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Sulfur Addition to the 1,1-Dithiolate Ligands in the $[Cu_8L_6]^{4-}$ Cubanes (L = 1,1-Dicarbo-*tert*-butoxy-2,2-ethylenedithiolate). Reversible $Cu_8(LS)_6{}^{4-}$ to $Cu_4(LS)_3{}^{2-}$ Transformations

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The cubic $[Cu_8L_6]^{4-}$ clusters (L = 1,1-dicarbo-*tert*-butoxy-2,2-ethylenedithiolate, *t*-Bu_2DED) undergo a sulfur-addition reaction with the formation of the "sulfur-rich" $[Cu_4(LS)_3]_n{}^{2-}$ clusters. Each of the ligands in these clusters has added a sulfur atom to form the perthiocarboxylate functional unit. ^{13}C NMR and infrared spectral evidence suggests that the counterions that accompany the $[Cu_4(LS)_3]_n{}^{2-}$ anions play an important role in the molecularity of the clusters. Thus with the noninteracting *n*-Bu_4N^+ cations the $[Cu_8(LS)_6]^{4-}$ clusters can be isolated. In the presence of alkali-metal ions the $[Cu_4(LS)_3]^{2-}$ clusters are stabilized. This stabilization, which is attributed to alkali-metal ion interactions with the carboxylate functions of the ligand, can be eliminated in solution by the addition of alkali-metal sequestering crown ethers to solutions of the $K(Ph_4P)Cu_4(LS)_3$ complex. The characterization of the $Cu_8(LS)_6{}^{4-}$ and $Cu_4(LS)_3{}^{2-}$ complexes in solution has been possible by ^{13}C NMR spectroscopy. For the $Cu_8(LS)_6{}^{4-}$ cluster containing the asymmetric (A–B) sulfur-rich ligands in the $Cu_8(A{-}B)_6$ unit, most of the expected (five) structural isomers are present in solution as evidenced by the presence of most of the expected ligand $^{13}CS_3$ resonances.

Introduction

The coordination chemistry of cuprous ions with sulfur-containing ligands is uniquely characterized by the formation of multinuclear aggregates with a wide variety in composition and structure. Some outstanding examples, which have been characterized structurally, are based on core units of the stoichiometry Cu_4S_6,[1-4] Cu_4S_8[5,6] Cu_5S_6,[7] Cu_5S_7,[8] Cu_8S_{12},[9-11] $Cu_8S_{12}Cl$,[12,13] and $Cu_{10}S_{16}O_2$.[14]

The existence of aggregates with the Cu_4S_6 and Cu_8S_{12} basic cores, which contain tetrahedral Cu_4 and cubic Cu_8 units, respectively, poses an interesting question regarding the factors that dictate the formation of structurally different cores with the same Cu/S ratio.

In previous reports,[2,11] we have suggested that with nonchelating ligands such as the RS^- mercaptides a Cu:S ratio of 2:3 favors the formation of the Cu_4S_6 "adamantane" type of unit and that the rather long S–S distances inherent in the adamantane structure ($\sim$4.0 Å)[2] preclude the ability of normal bidentate chelates to span the edges of the S_6 octahedron in the Cu_4S_6 core.

These suggestions are based on the fact that various dinegative 1,1-dithiolate chelates, with intraligand S–S distances close to 3.00 Å, invariably form the $[Cu_8L_6]^{4-}$ "cubane" clusters. In these clusters the Cu_8S_{12} unit of T_h symmetry contains a Cu_8 cube inscribed in an approximate S_{12} icosahedron. In either of the two cores, Cu_4S_6 or Cu_8S_{12}, the trigonal-planar coordination of the CuS_3 units is maintained and the Cu–S and Cu–Cu nearest neighbor distances are similar.

The coordinated 1,1-dithiolate ligands are known to undergo a sulfur-addition reaction,[15a] which results in the formation of the corresponding perthiolate ligands (Figure 1). In comparison to the 1,1-dithio ligands the perthio ligands are characterized by larger intramolecular S–S "bite" distances such as 3.173[15b] or 3.052 Å.[15c] The question regarding the effects of a larger intraligand S–S distance on the aggregation preference of the $(Cu_4L_3)_n{}^{2-}$ units (n = 1 vs. n = 2) prompted us to carry out the sulfur-addition reaction on the bridging ligands in the $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$ cubane.[16]

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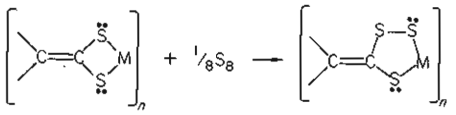

Figure 1. Sulfur addition to 1,1-dithiolate ligands.

In this paper we present evidence that suggests that as the "bite" size of the dithiolate ligand increases, the relative thermodynamic stabilities of the $[Cu_4L_3]^{2-}$ and $[Cu_8L_6]^{4-}$ clusters become similar. With the S-*t*-Bu_2DED ligand, a facile reversible conversion of one cluster to the other is affected by the introduction or removal of the interacting K^+ cation.

Experimental Section

The chemicals in this research were used as purchased. Analyses (C, H, and N) were performed by the analytical services laboratory of the Chemistry Department of The University of Iowa. Copper analyses were obtained locally by EDTA titration using murexide as an indicator. Sulfur, phosphorus, and potassium analyses were obtained from Clark Microanalytical Laboratory, Urbana, Ill. melting points are uncorrected.

