Metallocubanes. Crystal and Molecular Structures of $[(C_6H_5)_4P]_4[Cu_8(S_2C_4O_2)_6]$ and $[(C_4H_9)_4N]_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]$ Clusters with a Common Cu_8S_{12} Core

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Abstract: The synthesis and structural characterization of two cluster compounds with the Cu_8S_{12} core are described. Tetrakis-(tetraphenylphosphonium) hexakis(dithiosquarato)octacuprate(I)-acetonitrile, $[(C_6H_5)_4P]_4[Cu_8(S_2C_4O_2)_6]\cdot CH_3CN$ (I), crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell. The cell dimensions are a = 29.952 (13) Å, b = 14.457 (6) Å, c = 28.003 (13) Å, and β = 106.87 (3)°. Tetrakis(tetrabutylammonium) hexakis(1,1-dicarboethoxyethylene-2,2-dithiolato)octacuprate(I), $[(C_4H_9)_4N]_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]$ (II), crystallizes in the monoclinic space group $C2/c$ with two molecules per unit cell. The cell dimensions are a = 30.459 (4) Å, b = 19.724 (2) Å, c = 24.183 (2) Å, and β = 97.38 (3)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer using the θ-2θ scan technique. In both I and II the carbon atoms in the cations were constrained to refine as groups of fixed geometry. In I all the remaining atoms were refined with anisotropic thermal parameters. In II the copper and sulfur atoms were refined with anisotropic thermal parameters, while the rest of the nonhydrogen atoms in the anion were refined with isotropic thermal parameters. Refinement by full-matrix least squares of 367 parameters on 4064 data for I and 330 parameters on 1711 data for II gave final R values of 0.050 for I and 0.078 for II. The overall description of the Cu_8S_{12} cores in both I and II can be considered as a cube of copper atoms inscribed in a distorted icosahedron of sulfur atoms. Each sulfur atom is coordinated to two copper atoms across an edge of the cube, and each copper is trigonally coordinated by three sulfur atoms of three different ligands. Average values of selected structural parameters and the standard deviations of the mean for the two structures are as follows. For I: Cu-Cu, 2.844 (20) Å; Cu-S, 2.247 (10) Å; S-S (bite), 3.922 (10) Å; S-S (other), 3.814 (12) Å; Cu-Cu-Cu 90.0 (2)°; S-Cu-S, 116.2 (6)°; Cu-S-Cu, 78.6 (8)°. For II: Cu-Cu, 2.790 (11) Å; Cu-S, 2.258 (10) Å; S-S (bite), 3.043 (12) Å; S-S (other), 3.88 (1) Å; Cu-Cu-Cu, 90.0 (4)°; S-Cu-S, 118.4 (5)°; Cu-S-Cu, 76.3 (4)°. An analysis of the data and a comparison with the structural features of the $[Cu_4(SC_6H_5)_6]^{2-}$ cluster lead to the suggestion that the Cu-Cu distances in the Cu_8S_{12} cores represent the optimum conditions where the attractive interactions prevail, with repulsions arising at closer Cu-Cu distances.

Introduction

Polymetallic "cluster" compounds with eight metal atom cores were virtually unknown until the synthesis[2] and structural characterization[3] of the $Cu_8(i\text{-}MNT)_6^{4-}$ tetraanion[4] appeared in the literature. In the structure of this ionic cluster, the eight copper(I) ions are arranged in the corners of a nearly perfect cube which is inscribed in a distorted icosahedron defined by the 12 sulfur atoms contributed by the 6 dithiolate ligands. On the basis of simple closed-shell configuration arguments, it was suggested that each copper atom was bonded to the three nearest neighbor copper atoms by a bond order of two-thirds. A different interpretation of the bonding was advanced at a later date which suggested slightly repulsive rather than attractive copper-copper interactions.[5] This interpretation was the result of a molecular orbital calculation based on atomic functions of the 8 copper and 12 sulfur atoms and idealized O_h symmetry.

Following the structural characterization of the $Cu_8(i\text{-}MNT)_6^{4-}$ cluster, the octameric m-(trifluoromethyl)phenylcopper(I) was synthesized and chemically characterized.[6] For this cluster also, a cubic arrangement has been proposed for the copper atom framework. A report[7] of an apparently multinuclear copper(I) 1,1-dithiolate complex, $[Cu_4(S_2CC(CN)CONH_2)_3]^{2-}$, and the synthesis in our laboratory[7b] of $[Cu_8(S_2CNCN)_6]^{4-}$, with the cyanodithiocarbimate ligand, and of $[Cu_8(S_2CCHNO_2)_6]^{4-}$ with the nitroethylene-1,1 dithiolate ligand, prompt us to investigate the possibility that these as well as other copper(I) dithiolate compounds are members of a general class of octanuclear clusters which possess the Cu_8S_{12} core as a common characteristic.

Synthetic and crystallographic studies of copper(I) complexes with the dicarboethoxy-2,2-ethylenedithiolate (DED) and dithiosquarate (DTS) ligands resulted in the complete characterization of the $[Cu_8(DED)_6]^{4-}$ and $[Cu_8(DTS)_6]^{4-}$ clusters and lead us to conclude that (a) the Cu_8S_{12} structural unit appears to be a rather common feature of Cu(I) complexes with dianionic sulfur chelates, and (b) the stability of the copper cube must result at least in part from copper-copper attractive interactions. Very recently the synthesis and crystal molecular structure of the $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ cluster was communicated.[9] In this cluster the nickel atoms are "completely bonded" to each other to form an "electron precise" metal cube.

The synthesis and characterization of cluster compounds with "large" metal cores may eventually provide basic information pertinent to highly dispersed metal particles, widely used as heterogeneous catalysts.[10] The isolation of uniform size metal particles of small size (10 to 100 Å in diameter) has not been accomplished experimentally, and consequently studies of their electronic and structural properties are restricted to theoretical models.

In one such model, cubic Cu_8 and Ni_8 atomic clusters are assumed to represent small catalyst particles where all atoms are surface atoms. Calculations of the electronic energy levels of these clusters have been carried out by the x-α (SCF-Xa) scattered wave method.[11]

A study of the electronic and structural properties of molecular cluster, metal cores, which are large enough, and possibly comparable with the smaller microdispersed metallic particles, may allow for experimental testing of theoretical calculations. In this paper we report on the detailed synthesis and structural characterization of the $Cu_8(DED)_6^{4-}$ and $Cu_8(DTS)_6^{4-}$ cubanes.

Experimental Section

The chemicals in this research were used as purchased. Syntheses reported previously were used to obtain potassium dithiosquarate[12] and potassium 1,1-dicarboethoxy-2,2-ethylenedithiolate.[13] Analyses were performed by the analytical services laboratory of the Chemistry Department of the University of Iowa.

Preparation of Clusters. Tetrakis(tetraphenylphosphonium) Hexakis(dithiosquarato)octacuprate(I)-Acetonitrile, $[(C_6H_5)_4P]_4[Cu_8(S_2C_4O_2)_6]\cdot CH_3CN$. Bis(tetraphenylphosphonium) dithiosquarate, 2 g (2.5 mmol), or bis(tetraphenylphosphonium) bis(dithiosquarato)zincate(II),[12] 2.7 g (2.5 mmol), were dissolved in 20 mL of hot acetonitrile. This solution was added to a solution of 2.4 g (6.5 mmol) of tetrakis(acetonitrile)copper(I) perchlorate[14] in 60 mL of hot CH_3CN. The dark red crude product that was isolated following cooling and partial solvent evaporation was redissolved in hot acetonitrile, and the solution was allowed to cool slowly. Dark red crystals were obtained. Anal. Calcd: C, 52.86; H, 3.01; N, 0.51. Found: C, 52.71; H, 2.87; N, 0.74 (with esds of ±0.3% absolute).

