found: Cu, 14.35; Cl, 10.18; C, 22.30; H, 4.74. *Caution:* explodes when subjected to heat or shock.

Physical Measurements. Electric conductance measurements were performed by using a four-probe conductivity measuring device^{6a} for a single crystal of the mixed-valence species and a polycrystalline compaction for a pale green sample of the Cu(I) species.^{6b} Susceptibility measurements were performed on a PAR Model 155 Foner magnetometer calibrated with $\text{HgCo}(\text{NCS})_4$ between 5 and 75 K and a standard Gouy balance at 295 K.

ESR spectra were recorded at 77 K with a Bruker ER 200D spectrophotometer equipped with a Varian 2500 9-in. magnet.

X-ray Data Collection and Solution and Refinement of Structures. Crystals of all three complexes were isolated from cooled methanol solutions as described in the previous section. Intensity measurements were carried out in each case on a Syntex P2₁ diffractometer and a crystal cooled to 140 K. Comparative crystal data, as well as data collection and refinement procedures, are summarized in Table I. Only those details of the solution of the structure which differ from one complex to another will be discussed separately. The basic method of data collection and reduction were as reported previously.⁷ Calculations were performed on a Data General Eclipse computer using a program library developed in this laboratory. The agreement factor, R , is defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$.

$\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_{4/3}$. The determination of the structure of this species has been reported in a recent communication.⁴ Black, shiny crystals of this material (dark green when crushed) have been observed as needles and as nearly equidimensional polyhedra. Under the microscope it is clear that the needles are derived from growth along one face of the tetrahedron while the rounder crystals are more difficult to classify. This tetrahedral form is unique to classes 23 and $\bar{4}3m$ of the cubic system.⁸ The cubic space group $I\bar{4}3d$ (No. 220), a member of the class $\bar{4}3m$, was determined from axial photographs and the conditions hkl , $k + k + l = 2n$, and hhl ($l = 2n$), $2h + l =$

4n. A further check was supplied by Weissenberg photographs and by the agreement between a Patterson map generated from the final Cu, S, and Cl positions and the original Patterson map based on F_o^2 .

Once the space group had been unambiguously determined, it was clear from the cell volume and crystal density that the stoichiometry could not be $\text{Cu}(2,5\text{-DTH})_3(\text{ClO}_4)_2$. However, by placing copper at one of the two sets of 12 special positions (b) with point symmetry $\bar{4}$ and computing a Fourier map, chlorine was located at the set of 16 equivalent positions with point symmetry 3. The 12:16 Cu:Cl ratio in the unit cell suggested the stoichiometry $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_{4/3}$, which agrees with both the computed molecular weight and the elemental analysis. Other evidence for this mixed-valence formulation will be discussed later. The position of the sulfur atom was also found in this Fourier map, and full-matrix, least-squares refinement of Cu, Cl, and S was carried out, bringing R to 0.26. The remaining atoms were located on a subsequent Fourier map. The oxygen atoms are severely disordered, with one (O(1)) bonded to Cl along the threefold axis and the other (O(2)) nearly freely rotating around the threefold

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Table I. Crystal Data

	Cu(2,5-DTH) ₂ ClO ₄	Cu(2,5-DTH) ₂ (ClO ₄) _{4/3}	Cu(2,5-DTH) ₂ (ClO ₄) ₂
fw	407.49	440.64	506.95
space group	143d (cubic, No. 220)	143d	P2 ₁ /n
cryst dimens, mm	diameter, 0.25	0.15 × 0.20 × 0.12	0.20 × 0.275 × 0.35
color	pale green	dark green	dark red-brown
unit cell dimens ^a			
<i>a</i> , Å	17.214 (1)	17.273 (2)	8.249 (3)
<i>b</i> , Å			10.185 (4)
<i>c</i> , Å			11.169 (3)
β, deg			108.26 (2)
unit cell dimens ^b			
<i>a</i> , Å	17.536 (26)	17.435 (29)	
density, g cm ⁻³			
measd, 298 K	1.55 (2)	1.60 (2)	1.86 (1)
calcd, 298 K	1.51	1.66	
calcd, 140 K	1.59	1.70	1.89
<i>Z</i>	12	12	2
radiatn, Å	Mo Kα, λ = 0.710 69	Mo Kα, λ = 0.710 69	Mo Kα, λ = 0.710 69
μ _{Mo Kα} , cm ⁻¹	19.1	19.2	19.5
width of peak at half-height on ω scan, deg	0.32	0.28	0.37
scan type (2θ _{max} , deg)	ω (45)	ω (45)	ω (45)
scan range, deg	0.8	0.8	1.0
scan speed, deg min ⁻¹	1-30	0.5-10	3-60
no. unique data	314	320	1248
no. data with <i>I</i> > 3σ(<i>I</i>)	284	288	1195
<i>R</i>	0.064	0.074	0.041

^a 140 K; diffractometer. ^b 298 K; Weissenberg.