Physical Measurements. All infrared spectra were recorded on Beckman IR 20A and IR-11 spectrophotometers. Electronic spectra were recorded on a Cary Model 118 spectrophotometer. Proton NMR spectra were obtained on Varian A-60 or HA-100 spectrometers with tetramethylsilane, Me_4Si, as an 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 deterium signal as an internal lock. Chemical shifts are given in parts per million downfield from internal Me_4Si. Potentiometric titrations were performed with a Fisher Accument pH meter, Model 210, equipped with a Corning combination electrode adapted with 2-propanol–KCl for nonaqueous titrations. Acetonitrile solutions 0.1 M in HCl or 0.1 M in $HClO_4$ were prepared and standardized against pure diphenylguanidine.[17]

Syntheses. Dipotassium 1,1-Dicarbo-*tert*-butoxyethylene-2,2-dithiolate, K_2*t*-Bu_2DED. Malonyl chloride (14.1 g, 0.1 mol) was added to 18.8 g (0.2 mol) of *tert*-butyl alcohol in 50 mL of CH_2Cl_2. The HCl that was generated was removed by flushing the solution with N_2, and the solvent was removed on a rotary evaporator. The yellow oil that remained was dissolved in 200 mL of THF. Powdered potassium hydroxide (11.2 g, 0.2 mol) and CS_2 (7.2 g, 0.1 mol) were added. The mixture was stirred while cooling in an ice bath until all the KOH reacted. The yellow precipitate was filtered, washed with ether, and dried in vacuo. The product was stored at 0 °C when not in use.

Tetrapotassium Hexakis(1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolato)octacuprate(I), K_4Cu_8(*t*-Bu_2DED)$_6$. A mixture of 10 g (0.028 mol) of $Cu(CH_3CN)_4ClO_4$[18] and 10 g (0.027 mol) of K_2*t*-Bu_2DED in 150 mL of acetonitrile was allowed to react by stirring for $^1/_2$ h. The solution was filtered, and the solvent was removed on a rotary evaporator. The crude product was dissolved in a minimum amount of acetone and dried by adding 1 mL of dimethoxypropane and heating the solution to its boiling point. Pentane was added to incipient crystallization. Orange crystals were obtained on standing and cooling to 0 °C: yield 94%; mp 179–180 °C dec. Anal. Calcd for $K_4Cu_8S_{12}O_{24}C_{72}H_{108}$: C, 35.93; H, 4.49; Cu, 21.12; S, 15.97. Found: C, 35.69; H, 4.88; Cu, 21.0; S, 15.35.

Tetrakis(benzyltriphenylphosphonium) Hexakis(1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolato)octacuprate(I), $(BzPh_3P)_4Cu_8$(*t*-Bu_2DED)$_6$. The potassium cluster K_4Cu_8(*t*-Bu_2DED)$_6$ (2.41 g, 0.001 mol) was dissolved in 50 mL of warm acetonitrile. Benzyltriphenylphosphonium chloride (1.44 g, 0.0037 mol) was added. After the mixture was stirred for 20 min, the KCl was removed by filtration. Addition of an equal volume of ether and 100 mL of pentane gave yellow crystals: mp 113–114 °C dec; yield 73%. Anal. Calcd for $Cu_8S_{12}P_4O_{24}C_{172}H_{196}$: C, 56.37; H, 5.39; Cu, 13.9. Found: C, 56.16; H, 5.61; Cu, 14.0.

Tetrakis(tetraphenylphosphonium) Hexakis(1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolato)octacuprate(I), $(Ph_4P)_4Cu_8$(*t*-Bu_2DED)$_6$. This salt was prepared as the preceding benzyltriphenylphosphonium complex and was recrystallized from CH_3CN–ether; mp 103–104 °C dec. Anal. Calcd for $Cu_8S_{12}P_4O_{24}C_{168}H_{188}$: C, 55.92; H, 5.25; Cu, 13.9. Found: C, 55.63; H, 5.31; Cu, 14.1.

Potassium Tetraphenylphosphonium Tris(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)tetracuprate(I) Triacetonate, K$(Ph_4P)Cu_4$(S-*t*-Bu_2DED)$_3$·3$(CH_3)_2$CO (I). A 2.4-g (1 mmol) quantity of K_4Cu_8(*t*-Bu_2DED)$_6$, 0.759 g (2 mmol) of Ph_4PCl, and 0.38 g (12 mmol) of sulfur were suspended in a mixture of 30 mL of acetone and 20 mL of absolute ethanol. When the mixture is stirred, the suspension changes color from orange to yellow-brown. After filtration the solvent was removed on a rotary evaporator. The yellow-brown oil that remained was triturated with ether (~5–8 mL) and ethanol (~5–8 mL) for 5–8 min. The liquid was decanted off, and the crude solid was dried in vacuo. This material was crystallized by dissolving it in hot acetone (~25 mL), filtering, and adding 15 mL of ethanol, 90 mL of diethyl ether, and 90 mL of pentane. The yellow crystals obtained upon cooling were washed with ether and dried in vacuo: yield ~40%; mp 139–140 °C dec. Anal. Calcd for $Cu_4KS_9PO_{15}C_{69}H_{92}$: C, 46.71; H, 5.23; S, 16.26; P, 1.75; K, 2.20; Cu, 14.32. Found: C, 46.29; H, 5.65; S, 16.82; P, 2.08; K, 1.85; Cu, 14.3.

Tetrakis(tetrabutylammonium) Hexakis(1,1-dicarbo-*tert*-butoxyethylene-2-thio-2′-perthiolato)octacuprate(I), $(Bu_4N)_4Cu_8$(S-*t*-Bu_2DED)$_6$ (II). The synthetic procedure was identical with that employed for the synthesis of I above using Bu_4NCl instead of Ph_4Cl. The crude product obtained, following the trituration step, was crystallized by dissolving in dichloromethane, filtering, and adding pentane, until the first permanent cloudiness appeared in solution. After the solution was cooled to 0 °C and it stood for ca. 12 h, a yellow microcrystalline solid formed. The product was isolated by filtration, washed with ether, and dried in vacuo: yield ~50%; mp 142–143 °C dec. Anal. Calcd for $C_{136}H_{252}Cu_8N_4O_{24}S_{18}$: C, 47.88; H, 7.39; N, 1.64; S, 16.90; Cu, 14.9. Found: C, 47.68; H, 7.82; N, 1.65; S, 17.02; Cu, 14.9.

