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Mixed-Valence Coinage Metal Clusters with 1,1-Thioperthio Ligands. Syntheses and Molecular Structures of the $[Cu_4L_3]^{2-}$, $[Cu_5L_4]^-$, and $[AuCu_4L_4]^-$ Anions (L = 1,1-Dicarbo-*tert*-butoxyethylene-2,2-thioperthiolate). A Geometrically-Locked, Charge-Separated Valence State in the $[Cu_5L_4]^-$ Anion

D. Coucouvanis,* S. Kanodia, D. Swenson, S.-J. Chen, T. Stüdemann, N. C. Baenziger, R. Pedelty, and M. Chu

Contribution from the Departments of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109-1055, and University of Iowa, Iowa City, Iowa 52240

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Abstract: Sulfur addition to the coordinated dithiolene ligands in the known $[Cu_8(^tBuDED)_6]^{4-}$ cluster results in the formation of the $\{[Cu_4(S^tBuDED)_3]_n\}^{m-}$ "sulfur-rich" clusters. The molecularity of these clusters depends on the nature of the counterions. With Bu_4N^+ as counterions, $n = 2$ and $m = 4$ (**I**), while with K^+ as one of the counterions, $n = 1$ and $m = 2$ (**II**). The oxidation of either **I** or **II** with Cu(II) ions or with $HAuCl_4{\cdot}3H_2O$ affords the mixed-valence $[Cu_5(S^tBuDED)_4]^-$ (**III**) and the mixed-valence, mixed-coinage metal $[Cu_4Au(S^tBuDED)_4]^-$ (**IV**) clusters. The crystal and molecular structures of $K(Ph_4P)[Cu_4(S^tBrDED)_3]{\cdot}[(CH_3)_2C{=}O]_3$, $(BzPh_3P)[Cu_5(S^tBuDED)_4$, and $(Bu_4N)_2[Cu_4Au(S^tBuDED)_4]{\cdot}CuCl_2{\cdot}(CH_2Cl_2)_{0.5}$ have been determined. The compounds that contain **II**, **III**, and **IV** crystallize in the space groups $R3m$, $P2_1/n$, and $C2/c$, respectively. The cell dimensions for **II** are $a = 12.846(2)$ Å, $\alpha = \beta = \gamma = 83.92(1)°$, and $Z = 1$, for **III**, $a = 17.042(4)$ Å, $b = 31.133(10)$ Å, $c = 18.326(5)$ Å, $\beta = 97.03(2)°$, and $Z = 4$, and for **IV**, $a = 39.172(6)$ Å, $b = 9.8553(9)$ Å, $c = 30.745(4)$ Å, $\beta = 108.69(1)°$, and $Z = 4$. Crystallographic data for the three structures were obtained on an automatic diffractometer employing Mo Kα radiation for **II** and **III** and Cu Kα for **IV**. The refinement of the structures by full-matrix least-squares methods was based on 2507 unique reflections ($2\theta_{max} = 40°$, $I > 3\sigma(I)$) for **II**, on 4215 unique reflections ($2\theta_{max} = 40°$, $I > 3\sigma(I)$) for **III**, and on 4172 unique reflections ($2\theta_{max} = 103°$, $I > 3\sigma(I)$) for **IV**. Refinements on 206 parameters for **II**, 551 parameters for **III**, and 477 parameters for **IV**, with all atoms present in the asymmetric units, have converged to R values of 0.049, 0.109, and 0.085, respectively. The structure of **II** shows a tetrahedral Cu_4 core with three S^tBuDED ligands in a symmetric fashion roughly bisecting three of the Cu_4 tetrahedron faces. The arrangement of the ligands results in a unique Cu(I) atom that is located on a 3-fold axis of symmetry with the three other Cu atoms situated in a plane perpendicular to the 3-fold axis. The S–S "arms" of the sulfur-rich ligands are used to bridge the Cu atoms in this plane. The mean Cu–Cu distance of **II** is 2.729 Å, and the Cu–S distances range from 2.211(3) Å (involving the S atoms bridging the Cu atoms in the plane perpendicular to the 3-fold axis) to 2.268(3) Å (involving the the S atoms bridging the unique axial copper to the basal copper atoms). The potassium cation in **II** is located on the 3-fold axis of symmetry and is coordinated to three carbonyl groups, one from each ligand, and to the three acetone molecules of solvation. The structures of **III** and **IV** consist of rectangular pyramidal Cu_5 and Cu_4Au cores. Each of the square pyramidal faces are bisected by the S^tBuDED ligands. The persulfido S–S arm of each ligand binds to the unique axial atoms (Cu(III) in **III** and Au(III) in **IV**) and bridges these atoms to the basal Cu(I) atoms. The other sulfur donor of each ligand bridges the basal Cu(I) atoms to give an octagonal $Cu(I)_4S_4$ crown with alternating Cu and S atoms. The basal Cu atoms are three coordinate and planar with Cu–S bonds within the $Cu(I)_4S_4$ crown that range from 2.181(5) to 2.229(9) Å. The axial Cu(III) and Au(III) atoms are four coordinate and planar with Cu(III)–S and Au(III)–S bonds of 2.283(9) and 2.400 Å, respectively, for **III** and **IV**. The mean Cu(III)–Cu(I) bonds in **III** and the Cu(III)–Au(III) bonds in **IV** are 2.83(2) and 3.029(7) Å, respectively. The reactions of **III** with thiolate ions result in the formation of the new $[Cu_4(S^tBuDED)_4]^{4-}$ cluster, **V**. This cluster is proposed to be structurally similar to **III** and **IV** and is obtained by the reductive removal of the axial Cu(III) to Au(III) ions. The ^{13}C-NMR spectra of **III**, **IV**, and **V** are discussed in terms of their structural electronic and solution dynamic characteristics.

Introduction

The coordination chemistry of monovalent copper with 1,1- or 1,2-dithio-chelating ligands is well represented by polynuclear clusters that contain either the Cu_4 (tetrahedral)[1] or the Cu_8 (cubic) core.[2] The chemistry of these clusters now appears to be biologically relevant following the recent discovery of an apparent $Cu_8(Cys)_{12}$ cluster in yeast metallothionein[3a] and a copper thiolate cluster in the protein CUP2 that regulates the expression of yeast metallothionein.[3b] For the latter, Cu K-edge EXAFS curve-fitting results reveal Cu–Cu distances of ~2.75 Å. These distances are quite similar to the ones found in the Cu_4 or Cu_8 clusters with thiolate ligands.[1,2]

In the past we have explored and reported on the chemistry of the $[Cu_8L_6]^{4-}$ clusters (L = 1,1- or 1,2-dithiolenes that contain

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* To whom correspondence should be addressed at the University of Michigan.