Tetrapotassium Hexakis(1,1-dicarboethoxyethylene-2,2-dithiolato)octacuprate(I) Hexahydrate, $K_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]\cdot 6H_2O$. A solution containing 5.80 g (16 mmol) of $Cu(CH_3CN)_4ClO_4\cdot 2H_2O$,[14] 5.61 g (18 mmol) of K_2DED, and 10 mL of CH_3CN, in 200 mL of water, was stirred in the air for 12 hr. The yellow precipitate was filtered, air-dried, and redissolved in 150 mL of warm CH_3CN, wet with 1 mL of water. Upon addition of ether the yellow crystalline complex was obtained in 70% yield. Anal. Calcd: C, 26.46; H, 3.33; K, 7.2. Found: C, 26.81; H, 3.10; K, 7.3.

Tetrakis(tetrabutylammonium) Hexakis(1,1-dicarboethoxyethylene-2,2-dithiolato)octacuprate(I), $[(C_4H_9)_4N]_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]$. Cation exchange of the potassium ions in the previous compound, by tetrabutylammonium cations, was accomplished by dissolving $K_4Cu_8(DED)_6\cdot 6H_2O$ in water and adding the correct stoichiometric amount of Bu_4NCl in acetonitrile. The solution was filtered to remove most of the KCl formed and evaporated to dryness. The crude product was dissolved in acetone and ether was added until the first cloudiness appeared. On standing, thin orange plates of the product formed which were isolated, washed with ether, and dried. Anal. Calcd: C, 45.56; H, 7.07; N, 1.92; S, 13.31; Cu, 17.6. Found: C, 46.55; H, 7.08; N, 1.85; S, 13.51; Cu, 17.8.

X-Ray Diffraction Measurements. Collection and Reduction of Data. Specific details concerning crystal characteristics and x-ray diffraction methodology are shown in Table I. The crystals of both compounds were mounted on a Picker-Nuclear four-circle diffractometer automated by a DEC-PDP8-I computer with FACS-I DOS software, and equipped with a molybdenum target x-ray tube, a graphite monochromator ($2\theta_m = 12.20°$), crystal detector, and pulse-height analyzer set to accept approximately 90% of Mo Kα radiation. All measurements were made at ambient temperature (ca. 24 °C). For both structures 12 reflections with 2θ values between 20 and 30° (Mo K$\bar{\alpha}$, λ 0.7107 Å) were centered on the diffractometer, and the preliminary cell dimensions were refined on the 2θ values of these reflections to yield the cell parameters shown in Table I. The diffraction peaks were scanned at a rate of 1.0°/min in 2θ, and backgrounds were measured with both crystal and counter stationary for 10 s at each end of the scan range. Zirconium attenuators were inserted in the diffracted beam whenever the peak count exceeded 10 000 cps, and the peak was remeasured and backgrounds were taken with the attenuators in place. The least-squares procedure used minimized the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$, and we assigned $w = 0.0$ if $F^2 < 3\sigma(F^2)$ or $F^2 < 2(F^2)$ depending on the structure (Table I) and $2 = 1/\sigma^2(F)$ for all other reflections. The atomic scattering factors of the neutral atoms were used,[15] and all except those for hydrogen[16] were corrected for both real and imaginary dispersion.[17]

I, $[(C_6H_5)_4P]_4[Cu_8(S_2C_4O_2)_6]\cdot CH_3CN$. A fresh crystal was mounted on a glass fiber in the air with the (1 0 1) direction approximately parallel to the spindle axis. Data were collected using a θ-2θ scan technique with a base width of 1.0° 2θ centered on the calculated Mo Kα_1 peak (λ 0.70926 Å) and expanded to the high 2θ side to allow for α_1-α_2 dispersion. Three "standard" reflections (0 6 0, 12 2 −13, and 8 0 8) were measured after every 100 data points to monitor crystal and instrumental stability. No systematic change over the data collection period was observed. Data were collected in the hemisphere of the reciprocal space $\pm h, +k, \pm l$ out to a 2θ value of 40° ($\sin\theta/\lambda \leqslant 0.48$). The agreement factors on F and F^2 between equivalent data were 0.034 and 0.029, respectively.[18] The structure was solved and initially refined on these data. At a late point in the refinement an absorption correction was applied to the data. The program used was ABSORB[19] which uses the analytical method of de Meulenaer and Tompa.[20] The absorption correction varied from 1.41 to 2.04 with an average correction of 1.58. Averaging equivalent reflections of the absorption corrected data reduced residuals on F and F^2 to 0.027 and 0.026.

II, $[(n\text{-}C_4H_9)_4N]_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]$. A freshly prepared crystal was mounted on a glass fiber and used for cell dimensions measurement and data collection. Data were collected as previously described for I with a scan width of 1.5° 2θ. All data in the quadrant of reciprocal space h, k, $\pm l$ were collected to a 2θ angle of 30°. Near 30° there were very few "observed" reflections and data collection was terminated.[21] During data collection three reflections (0 0 10, 14 0 0, 0 6 0) were measured after every 50 data points to monitor crystal and instrument stability. These showed no systematic trend over the data collection period.

Determination of the Structures. I, $[(C_6H_5)_4P]_4[Cu_8(S_2C_4O_2)_6]\cdot CH_3CN$. From the intensity data, corrected for background, Lorentz, and polarization effects,[22] a set of structure factors was obtained which was used to compute a three-dimensional Patterson map. A pattern of large peaks indicated clearly a Cu_8 cube centered at the origin of the unit cell. An electron density map phased on the input positions of the four independent copper atoms revealed the positions of the two independent phosphorus atoms and six sulfur atoms. Following three cycles of least squares on these 12 atoms ($R = 0.32$), a Fourier map showed the positions of all of the remaining nonhydrogen atoms of the complex anion and the Ph_4P cations. The R value on the unrefined values of all 78 atoms was 0.20.

Because of space limitations on the computer, the phenyl rings of the cations were refined as rigid bodies in a manner previously described.[23] Isotropic refinement of all atoms resulted in an R value of 0.098. The complex anion was then refined alternately with the cations with anisotropic thermal parameters used for all nongroup atoms. Hydrogen atom positions were located on a difference Fourier map and were included in the calculation of the structure factors with isotropic thermal parameters equal to the average of those of the phenyl ring to which they were attached. With the hydrogen atoms included, a cycle of full-matrix least squares reduced the R value to 0.064. It was at this point that our preliminary communication of our results was made.[8]

A difference Fourier map phased on the results of this last refinement showed a diffuse peak around the twofold axis at $y = 1/4$, and inspection of the listings of F_o and F_c showed many reflections with significant deviations from agreement. It was thus decided to perform an absorption correction on the data.

Refinement on the absorption corrected data yielded a new R value of 0.060, with the major changes in parameters occurring for the anisotropic thermal parameters B_{11}, B_{22}, and B_{13}. The difference Fourier map phased after this refinement showed a somewhat sharpened peak just off the twofold axis near $y = 1/4$ with a lower, but still positive area connecting it with its twofold-related neighbor. The separation of the two peaks on the map was 2.54 Å, just slightly shorter than the 2.60 Å predicted for the N-CH_3 distance of acetonitrile.[24] An attempt was made to fit a disordered acetonitrile across the twofold axis. This was attempted first with partial occupancy of the site and, followed by inspection of difference Fourier maps, led to assignment of full occupancy to the site (or half-occupancy of one orientation of the twofold disorder).