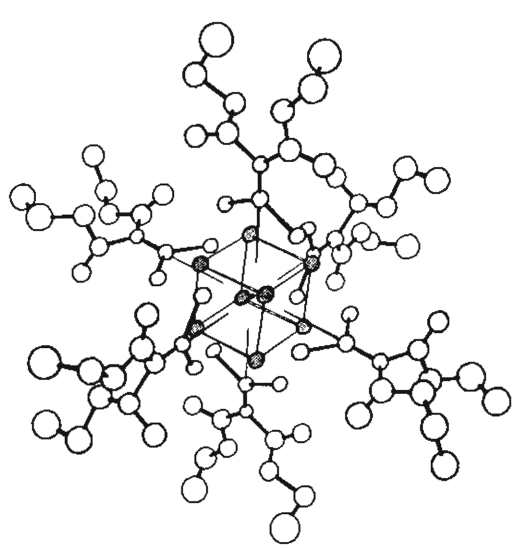

Figure 2. Molecular structure of the $[Cu_8(DED)_6]^{4-}$ anion showing the cube of copper atoms as shaded circles. DED is the abbreviation for the 1,1-dicarbethoxy-2,2-ethylenedithiolate ligand.

Results and Discussion

The existence of the Cu_8 cubic core in the $[Cu_8(Et_2DED)_6]^{4-}$ cluster[16] has been verified in a crystal structure determination of the tetrabutylammonium salt of this molecule[11] (Figure 2). With other disubstituted R_2DED ligands the same type of clusters are obtained.[19] The reaction of the *t*-Bu_2DED ligand with cuprous ions gives the $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$ cubane, which unlike the clusters obtained with other R_2DED ligands, is

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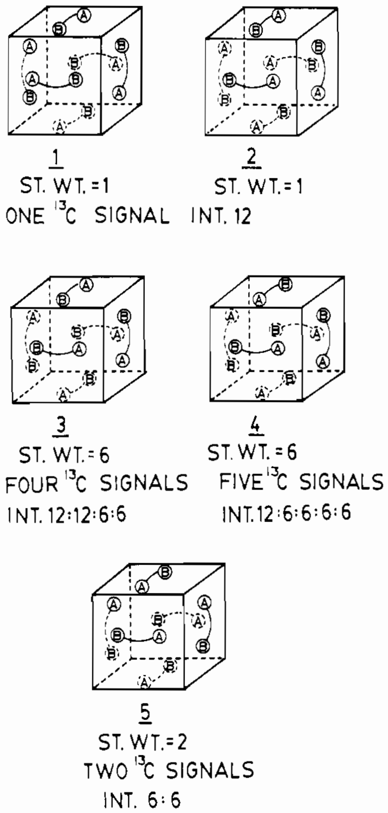
characterized by satisfactory solubility properties. Evidence that the *t*-Bu_2DED ligand gives a cluster with the $[Cu_8L_6]^{4-}$ stoichiometry is supplied by nonaqueous titration data in CH_3CN, which shows inflection points at 1 and 6 equiv of H^+ added[14] per mol of the $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$ cluster. The protonation of the R_2DED coordinated ligands occurs at the methine carbon of the ligand and has been reported previously.[14]

The sulfur addition reaction, initially reported for the coordinated 1,1-dithiolate ligands in the planar nickel(II) bischelate complexes[15] has been studied extensively for various 1,1-dithio complexes. Furthermore, crystallographic studies[20] on the "sulfur-rich" complexes have established the MSCS to MSCSS ring expansion that accompanies sulfur addition (Figure 1). This reaction proceeds readily with the coordinated *t*-Bu_2DED ligands in the $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$ cubanes to give products of the empirical formula $\{[Cu_4(S\text{-}t\text{-}Bu_2DED)_3]^{2-}\}_n$. The nature of the accompanying counterions seems to be important in the structure of these sulfur-rich clusters, where, very likely, sulfur insertion into the coordinated ligand has resulted in an expansion of the six $Cu_2S\text{–}SCu_2$ bridges (Figure 2).

With tetraphenylphosphonium (PPh_4^+) and K^+ as the counterions, the triacetone solvate of the stoichiometry $K(Ph_4P)Cu_4(S\text{-}t\text{-}Bu_2DED)_3\cdot 3[(CH_3)_2CO]$ (I) was isolated. With the tetrabutylammonium (Bu_4N^+) cation the cluster obtained had the empirical formula $(Bu_4N)_2Cu_4(S\text{-}t\text{-}Bu_2DED)_3$ (II). Subtle differences are apparent in the infrared spectra of I and II. In the spectrum of I the carbonyl stretching frequencies occur at 1714 (1) and 1669 (1) cm^{-1}. The corresponding frequencies in II were found at 1715 (1) and 1676 (1) cm^{-1}, respectively. These small differences and minor differences in other regions of the infrared spectra between I and II indicate interactions of the K^+ cation with the carbonyl groups of the ligands in I. A shift of the carbonyl stretching frequency to lower energies, as a result of K^+ interactions, has been noted for the antibiotic valinomycin[21] ($\Delta\nu = 7\ cm^{-1}$) and for the $K_2Ni(S_2C_2O_2)_2$ complex[22] when compared to the corresponding Ph_4P salt ($\Delta\nu = 15\ cm^{-1}$). The infrared spectra of the "sulfur-rich" clusters show many similarities to the "parent" cubane, $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$. Major differences are apparent in the region 490–390 cm^{-1}, where I and II show multiple absorptions. In the same region the "parent" cubane shows only a single band. The S–S stretching vibration usually occurs[23] between 490 and 430 cm^{-1}. It is very likely that the observed vibrations in this region, for I and II, are associated with the S–S vibration, although no definitive assignment can be made. The clusters I and II have nearly identical visible spectra with absorptions at 383 and 350 nm; both I and II obey Beer's law in acetonitrile, CH_3CN, and dichloromethane, CH_2Cl_2, solutions. A potentiomeric titration of II ($HClO_4$ in CH_3CN) shows very similar behavior to that observed with the parent cubane, with inflection points at 1 and 6 equiv of acid per *dimer* of II. These data are consistent with the molecular formula $(Bu_4N)_4Cu_8(S\text{-}t\text{-}Bu_2DED)_6$ for II.