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the Cu_8 core inscribed within a nearly regular icosahedron of 12 thiolate sulfur donor atoms.[2] Among the interesting reactions observed with some of these clusters are included ligand protonation[4] and sulfur addition.[5] Addition of elemental sulfur to the $[Cu_8({}^tBuDED)_6]^{4-}$ cluster (^{t}BuDED = 1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolate) results in the formation of the "sulfur-rich" $[Cu_8(S^tBuDED)_6]^{4-}$ cluster (I) and, depending on the counterions present, also the $[Cu_4(S^tBuDED)_3]^{2-}$ tetranuclear cluster[5] (II). In I and II, all of the dithiolene ligands contain an additional sulfur atom and have been converted to "sulfur-rich" 1,1-thioperthio dithiolenes. Sulfur addition to coordinated 1,1-dithiolate ligands originally was reported for the CS_3^{2-} ligand in the $[Ni(CS_3)_2]^{2-}$ anion.[6] The structures of "sulfur-rich" 1,1-dithio-chelating ligands and 1,1-dithiolenes have been established by X-ray crystallography in such complexes as FeL_3S (L = *p*-dithiotoluate[7]), NiL_2S, ZnL_2S_2 (L = *p*-dithiocumate[8]), *cis*- and *trans*-$[(CS_4)_2Mo{=}S]^{2-}$, the $[Mo_2S_2(\mu\text{-}S)_2(CS_4)_2]^{2-}$ and the $[Mo_2O_2(\mu\text{-}S)_2CS_3CS_4]^{2-}$ complexes,[9] the $[Ni(CS_4)_2]^{2-}$ complex,[10] and very recently, the $[Mn(CS_4)_2Cl]^{3-}$ complex.[11] Other sulfur complexes with a perthio S unit coordinated to a metal include the $[Mo_2O_2(\mu\text{-}S)_2L_2]^{2-}$ anion (L = vinyl disulfide),[12] the $[HB(Me_2pz)_3\}MoOS(\eta^1\text{-}SP(S)^iPr_2)$ complex,[13] the $Cp_2MoS_3C_2$(2-quinoxaline)(C(O)Me) complex that contains a "sulfur-rich" dithiolene ligand,[14a] and the $[Re_2((\mu\text{-}S)S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3]^+$ cation[14b] that contains a rather long S–S bond of 2.264(7) Å.

In this paper we report in detail the oxidation of I and II and the syntheses of the new mixed-valence and mixed-valence, mixed-coinage metal clusters $[Cu^I_4Cu^{III}(S^tBuDED)_4]^-$ (III) and $[Cu^I_4Au^{III}(S^tBuDED)_4]^-$ (IV), respectively. The crystal structures of $K(Ph_4P){\cdot}$II, $BzPh_3P{\cdot}$III, and $Bu_4N{\cdot}$IV are reported in detail. The synthesis of $K(Ph_4P){\cdot}$II has been reported previously.[5] Recently, the reactions of the $[Cu_8(\text{i-MNT})_6]^{4-}$ cubane[2c] (i-MNT = 1,1-dicyano-2,2-ethylenedithiolate) with elemental sulfur has been found[15] to give the hexanuclear $[Cu_6(\text{S-i-MNT})_6]^{6-}$ anion that contains the "sulfur-rich" i-MNT ligands.

Experimental Section

The chemicals in this research were used as purchased, $K_2{}^tBuDED$[16] and K_2DED[17] were prepared by previously published methods. K_2BzDED was made by the same method using benzyl alcohol instead of *tert*-butyl alcohol. The synthesis of the $K_4Cu_8({}^tBuDED)_6$ and $(n\text{-}Bu_4N)_4Cu_8({}^tBuDED)_6$ clusters have been published.[5] All compounds were prepared in air. Acetonitrile was distilled from calcium hydride under dinitrogen. Diethyl ether was distilled over sodium benzophenone. Analyses for C, H, and N were obtained from the Analytical Services Laboratories of the Chemistry Departments of the University of Michigan and the University of Iowa and by Oneida Research Services Inc., Whitesboro, NY. The copper content in some of the complexes was determined by EDTA titration using murexide as an indicator. Sulfur, phosphorous, and potassium analyses were obtained from Clark Microanalytical Laboratory, Urbana, IL. Melting points were uncorrected.

Physical Measurements. Infrared spectra were recorded on a Nicolet 60 SX FT-IR spectrometer at a resolution of 4 cm^{-1} in CsI disks or on a Beckman 20A infrared spectrophotometer using Nujol or hexachlorobutadiene mull between potassium bromide plates or potassium bromide disks. Electronic spectra were recorded on a Cary Model 118 spectrophotometer and on a Varian Cary 219 spectrophotometer using 1-mm path length quartz cells. Proton-NMR spectra were obtained on a Bruker 300-MHz Pulse FT NMR spectrometer with Me_4Si as internal standard. ^{13}C-NMR spectra were obtained with a Bruker HX90E spectrometer equipped for pulse-Fourier transform operation. Most of the spectra were obtained with broad-band proton decoupling employing the solvent deuterium signal as an internal lock. Chemical shifts (δ) are given in parts per million downfield from internal tetramethylsilane.

Conductivity measurements were carried out in purified and distilled dichloroethane, spectrophotometric grade acetone, and acetonitrile using an Industrial Instrument Inc. Model RC 16B2 conductivity bridge and a Beckman Instruments, Inc. conductivity cell. Molecular weights were determined osmometrically using a Mechrolab Inc. Model 301A vapor pressure osmometer, and benzil was used as a calibrant. Cyclic voltammetric measurements were performed on a Princeton Applied Research model 175 Universal programmer. The electrochemical cell used had platinum working and auxiliary electrodes. As the reference electrode, a saturated calomel electrode was used. All solvents used in the electrochemical measurements were property dried and distilled. The supporting electrolyte used was tetra-*n*-butylammonium perchlorate, $(C_4H_9)_4NClO_4$, (0.1 M solutions). Normal concentrations used were 0.001 M in electroanalyte. Purified argon was used to purge the solutions prior to the electrochemical measurements.

Syntheses. Tetrabutylammonium Tetrakis(1,1-Dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracopper(I)cuprate(III) ($Bu_4N[Cu^I_4Cu^{III}(S^tBuDED)_4]$, $Bu_4N{\cdot}$III). A mixture of 2.4 g (0.001 mol) of $K_4Cu_8(S^tBuDED)_6$,[5] 1.1 g (0.004 mol) of Bu_4NCl, and 0.38 g (0.012 mol) of S_8 in a mixture of 30 mL of acetone and 20 mL of EtOH was allowed to stir until the solution changed color from orange to yellow–brown. Finely powdered $Cu(NO_3)_2{\cdot}3H_2O$ (0.002 mol) was added slowly with vigorous shaking until the solution turned deep blue in color. The intensely blue colored solution was filtered into cold distilled water which was vigorously stirred. The blue solid that precipitated out was collected by filtration, washed with water, and dried. The crude product was crystallized by dissolving in a minimum amount of acetone and adding pentane to incipient crystallization. Upon cooling, dark blue crystals were obtained: yield 45%; mp, 139 °C (dec). Anal. Calcd for $C_{64}H_{108}Cu_5S_{12}O_{16}N$: C, 41.50; H, 5.99; N, 0.76. Found: C, 41.44; H, 5.95; N, 0.69.

Potassium Tetrakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracopper(I)cuprate(III) ($K[Cu^I_4Cu^{III}(S^tBuDED)_4]$). The $KCu_5(S^tBuDED)_4$ derivative was prepared by the above procedure without adding a salt of an organic cation. Anal. Calcd for $C_{48}H_{72}Cu_5S_{12}O_{16}K$: C, 34.99; H, 4.37. Found: C, 34.02; H, 4.20.

Bis(tetrabutylammonium)(Tetrakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracopper(I)monoaurate(III) Dichlorocuprate ($(Bu_4N)_2[Cu_4Au(S^tBuDED)_4]{\cdot}(CuCl_2){\cdot}(CH_2Cl_2)_{0.5}$, $(Bu_4N)_2{\cdot}$IV). An amount of $HAuCl_4{\cdot}3H_2O$, 0.243 g (6.15×10^{-4} mol), was dissolved in 20 mL of acetone and was added dropwise to a solution of $(Bu_4N)_4Cu_8(S^tBuDED)_6$, 1.2 g ($3.52 \times 10^{-4}$ mol), in 50 mL of acetone with stirring. The color of the solution changed from yellow to violet on addition of the gold reagent. The solution was filtered after addition of 50 mL of pentane. To the filtrate was added 50 mL of a 1:1 mixture of Et_2O and petroleum ether. The violet oil which formed on standing at 0 °C was separated by decanting the supernatant liquid. The oil was dissolved in EtOH, and a 4:1 Et_2O/pentane mixture was added to incipient crystallization. Violet crystals formed on standing at 0 °C and were isolated: yield, 40%. Anal. Calcd for $C_{80.5}H_{145}Cu_5AuS_{12}O_{16}N_2Cl_3$, (MW = 2400.1): C, 40.25; H, 6.04; N, 1.17. Found: C, 40.42; H, 5.87; N, 1.14.