Analysis of difference Fourier maps coupled with observations of the R value at various stages led to a shift of the center of gravity of the C-C-N backbone of the acetonitrile by 0.25 Å away from the twofold axis along the length of the molecule and in the direction of the nitrogen. Several cycles of least squares on the rest of the structure, leaving the contribution of the acetonitrile fixed, resulted in convergence (Table I). The extreme diffuseness of the peaks and the difficulties of interacting thermal and positional parameters across the twofold axis suggested strongly that the acetonitrile should not be refined.

In the final cycle of least squares all parameter shifts were less than 0.4 times their esd's as estimated by inversion of the least-squares matrix. Inspection of the data showed no indication of secondary extinction. The final difference Fourier map showed two peaks with heights of approximately 0.5 e/Å^3, one near the acetonitrile and one near a phenyl carbon. All other peaks on the map were lower than these, with the highest ones generally associated with phenyl carbons, indicating anisotropic thermal motion.

II, $[(n\text{-}C_4H_9)_4N]_4[Cu_8(S_2CC(COOC_2H_5)_2)_6]$. The data were corrected as described previously and a three-dimensional Patterson map was

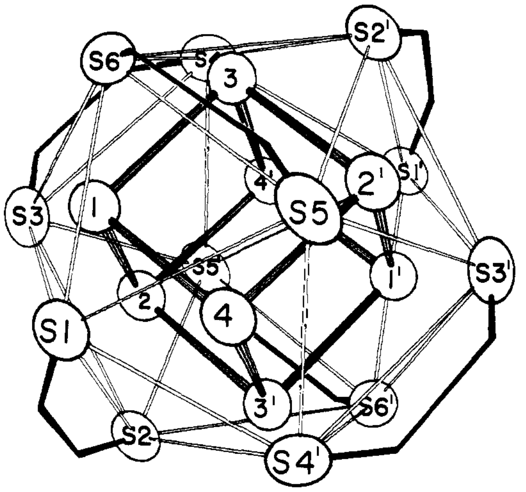

Figure 1. Structure and labeling of the Cu_8S_{12} core of the $Cu_8DTS_6{}^{4-}$ complex anion. Thermal ellipsoids are scaled to include 50% probability. The icosahedron formed by the sulfur atoms has been emphasized, and the ligands have been represented schematically for clarity. Primed atoms are related to unprimed atoms by the crystallographic inversion center at the center of the cluster.

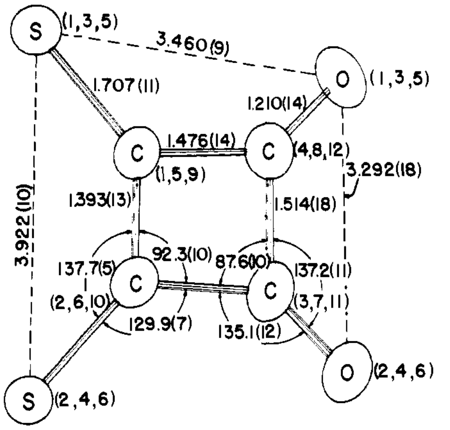

Figure 2. Labeling and average distances (Å) and angles (deg) for the dithiosquarate dianions. The atom numbers for the first, second, and third ligands are given in parentheses near the atom labels, e.g. (1, 3, 5). The esd's of the chemically equivalent bond distances and angles have been taken as the larger of $(\Sigma\sigma_i{}^2/N)^{1/2}$ or $(\Sigma\Delta_i{}^2/N(N-1))^{1/2}$, where σ_i is the esd of an individual distance or angle and Δ_i is the difference between an individual parameter and the average.

Table I. Crystal and Refinement Data

	$Cu_8(DTS)_6(Ph_4P)_4\cdot CH_3CN$	$Cu_8(DED)_6$-$(Bu_4N)_4$
Mol wt	2881	2770
Crystal dimensions, mm	0.23 × 0.32 × 0.48	0.25 × 0.25 × 0.08
Space group	$C2/c$[a]	$C2/c$[a]
a, Å	29.952(13)	30.459(4)
b, Å	14.457(6)	19.724(2)
c, Å	28.003(13)	24.183(2)
β, deg	106.87(3)	97.38(1)
V, Å^3	11 676	14.408 Å
Z	4	4
d_c, g/cm^3	1.58	1.30
d_o, g/cm^3[b]	1.56(5)[b]	1.35(5)[b]
λ, Å	0.7107 (Mo $K\bar{\alpha}$)	0.7107 (Mo $K\bar{\alpha}$)
μ, cm^{-1}	18.06	14.3
Data collected	10 900	3027
Unique data	5463	2929
Data used in refinement	4064 ($F^2 > 3\sigma(F^2)$)[c]	1711 ($F^2 > 2\sigma(F^2)$)
Parameters	367	330
R_1[d]	0.050	0.078
R_2[e]	0.067	0.076
SDOUW[f]	2.13	2.03

[a] Systematics absences: hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$. For both structures the centric space group was confirmed by the successful refinement of the structure. [b] Determined by flotation in a CCl_4/CBr_4 solution. [c] The "ignorance factor" p used throughout was 0.04. [d] $R_1 = \Sigma|\Delta|F||/\Sigma|F_o|$. [e] $R_2 = (\Sigma w(\Delta|F|)^2/\Sigma wF_o{}^2)^{1/2}$. [f] Standard deviation of an observation of unit weight ("goodness of fit"); $(\Sigma w(\Delta|F|)^2/(n_O - n_p))^{1/2}$.

computed. No pattern easily interpretable in terms of a cluster of Cu atoms could be observed, and an attempt was made to solve the structure using direct methods.

The data were scaled and converted to E values using Wilson's method and program FAME.[25] Statistics were intermediate between those for the centric and those for acentric distribution, so at first the centric case was assumed. Centric direct methods using the MAGIC-LINK-SYMPL[25] programs were applied to the data. A choice of starting reflections was taken which resulted in a large number of phase predictions, and high-consistency maps. Preliminary attempts at refinement of the positions of some of the peaks, assuming them to be Cu and S atoms, led to R values in the 40% range and phased Fourier maps which yielded further structure, but very poor distances across certain symmetry elements in the centric space group. The structure was then defined in the acentric space group Cc and the positions of all 8 Cu atoms and 12 S atoms were input to least squares. Three cycles of isotropic refinement on these 20 positions gave a conventional R value of 0.26. A Fourier map phased by the output of the least squares revealed peaks corresponding to the positions of the ethylenic carbons and the four oxygens of each of the ligands, and these showed a strong indication of a center of symmetry at the center of the cube of Cu atoms. The positions of the Cu and S atoms which were equivalent by this "center" were averaged, and the "center" was shifted so that it was at ¼, ¼, ½. An attempt was then made to refine the ten atoms in the centric space group. Three cycles of least squares gave an R value of 0.29, and a Fourier map phased from the results showed peaks corresponding to three ligands and one of the tetrabutylammonium cations. All further refinement took place in the centric space group, and the final refinement of the structure confirms this choice. A reinspection of the direct methods maps showed that the structure had indeed been present in essentially the same form, but shifted, for some reason, so that the center of the cube did not correspond to the center of symmetry on the map.

Following location of the second tetrabutylammonium cation, refinement proceeded with isotropic thermal parameters for all atoms. Convergence with isotropic refinement of individual atoms was finally obtained at an R value of 0.079, and refinement was continued with the Cu and S atoms refined with anisotropic thermal parameters to an R value of 0.068 on 1499 data with $F^2 > 3\sigma(F^2)$. However, many of the C–C distances in the cations and in the terminal portions of the DED ligands were unreasonable, and thermal parameters for the same atoms were large. Additionally there was one very close contact between C(40) and the same atom related by a two fold axis, but attempts to refine a disordered model failed to converge.