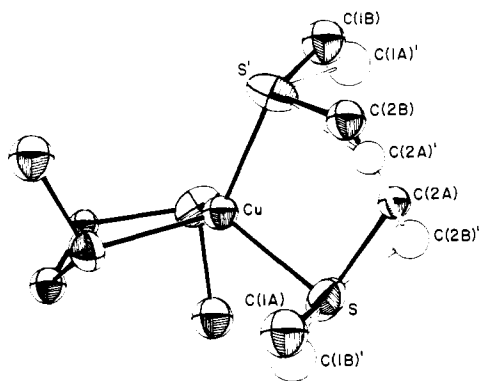


Figure 1. View of the mixed-valence cation indicating the disorder in the carbon atoms of one of the 2,5-DTH ligands.

axis, appearing as a toroid of low electron density. In addition, the entire anion appears to rock about the threefold axis. Although O(1) could be located with some certainty, its thermal parameter during refinement climbed to 18 Å². Three flat maxima for O(2) could also be seen, but its thermal parameter diverged with each cycle of refinement, so that ultimately its position was fixed and *B* set to 21 Å². The two carbon atoms also suffer disorder and appeared as distinct peaks of low density on the map. The methyl carbon atom (C(1)) has two disordered positions separated by 0.6 Å while the methylene carbon (C(2)) has two disordered positions separated by 0.7 Å. Refinement was attempted by using anisotropic thermal parameters for C(1) and C(2), but unreasonable thermal parameters resulted, and *R* increased ca. 2%. Improved agreement was obtained by using a disordered model of 0.50 weight for two alternative positions for each of the two carbon atoms. The sulfur atom can be made to fit either a disordered or anisotropic model with a 0.6% improvement in *R* for the anisotropic model. When refinement was done by using disordered positions, the separation between the two disordered sulfur atoms amounted to 0.47 Å; distinct peaks in the Fourier map were also not observed. It is tempting to assume that the presence of this disorder reflects an attempt on the part of the one-third copper(II) atoms to "flatten" out the tetrahedral geometry provided by the four-coordinated sulfur atoms; however, careful examination of models reveals that the disorder corresponds rather to a sideways displacement of the ligand in a plane that is perpendicular to the CuS₂ plane of the other ligand. This disorder is illustrated in Figure 1, where the open circles represent one arrangement and the shaded circles represent the other arrangement for the 2,5-DTH ligand on the right. It can

Table II. Atomic Positional and Isotropic Thermal Parameters for Cu(2,5-DTH)₂(ClO₄)_{4/3} and Anisotropic Thermal Parameters^a for Cu, Cl, and S

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²		
Cu	0.2500	0.6250	0.5000			
Cl	0.2773 (1)	0.2773 (1)	0.2773 (1)			
S	0.2897 (3)	0.5363 (3)	0.4115 (2)			
O(1)	0.320 (1)	0.320 (1)	0.320 (1)	18 (1)		
O(2)	0.322	0.213	0.231	21 ^b		
C(1A)	0.188 (2)	0.516 (3)	0.361 (3)	7 (1)		
C(1B)	0.215 (3)	0.526 (3)	0.345 (3)	7 (1)		
C(2A)	0.271 (1)	0.449 (1)	0.484 (1)	3.5 (5)		
C(2B)	0.302 (2)	0.452 (2)	0.457 (2)	4.9 (5)		
atom	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cu	4.1 (1)	5.2 (2)	4.1 (1)	0.0	0.0	0.0
Cl	4.7 (1)	4.7 (1)	4.7 (1)	-0.4 (1)	-0.4 (1)	-0.4 (1)
S	6.7 (2)	7.6 (2)	5.4 (2)	1.9 (2)	-0.6 (2)	-2.1 (2)

^a The anisotropic thermal parameter is of the form $\exp[-1/4 \cdot (h^2 a^{*2} B_{11} + \dots + 2klb^* c^* B_{23})]$. ^b After several cycles of refinement the parameters for O(2) were fixed since they diverged with each cycle.

also be seen in Figure 1 that the disorder is about the horizontal twofold axis that passes through copper.

The question of handedness for the structure was resolved by the following procedure. Refinement to convergence (*R* = 0.073) was carried out with no correction applied for the imaginary part of anomalous dispersion. A structure factor calculation was then made for the original coordinates and the inverted (1 - *x*, 1 - *y*, 1 - *z*) coordinates with the correction for anomalous dispersion applied to Cu, Cl, and S. Since the original set of coordinates yielded an *R* of 0.074 while the inverted set gave an *R* of 0.077, the original choice was taken as correct.