NMR Spectra

The proton magnetic resonance, ^1H NMR, spectrum of the parent $(Bu_4N)_4Cu_8(t\text{-}Bu_2DED)_6$ compound shows a sharp single resonance at δ 1.47 for the *tert*-butyl protons in CD_2Cl_2 solution and indicates the presence of equivalent ligands in the cluster. The ^1H NMR spectra of the "sulfur-rich" clusters I and II also are quite simple. The spectra of II in CD_2Cl_2 solution at ambient as well as low temperatures (288–230 K) show two sharp resonances of equal intensity for the protons of the *tert*-butyl groups at δ 1.52 and 1.44. The two resonances correspond to the two different *tert*-butyl groups for each ligand (cis and trans to the perthio group). The ^1H NMR spectrum of I is similar, with *tert*-butyl peaks at δ 1.46 and 1.43 relative to Me_4Si and a single resonance for the acetone protons at δ 2.13. Complex multiplets centered at δ 7.77 and 7.63 are assigned to the Ph_4P^+ protons. The integrated intensities of the peaks for the *tert*-butyl and cation protons yield a ligand:cation ratio of 3.0:1, which is in excellent agreement with the theoretically calculated value of 3:1 for I.


1 ST. WT. = 1 ONE ^{13}C SIGNAL

2 ST. WT. = 1 INT. 12

3 ST. WT. = 6 FOUR ^{13}C SIGNALS INT. 12:12:6:6

4 ST. WT. = 6 FIVE ^{13}C SIGNALS INT. 12:6:6:6:6

5 ST. WT. = 2 TWO ^{13}C SIGNALS INT. 6:6

Figure 3. Structural isomers and S_2CS ^{13}C NMR signal analysis for the $[Cu_8(S\text{-}t\text{-}Bu_2DED)_6]^{4-}$ cluster.

The lack of ^1H NMR evidence for the geometrical isomers expected for II in the distribution of six asymmetric ligands on the faces of the Cu_8 cube with a $[Cu_8L_6]^{4-}$ structure (Figure 3) can be rationalized by any of the following arguments. (a) The perthio ligands in all of the clusters in solution are disposed in a centrosymmetric fashion (isomers **1** or **2**, Figure 3). (b) Structural isomers are present, but the differences in the chemical shifts of the nonequivalent ligand protons are too small to be resolved. (c) The structure of the clusters in solution is $[Cu_4L_3]^{2-}$ with three symmetry-equivalent ligands (an argument that is contradicted by the titration data for II!). (d) Very fast ligand exchange equalizes the environments of the ligands.

In ^{13}C magnetic resonance spectra of I and II were obtained with the anticipation that an improvement in resolution might reveal the presence of geometrical isomers provided that fast ligand exchange was not taking place. The broad-band, hydrogen-decoupled ^{13}C NMR spectrum of II (Figure 4) is quite complex. The seven resonances observed in the region between 174.9 and 179.4 ppm (downfield from internal Me_4Si) are attributed to the carbon atoms of the carbon disulfide moieties of the ligands. Complex multiplets also were observed for all of the other carbon atoms in the S-*t*-Bu_2DED ligand in II. The

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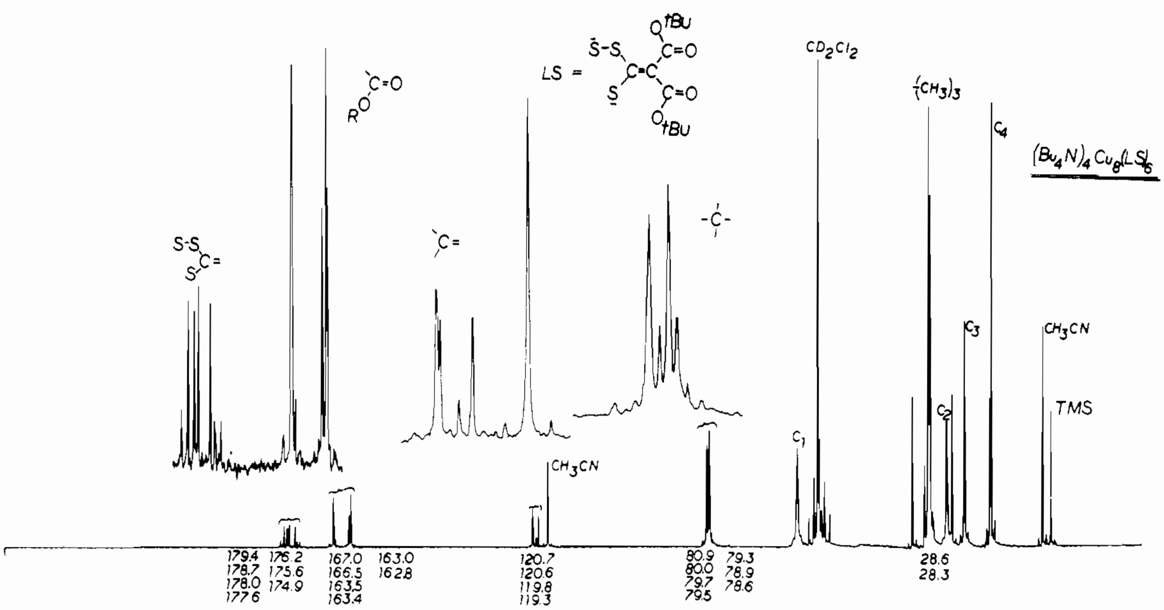


Figure 4. Proton-decoupled ^{13}C NMR spectrum of $(Bu_4N)_4Cu_8(S\text{-}t\text{-}Bu_2DED)_6$ in CD_2Cl_2 at ambient probe temperature.