The criterion for rejection of data as "unobserved" was reduced in hope that the increased number of data would improve the refinement. This hope was not validated. An absorption correction using the analytical program ABSORB[19,20] was attempted. The absorption coefficient, μ, is 14.3 cm^{-1} and the absorption corrections varied from 1.12 to 1.35 with an average of 1.18 ($I = \mathrm{corr}^* I_0$). Refinement on the corrected data yielded no significant change in any of the parameters or improvement in distances and angles.

At this point it was decided to refine the n-butyl groups as rigid bodies, with the justification that the carbon-carbon bond distances and angles were known to far better precision than could be refined and that the carbon chain would, in the absence of relatively strong outside forces, remain in a planar, trans configuration.[26] The thermal parameters for C(40) and for C(48) showed anomalously large values, and peaks were revealed on a difference Fourier map which suggested orientational disorder for C(40) and suggested that C(48) did not lie in the same plane as C(45)–C(47) (Butyl 6). Changes were made to allow C(48) to refine as an individual atom with full occupancy, and C(40) was given an occupancy of 0.5 and an individual atom, C′(40), was placed in the position indicated by the peak on the difference

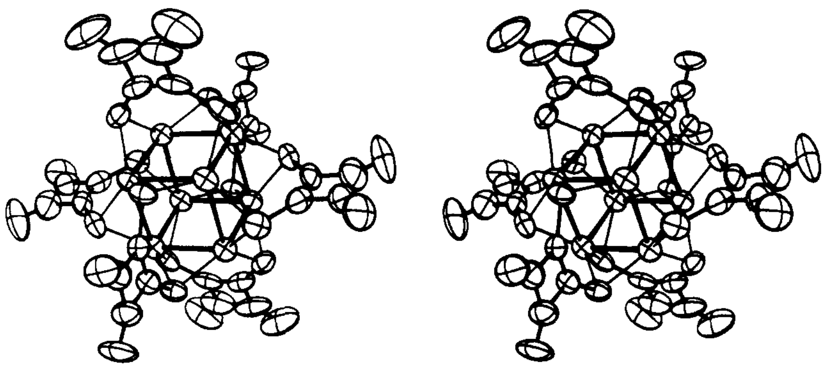

Figure 3. Stereographic pair illustrating the structure of the $Cu_8DTS_6^{4-}$ complex anion. Thermal ellipsoids are scaled to include 50% probability.

Table II. Positional[a] and Thermal Parameters[b] and Their Standard Deviations in Tetraphenylphosphonium Hexa(dithiosquarato)octacuprate'(I)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.01597(4)	0.16220(7)	−0.01263(4)	4.34(6)	4.74(5)	4.60(6)	0.11(4)	1.50(4)	−0.28(4)
Cu(2)	−0.05977(4)	0.09422(7)	0.02174(4)	4.19(6)	5.08(6)	4.93(6)	−0.14(4)	1.10(5)	−0.78(5)
Cu(3)	−0.00387(4)	0.02782(7)	−0.08880(4)	4.49(5)	4.52(5)	4.68(6)	−0.12(4)	1.24(4)	−0.37(4)
Cu(4)	0.07811(4)	0.04258(7)	0.05128(4)	4.10(5)	5.11(6)	4.51(6)	0.34(4)	1.22(4)	−0.82(5)
P(1)	0.21451(8)	0.1470(2)	0.28007(8)	3.55(11)	4.84(11)	3.94(12)	0.87(9)	1.26(9)	0.15(9)
P(2)	0.09959(8)	0.4822(2)	0.40258(9)	4.85(12)	4.27(11)	4.16(12)	−0.19(9)	1.73(10)	−0.36(9)
S(1)	0.07094(7)	0.1953(2)	0.05934(9)	3.76(11)	4.97(11)	5.15(13)	−0.85(9)	2.05(10)	−1.09(10)
S(2)	−0.03229(7)	0.0986(2)	0.10533(9)	3.72(11)	5.00(11)	4.94(12)	−0.91(9)	1.86(9)	−1.38(10)
S(3)	−0.05497(9)	0.2224(2)	−0.02031(10)	4.87(12)	4.39(12)	6.99(16)	0.98(10)	1.51(11)	−0.38(11)
S(4)	−0.08128(8)	0.0314(2)	−0.12266(9)	4.52(12)	6.88(14)	3.88(12)	0.32(11)	−0.03(9)	−0.21(10)
S(5)	0.12461(7)	−0.0062(2)	0.00688(10)	3.13(10)	6.60(13)	5.86(14)	0.29(10)	0.87(9)	−2.34(12)
S(6)	0.03635(9)	0.1605(2)	−0.08361(9)	7.02(15)	4.77(12)	4.69(13)	−0.82(11)	2.53(11)	0.21(10)
O(1)	0.0941(3)	0.3292(5)	0.1657(3)	9.5(5)	8.1(4)	7.7(5)	−5.8(4)	3.5(4)	−4.4(4)
O(2)	−0.0023(3)	0.2754(4)	0.1919(3)	8.5(4)	6.2(4)	6.1(4)	−1.4(3)	4.2(4)	−2.3(3)
C(1)	0.0470(3)	0.2137(6)	0.1070(3)	4.0(4)	4.0(4)	4.0(4)	0.1(3)	1.4(4)	−0.6(4)
C(2)	0.0091(3)	0.1822(5)	0.1217(3)	3.8(4)	3.9(4)	3.5(4)	0.3(3)	1.2(3)	−0.1(3)
C(3)	0.0176(3)	0.2505(6)	0.1631(4)	6.1(6)	4.7(5)	4.0(5)	0.0(4)	2.0(4)	−0.9(4)
C(4)	0.0615(4)	0.2794(7)	0.1488(4)	6.7(6)	4.9(5)	5.4(6)	−1.5(5)	2.5(5)	−1.4(5)
O(3)	−0.1406(3)	0.3458(6)	−0.1037(4)	6.1(4)	6.8(5)	16.3(8)	2.7(4)	−0.3(5)	2.5(5)
O(4)	−0.1576(4)	0.1921(9)	−0.1953(4)	9.5(6)	18.3(9)	7.1(6)	4.5(6)	−2.0(5)	2.2(6)
C(5)	−0.0902(3)	0.2083(7)	−0.0788(5)	3.8(5)	4.5(5)	9.5(7)	1.6(4)	2.3(5)	2.3(6)
C(6)	−0.0996(3)	0.1419(7)	−0.1163(4)	3.0(4)	7.2(6)	5.4(5)	0.9(4)	0.8(4)	1.7(5)
C(7)	−0.1338(4)	0.2018(11)	−0.1517(6)	4.8(6)	11.2(10)	9.2(10)	1.6(7)	1.7(7)	2.6(9)
C(8)	−0.1254(4)	0.2702(10)	−0.1109(5)	4.3(5)	6.8(7)	10.1(9)	0.8(6)	0.6(6)	2.8(7)
O(5)	0.1981(4)	0.0483(9)	−0.0635(4)	6.8(5)	20.5(10)	12.0(7)	−2.4(6)	5.9(5)	−5.5(7)
O(6)	0.1274(4)	0.1972(8)	−0.1350(4)	17.4(10)	11.1(6)	12.5(7)	−5.1(6)	11.4(8)	−1.4(6)
C(9)	0.1232(3)	0.0659(7)	−0.0435(4)	4.5(5)	6.5(6)	6.4(6)	−2.7(5)	3.2(5)	−3.9(5)
C(10)	0.0914(4)	0.1253(7)	−0.0749(4)	7.6(7)	5.5(5)	5.1(6)	−2.5(5)	4.2(5)	−1.7(4)
C(11)	0.1262(6)	0.1482(10)	−0.1015(6)	12.0(11)	7.7(8)	9.2(9)	−5.4(8)	8.0(10)	−4.2(7)
C(12)	0.1587(6)	0.0781(12)	−0.0687(6)	6.8(8)	11.2(10)	9.7(10)	−2.9(7)	5.7(8)	−4.2(8)
N	0.5249	0.2656	0.2086	15.000					
−C−	0.5063	0.2656	0.2396	15.000					
CH3	0.4831	0.2656	0.278	15.000					

[a] In this and the following tables the estimated standard deviation of the least significant digit(s) is given in parentheses. [b] The form of the temperature factor (B's in units of $Å^2$) is $T = \exp(-0.25\ (B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)$ for anisotropic and $T = \exp(-B \sin^2\theta/\lambda^2)$ for isotropic thermal parameters.