The function minimized during refinement was $\sum w(F_o - k|F_c|)^2$, with the weighting factor, *w*, given by a Hughes weighting scheme⁹ and *k*, an adjustable parameter.

The scattering factors employed were those of Cromer and Waber for Cu(I) and neutral Cl, S, O, and C.^{10a} The corrections for the real and imaginary parts of anomalous dispersion were made for Cu, Cl, and S^{10b} in the final refinement. Anisotropic thermal parameters were assigned to Cu, Cl, and S; the position of O(2) was fixed; the

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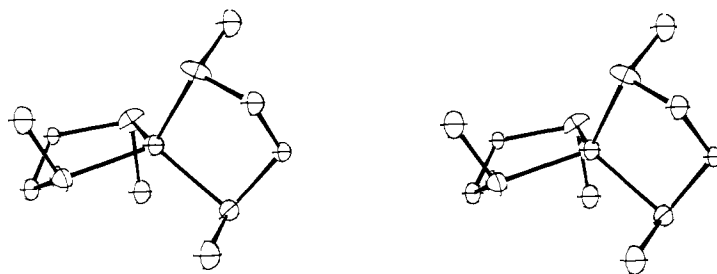


Figure 2. Stereoscopic view of the mixed-valence cation at the 20% thermal ellipsoid level.

two carbon atoms were divided into disordered pairs. This brought the number of parameters being refined to 33 and yielded an R of 0.074 for 288 data with $I > 3\sigma(I)$. A final difference map was devoid of any features. The last shift in any parameter in the final cycle of full-matrix least-squares refinement was less than $1/20$ the esd. The final positional and thermal parameters are reported in Table II.

Cu(2,5-DTH)₂ClO₄. Very pale green, almost colorless crystals of this complex were isolated in the same two crystal forms as the black mixed-valence crystals. A zero-layer Weissenberg photograph displayed the same symmetry as the mixed-valence species although individual intensities differed. Diffractometer measurements confirmed the space groups to be the same. Solution of the structure was facilitated by taking advantage of the similarity between these two structures. The assumption was made that the Cu(I) salt differed in the occupancy of the perchlorate position, which for pure Cu(I) would be $12/16$ of the full occupancy. Refinement was carried out under this assumption. The chirality of the crystal was established as for the mixed-valence salt. Form factor tables for Cu(I) and neutral Cl, S, O, and C^{10a} were employed with corrections for the real and imaginary parts of anomalous dispersion applied to Cu, Cl, and S.^{10b} No attempt was made to include hydrogen atoms, as the structure was subject to the same disorder as noted in the mixed-valence structure. Anisotropic thermal parameters for C(1) and C(2) gave slightly better agreement than disordered positions. The shift in the parameters of O(1) and O(2) in the last cycle of full-matrix least-squares refinement was $1/2$ the esd and less than $1/10$ the esd for the remaining atoms. With 284 reflections for which $I > 3\sigma(I)$ and 39 parameters, the final cycle of refinement brought R to 0.064. A final difference map revealed no atom as large as a hydrogen atom. Table III presents the final positional and thermal parameters for this structure.

Cu(2,5-DTH)₂(ClO₄)₂. Crystals of the Cu(II) species appear as black, four-sided needles but are actually red-brown when crushed. Crystal data are reported in Table I. Anomalous dispersion corrections for Cu, Cl, and S, together with form factor tables^{5a,b} for Cu(II) and neutral Cl, S, O, and C, were used. The copper atom was arbitrarily placed at the origin and a Fourier map calculated to find the two sulfur atoms. Another Fourier map calculated from refined Cu, S(1), and S(2) positions yielded all the remaining nonhydrogen atoms. Full-matrix least-squares refinement of these atoms with isotropic thermal parameters brought R to 0.053. Since the isotropic B 's were quite small, further refinement with anisotropic B 's was considered unnecessary. No atoms larger than hydrogen appeared in the final difference Fourier map. In the final cycle of full-matrix least-squares refinement the 10 hydrogen atoms were included at calculated positions but not refined. This brought R to 0.041, and the last shift in the value of any of the 46 parameters being refined was $< 1/9$ the esd. Positional and thermal parameters are reported in Table IV.