Tetraphenylphosphonium Tetrakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracopper(I)monoaurate(III) Potassium Chloride ($(Ph_4P)[Cu_4Au(S^tBuDED)_4]{\cdot}KCl$). The complex was prepared by following the same procedure as that with $(Bu_4N)_4Cu_8(LS)_6$ except that $K(Ph_4P)Cu_4(S^tBuDED)_3$ was used in acetone solution. Violet colored crystals formed by cooling the solution of 0 °C. After filtration, the crystals were washed with acetone and Et_2O and then dried unver vacuum.

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement of $K(Ph_4P)[Cu_4(S^tBuDED)_3]\cdot[(CH_3)_2C{=}O]_3$ (II), $(BzPh_3P)[Cu_5(S^tBuDED)_4]$ (III), and $(Bu_4N)_2[Cu_4Au(S^tBuDED)_4]\cdot CuCl_2\cdot(CH_2Cl_2)_{0.5}$ (IV)

	II	III	IV
formula	$C_{69}H_{92}Cu_4S_9O_{15}PK$	$C_{73}H_{94}Cu_5S_{12}PO_{16}$	$C_{80.5}H_{145}Cu_5AuS_{12}O_{16}N_2Cl_3$
MW	1772.2	1961.1	2400.1
a, Å	12.846(2)	17.042(4)	39.172(6)
b, Å	12.846(4)	31.133(10)	9.8553(9)
c, Å	12.846(1)	18.326(5)	30.745(4)
α, deg	83.92(1)	90.00	90.00
β, deg	83.92(1)	97.03(2)	108.69(1)
γ, deg	83.92(1)	90.00	90.00
V, Å^3; *Z*	2086.6 (3); 1	9650.5(48); 4	11 243.3(30); 4
d_{calcd}, g/cm^3	1.41	1.35	1.38
d_{obsd},[a] g/cm^3	1.40	1.34	1.37[b]
space group	*R*3*m*	$P2_1/n$	*C*2/*c*
cryst dimens, mm	0.3 × 0.3 × 0.3	0.4 × 0.5 × 0.01	0.051 × 0.079 × 0.220
μ, cm^{-1}	16.4	14.05	62.9
radiation	Mo Kα[c]	Mo Kα[c]	Cu Kα[d]
data collection	$2\theta_{max} = 40°$	$2\theta_{max} = 40°$	$2\theta_{max} = 103°$
no of data used, $F_o^2 > 3\sigma(F_o^2)$	2507	4215	4172
parameters	206	551	477
R_c[e]	0.049	0.109	0.085
R_2[f]	0.049	0.113	0.136

[a] Obtained by flotation in a CCl_4/pentane mixture. [b] Obtained by flotation in a CBr_4/pentane mixture. [c] λ = 0.710 69 Å. [d] λ = 1.5418 Å. [e] $R = \Sigma|F_o| - |F_c|/|F_o|$. [f] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

Anal. Calcd for $C_{72}H_{92}Cu_4AuS_{12}PClKO_{16}$: C, 40.14; H, 4.27. Found: C, 39.57; H, 4.37.

Dipotassium Bis(tetrabutylammonium) Tetrakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracuprate(I) ($K_2(Bu_4N)_2[Cu_4(S^tBuDED)_4]$, $K_2(Bu_4N)\cdot V$). An amount of $Bu_4NCu_5(S^tBuDED)_4$, 1.8 g (0.001 mol), was dissolved in 20 mL of warm acetonitrile under nitrogen. To this solution 0.74 g (0.005 mol) of solid potassium thiophenolate was added KSPh in small portions while the solution was frequently agitated. The solution changed color from blue to orange. It was filtered after warming for 5 min. The oil that was obtained by complete removal of the solvent was washed with 5–8 mL of Et_2O and was triturated with 2–3 mL of EtOH until it solidified. The solid obtained after decanting off the ethanol was crystallized from acetone by adding pentane to incipient crystallization. Yellow crystals formed upon standing. The product was collected by filtration, washed with Et_2O, and dried in vacuum: yield, 20%; mp, 120 °C (dec). Anal. Calcd for $C_{80}H_{1444}Cu_4S_{12}O_{16}N_2K_2$: C, 45.62; H, 6.8; S, 18.25; N, 1.33; K, 3.71; Cu, 12.08. Found: C, 45.46; H, 6.86; S, 18.20; N, 1.24; K, 3.93; Cu, 11.9.

Dipotassium Bis(tetraphenylphosphonium) Tetrakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracuprate(I) ($K_2(Ph_4P)_2[Cu_4(S^tBuDED)_4]$. This compound was prepared as indicated above for the Bu_4N^+ derivative using $Ph_4P[Cu_5(S^tBuDED)_4]$ as a reagent. Anal. Calcd for $C_{80}H_{144}Cu_4S_{12}O_{16}N_2K_2$ (MW 2298.16): C, 50.13; H, 4.87; S, 16.71; P, 2.70; Cu, 11.05. Found: C, 49.45; H, 4.86; S, 16.25; P, 2.24; Cu, 10.6.

$Na_2(Bu_4N)_2[Cu_4(S^tBuDED)_4]$. The synthesis of this derivative was carried out as in the previous case except that NaSPh was used instead of KSPh. Anal. Calcd for $C_{80}H_{144}N_2S_{12}O_{16}Na_2Cu_4$: C, 46.33; H, 7.00; N, 1.35. Found: C, 47.01; H, 7.65; N, 1.70.

Collection and Reduction of X-ray Diffraction Data. Single crystals of $K(Ph_4P)[Cu_4(S^tBuDED)_3]\cdot[(CH_3)_2C{=}O]_3$ ($K(Ph_4P)\cdot II$) were obtained as yellow tetrahedra by the addition of pentane into a warm acetone/ethanol solution of the complex as described previously.[5] One of these crystals was mounted on a glass fiber and was used for cell dimension measurements and data collection. Single crystals of III and IV were obtained by the slow diffusion of *n*-pentane into CH_2Cl_2 solutions of the clusters. Details concerning crystal characteristics, the data collection, and structure refinement are shown in Table I.

Intensity data for II and IV were obtained on a Picker–Nuclear four-circle diffractometer as described previously.[4] Graphite monochromatized Mo Kα radiation (Kα, λ = 0.7107 Å) was used for data collection for II ($2\theta_{max} = 40°$), and Cu Kα radiation (Kα, λ = 1.5417 Å) was used for data collection for IV ($2\theta_{max} = 103°$). Unit cell dimension determinations and data collection and reduction were carried out according to a previously published protocol.[4]

Diffraction data on III were collected with a Nicolet P3/F four-circle computer-controlled diffractometer, equipped with a molybdenum X-ray tube and a graphite monochromator using Mo Kα radiation. Crystal data and data collection parameters are summarized in Table I and were obtained as described previously.[18] An absorption correction was applied to the data.