Fourier map and allowed to refine as an individual atom.

After the group refinement of the cations had converged, the results were compared with those of the unconstrained refinement of the cations. There was no change in the R value despite the fact that 57 fewer parameters were being refined, and none of the thermal parameters had changed by more than twice its esd (admittedly large). We feel that this supports our choice of group refinement of the n-butyl groups in the face of low-resolution data; furthermore, the sensitivity of the temperature factors to the disorder at C(40) and the displacement of C(48) from the plane of its group lend confidence that the model chosen is as correct as the data warrant.[21]

All parameter shifts in the last cycle of refinement were less than 20% of their esd's as calculated from the least-squares matrix, and only nine parameters were shifted by more than 10% of their esd's. A final difference Fourier shows many small peaks in the region of the cations, undoubtedly due to contributions from the hydrogens mixed with anisotropic thermal motion of the butyl groups. The maximum peak height on the difference map was 0.6 e/Å^3.

Crystallographic Results. The final atomic positional and thermal parameters for I with standard deviations derived from the inverse matrix of the last least-squares refinement are compiled in Table II, and the parameters of the refined groups are given with their esd's in Table III. The corresponding data for II are tabulated in Tables IV and V.

Intramolecular and selected intermolecular distances and angles for I are given in Tables VI-IX. Corresponding results for II are presented in Tables X-XIII. The atom labeling schemes are shown in Figures 1, 2, 5, and 6.

The generated atomic parameters of the group carbon atoms and hydrogen atoms have been deposited together with a table of the observed values of F, their esd's, and the $|F_o| - |F_c|$ values. (See paragraph at the end of the paper for supplementary material.)

Description of the Structures

In both structures discrete, anionic, $Cu_8(DED)_6^{4-}$, and $Cu_8(DTS)_6^{4-}$ clusters are surrounded by the large counterions

Table III. Group Parameters for $[(Ph_4P)_4][Cu_8(DTS)_6]\cdot CH_3CN$[a]

Group	x	y	z	φ	θ	ρ
			Positional			
Phen-1	0.1136(2)	0.0648(4)	0.2689(2)	113.6(3)	−4.4(3)	175.2(3)
Phen-2	0.2319(1)	0.1827(3)	0.1752(2)	−71.7(5)	−61.0(2)	72.6(5)
Phen-3	0.2320(2)	0.3358(3)	0.3384(2)	−2.3(3)	28.1(2)	−64.9(3)
Phen-4	0.2866(1)	−0.0018(3)	0.3405(1)	−143.1(2)	30.8(2)	−48.8(2)
Phen-5	−0.0013(2)	0.5008(3)	0.4164(2)	83.4(2)	7.8(2)	33.2(2)
Phen-6	0.1472(2)	0.2896(3)	0.4382(2)	−156.2(3)	18.7(2)	−98.2(3)
Phen-7	0.1674(1)	0.6250(3)	0.4731(2)	−37.2(2)	36.5(2)	−163.0(3)
Phen-8	0.0925(1)	0.5296(3)	0.2896(2)	−43.4(7)	−72.3(2)	−99.6(7)

Thermal[b]

Phen-1	*C(13)	5.3(2)	Phen-5	*C(37)	4.7(2)
	C(14)	7.4(3)		C(38)	5.7(2)
	C(15)	9.0(3)		C(39)	7.0(3)
	C(16)	11.3(4)		C(40)	6.5(2)
	C(17)	10.8(4)		C(41)	6.8(2)
	C(18)	7.7(3)		C(42)	6.4(2)
Phen-2	*C(19)	4.3(2)	Phen-6	*C(43)	4.9(2)
	C(20)	5.0(2)		C(44)	6.2(2)
	C(21)	5.9(2)		C(45)	7.1(3)
	C(22)	7.1(3)		C(46)	6.5(2)
	C(23)	7.3(3)		C(47)	10.3(4)
	C(24)	5.9(2)		C(48)	8.2(3)
Phen-3	*C(25)	4.6(2)	Phen-7	*C(49)	4.4(2)
	C(26)	8.2(3)		C(50)	4.4(2)
	C(27)	9.0(3)		C(51)	6.6(2)
	C(28)	8.4(3)		C(52)	6.8(2)
	C(29)	8.3(3)		C(53)	6.2(2)
	C(30)	5.6(2)		C(54)	5.2(2)
Phen-4	*C(31)	3.3(2)	Phen-8	*C(55)	4.2(2)
	C(32)	4.5(2)		C(56)	5.5(2)
	C(33)	4.8(2)		C(57)	6.7(2)
	C(34)	5.2(2)		C(58)	6.3(2)
	C(35)	5.5(2)		C(59)	6.3(2)
	C(36)	5.4(2)		C(60)	5.3(2)

[a] The equivalent coordinates of the phenyl group carbon atoms have been deposited. [b] The asterisk indicates the phenyl ring carbon attached to the phosphorus.

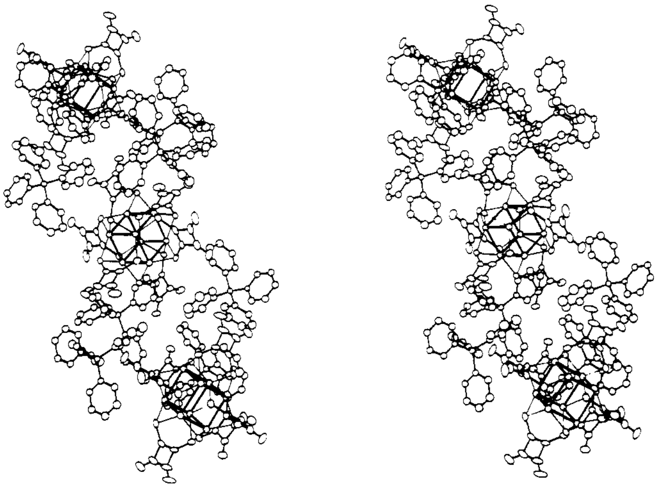

Figure 4. Packing of the cations and complex anions. View is roughly perpendicular to the *a*-*c* plane, with the positive *c* direction pointing down and slightly into the page, relating the top and bottom clusters.

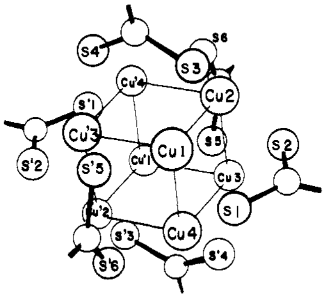

Figure 5. Structure and labeling of the Cu_8S_{12} core of the $Cu_8(DED)_6{}^{4-}$ complex anion. The DED ligands have been indicated schematically for clarity. Primed atoms are related to unprimed atoms by the crystallographic center of inversion at the center of the cluster.