Results

Structure Determinations. **Cu(2,5-DTH)₂(ClO₄)_{4/3}.** The general structure description of the mixed-valence complex will be summarized first since the structure of the copper(I) complex is a natural extension of it. Each of the 12 cations per unit cell (Cu(2,5-DTH)₂^{*n*+}, $n = 1, 2$), has crystallographically imposed $\bar{4}$ symmetry. In the absence of disorder, the cation is generated by one copper, one sulfur, and two carbon atoms (omitting hydrogen) in the asymmetric unit. The fourfold inversion axis bisects the CH₂-CH₂ bridge between the two sulfur atoms of one of the ligands, passes through copper, and bisects the CH₂-CH₂ bridge of the other ligand,

Table III. Atomic Positional and Isotropic Thermal Parameters for Cu(2,5-DTH)₂ClO₄ and Anisotropic Thermal Parameters^a for Cu, Cl, S, C(1), and C(2)

atom	x	y	z	$B, \text{\AA}^2$
Cu	0.2500	0.6250	0.5000	
Cl	0.2761 (2)	0.2761 (2)	0.2761 (2)	
S	0.2900 (3)	0.5371 (3)	0.4107 (3)	
O(1)	0.321 (3)	0.321 (3)	0.321 (3)	17 (2)
O(2)	0.298 (3)	0.208 (3)	0.280 (3)	21 (2)
C(1)	0.205 (2)	0.519 (2)	0.349 (1)	
C(2)	0.287 (2)	0.451 (1)	0.472 (2)	

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3.3 (1)	3.7 (2)	3.3 (1)	0.0	0.0	0.0
Cl	2.3 (1)	2.3 (1)	2.3 (1)	-0.2 (1)	-0.2 (1)	-0.2 (1)
S	6.2 (3)	6.7 (3)	5.6 (2)	1.8 (2)	-0.3 (2)	-2.6 (2)
C(1)	15 (2)	12 (2)	6 (1)	-2 (2)	-8 (1)	1 (1)
C(2)	13 (2)	1 (1)	12 (2)	1 (1)	-4 (2)	-1 (1)

^a The anisotropic thermal parameter is of the form $\exp[-1/4 \cdot (h^2 a^{*2} B_{11} + \dots + 2klb^* c^* B_{23})]$.

Table IV. Atomic Positional and Isotropic Thermal Parameters for Cu(2,5-DTH)₂(ClO₄)₂

atom	x	y	z	$B, \text{\AA}^2$
Cu	0.0	0.0	0.0	0.94 (3)
Cl	-0.1935 (1)	0.2927 (1)	0.0777 (1)	1.14 (3)
S(1)	0.1306 (1)	-0.0612 (1)	0.2082 (1)	1.03 (3)
S(2)	0.2719 (1)	0.0617 (1)	-0.0071 (1)	1.11 (3)
O(1)	-0.0354 (4)	0.2271 (3)	0.0843 (3)	1.5 (1)
O(2)	-0.1724 (4)	0.4312 (3)	0.0682 (3)	1.7 (1)
O(3)	-0.3250 (5)	0.2465 (3)	-0.0330 (3)	2.2 (1)
O(4)	-0.2394 (5)	0.2619 (4)	0.1890 (4)	2.7 (1)
C(1)	0.0037 (6)	-0.0007 (4)	0.3024 (5)	1.2 (1)
C(2)	0.3046 (6)	0.0564 (4)	0.2485 (4)	1.3 (1)
C(3)	0.4036 (6)	0.0406 (5)	0.1563 (4)	1.3 (1)
C(4)	0.2629 (6)	0.2387 (4)	-0.0211 (4)	1.4 (1)

now oriented 90° to the first. In other words, the two S-Cu-S planes are required by symmetry to have a dihedral angle of 90° between them. This arrangement is depicted in Figure 2. The geometry about copper differs from that of a regular tetrahedron by virtue of the bite angle of the ligand (95 (1)°) and an external S-Cu-S angle of 117°. The cation itself has a compact, nearly spherical shape which arises from a folding of the ligand as required by the $\bar{4}$ axis. This results in an alternation of the methyl groups above and below the CuS₂ planes. The 16 perchlorate groups per unit cell occupy a site of threefold point symmetry. Chlorine and O(1) lie on the threefold axis, and the other three oxygen atoms are generated by rotation of O(2) about this axis. Since both cation and anion have a roughly spherical shape, it is not unexpected that both are subject to disorder or large thermal motion. This aspect of the structure has been discussed in a prior communication.⁴

Each copper atom is surrounded by one flattened tetrahedron of chlorine atoms at 5.10 Å and another at 7.14 Å. These eight chlorine atoms form a dodecahedron with Cl-Cl separations of 7.48 to 7.75 Å. Each chlorine atom, in turn, is

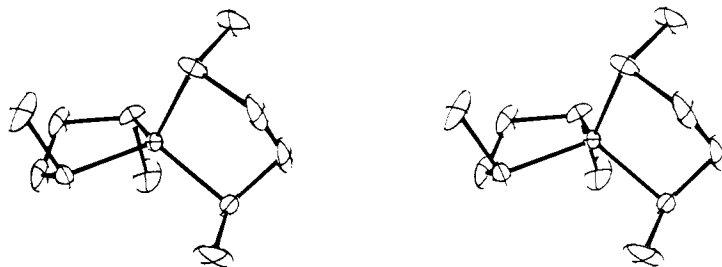


Figure 3. Stereoscopic view of the $\text{Cu}(2,5\text{-DTH})_2^+$ cation in the copper(I) salt at the 20% thermal ellipsoid level.