Solution and Refinement of the Structures. Three-dimensional Patterson synthesis maps were obtained for II and IV in the appropriate space groups (Table I) and were solved to yield the positions of one or more of the heavy atoms. The other non-hydrogen atoms were located on subsequent Fourier synthesis maps following least-squares refinements of input atomic coordinates. In the structure of II, the anion is located on a special position in the space group *R*3*m* with 3*m* site symmetry. The site symmetry is satisfied by two mirror-related anions (enantiomers) occupying (each with half occupancy) the crystallographic 3-fold axis at 0,0,*z*. The pentanuclear cluster in IV is located on a crystallographic 2-fold axis of symmetry in the space group *C*2/*c*. For both II and IV, the correct choice of space group was validated by the successful refinement of the structures. Refinement of the structure of II in the space group *R*3, with a disorder model as described above, was unsatisfactory and resulted in R_c and R_2 values of 0.09 and 0.11, respectively, and unacceptably high standard deviations in both distances and angles.

The procedures and programs employed in the refinement of II and IV have been described previously.[4] The structure of II was refined with anisotropic temperature factors for the Cu, P, K, S, and O atoms and for the four skeletal ligand carbon atoms. The phenyl group of the cation on the 3-fold axis and the ^{t}Bu groups of the ligand were refined with isotropic temperature factors. The acetone molecule of solvation and the phenyl ring of the cation not lying on the 3-fold axis were refined as rigid groups as described previously.[19]

The direct method routine SOLV of the SHELXTL package was used to solve the structure of III. Trial positions for the copper atoms were taken from the *E* map derived from the phase set with the highest combined figure of merit. The remaining non-hydrogen atoms were determined by difference Fourier maps. With the exception of all carbon atoms that were refined isotropically, all non-hydrogen atoms were refined with anisotropic thermal parameters according to a protocol described previously.[18] The anion occupies a general position.

Crystallographic Results. The fractional atomic coordinates and equivalent isotropic thermal parameters, with standard deviations, for the non-hydrogen atoms in II, III, and IV have been deposited in the supplementary material together with the observed and calculated structure factors. The structures of the anions are shown in Figures 2 and 3 for II, Figure 4 for III, and Figure 5 for IV.

Results and Discussion

Synthesis. The syntheses and spectroscopic characterizations of the $[Cu_8(S^tBuDED)_6]^{4-}$ (I) and $[Cu_4(S^tBuDED)_3]^{2-}$ (II) anionic clusters have been reported previously.[5] Yellow solutions

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(18) Al-Ahmad, S. A.; Salifoglou, A.; Kanatzidis, M. G.; Dunham, W. R.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 927.

(19) Hollander, F. J.; Coucouvanis, D. *Inorg. Chem.* **1974**, *13*, 2381.

of either **I** or **II** undergo a dramatic color change to intense blue upon reaction with either Cu(II) or Fe(III) ions. The color change is due to the $[Cu_5(S^tBuDED)_4]^-$ anion (**III**), that is the stable oxidation product of either **I** or **II**. The synthesis of the *diamagnetic* **III** in moderate yield is accomplished readily by the oxidation of **I** with $Cu(NO_3)_2{\cdot}3H_2O$ in acetone solution and can be obtained in crystalline form with various counterions. The stoichiometry and overall charge of **III** indicate that the compound is a mixed-valence cluster that contains either a $(Cu^{II})_2(Cu^I)_3$ or a $Cu^{III}(Cu^I)_4$ core. The latter appears to be a more accurate description and is supported by the coordination geometries of the metal ions, by the diamagnetic nature of **III**, and as described below, by the existence of an isostructural cluster that contains the $Au^{III}(Cu^I)_4$ aggregate. The reaction of **III** with OH^- results in the internal oxidation of some of the S^{t}BuDED ligands to $(SC{=}C(COOR)_2)_2$ and formation of **I** (eq 1.). The 2:1 **III**:**I** stoichiometry shown (eq 1) for this reaction is based on a spectrophotometric titration of **III** with Bu_4NOH, and the 1:2 **III**:OH stoichiometry was established by a potentiometric titration.[20] 2,4-Bis(dicarbo-*tert*-butoxymethylene)-1,3-dithiacyclobutane ($(SC{=}C(COOR)_2)_2$) was characterized spectroscopically[21] and has been reported previously.[22] The other products of this reaction have not been identified. The reaction of either $(Bu_4N)_4{\cdot}$**I** or $K(Ph_4P){\cdot}$**II** with $HAuCl_4{:}3H_2O$ in acetone solution is evident by the appearance of an intense violet color. A violet crystalline *diamagnetic* compound forms upon addition of ether to a solution obtained from the reaction of **I** with $HAuCl_4{\cdot}3H_2O$. The elemental analysis of this compound is consistent with the stoichiometry $[Bu_4N]\{[Cu^I_4Au^{III}(S^tBuDED)_4]{\cdot}[Bu_4N][Cu(Cl_2)]{\cdot}(CH_2Cl_2)_{0.5}\}$. This formulation has been confirmed by a crystal structure determination (vide infra).

$$2[Cu_5(S^tBuDED)_4]^- + 4OH^- \rightarrow [Cu_8(S^tBuDED)_6]^{4-} + (SC{=}C(COOR)_2)_2 + \text{other products} \quad (1)$$

The reactions of **III** with thiolate ions (PhS^-, p-CH_3PhS^-, or $PhCH_2S^-$) result in the formation of a new yellow crystalline product. This compound has been obtained with various counterions or mixtures of counterions such as K^+, Ph_4P^+/K, Et_4N^+/K^+, or Bu_4N^+/K^+. In all cases, the best fit of the analysis is consistent with the presence of the $[Cu_4(S^tBuDED)_4]^{4-}$ anion (**V**). The isolation and positive identification of RSSR disulfides as reaction byproducts suggest that **III** is reduced by the RS^- ions. A molecular weight determination of the $K_2(Ph_4P)_2{\cdot}$**V** salt was carried out in CH_3CN and $C_2H_4Cl_2$. The results[23] show that the number of particles in solution as expected for a weak electrolyte increases with dilution and also with increasing polarity of the solvent. A calculation of M_o/M_c based on the $K(Ph_4P)[Cu_2(S^tBuDED)_2]$ empirical formula gave values less than unity for the measurements in $C_2H_4Cl_2$ solution and indicates that, in $C_2H_4Cl_2$ solution, the undissociated cluster is at least a dimer, i.e. $K_2(Ph_4P)_2[Cu_4(S^tBuDED)_4]$. Indeed, the molecular weight at the highest attainable concentration in $C_2H_4Cl_2$ was determined to be 2092 ± 110, which is reasonably close to the value of 2298 expected for the $K_2(Ph_4P)_2{\cdot}$**V** tetramer. The molecular weight data strongly support the dimeric formulation but cannot exclude a $K_3(Ph_4P)_3[Cu_6(S^tBuDED)_6]$ hexamer. The latter has a precedent in the structure of the $[Cu_6(S\text{-}i\text{-}MNT)_6]^{6-}$ anion, which has been structurally characterized.[15] Possible structures for **V** are shown in Figure 1 as derivatives of **III** following reduction and the subsequent loss of the apical Cu(III) ion. The ^{13}C-NMR data (vide infra) indicate a comparatively greater double bond character for the C–S ligand bonds in **V** and would favor a structure where, following a minor rearrangement, the S^{t}BuDED ligands employ the perthio group as a bridge and reserve the "C=S" group for terminal ligation (Figure 1B). The oxidation of **V** with Cu^{2+}, like the corresponding oxidations of **I** and **II**, affords **III** in modest yield. The utility of **V** as a metalloligand is illustrated in its reaction with $HAuCl_4$ that readily gives **IV**. Similar reactions with Ni^{2+} or Rh^+ ions show intense color changes. The red compounds that can be isolated from these reactions are noncrystalline and are rather difficult to purify.