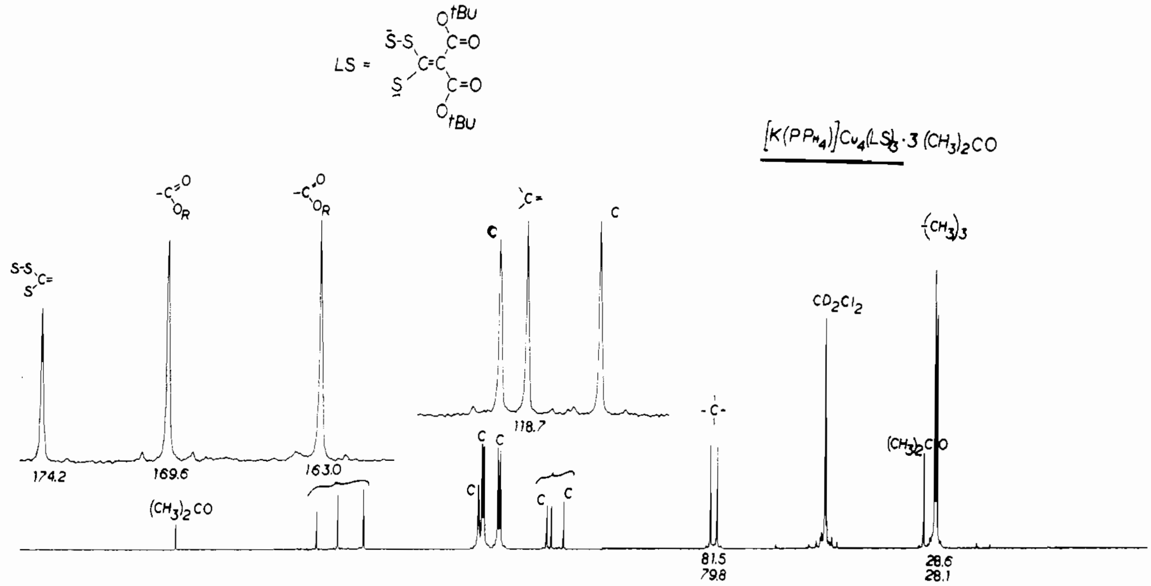


Figure 5. Proton-decoupled ^{13}C NMR spectrum of $K(Ph_4P)Cu_4(S\text{-}t\text{-}Bu_2DED)_3{\cdot}3(CH_3)_2CO$ in CD_2Cl_2 at ambient probe temperature. Signals labeled "c" arise from the Ph_4P^+ cation.

assignment of the signals between 174.9 and 179.4 ppm to the SCSS carbon was verified by isotopic enrichment. Thus, the synthesis of the t-Bu_2DED ligand with ^{13}C-enriched CS_2 and the subsequent synthesis of II gave a product that showed a ^{13}C NMR spectrum with dramatically enhanced resonances in that region.

By contrast the ^{13}C NMR spectrum of I shows only a single resonance in the CS_2 region (verified by isotopic substitution) and a single resonance for each equivalent carbon atom of all the "sulfur-rich" ligands (Figure 5). It should be noted that because of the asymmetry in the CS_3 unit of the ligand, two sets of carbo-*tert*-butoxy carbon atom resonances are observed in the spectrum (cis and trans to the perthio S–S unit).

The ^{13}C NMR spectrum of the "parent" $Cu_8(t\text{-}Bu_2DED)_6^{4-}$ cubane (Figure 6) (with a symmetric CS_2 unit) as expected shows single resonances for each of the equivalent carbon atoms. The different ^{13}C NMR spectra for "sulfur-rich" I and II strongly suggest that the two compounds have different structures in solution.

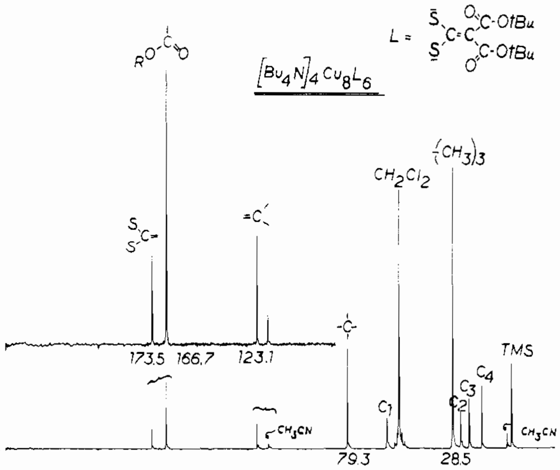


Figure 6. Proton-decoupled ^{13}C NMR spectrum of $(Bu_4N)_4Cu_8L_6$ in CD_2Cl_2 at ambient probe temperature.

The structural difference between I and II, in solution, must arise because of the presence of K^+ in the former. The K–O interaction in I, suggested by the small bathochromic shift in the C=O stretching frequency, also is consistent with the downfield shift (~3 ppm) of the ^{13}C NMR absorption as-