(Figures 4 and 8). In each cluster the six ligands bridge the faces of a cube of copper atoms in a manner entirely similar to that observed in the $Cu_8(i\text{-}MNT)_6$ structure.[3] (Figures 1 and 5.) The overall description of the Cu_8S_{12} core can be considered as a cube of copper atoms inscribed in a distorted icosahedron of sulfur atoms. Each sulfur atom is coordinated to two copper atoms across an edge of the cube, and each copper is trigonally coordinated by three sulfur atoms of three different ligands.

I, $[Ph_4P][Cu_8(DTS)_6]\cdot CH_3CN$. The copper-sulfur distances in this structure average to 2.247 ± 0.010 Å with a deviation from the average which is approximately three times the esd of each individual distance (±0.003 Å). This value is comparable to Cu(I)-S bond lengths for trigonally coordinated copper observed in other copper clusters such as the copper(I) diethyl dithiocarbamate tetramer[28] (2.25 (1)-2.29 (1) Å), the dipropyl thiocarbamate hexamer[29] (2.20 (1)-2.25 (1) Å), the $Cu_8(i\text{-}MNT)_6{}^{4-}$ cubane[3] (2.239 (4)-2.261 (4) Å), the $Cu_5(\mu\text{-}S(t\text{-}C_4H_9))_6{}^-$ cluster[30] (2.27 (1) Å), and the $Cu_5(SC_6H_5)_7{}^{2-}$ cluster[31] (2.27 (3) Å).

Table IV. Positional and Thermal Parameters and Their Standard Deviations in the Compound Tetra(*n*-butylammonium) Hexakis(DED) octacuprate (4--)

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.2260(1)	0.2141(2)	0.4052(2)	6.0(3)	5.1(3)	5.9(3)	−0.8(2)	1.4(2)	0.2(2)
Cu(2)	0.2958(1)	0.1575(2)	0.4742(2)	6.1(3)	5.1(3)	5.4(3)	−0.2(2)	1.5(2)	−0.1(2)
Cu(3)	0.2461(1)	0.1540(2)	0.5630(2)	5.0(3)	4.9(3)	5.7(3)	−0.1(2)	1.2(2)	0.1(2)
Cu(4)	0.1752(1)	0.2142(2)	0.4936(2)	5.9(3)	4.6(3)	5.6(3)	−0.7(2)	0.9(2)	0.1(2)
S(1)	0.1768(3)	0.1346(5)	0.4260(4)	5.4(5)	5.9(7)	5.5(6)	−0.3(5)	1.1(4)	0.9(5)
S(2)	0.2545(3)	0.0720(5)	0.5004(3)	5.3(6)	6.1(7)	4.1(5)	−1.0(5)	0.9(4)	−0.2(5)
S(3)	0.2923(3)	0.1822(5)	0.3822(4)	6.7(6)	4.5(6)	5.5(6)	−1.0(5)	2.4(5)	−0.7(5)
S(4)	0.3233(3)	0.3239(5)	0.4184(4)	6.0(6)	4.2(6)	4.9(6)	−0.6(5)	1.0(5)	−0.8(5)
S(5)	0.3013(3)	0.1860(5)	0.6285(4)	5.2(6)	5.8(7)	5.7(6)	−0.2(5)	0.7(5)	0.6(5)
S(6)	0.3572(3)	0.1854(4)	0.5328(4)	5.2(5)	5.0(6)	5.8(6)	−0.0(5)	2.1(5)	0.6(5)
O(1)	0.1150(11)	0.015(2)	0.396(1)	12.7(10)					
O(2)	0.1521(9)	−0.081(2)	0.388(1)	10.5(8)					
O(3)	0.2514(9)	−0.083(1)	0.443(1)	8.4(7)					
O(4)	0.1997(9)	−0.091(2)	0.499(1)	11.5(8)					
C(1)	0.149(2)	−0.013(3)	0.403(2)	11.0(14)					
C(2)	0.190(1)	−0.000(2)	0.439(1)	4.7(8)					
C(3)	0.219(1)	−0.062(2)	0.457(2)	7.9(11)					
C(4)	0.206(1)	0.064(2)	0.452(1)	4.6(8)					
C(5)	0.108(1)	−0.110(2)	0.353(2)	11.1(13)					
C(6)	0.084(1)	−0.143(3)	0.397(2)	13.2(14)					
C(7)	0.223(2)	−0.157(4)	0.525(2)	17.0(19)					
C(8)	0.194(2)	−0.210(3)	0.502(2)	18.1(21)					
O(5)	0.3402(8)	0.153(2)	0.285(1)	9.6(8)					
O(6)	0.3749(8)	0.236(1)	0.247(1)	8.6(7)					
O(7)	0.3443(8)	0.374(1)	0.290(1)	8.6(7)					
O(8)	0.4081(9)	0.336(1)	0.334(1)	8.5(7)					
C(9)	0.351(1)	0.211(3)	0.288(2)	8.5(12)					
C(10)	0.344(1)	0.265(2)	0.327(1)	4.5(8)					
C(11)	0.366(1)	0.331(2)	0.314(2)	7.9(11)					
C(12)	0.321(1)	0.258(2)	0.373(1)	4.5(8)					
C(13)	0.384(2)	0.186(3)	0.200(2)	14.9(17)					
C(14)	0.429(2)	0.184(3)	0.210(3)	20.1(24)					
C(15)	0.425(2)	0.410(2)	0.316(2)	12.1(14)					
C(16)	0.466(2)	0.388(4)	0.310(3)	21.0(25)					
O(9)	0.3644(8)	0.129(1)	0.725(1)	8.9(7)					
O(10)	0.4318(10)	0.102(1)	0.713(1)	10.7(8)					
O(11)	0.4564(8)	0.164(1)	0.607(1)	9.3(7)					
O(12)	0.4275(9)	0.057(2)	0.590(1)	10.4(8)					
C(17)	0.391(2)	0.124(2)	0.689(2)	11.4(14)					
C(18)	0.386(1)	0.141(2)	0.634(2)	6.2(9)					
C(19)	0.430(1)	0.111(3)	0.609(2)	7.9(11)					
C(20)	0.353(1)	0.172(2)	0.604(1)	4.3(8)					
C(21)	0.445(1)	0.084(2)	0.777(2)	10.1(12)					
C(22)	0.441(2)	0.005(3)	0.764(2)	16.5(19)					
C(23)	0.474(2)	0.033(3)	0.574(2)	15.6(18)					
C(24)	0.462(2)	−0.030(4)	0.565(3)	19.7(25)					
N(1)	0.473(1)	0.335(2)	0.539(1)	8.5(8)					
N(2)	0.232(1)	0.484(2)	0.226(1)	8.4(8)					
C′(40)	0.445(4)	0.296(7)	0.711(5)	19.3(45)					
C(48)	0.176(2)	0.543(3)	0.394(2)	13.7(16)					

Atom	*x*	*y*	*z*
C(25)	0.4673	0.402	0.5087
C(26)	0.4198	0.4203	0.4832
C(27)	0.4196	0.4915	0.4570
C(28)	0.3721	0.5097	0.4315
C(29)	0.523	0.3268	0.5488
C(30)	0.5406	0.2644	0.5829
C(31)	0.5908	0.2575	0.5812
C(32)	0.6084	0.195	0.6153
C(33)	0.4528	0.276	0.5039
C(34)	0.4694	0.2600	0.4478
C(35)	0.4455	0.1965	0.4219
C(36)	0.4621	0.1805	0.3658
C(37)	0.4524	0.3329	0.5908
C(38)	0.4697	0.3883	0.633
C(39)	0.445	0.3835	0.6846
C(40)	0.4622	0.4389	0.7268
C(41)	0.2596	0.427	0.212
C(42)	0.2366	0.3576	0.2039
C(43)	0.2705	0.3037	0.1912
C(44)	0.2475	0.2343	0.183
C(45)	0.2329	0.475	0.2883
C(46)	0.2087	0.5335	0.3139
C(47)	0.2136	0.525	0.3777
C(49)	0.1873	0.4961	0.1914
C(50)	0.1795	0.4855	0.1278
C(51)	0.1314	0.5044	0.1056
C(52)	0.1236	0.4937	0.042
C(53)	0.2611	0.5384	0.2085
C(54)	0.2998	0.5574	0.2532
C(55)	0.3244	0.6192	0.2334
C(56)	0.3631	0.6382	0.2781