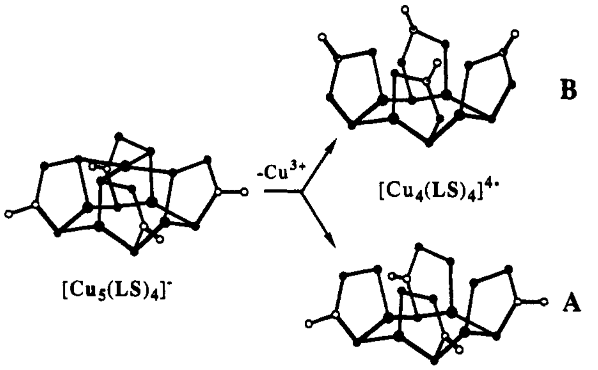

Figure 1. Formation and two probable structures of the $[Cu^I_4(S^tBuDED)_4]^{4-}$ anion.

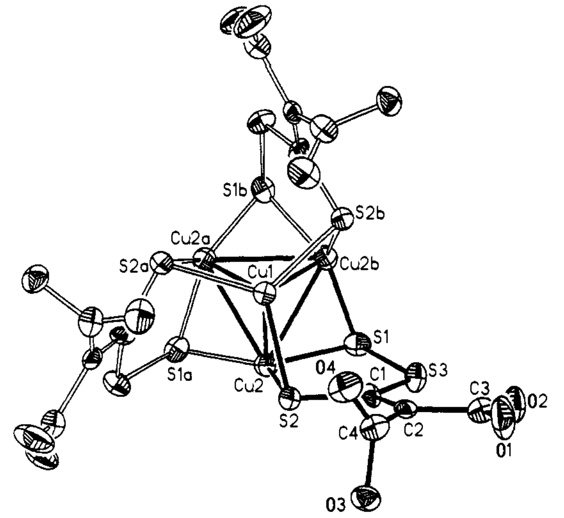

Figure 2. Structure of the $[Cu_4(S^tBuDED)_3]^{2-}$ anion in $K(Ph_4P){\cdot}$**II**. The *tert*-butyl groups of the S^{t}BuDED ligands have been omited for clarity. Thermal ellipsoids as drawn by ORTEP represent the 30% probability surfaces.

Crystal Structures of II, III, and IV. In the X-ray crystal structure of $KPh_4P{\cdot}$**II**, two $[Cu_4(S^tBuDED)_3]^{2-}$ anions (Figure 2) are located with half occupancy on a crystallographic 3-fold axis of symmetry, sharing the apical copper atom (Cu(1)) at 0,0,0 and related to each other by the crystallographic mirror plane of the special position ($3m$ symmetry) in the $R3m$ space group. The two half-occupancy anions are rotated around the 3-fold axis by 37.4° relative to each other (Figure 3). The K^+ cation, the P atom of the Ph_4P^+ cation, and two carbons of one of the phenyl rings of the cation also are located on the 3-fold, z axis. The six-coordinate K^+ cation is coordinated to three carbonyl groups of the ligands (one from each ligand: O4L, O4L′, and O4L″, Figure 2) and to the three acetone molecules of solvation. The alkali metal/cluster interactions apparently "drive" the facile dissociation of the $[Cu_8(S^tBuDED)_6]^{4-}$ cubic cluster (**I**) into two $[Cu_4(S^tBuDED)_3]^{2-}$ anions when Na^+ or K^+ ions are added to solutions of **I**. As demonstrated previously by ^{13}C-

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[20] Huber, W. *Titrations in Non-Aqueous Solvents*; Academic Press: New York, 1967.

[21] This compound was characterized by elemental analysis, infrared spectroscopy (a single carbonyl absorption at 1661 cm^{-1}), and ^{13}C-NMR spectroscopy (*C*—S, δ 165.81; *C*=O, δ 162.69; =*C*(R$_2$), δ 114.81; *C*(CH$_3$)$_3$, δ 83.03; C(*C*H$_3$), δ 28.33.

[22] (a) Gompper, R.; Toepfl, W. *Chem. Ber.* **1962**, *95*, 2861. (b) Kelber, C.; Schwartz, A. *Chem. Ber.* **1912**, *45*, 137.

[23] A table and a figure that show these results have been deposited with the supplementary material.

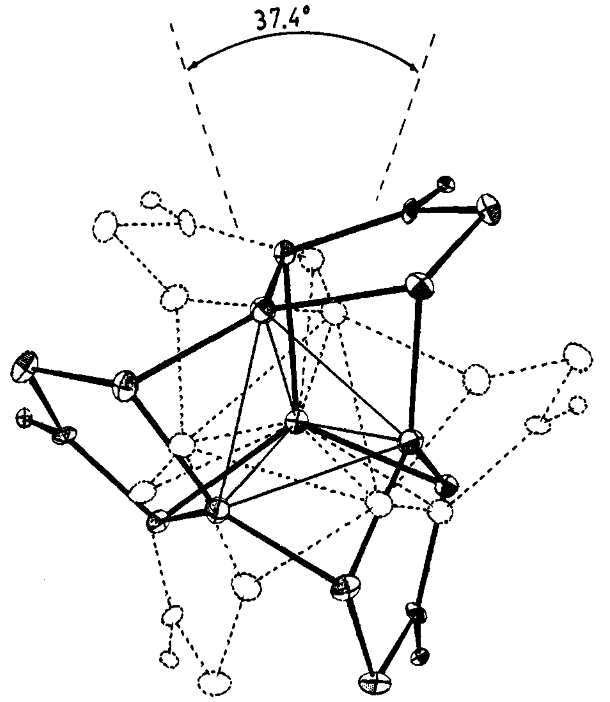

Figure 3. Occupation of the $3m$ site in the space group $R3m$ by the two enantiomers of the $[Cu_4(S^tBuDED)_3]^{2-}$ anion each at one-half occupancy.

Table II. Summary of Interatomic Distances (Å) and Angles (deg) for $K(Ph_4P)[Cu_4(S^tBuDED)_3]$ (II)

Metal Core			
Distances (Å)			
Cu(1)–Cu(2)	2.724(2)	S(1)–S(2)	3.440
Cu(2)–Cu(2′)	2.733(3)	S(2)–S(3)	3.991
Cu(1)–S(2)	2.263(4)	S(1)–S(2′)	3.975
Cu(2)–S(2)	2.272(3)	S(2)–S(2′)	3.916
Cu(2)–S(1)	2.211(3)	S(1)–S(1′)	4.132(4)
Cu(2)–S(1′)	2.246(3)	K–O4L′	2.655(9)
Cu(2)–S(3)	3.366(3)	K–OA	2.795(9)
Cu(2′)–S(3)	3.381(3)		
Angles (deg)			
S(2)–Cu(1)–S(2)	119.8(2)	Cu(2)–Cu(2)–Cu(1)	54.69(3)
S(1)–Cu(2)–S(2)	124.2(2)	Cu(2)–Cu(1)–Cu(2)	60.21(5)
S(1)–Cu(2)–S(1′)	136.0(1)	O4L–K–O4L′	102(1)
S(2)–Cu(2)–S(1′)	99.0(1)	OA–K–OA′	72(1)
Cu(2)–Cu(2)–Cu(2)	60.00	O4L–K–OA	98(1)
Cu(2)–Cu(2)–Cu(1)	59.89(4)	O4L–K–OA′	85(1)
Ligands			
Distances (Å)			
S(1)–S(3)	2.076(4)	C3L–O2L	1.173(13)
S(3)–C1L	1.766(10)	C3L–O1L	1.357(15)
S(2)–C1L	1.716(9)	C4L–O4L	1.203(11)
C1L–C2L	1.392(13)	C4L–O3L	1.363(10)
C2L–C3L	1.530(15)	O1L–C5L	1.413(16)
C2L–C4L	1.476(12)	O3L–C9L	1.501(13)
Angles (deg)			
S(2)–C1L–S(3)	125.0(4)	S1–S3–C1L	107.3(4)
S(2)–C1L–C2L	118.0(6)	S3–S1–Cu(2)	102.9(1)
S3–C1L–C2L	117.0(5)	S3–S1–Cu2′	103.5(1)
C1L–S(2)–Cu(1)	101.3(4)	C1L–C2L–C3L	
C1L–S(2)–Cu(2)	104.3(4)	C1L–C2L–C4L	

NMR spectroscopy,[5] the sequestering of the K^+ ions in solutions of **II** by crown ether molecules reverses the dissociation process and **I** reappears in solution.