Table V. Interatomic Distances (Å) and Angles (Deg) for $\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$, $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_{4/3}$, and $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$

	$\text{Cu}(2,5\text{-DTH})_2\text{-ClO}_4$	$\text{Cu}(2,5\text{-DTH})_2\text{-}(\text{ClO}_4)_{4/3}$	$\text{Cu}(2,5\text{-DTH})_2\text{-}(\text{ClO}_4)_2$
Cu-S	2.263 (6)	2.27 (2)	2.320 (1), 2.354 (1)
Cu...O	3.9 (1)	3.8 (1)	2.549 (3)
C(2)-C(3) [C(2)']	1.59 (5)	1.62 (4)	1.510 (7)
Cl-O(1)	1.3 (2)	1.3 (2)	1.446 (4)
Cl-O(2)	1.2 (2)	1.6 (2)	1.429 (3)
Cl-O(3)			1.444 (4)
Cl-O(4)			1.443 (4)
S(1)-C(1)	1.83 (3)	1.99 (10), 1.74 (10)	1.809 (5)
S(1)-C(2)	1.82 (2)	1.98 (10), 1.66 (10)	1.814 (5)
S(2)-C(3)			1.820 (5)
S(2)-C(4)			1.809 (5)
S-Cu...O			86.8 (1), 89.5 (1)
S-Cu-S(int)	96.2 (4)	95 (1)	89.5 (1)
S-Cu-S(ext)	116.5 (4)	117 (1)	90.5 (1)
Cu-S-C(int)	98 (1)	92 (1)	98.8 (2), 102.1 (2)

surrounded by three copper atoms at 5.10 Å and another three at 7.14 Å. A given copper atom is surrounded by eight equivalent copper atoms at 8.08 Å that describe an irregular dodecahedron. There is no obvious grouping into multiples of three copper atoms, or clusters, as might be expected from the mixed-valence stoichiometry. One must simply conclude that this is a lattice of high stability. The crystallographic results represent an average of indistinguishable copper(I) and copper(II) ions in identical tetrahedral sites. Interatomic distances and angles are reported in Table V. A stereoscopic view of one set of disordered positions is presented in Figure 2.

$\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$. The crystal structure of this complex is isomorphous with that of the mixed-valence complex. The density is less; thus the computed molecular weight agrees with the copper(I) formulation. In color, but not in shape, there is a striking difference between the two crystals. As mentioned in the Experimental Section, these crystals are nearly white, while those of the mixed-valence complex are shiny black. The evidence accumulated so far supports the view that this complex differs from the mixed-valence complex only in the occupancy of the perchlorate site; i.e., 12 out of the 16 possible sites are occupied. This structure therefore possesses additional disorder stemming from 0.75 occupancy in this position. Bond distances and angles are given in Table V, where they may be compared to those of the mixed-valence species. A stereoscopic drawing of the cation is shown in Figure 3.

The bonding within the cation can be compared to the similar structure $\text{Cu}(3,6\text{-DTO})_2\text{BF}_4$,¹¹ which, while not in a cubic lattice, contains a ligand which differs only in the re-

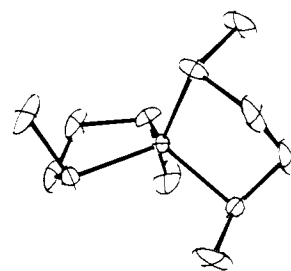


Figure 4. ORTEP drawing of $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$ using 50% thermal ellipsoids.

placement of the methyl groups by ethyl groups (3,6-DTO = 3,6-dithiaoctane). The cation in the 3,6-DTO complex is not disordered, but the BF_4^- anion is. The Cu-S distances in the 3,6-DTO cation average 2.303 Å, while the 2,5-DTH cation has a distance of 2.263 (6) Å, the shortest reported for a copper-thioether link. Even though the 3,6-DTO complex has no crystallographically imposed symmetry (2,5-DTH has $\bar{4}$), the distortions from ideal tetrahedral angles are only those imposed by the ligand "bite"; the dihedral angle between the CuS_2 planes is 84.7°, very close to the required 90° in the 2,5-DTH complex.