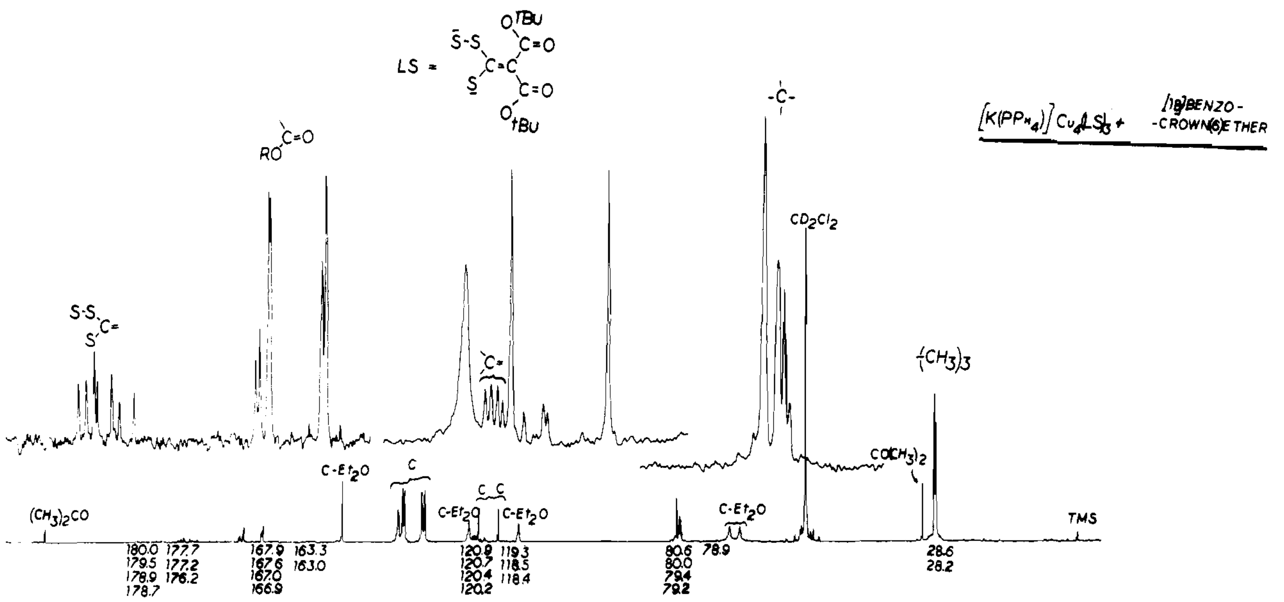


Figure 7. Proton-decoupled ^{13}C NMR spectrum of $K(Ph_4P)Cu_4(S\text{-}t\text{-}Bu_2DED)_3$ in CD_2Cl_2 at ambient probe temperature after the addition of dibenzo-18-crown-6 ether.

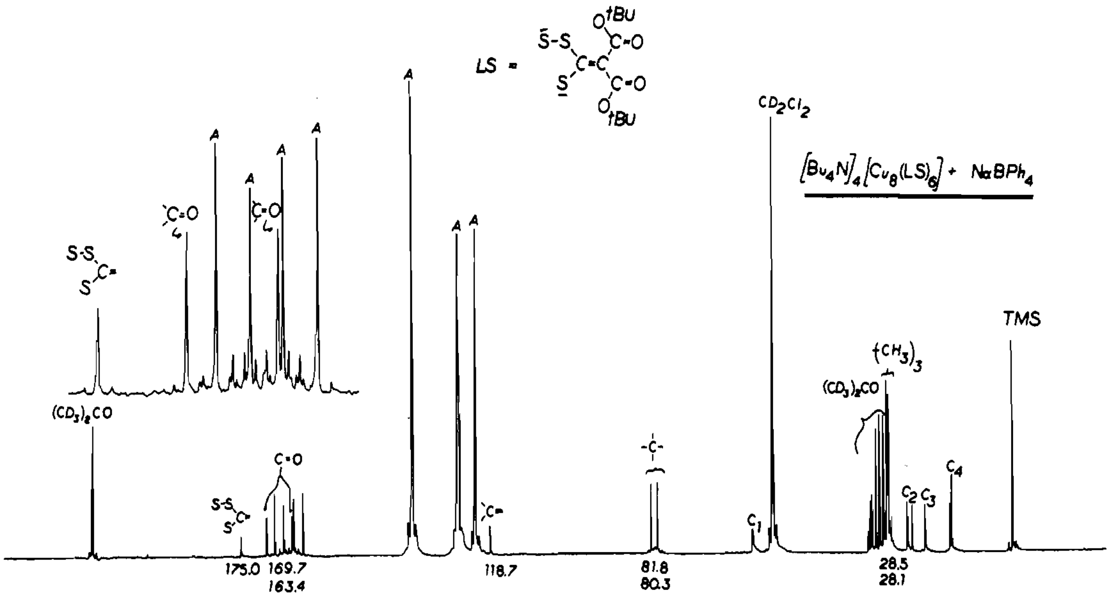


Figure 8. Proton-decoupled ^{13}C NMR spectrum of $(Bu_4N)_4Cu_8(S\text{-}t\text{-}Bu_2DED)_6$ in $CD_2Cl_2/(CD_3)_2CO$ at ambient probe temperature after the addition of $NaB(C_6H_5)_4$. Resonances labeled "A" are due to the $B(C_6H_5)_4^-$ anion.

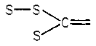
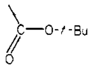
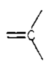
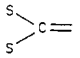
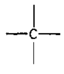
signed to the carbonyl carbon of the ligand. The observed shift (by comparison to the corresponding resonance in II) can be explained in terms of a K^+–O interaction, which results in a decrease of electron density at the carbonyl carbon atoms. Similar downfield shifts have been reported for the ester carbonyl carbon atoms of the antibiotic valinomycin upon complexation with K^+ ions.[21]

The effects of the K^+ ion in the ^{13}C NMR spectra of I and II are illustrated dramatically when the K^+ ion in solutions of I is sequestered or when alkali metal cations are added to solutions of II. The ^{13}C NMR spectrum of I, obtained following the addition of an equimolar amount of dibenzo-18-crown-6 ether, is shown in Figure 7. The apparent binding of the K^+ ion in I by the crown ether results in a spectrum that is very similar to that obtained for II.

The nearly quantitative sequestering of the K^+ ions in the solution of I by the crown ether is evident in the conductometric titration curve of I with the crown ether. This curve shows a "clean" break after 1 equiv of the crown ether has been added. Evidence for the transformation of II to I following the addition of Na^+ ions is apparent in the ^{13}C NMR spectral changes that accompany the addition of $NaBPh_4$ to solutions of II (Figure 8). The spectra of these solutions are virtually identical with those obtained for I (Table I, Figure 5).