Structural details of the $[Cu_4(S^tBuDED)_3]^{2-}$ anion are presented in Table II. The four copper atoms in the anion define a nearly regular tetrahedron, and one of the four copper atoms in the tetrahedron is structurally unique. The unique, apical, copper atom of the anion in **II** is coordinated by the thio groups of the ligands (one from each ligand), and the remaining three copper atoms in the basal plane of the Cu_4 tetrahedron are bridged pairwise by each of the three perthio groups. Two sets of nearly planar CuS_3 units (Table II) are present in the Cu_4S_6 core of the anion in **II**. One has crystallographically imposed C_3 symmetry with Cu–S bond lengths of 2.263(4) Å and is associated with the unique Cu(II) atom. The other CuS_3 unit (off the 3-fold axis) shows a wide variation in Cu–S bond lengths (2.211(3), 2.246(3), and 2.272(3) Å) and S–Cu–S angles (124.2(2), 136.0(1), and 99.0(1)°). The Cu–Cu distances in **II** of 2.724(2) and 2.733(2) Å are shorter than the Cu–S distances in the $[Cu_8L_6]^{4-}$ cubanes (L = dithiosquarate,[2a,b] 2.844(20) Å; L = EtDED,[2a,b] 2.790(11) Å; L = $(S_2C{=}C(CN)_2)^{2-}$,[2c,d] 2.829(14) Å) and similar to those in the $[Cu_4(\mu\text{-}SPh)_6]^{2-}$ cluster[24] (2.76(4) Å).

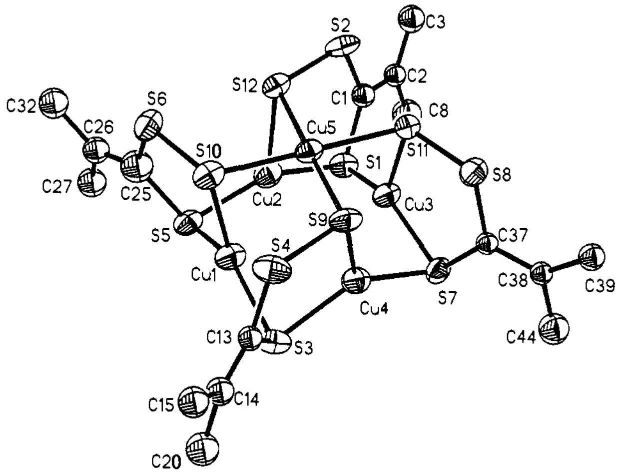

Figure 4. A view of the anion **III** in $(BzPh_3P)[Cu_5(S^tBuDED)_4]$. The oxygen atoms and the *tert*-butyl groups of the S^tBuDED ligands have been omited for clarity. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

The structures of the anions in **III** and **IV** are shown in Figures 4 and 5, and bond distances and angles are presented in Table III. The structures of both anions are similar and consist of Cu_5 and $AuCu_4$ rectangular pyramids with four bridging sulfur-rich ligands spanning and nearly bisecting the triangular faces. In both structures, the trivalent ion at the apex of the pyramid (Cu(III) in **III** and Au(III) in **IV**) is four coordinate and square planar. The basal Cu(I) ions in both **III** and **IV** are trigonal and nearly planar. The two, crystallographically independent, Cu–Cu distances in **IV** at 3.056(4) and 2.755(4) Å define the skewed rectancular shape of the planar Cu_4 subunits. The same subunit in the structure of **III** is closer to a square geometry with a mean Cu–Cu distance of 2.83(2) Å.[25] The mean Au(III)–Cu(I) distances in **IV** at 3.07 Å are within 3σ from the Cu(III)–Cu(I) distances in **III** of 3.029(7) Å.

The two independent Au–S bonds in **IV** at 2.406(5) and 2.393(4) Å are longer than other Au(III)–S bonds usually found close to 2.33 Å in square complexes.[1] The mean Cu–S bond in **III** (2.283(9) Å) also is longer than "typical" Cu(III)–S bond lengths usually found near 2.22 Å.[1] Indeed the Au–S and the axial Cu–S bond lengths in **III** and **IV** are closer to those expected for the divalent metal ions. The apparent lengthening of the M(III)–S bonds in **III** and **IV** may be due to the ligand bridging mode, or perhaps to an electronic description of the M(III)–S chromophore as a Cu(II)–S• antiferromagnetically coupled cupric ion–free radical pair (vide infra). This extensive $S_2 \rightarrow M$ charge

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(24) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993–2998. (b) Dance, I. G.; Calabrese, J. C. *Inorg. Chim. Acta* **1976**, *19*, L41.

(25) The numbers in parentheses following mean values of crystallographically independent, chemically equivalent, structural parameters represent the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}(x_i - x)^2/N(N-1)]^{1/2}$.

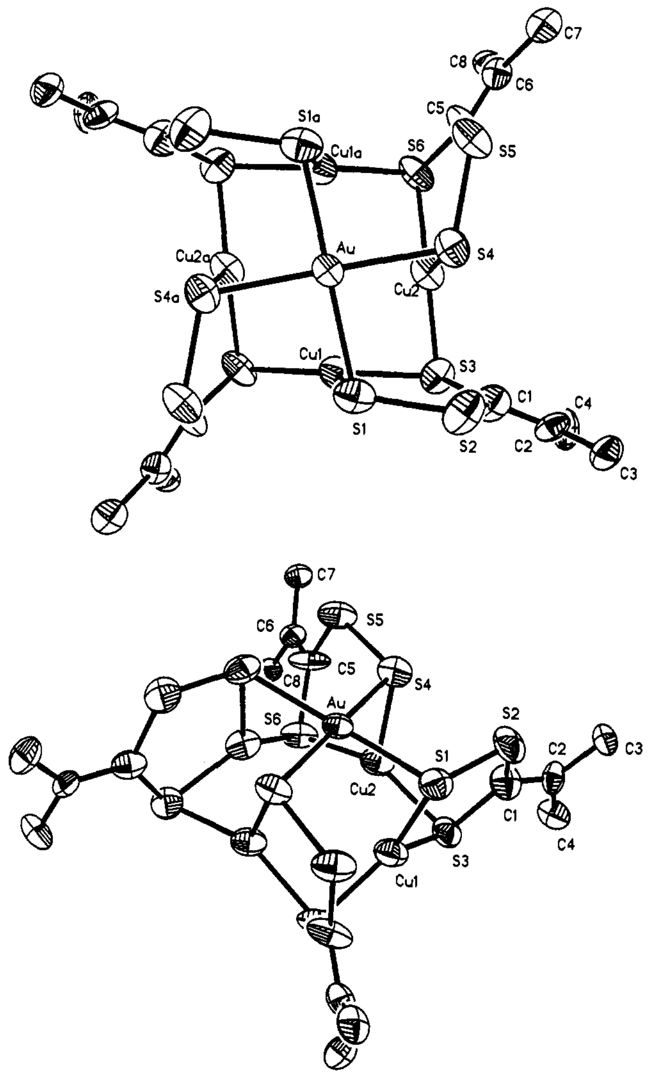

Figure 5. Two views of the anionic cluster IV in the $(Bu_4N)_2$-$\{[Cu^I_4Au^{III}(S^tBuDED)_4]^- \cdot CuCl_2\}$ double salt. The oxygen atoms and the *tert*-butyl groups of the S^tBuDED ligands have been omited for clarity. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

transfer, may be the origin of the low-energy, high-intensity, charge-transfer electronic transitions in III[26] and IV[27] (Figure 6).