$\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$. The structure of $\text{Cu}(2,5\text{-DTH})_2\text{-}(\text{ClO}_4)_2$ reported here is isomorphous with that of $\text{Cu}(2,5\text{-DTH})_2(\text{BF}_4)_2$.^{11,12} The copper atom is located on a center of inversion and thus is coordinated to a rigorous plane of four sulfur donor atoms. It is weakly coordinated to two perchlorate groups above and below this plane. In contrast to the tetrafluoroborate structure, we observed no disorder in the C-C bond for which a distance of 1.37 (1) Å was reported. Our value of 1.510 (7) Å for this bond is closer to what would be expected for a normal C-C single bond. For the Cu-S bonds we obtained values of 2.320 (1) and 2.354 (1) Å, compared to 2.315 (2) and 2.319 (2) Å in the tetrafluoroborate structure. The Cu-O distance of 2.549 (3) Å is similar to that of Cu-F, 2.579 (5) Å. Other interatomic distances and angles are normal and are reported in Table V. The arrangement of the methyl groups differs from the tetrahedral cation in that both methyl groups within a given ligand lie on the same side of the CuS_2 plane (Figure 4). In order to minimize steric in-

(11) Baker, E. N.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* 1977, 877.

(12) The space group is $P2_1/n$, a different setting of $P2_1/c$.

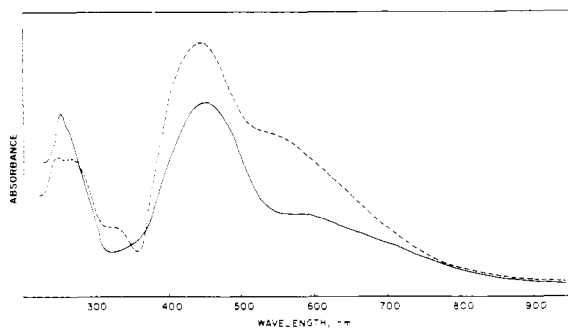


Figure 5. Mull spectra at room temperature of $\text{Cu}(\text{2,5-DTH})_2(\text{ClO}_4)_{4/3}$ and $\text{Cu}(\text{2,5-DTH})_2(\text{ClO}_4)_2$ (dotted line).

teractions the perchlorate groups bend to the opposite side of the complex, away from these methyl groups.

ESR and Magnetic Susceptibility Results. The magnetic susceptibility in the mixed-valence species displays normal Curie behavior between 5.5 and 295 K with $\mu_{\text{eff}} = 0.98$ (6) μ_{B} . In contrast, the all-copper(II) distorted octahedral complex is antiferromagnetic below 11 K; between 35–75 K the susceptibility follows Curie–Weiss behavior with $\theta = 11.4$ K and $\mu_{\text{eff}} = 1.85$ (5) μ_{B} .

Dissimilar powder ESR spectra at 77 K are observed for the mixed-valence and all-copper(II) species. For tetrahedral copper(II) incorporated in the mixed-valence compound the spectrum displays line broadening and what appears to be extra features.⁴ The most prominent peaks, however, yield $g_{\parallel} = 2.22$ and $g_{\perp} = 2.053$; $A_{\parallel} = 153$ G. A small high-field peak corresponding to $g = 1.98$ at its maximum may be an overshoot peak. Some variation in the fine structure from sample to sample has been observed, but a typical spectrum shows additional splitting in the A_{\parallel} region of 105 G. The spectrum of a powdered sample of $\text{Cu}(\text{2,5-DTH})_2(\text{ClO}_4)_2$ displays full anisotropy with $g_x = 2.025$, $g_y = 2.039$, and $g_z = 2.095$. The lines are quite narrow, and there is no hyperfine structure.

Electrical Conductance Measurements. Electrical conductance measurements were performed on a single crystal, 1 mm in length, of the mixed-valence complex and also on a polycrystalline compaction of pale green $\text{Cu}(\text{2,5-DTH})_2\text{ClO}_4$. Both samples behaved as insulators, with conductances less than 10^{-10} mho cm^{-1} .

Electronic Spectral Measurements. Spectroscopic measurements on these complexes are limited to the solid state since the affinity of thioether ligands for copper(II) in solution is low, and the species in solution is probably the solvated mono complex.^{13,14} Therefore, only the Nujol mull spectra were recorded, and these are shown in Figure 5. There is no direct evidence for an “intervalence” transition in the mixed-valence complex. The mull spectrum can be satisfactorily explained by $\text{S} \rightarrow \text{Cu}$ charge transfer,¹⁵ which produces a broad maximum at 450 nm and a shoulder near 595 nm. The expected $d \rightarrow d$ band due to tetrahedral copper(II) is probably masked by tailing of the charger-transfer bands into the near IR or else is too weak to be detected. The red-brown, all-copper(II) distorted octahedral complex has a mull spectrum very similar to that of the mixed-valence complex. It, too, is dominated by intense $\text{S} \rightarrow \text{Cu}$ charge transfer centered at 442 nm and a shoulder at ca. 560 nm.