The Cu-Cu distances average to 2.844 ± 0.020 Å with a deviation from the average considerably greater than the esd's of individual distances but still small enough to form quite a regular cube. The icosahedron of the sulfur atoms is distorted by the restrictions on the "bite" of the ligand which is very similar for the three independent ligands ($\bar{S}$-$\bar{S}_{\text{intraligand}}$, 3.922 (10) Å). The interligand S- - -S contacts are regular and average to 3.814 (12) with a range from 3.866 (4) to 3.715 (4) Å. These distances are greater than the normal ver der Waals S-S contact of 3.6-3.7 Å.[32] The small distortion of the icosahedron of sulfurs consists of a slight lengthening of six of the 30 edges to reduce the symmetry of the Cu_8S_{12} core close to T_h, even though the only required symmetry from crystallographic considerations is a center of inversion. The three Cu_4 planes that define the cube with their centrosymmetrically related pairs are planar within 8σ (0.008 Å), 20σ (0.020 Å), and 6σ (0.006 Å), respectively, and form close to right angles with each other. The actual angles (absolute value) are 90.0, 89.8, and 89.8°. The average distance for these planes from the center of the cube is 1.42 (2) Å. Four other reference planes can be defined by the three sulfur atoms which are coordinated to each copper atom. These form close to octahedral angles with each other, as expected, and the copper atoms lie inside these planes, toward the center of the cube. The average dis-

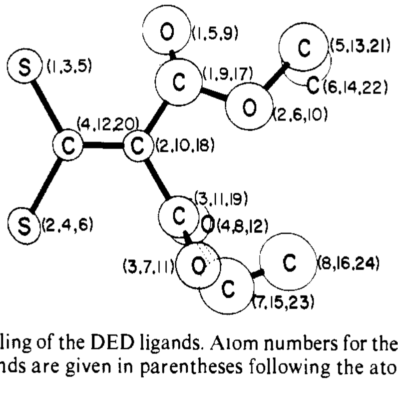

Figure 6. Labeling of the DED ligands. Atom numbers for the first, second, and third ligands are given in parentheses following the atom label, e.g., S(1,3,5).

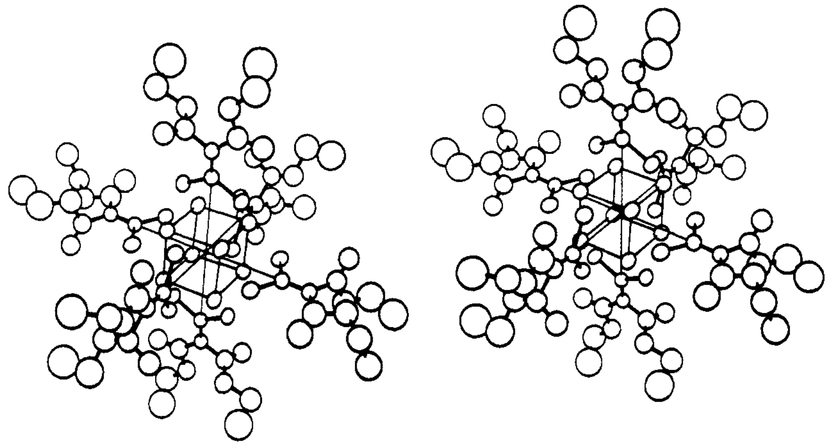

Figure 7. Stereographic pair showing the structure of the $Cu_8(DED)_6^{4-}$ complex anion. The view is approximately down the pseudo-threefold inversion axis. The thermal ellipsoids have been scaled to represent the 40% probability surfaces. The view is the same as that shown in Figure 5 for the labeling of the cluster.

Table V. Final Coordinates of the Refined Butyl Groups in $((n\text{-}C_4H_9)_4N)_4Cu_8(DED)_6$

Group	x	y	z	ϕ[a]	θ	ρ
Butyl 1	0.4197(7)	0.4559(10)	0.4701(7)	−3.0(10)	−24.1(18)	162.3(18)
Butyl 2	0.5657(9)	0.2609(14)	0.5820(10)	−95.0(16)	−1.6(21)	−35.0(28)
Butyl 3	0.4575(6)	0.2283(11)	0.4349(9)	152.6(19)	−23.8(13)	121.1(15)
Butyl 4	0.4573(8)	0.3859(14)	0.6588(12)	95.9(33)	53.5(19)	−43.9(20)
Butyl 5	0.2536(9)	0.3307(23)	0.1975(10)	225.3(13)	−11.4(32)	3.7(37)
Butyl 6[b]	0.2112(13)	0.5293(19)	0.3458(19)	33.5(46)	4.1(20)	−94.9(33)
Butyl 7	0.1555(9)	0.4949(12)	0.1167(14)	75.1(30)	−20.3(11)	98.4(23)
Butyl 8	0.3121(12)	0.5883(17)	0.2433(13)	−33.6(31)	−18.0(20)	−63.1(45)

Butyl 1	B, Å^2	Butyl 2	B, Å^2	Butyl 3	B, Å^2
C(25)	7.7(10)	C(29)	10.6(13)	C(33)	7.0(10)
C(26)	7.6(10)	C(30)	10.0(12)	C(34)	7.0(10)
C(27)	8.2(10)	C(31)	14.6(16)	C(35)	10.3(12)
C(28)	10.5(12)	C(32)	20.4(23)	C(36)	14.2(16)
Butyl 4		Butyl 5		Butyl 6[b]	
C(37)	8.4(11)	C(41)	20.0(23)	C(45)	13.7(16)
C(38)	10.7(12)	C(42)	12.4(14)	C(46)	21.3(25)
C(39)	14.3(16)	C(43)	21.5(26)	C(47)	15.6(18)
C(40)[c]	12.6(27)	C(44)	21.6(25)		
Butyl 7		Butyl 8			
C(49)	13.5(15)	C(53)	19.6(22)		
C(50)	13.9(16)	C(54)	14.2(16)		
C(51)	13.0(15)	C(55)	19.0(21)		
C(52)	20.6(23)	C(56)	26.9(32)		

[a] ϕ, θ, and ρ are given in degrees. The angular coordinates are those defined by Scheringer,[27] and details of the program can be found in ref 23. [b] This group only contains three carbon atoms. The fourth atom, C(48), was refined individually. See text for details. [c] This atom has an occupancy factor of 0.5. An additional carbon atom with occupancy 0.5 was refined individually. See text for details.

tance from the copper to the plane is 0.44 Å.

The three crystallographically independent ligands in the structure are significantly nonplanar and an overall "saddle" pattern of distortion is apparent. The approximate DTS ligand planes are close to being orthogonal to appropriate Cu_4 planes, and dihedral angles of 3.3, 3.0, and 12.0° are calculated for ligands 1, 2, and 3, respectively. (Figures 1 and 2.) In the same order the ligand planes pass 0.17, 0.15, and 0.68 Å from the center of the cube. The other parameters within the dithiosquarate ligands are similar to those observed in the structure of the $Ni(DTS)_2^{2-}$ complex anion, and a comparison has been made already.[33] It is interesting to point out that while the cyclobutenone intra-ring angles are very similar in the present structure and the structure of the $Ni(DTS)_2^{2-}$ complex,[33] the S-S "bites" differ greatly, being 3.922 Å in the former and 3.257 Å in the latter.