The similarities in the structures of IV and III, with a Au(III) in the former replacing a Cu(III) in the latter, are evident and suggest that the common $[Cu^I_4(S^tBuDED)_4]^{4-}$ unit in III and IV (a "cluster ligand") may have an independent existence. As indicated previously, such a "cluster ligand" has been isolated (V) and has been found effective in the syntheses of III and IV.

^{13}C- and ^1H-NMR Spectroscopic Studies. The ^{13}C-NMR spectrum of II has been published,[5] and the spectra of III and IV have been obtained in CD_2Cl_2 solution.[28] The carbons of the CS_3 units in III and IV show resonances (168.22 and 167.31 ppm, respectively) shifted upfield by comparison to the corresponding resonances in II and V. These data (Table IV) together with a downfield shift of the olefinic carbon resonances (127.81 and 127.26 ppm) suggest extensive charge localization on the sulfur atoms, a pronounced single bond character of the C–S bonds, and a corresponding increase in the double bond character of the "olefinic" bond of the sulfur-rich ligands.

Table III. Summary of Interatomic Distances (Å) and Angles (deg) for $(BzPh_3P)[Cu_5(S^tBuDED)_4]$ (III) and $(Bu_4N)_2[Cu_4Au(S^tBuDED)_4] \cdot CuCl_2 \cdot (CH_2Cl_2)_{0.5}$ (IV)

	III	IV
	Distances[a]	
M(III)–Cu(I)	3.029(7,4)	3.069
range	3.022(5)–3.037(5)	3.051(3), 3.087(3)
Cu(I)–Cu(I)	2.83 (2,4)	2.91
range	2.776(5)–2.868(6)	2.755(4), 3.056(4)
M(III)–S_{ax}[b]	2.283(9,4)	2.400
range	2.268(9)–2.300(9)	2.393(4), 2.406(5)
Cu(I)–S_{eq}[c]	2.205(10,8)	2.200(8,4)
range	2.182(10)–2.229(9)	2.181(5)–2.215(5)
Cu(I)–S_{ax}[b]	2.340(9,4)	2.313
range	2.326(9)–2.351(9)	2.284(5), 2.343(5)
S–S[e]	2.055(12,4)	2.094
range	2.045(12–2.069(13)	2.087(7), 2.098(7)
C–S_{eq}	1.78(4,4)	1.77
range	1.74(3)–1.82(4)	1.74(2), 1.79(2)
C–S_{ax}	1.80(3,4)	1.76
range	1.78(3)–1.81(3)	1.76(2), 1.76(2)
C═C	1.34(5,4)	1.37
	Angles	
S–M(III)–S (cis)	90.0(3,4)	90.0
range	89.4(3)–91.1(3)	88.8(2), 91.2(2)
S_{eq}–Cu(I)–S_{ax} (intraligand)	98.6(3,4)	99.5
range	98.3(3)–98.8(3)	99.5(2), 99.6(2)
S_{eq}–Cu(I)–S_{ax} (interligand)	118.9(4,4)	118.0
range	118.1(3)–119.6(3)	115.1(2), 120.9(2)
S_{eq}–Cu(I)–S_{eq}	141.5(4,4)	142
range	140.7(3)–142.4(3)	139.1(1), 144.8(2)
M(III)–S_{ax}–Cu(I)	81.8(4,4)	81.3
range	· 81.0(3)–82.7(3)	81.1(1), 81.4(1)
Cu(I)–S_{eq}–Cu(I)	79.7(7,4)	82.8
range	77.8(3)–80.7(3)	77.6(2), 87.9(2)
M(III)–S_{ax}–S_{ax} (disulfide)	113.0(6,4)	110.5
range	112.2(4)–114.0(5)	109.6(2), 111.3(2)
Cu(I)–S_{ax}–S_{ax} (disulfide)	102.5(4,4)	101.1
range	102.3(4)–102.9(4)	102.8(2), 99.3(2)
S_{ax}–S_{ax}–C (disulfide)	107.9(10,4)	107.3
range	106.6(10)–109.0(13)	106.4(7), 108.2(6)

[a] Mean values of crystallographically independent, chemically equivalent, structural parameters. The first number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. The second number is the number of independent measurements. [b] Atoms located in the M(III) planes are designated as axial. [c] Atoms located at the base of the rectangular M_t pyramid are designated as equatorial.

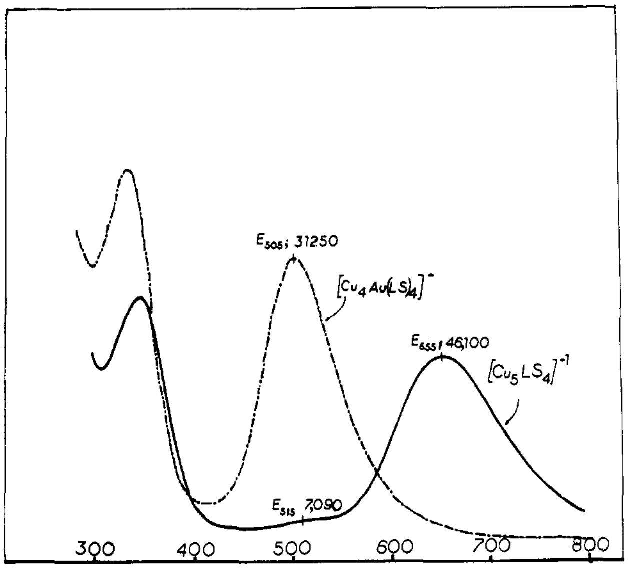

Figure 6. Electronic spectra of $(Bu_4N)[Cu^I_4Cu^{III}(S^tBuDED)_4]$ (III) and $(Bu_4N)_2\{[Cu^I_4Au^{III}(S^tBuDED)_4]^- \cdot CuCl_2\}$ (IV) in CH_2Cl_2 solution.

The variable-temperature ^1H- and ^{13}C-NMR spectra of V in CD_2Cl_2 solution[28] are characteristic of a fluxional system and may be explained in terms of hindered rotation of the $(^tBuOOC)_2C$

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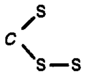
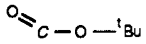
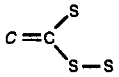
[26] Electronic spectrum in acetone solution: λ_{max} 655 nm, ϵ = 46 100; 525 nm, ϵ = 7090; 330 nm, ϵ = 80 000.

[27] Electronic spectrum in acetone solution: λ_{max} 505 nm, ϵ = 31 250; 320 nm, ϵ = 90 000.

[28] The ^{13}C-NMR spectra of III, IV, and V have been deposited with the supplementary material.