Discussion

Cubic space groups are rare for transition-metal complexes with organic ligands. One of the few examples, *F*432, is found for the copper mixed-valence penicillamine complex¹⁵ Tl_5 -

$[\text{Cu}^{\text{I}}_8\text{Cu}^{\text{II}}_6(\text{D-Pen})_{12}\text{Cl}] \cdot n\text{H}_2\text{O}$. In this cluster the copper(I) atoms are separated by an average distance of 3.30 Å, the copper(II) atoms are separated by an average distance of 6.71 Å, and the minimum Cu(I)–Cu(II) distance is 3.80 Å. An unexpected aspect of the cubic mixed-valence 2,5-DTH structure is that the copper atoms are separated by 8 Å, and electron transfer between them would have to be mediated by groups normally thought of as insulators. There is one other reported instance of a mixed-valence compound with equivalent copper(I) and copper(II), $\text{KCu}_3\text{Cu}^{\text{II}}\text{S}_3$,¹⁶ but here sulfide would be expected to play a role in electron transport. In the results it was pointed out that the anion and cation have a spherical shape; this may predispose crystallization in a cubic lattice. Furthermore, this particular lattice is found for compounds with ion radius ratios of 2:1, as in Th_4P_3 ¹⁷ and $\text{Bi}_4(\text{SiO}_3)$,¹⁸ with the larger ion occupying the site with 12 equivalent positions. The same radius ratio is found for $\text{Cu}(\text{2,5-DTH})_2^{n+}$ and ClO_4^- on the basis of estimated sizes of 4.0 and 2.0 Å, respectively.

One naturally questions whether a continuous range of composition for $\text{Cu}(\text{2,5-DTH})_2(\text{ClO}_4)_x$, with x ranging from 1.00 to 1.33, can occur. The answer is likely to be yes, and is currently under further study. For example, we have recently observed fresh samples of “ $\text{Cu}(\text{2,5-DTH})_2\text{ClO}_4$ ” of varying degrees of green. These display a very weak ESR signal, while the whitest samples have no detectable signal under high amplification. In addition, the greener the crystal, the higher the density. The data presented in Table I show that the computed density for $\text{Cu}(\text{2,5-DTH})_2(\text{ClO}_4)_{4/3}$ is higher than that determined by flotation and that of $\text{Cu}(\text{2,5-DTH})_2\text{ClO}_4$ is lower. This is in keeping with a composition that deviates somewhat from the ideal. The incorporation of any large or stoichiometric amount of methanol into the lattice vacancies has been ruled out from chemical analysis, but small amounts of methanol would be indistinguishable from perchlorate if the C–O bond were located where Cl–O(1) is found, along the threefold axis.

Comparison of Copper(I), Mixed-Valence, and Copper(II) Crystal Structure Results. This series of compounds, encompassing tetrahedral copper(I), mixed-valence tetrahedral copper(I)/copper(II), and tetragonally distorted octahedral copper(II), provides a unique opportunity for comparing bond distances and angles with the same ligand and counterion. Due to disorder, the estimated standard deviations for the two cubic structures are larger than one would like, yet the trends are all in the expected direction. Our results substantiate those of Baker and Norris¹¹ that Cu^I–S bonds are shorter than or comparable to Cu^{II}–S bonds when S is part of a thioether ligand. Their suggestion that a greater π component in Cu^I–S bonds compensates for the larger Cu^I radius deserves further theoretical investigation, but it should be kept in mind that the concomitant change in coordination number from 4 to 6 in going from copper(I) to copper(II) can also have a large effect on bond distance. The difference that we observe, 0.06 Å, is even larger than the 0.01 Å they observe. Other Cu^I–S(thioether) bond lengths are, for comparison, 2.345 (1) Å for $[\text{Cu}(\text{pdto})]\text{PF}_6$ ² and 2.260 (4), 2.338 (4), 2.327 (4), and 2.342 (3) Å for $[\text{Cu}(\text{14-ane-S}_4)(\text{ClO}_4)]_x$.^{1a} Cu^{II}–S(thioether) bond lengths are 2.311 (2) Å for $[\text{Cu}(\text{pdto})\text{ClO}_4]\text{ClO}_4$,² 2.369 (2) and 2.308 (2) Å for $[\text{Cu}(\text{BBTE})\text{Cl}_2]_2$,¹⁹ 2.325 (2) and