From the available ^{13}C NMR data it is apparent that sulfur addition to the six ligands in the "parent" $[Cu_8L_6]^{4-}$ cubane occurs in a nearly random fashion. Such an event is expected to give a distribution of structural isomers for the $[Cu_8(LS)_6]^{4-}$ product. Since LS is an unsymmetrical bidentate chelate, five geometric isomers of the $[Cu_8(LS)_6]^{4-}$ cubane are possible (Figure 3). Analysis of the "carbon disulfide" environments in these isomers indicates that, if all isomers were present and all expected resonances were well resolved, the spectrum should show twelve peaks. Of these, four should be twice as intense as the remaining eight. The observation of seven "CS_3" carbon atoms in the ^{13}C NMR spectrom of II suggests that II very likely exists as a Cu_8L_6 "cubane" cluster in solution. Failure to detect five of the twelve possible resonances may be due to (a) the absence of one or more of the expected isomers, (b)

Table I. Carbon-13 NMR Data[a] for the $(Bu_4N)_4Cu_8L_6$ Cluster and the Sulfur-Rich Variants Obtained from This Molecule

assignt	$(Bu_4N)_4Cu_8L_6$[b]	$K(Ph_4P)Cu_4(LS)_3$[c]	$(Bu_4N)_4Cu_8(LS)_6$[c]	$K(Ph_4P)Cu_4(LS)_3$[c] + dibenzo-18-crown-6 ether	$(Bu_4N)_4Cu_8(LS)_6$[d] + $NaBPh_4$
		174.20	...	180.04 (w)	174.21
			179.43 (w)	179.47 (w)	
			...	178.95 (s)	
			178.75 (s)	178.74 (w)	
			178.08 (s)	...	
			177.59 (s)	177.75 (s)	
			...	177.19 (w)	
			176.16 (s)	176.21 (s)	
			175.63 (w)	...	
			175.06 (w)	...	
	166.7	169.62	166.69	167.86	169.65
		163.02	166.53	167.57	163.35
			163.49	167.02	
			163.45	166.92	
			162.96	163.28	
			162.83	163.02	
	123.1	118.68	120.72	120.89	118.65
			120.63	120.66	
			119.82	120.40	
			119.30	120.17	
				119.30	
				118.52	
				118.35	
	173.5				
	79.3	81.54	80.93	80.41	81.80
		79.82	80.05	79.95	80.31
			79.73	79.40	
			79.50	79.17	
			79.27	78.95	
			78.95		
			78.59		
$(CH_3)_3$	28.5	28.59	28.59	28.56	28.50
		28.10	28.26	28.20	28.07

[a] The chemical shift values are in ppm downfield from Me_4Si as an internal standard. [b] Spectrum obtained in CH_3CN. [c] Spectrum obtained in CH_2Cl_2. [d] Spectrum obtained in $(CD_3)_2CO$.

the presence of the expected isomers in a ratio different than that shown in Figure 3, and (c) the overlapping of the expected resonances.

A tabulation of the "CS_3" resonances in the ^{13}C NMR spectra of II obtained by (a) the sulfur addition reaction and (b) the sequestering of the potassium ions in solutions of I is included in Table I. The chemical shifts and relative intensities of the seven "CS_3" resonances in the spectrum of the "crown ether treated" I show coincidence with only four of the resonances in the ^{13}C NMR spectrum of II. We suggest that the assembly of II from the apparently symmetric units in I would favor the formation of certain structural isomers (such as **1** and **2**, Figure 3) with the possible exclusion of others.

It is significant to point out that in the ^{13}C NMR spectra of II, obtained by two different synthetic procedures, 10 of the expected 12 "$=CS_3$" resonances are accounted for. This observation is sufficient to rule out a solution structure such as $[Cu_4(LS)_3]^{2-}$ for II. Formation of a tetranuclear cluster of this type with the asymmetric (LS) ligands is expected to give four structural isomers and only six ^{13}C signals for the "$=CS_3$" units in the ^{13}C NMR spectrum (Figure 9).

The simplicity of the ^{13}C NMR spectrum of I indicates a structure where all ligands are symmetry equivalent. A centrosymmetric $Cu_8(LS)_6$ structure such as **1** or **2** stabilized by K^+ interactions (Figure 3) could give rise to such a spectrum. An alternate explanation for the simple ^{13}C NMR spectrum of I is that the potassium counterion facilitates a deaggregation of the Cu_8L_6 unit to two Cu_4L_3 units with structurally equivalent ligands. On the basis of the available data we cannot rule out either of these two structures in solution. However, the solid-state molecular structure of I[24] reveals that the $[Cu_4(LS)_3]^{2-}$ tetramer (Figure 10) is the actual solid-state structure. In this structure the K^+ cation is coordinated to three carbonyl groups of the ligands (one from each ligand) and to the three acetone molecules of solvation. In the two reasonable symmetric structures possible for the $[Cu_4(LS)_3]^{2-}$ cluster (Figure 9; **1**, **2**) the unique copper atom would be coordinated by either three thio or three perthio groups. The former type of coordination is found in the structure shown in Figure 10.

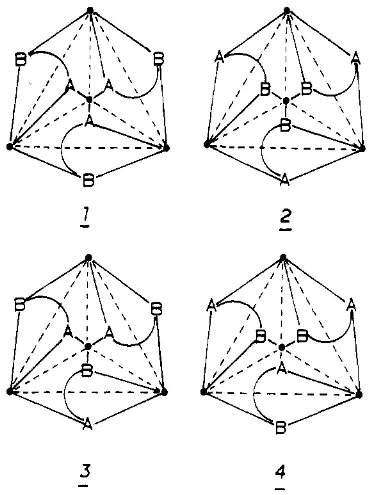


Figure 9. Structural isomers for the $[Cu_4(S\text{-}t\text{-}Bu_2DED)_3]^{2-}$ cluster.

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[24] Coucouvanis, D.; Swenson, D.; Kanodia, S., manuscript in preparation.

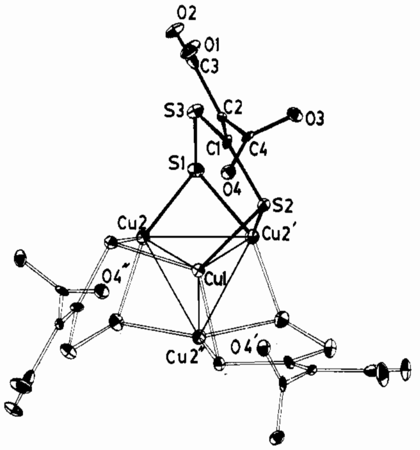

Figure 10. Molecular structure of the $(Ph_4P)KCu_4(S$-*t*-$Bu_2DED)_3$ cluster. The K^+ ion is located exactly above Cu1 on a crystallographic 3-fold axis perpendicular to the paper. The K^+ ion is octahedrally coordinated by the three acetone molecules of solvation and the ligand carbonyl oxygens O4, O4′, and O4″. The *t*-Bu groups have been omitted for clarity.