Table IV. ^{13}C-NMR (ppm) and Infrared Spectra (cm^{-1}) of the Clusters $[Cu_4(S^tBuDED)_3]^{2-}$ (II), $[Cu_5(S^tBuDED)_4]^-$ (III), $[Cu_4Au(S^tBuDED)_4]^-$ (IV), and $[Cu_4(S^tBuDED)_4]^{4-}$ (V)

	II^a	III^a	IV^a	V (310 K)^a	V (240 K)^a	V (333 K)^b
			^{13}C-NMR Spectra			
	174.20	168.22	167.31	185.18	184.08	188.17
	169.62 163.02	164.74 162.50	164.88 162.44	169.72 163.38	169.78 162.89	164.97
	118.68	127.81	127.26	115.85	115.85	113.16
O—C(CH$_3$)$_3$	81.54 79.82	82.13 81.93	82.16 81.97	79.21	80.18 78.10	77.05
OC(*C*H$_3$)$_3$	28.59 28.10	28.36 28.13	28.33 28.10	28.46	28.59 27.74	28.20
			IR Spectra^c			
C=O	1714 (s) 1669 (s)	1713 (s) 1685 (s)	1716 (s) 1690 (s)	1697 (s) 1656 (s)		
C=CS$_2$	1460 (s, bv)	1500 (s) 1474 (s, sh) 1454 (m, sh) 1367 (s)	1495 (s) 1462 (s, sh) 1452 (m, sh) 1368 (s)	1460 (sh) 1448 (s, bv)		

^{a} In CD_2Cl_2 solution. ^{b} In DMSO-d^6 solution. ^{c} In KBr disks.

groups around the "ethylenic" C–C bonds of the ligands. At low temperatures, hindered rotation around this bond would differentiate the two ester groups per ligand as *cis* and *trans* to the perthio group of the sulfur-rich ligand. Similar fluxional behavior has been reported previously for nitroketene mercaptals[29] and related compounds.[30,31] The low barrier to rotation was qualitatively explained by the low bond order of the double bond. By comparison to V, the ^{13}C-NMR spectra of II, III, and IV indicate a higher barrier to rotation and show very sharp doublets for the carbonyl, quaternary, and ^{t}Bu methyl carbon atoms (Table IV). An examination of the ambient temperature chemical shifts of the CS_3 and olefinic carbon atoms in V (at 185.18 and 115.85 ppm, respectively) shows the former shifted downfield and the latter upfield relative to those of II, III, and IV. This comparison shows that in V the double bond character of the C–S bond is higher and of the C–C bond lower than that of the corresponding bonds in II, III, and IV and may account for the lower barrier to rotation in V.

Of the two possible structures for V (Figure 1), the one that shows bridging perthio and terminally bound thio groups appears more realistic and consistent with an increased bond order for the C–S bond (and consequently a decrease in the bond order of the C=C bond).

Mixed-Valence States in III and IV. The oxidation of the $\{[Cu_4L_3]^{2-}\}_n$ clusters (n = 1 or 2; L = S^{t}BuDED) with either Cu(II) or Au(III) results in the formation of the mixed-valence coinage metal clusters $[Cu_5L_4]^-$ and $[AuCu_4(L)_4]^-$ that contain the 1,1-thioperthio ligands and both monovalent and trivalent coinage metal ions at close proximity *within the same molecule.* Homonuclear or heteronuclear mixed-valence complexes of the type M^n/M^{n+1} that contain Cu(I)/Cu(II),[32,33] Cu(II)/Cu(III),[34] or Cu(II)Cu(III)Au(III)[35] have been reported previously. Homonuclear, mixed-valence delocalized complexes of the M^n/M^{n+2} type also are known and include complexes with M = Rh, *n* = 1 or 3,[36] M = Ir, n = 1 or 3,[37] and M = Ni, Pd, or Pt, n = 2 or 4.[38] With the exception of a "salt" like compound[39] that contains the linear dichloroaurate monoanion and the square 2,3-butanedione dioximate gold(III) monocation (Au–Au separation, 3.26 Å), coinage metal complexes that contain both M(III) and M(I) with different coordination geometries within the same molecule have not been reported. The absence of electron transfer to the trivalent ions from potentially reducing Cu(I) centers (at 3.029(7) and 3.069(3) Å, respectively, for III and IV) is remarkable. A barrier to intramolecular electron transfer accounts for the exceptional stability of essentially a charge-separated state in III and may be explained in terms of geometric constraints that do not allow for a change in coordination geometry of the three-coordinate Cu^I centers following oxidation. A bonding description that cannot be ruled out at present is one that places a significant contribution of a Cu(II)–S$^•$ form to the electronic structure of III. This form derives from intramolecular electron transfer from the coordinated S atom to the Cu(III) center with the formation of a strongly antiferromagnetically coupled cupric ion–sulfur radical pair. The pairing of Cu(II) with an organic free radical has been found in galactose oxidase. Galactose oxidase catalyzes the oxidation of primary alcohols to aldehydes and couples this reaction to the reduction of dioxygen to hydrogen peroxide.[40] The one-electron oxidized form of galoctose oxidase (catalytically inactive) shows a "normal" EPR signal typical of type 2 copper.[41] Oxidation by an additional electron (of the catalytically active state) results in an EPR silent form of the enzyme. This form originally was proposed to contain Cu(III).[42] Recent studies have shown that the center in the two-electron oxidized form of galactose oxidase can best be described by a model where a Cu(II) is strongly antiferromagnetically coupled to an organic free radical metabolically derived from tyrosine.[43] Upon removal of the copper,

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the organic radical can be seen in large amounts.[41] The Cu(II)–radical pair model is supported further by X-ray absorption edge studies that have revealed the existence of Cu(II) in the two-electron oxidized form of the enzyme.[44]

A significant contribution to the electronic structure of **III** by the Cu(II)–S$^\bullet$ description also finds support in the length of the Cu–S bond (somewhat long and more appropriate for Cu(II)). It should be noted that the very intense blue color of **III** is similar to the color associated with the S_3^- radical anion (620 nm).[45] This similarity is very likely coincidental since in S_3^- the electronic absorption is due to a doublet–doublet transition.[46]

An alternate, albeit less specific, explanation for the stability of the Cu(III) center in **III** may be the extensive covalency of the Cu(III)–S bonds with the S^{t}BuDED ligands. Covalency has been suggested as a possible reason for the unusual stability of the planar $[Cu^{III}(EtDED)_2]^-$ complex[47] (Cu(III)–S = 2.195(5) Å) and also of the distorted octahedral $[Fe^{IV}(EtDED)_3]^{2-}$ complex.[48] The difficulty of reducing the Cu(III) center in **III** (irreversible reduction at –0.40 V vs SCE) has a precedent in the reduction of the $[Cu^{III}(EtDED)_2]^-$ complex[47] (reversible reduction at –0.50 V vs Ag/AgI) and is not unexpected in view of the fact that the electron is added to the empty, antibonding $d_{x^2-y^2}$ orbital. Irreversibility in the chemical reduction of **III** is evident in the synthesis of **V**. The latter forms following the release of a copper atom as the Cu(III) ion in **III** undergoes reduction. At present it is not known whether clusters similar to **III** or **IV** can be obtained by oxidation of other "sulfur-rich" 1,1-dithiolene ligand (SL, S-i-MNT[15]) derivatives such as the $[Cu_6(S\text{-}i\text{-}MNT)_6]^{6-}$ hexamer[15] or other $[(Cu_4(SL)_3)_n]^{2n-}$ sulfur-rich 1,1-dithiolene clusters.

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Supplementary Material Available: Tables S1–S4 containing listings of crystal data, positional parameters, thermal parameters, and selected distances and angles and drawings showing structures of $K(Ph_4P)[Cu_4(S^tBuDED)_3]\cdot[(CH_3)_2C{=}O]_3$ (**II**), $(BzPh_3P)[Cu_5(S^tBuDED)_4]$ (**III**), and $(Bu_4N)_2[Cu_4Au(S^tBuDED)_4]\cdot CuCl_2\cdot(CH_2Cl_2)_{0.5}$ (**IV**), ^{13}C-NMR spectra of **II**, **IV**, and **V** and a table and plot of the molecular weight data for **V** (41 pages); tables S5–S7 listing calculated and observed structure factors for **II**, **III**, and **IV** (76 pages). Ordering information is given on any current masthead page.

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