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2.313 (2) Å for $[\text{Cu}(3,6\text{-DTH})_2(\text{ClO}_4)_2]_2$,²⁰ 2.297 (1) and 2.308 (1) Å for $[\text{Cu}(14\text{-ane-S}_4)(\text{ClO}_4)]_2$,^{1b} 2.410 (5) for $[\text{Cu}[(\text{Me}_2\text{NCOCH}_2)_2\text{S}]\text{Cl}_2]$,²¹ 2.366 (1) Å for $[\text{Cu}(\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{SCH}_3)_2](\text{ClO}_4)_2$,²² and 2.445 (6) and 2.431 (6) Å for μ -chloro-chlorobis[3,4-bis((2-aminoethyl)thio)toluene]dicopper(II) diperchlorate.²³

The broad absorption of both the tetrahedral and distorted octahedral copper(II) species throughout the visible region explains why both kinds of crystals appear black. It is not clear why the slight differences in their spectra cause the colors of the powders to be so different: red-brown for the distorted octahedral and green for the tetrahedral geometry. However, we have found these colors to be characteristic of other thioether-copper(II) complexes in our laboratory, with green colors extending to distorted five- and six-coordinate species. The broad peak ca. 350 nm and the smaller, lower energy peak, which have been assigned to $\text{S}(\sigma) \rightarrow \text{Cu}$ and $\text{S}(\pi) \rightarrow \text{Cu}$, respectively,²⁴ shift toward the red as the geometry changes from distorted octahedral to tetrahedral. However, the shift is small—only 400 cm^{-1} —and conflicts with the 5200-cm^{-1} value that has been estimated from solution spectra to dissimilar thioether complexes.²⁵

The low magnetic moment for the mixed-valence species agrees well with its formulation as $\text{Cu}^1_2\text{Cu}^{\text{II}}(2,5\text{-DTH})_6(\text{ClO}_4)_{4/3}$. Since all copper atoms are separated by at least 8.08 Å and, on the average, two-thirds of these are diamagnetic, it is not surprising that it behaves as a magnetically dilute substance. Its ESR spectrum bears some resemblance to certain biological systems containing two types of copper.^{26,27} One possible interpretation would assign a major contribution from $\text{Cu}^{\text{II}}\text{-S}^0$ together with a smaller contribution from $\text{Cu}^{\text{II}}\text{-S}^-$ or $\text{Cu}^1\text{-S}^+$. It can be noted that the g_{\parallel} and A_{\parallel} values are not inconsistent with those found for tetrahedral copper(II).²⁸

In the all-copper(II) $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$, both the susceptibility and ESR results suggest the presence of long-range

exchange interactions. It has already been noted²⁹ that the line narrowing in the powder ESR spectrum of $\text{Cu}(2,5\text{-DTH})_2(\text{BF}_4)_2$, which is in appearance identical with that of the perchlorate, is likely the result of an electron-exchange process. The absence of hyperfine structure can also be attributed to exchange coupling which averages the hyperfine interaction to zero. Although the minimum distance between copper(II) atoms in the crystal is 7.73 Å, apparently it is sufficiently small for such interactions to occur.³⁰

Conclusion

From these crystal structures and the other data reported on these and similar complexes we tentatively conclude that the thioether coordination to copper differs from thiolate. Not only is the bond to sulfur sometimes shorter in copper(I) complexes than in copper(II) but also there is very little red shift in the position of the $\text{R}_2\text{S} \rightarrow \text{Cu}^{\text{II}}$ transition as the geometry changes from distorted octahedral to tetrahedral.

The structure of $\text{Cu}^1(2,5\text{-DTH})_2\text{ClO}_4$ provides a rationale for the crystallization of the unusual mixed-valence complex. As reduction of copper(II) in a methanol solution containing 2,5-dithiahexane and perchlorate proceeds, the incipient copper(I) lattice is doped with one-third copper(II) cations in order to achieve charge balance when all the perchlorate sites are filled. If reduction occurs rapidly enough, only the copper(I) salt results. If the solution is sufficiently concentrated and the reducing agent is not present in excess, the solubility of the copper(II) salt is exceeded and it will be the solid isolated. Other experiments conducted in our laboratory indicate that the difficulty in isolating thioether complexes of copper(II) may often be surmounted by careful choice of reaction conditions. This work will appear in a subsequent publication.

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Registry No. $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_2$, 75149-74-5; $\text{Cu}(2,5\text{-DTH})_2\text{ClO}_4$, 62207-32-3; $\text{Cu}(2,5\text{-DTH})_2(\text{ClO}_4)_{4/3}$, 75196-79-1.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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