Summary

The 1,1-dicarbo-*tert*-butoxyethylene-2,2-dithiolate ligands (*t*-Bu_2DED) in the $[Cu_8(t\text{-}Bu_2DED)_6]^{4-}$ cubane clusters undergo a sulfur addition reaction that results in the formation of the new "sulfur-rich" $Cu_8(S\text{-}t\text{-}Bu_2DED)_6{}^{4-}$ cluster.

Solution ^{13}C NMR spectra of this compound indicate that, when noninteracting counterions are present, the cluster maintains an octameric structure as evidenced by the presence of most of the structural isomers expected for a $[Cu_8L_6]^{4-}$ cubic cluster with six asymmetric ligands (Figure 3).

When Na^+ or K^+ ions are present, the basic $[Cu_8L_6]^{4-}$ unit dissociates into two $[Cu_4L_3]^{2-}$ units that appear to be stabilized by Lewis acid–Lewis base interactions between the alkali-metal counterions and the carbonyl groups of the ligands. A simple ^{13}C NMR spectrum similar to the spectrum of $[Cu_4L_3]^{2-}$ (Figure 5) would be expected for either of the centrosymmetric isomers (Figure 3; **1**, **2**) of a $[Cu_8L_6]^{4-}$ cluster. The possibility that the potassium ion interactions result in the conversion of all isomers for the $[Cu_8L_6]^{4-}$ to a centrosymmetric one is not very likely. This contention finds support in the fact that the ^{13}C NMR spectra of preisolated $[Cu_4L_3]^{2-}$ (Figure 10) and "potassium-treated" $[Cu_8L_6]^{4-}$ are virtually identical.

As indicated previously,[2b,11] the small S–S intraligand distances in the 1,1-dithiolate ligands preclude the formation of the $[Cu_4L_3]^{2-}$ tetranuclear clusters and instead favor formation of the $[Cu_8L_6]^{4-}$ "cubanes" with the Cu_8S_{12} core. With monodentate ligands (such as $C_6H_5S^-$) and in the absence of ligand constraints, the $[Cu_4(SR)_6]^{2-}$ cluster forms[2] and contains the adamantane type Cu_4S_6 core. Our present studies indicate that as the S–S intraligand distances become larger in the 1,1-dithiolate ligands, a situation can arise where the thermodynamic stabilities of the $[Cu_4L_3]^{2-}$ and $[Cu_8L_6]^{4-}$ clusters are of comparable magnitude. In such a situation, the transformation of one type of cluster to the other is affected by relatively weak perturbations.

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Registry No. I, 79953-44-9; II, 80317-36-8; $K_4Cu_8(t\text{-}Bu_2DED)_6$, 80105-67-5; $(BzPh_3P)_4Cu_8(t\text{-}Bu_2DED)_6$, 80317-37-9; $(Ph_4P)_4Cu_8(t\text{-}Bu_2DED)_6$, 80317-94-8; K_2-*t*-Bu_2DED, 79952-99-1; $Cu(CH_3CN)_4ClO_4$, 14057-91-1; malonyl chloride, 1663-67-8; *tert*-butyl alcohol, 75-65-0; CS_2, 75-15-0; S_8, 10544-50-0.

Contribution from Departamento de Quîmica, Universidad Autônoma de Guadalajara, A. P. 1-440, Guadalajara, Jal., Mêxico, and and the Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Molecular Species Formed by the Reaction of Copper(I) Trifluoroacetate with Alkenes and Benzene in the Solid and Liquid State

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It has been shown that the only products that are formed by the reaction of solid copper(I) trifluoroacetate (CuT) with gaseous ethene or benzene are $CuTC_2H_4$ and $Cu_2T_2C_6H_6$. Vapor pressure osmometry, in vacuo, was used to determine the species present in solutions of copper(I) trifluoroacetate in benzene and cyclohexane. It was found that an equilibrium mixture of monomeric and tetrameric species is formed at room temperature. A gas chromatographic technique was used to show that the monomers had the composition $CuT(C_6H_6)_2$ and $CuT(C_6H_{10})_2$ and the tetramers $Cu_4T_4(C_6H_6)_2$ and $Cu_4T_4(C_6H_{10})_4$. The enthalpy and entropy changes that accompanied the tetramer formation from the monomer were 77.2 kJ·mol^{-1} and 87.0 J·mol^{-1}·K^{-1}, respectively, in benzene and were 32.9 kJ·mol^{-1} and 66.9 J·mol^{-1}·K^{-1}, respectively, in cyclohexene.

Some copper(I) complexes of the simplest alkene, ethene, have been isolated and characterized.[2-6] These have been found to have markedly different properties. $CuCl\cdot C_2H_4$ is so unstable[2,3] that the dissociation pressure of ethene in equilibrium with the complex is 2 atm at 0 °C; $CuBr\cdot C_2H_4$, however, is much more unstable.[2] The coordinated C_2H_4 can be liberated from $CuClO_4(H_2O)_2\cdot C_2H_4$ by removing the gas phase that is in equilibrium with the complex, but the copper(I) salt that is left behind undergoes disproportionation. $CuCF_3SO_3\cdot CH_3CN$ absorbs ethene and forms the complexes $CuCF_3SO_3\cdot CH_3CN\cdot C_2H_4$ and $(CuCF_3SO_3\cdot CH_3CN)_2C_2H_4$, liquids at room temperature, from which the coordinated ethene can be freed reversibly.[5]

Of all of the copper(I)–benzene complexes that have been isolated,[7-9] the copper(I) trifluoroacetate complex has been

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