The structure of the tetraphenylphosphonium cation is normal and will not be discussed.

II, $[(Bu_4N)_4][Cu_8(DED)_6]$. Analogous structural parameters to those already discussed for the Cu_8S_{12} core in the dithiosquarate cluster are shown in Table XIV. The "icosahedron" of the sulfur atoms is also distorted by the restrictions on the "bite" of the ligand which is 3.04 (1) Å. Shortening of six of the 30 edges of the icosahedron reduces the possible symmetry of the core to T_h.

The Cu_4 planes as in the previous structure are all planar within 4σ, and the three independent dihedral angles between these planes are (absolute values): 88.8, 88.4, and 89.3°. Each of the planes is 1.39 (1) Å from the cube center. The CuS_3 units are octahedrally arranged. The copper atoms in each unit are displaced out of the S_3 plane and toward the cube center by 0.29 Å.

Table VI. Distances and Angles in the Cu_8S_{12} Core of $Cu_8(DTS)_6^{4-}$

Distances, Å		Angles, deg	
Cu(1)-Cu(2)	2.884(2)	Cu(2)-Cu(1)-Cu(3)	90.07(5)
Cu(1)-Cu(3)	2.826(2)	Cu(2)-Cu(1)-Cu(4)	90.86(5)
Cu(1)-Cu(4)	2.786(2)	Cu(3)-Cu(1)-Cu(4)	90.44(5)
Cu(2)-Cu′(3)[a]	2.869(2)	Cu(1)-Cu(2)-Cu′(3)	89.60(5)
Cu(2)-Cu′(4)	2.791(2)	Cu(1)-Cu(2)-Cu′(4)	90.38(5)
Cu(3)-Cu′(4)	2.907(2)	Cu′(3)-Cu(2)-Cu′(4)	89.45(5)
Cu(1)-Cu′(2)	3.987(2)	Cu(1)-Cu(3)-Cu′(2)	88.84(6)
Cu(1)-Cu′(3)	4.054(2)	Cu(1)-Cu(3)-Cu′(4)	89.21(5)
Cu(1)-Cu′(4)	4.027(2)	Cu′(2)-Cu(3)-Cu′(4)	88.75(5)
Cu(2)-Cu(3)	4.040(2)	Cu(1)-Cu(4)-Cu′(2)	91.26(6)
Cu(2)-Cu(4)	4.040(2)	Cu(1)-Cu(4)-Cu′(3)	90.78(5)
Cu(3)-Cu(4)	3.984(2)	Cu′(2)-Cu(4)-Cu′(3)	90.29(5)
Cu(1)-S(1)	2.254(3)	S(1)-Cu(1)-S(3)	115.28(12)
Cu(1)-S(3)	2.250(3)	S(1)-Cu(1)-S(6)	118.61(12)
Cu(1)-S(6)	2.242(3)	S(3)-Cu(1)-S(6)	114.34(14)
Cu(2)-S(2)	2.246(3)	S(2)-Cu(2)-S(3)	117.76(12)
Cu(2)-S(3)	2.232(3)	S(2)-Cu(2)-S′(5)	113.68(12)
Cu(2)-S′(5)	2.269(3)	S(3)-Cu(2)-S′(5)	117.67(14)
Cu(3)-S′(2)	2.250(2)	S′(2)-Cu(3)-S(4)	115.70(12)
Cu(3)-S(4)	2.236(3)	S′(2)-Cu(3)-S(6)	115.62(12)
Cu(3)-S(6)	2.257(3)	S(4)-Cu(3)-S(6)	118.39(13)
Cu(4)-S(1)	2.250(3)	S(1)-Cu(4)-S′(4)	111.37(12)
Cu(4)-S′(4)	2.248(3)	S(1)-Cu(4)-S(5)	117.56(12)
Cu(4)-S(5)	2.235(3)	S′(4)-Cu(4)-S(5)	118.04(14)
S(1)-S(3)	3.804(4)	Cu(1)-S(1)-Cu(4)	76.43(7)
S(1)-S(6)	3.866(4)	Cu(2)-S(2)-Cu′(3)	79.32(8)
S(3)-S(6)	3.775(4)	Cu(1)-S(3)-Cu(2)	80.11(8)
S(2)-S(3)	3.833(4)	Cu(3)-S(4)-Cu′(4)	80.83(8)
S(2)-S′(5)	3.779(4)	Cu′(2)-S(5)-Cu(4)	76.59(8)
S(3)-S′(5)	3.852(4)	Cu(1)-S(6)-Cu(3)	77.82(8)
S′(2)-S(4)	3.799(3)		
S′(2)-S(6)	3.815(4)	Cu(1)-S(1)-C(1)	111.6(3)
S(4)-S(6)	3.860(4)	Cu(4)-S(1)-C(1)	107.9(3)
S(1)-S′(4)	3.715(4)	Cu(2)-S(2)-C(2)	108.6(3)
S(1)-S(5)	3.835(3)	Cu′(3)-S(2)-C(2)	106.4(3)
S′(4)-S(5)	3.843(4)	Cu(1)-S(3)-C(5)	110.7(3)
		Cu(2)-S(3)-C(5)	107.0(3)
S(1)-S(2)	3.938(3)[b]	Cu(3)-S(4)-C(6)	107.5(3)
S(3)-S(4)	3.904(4)[b]	Cu′(4)-S(4)-C(6)	106.7(3)
S(5)-S(6)	3.925(4)[b]	Cu′(2)-S(5)-C(9)	103.6(3)
		Cu(4)-S(5)-C(9)	112.6(3)
		Cu(1)-S(6)-C(10)	112.6(4)
		Cu(3)-S(6)-C(10)	103.4(3)

[a] For labeling, see Figure 1. [b] Intraligand S- - -S "bite".

Table VII. Distances and Angles in the Dithiosquarate Ligands in $Cu_8(DTS)_6^{4-}$

	Ligand 1	Ligand 2[a]	Ligand 3[a]
	Distances (Å)		
C(1)-S(1)	1.711(9)	1.684(13)	1.748(12)
C(2)-S(2)	1.701(9)	1.723(11)	1.676(12)
C(4)-O(1)	1.197(11)	1.230(14)	1.226(16)
C(3)-O(2)	1.190(10)	1.231(16)	1.186(16)
C(1)-C(4)	1.475(13)	1.475(15)	1.447(15)
C(2)-C(3)	1.492(12)	1.483(16)	1.485(15)
C(1)-C(2)	1.392(11)	1.395(14)	1.393(14)
C(3)-C(4)	1.542(14)	1.479(19)	1.520(20)
S(1)-O(1)	3.456(7)	3.432(9)	3.445(10)
S(2)-O(2)	3.469(7)	3.482(10)	3.475(10)
S(1)-S(2)	3.938(3)	3.904(4)	3.925(4)
O(1)-O(2)	3.274(10)	3.329(16)	3.273(18)
	Angles (deg)		
S(1)-C(1)-C(2)	137.9(5)	138.5(5)	137.2(5)
S(2)-C(2)-C(1)	138.4(4)	136.3(5)	138.1(5)
S(1)-C(1)-C(4)	128.7(5)	130.8(7)	128.1(9)
S(2)-C(2)-C(3)	129.2(5)	131.2(8)	131.5(9)
C(2)-C(1)-C(4)	93.4(7)	90.7(10)	94.6(12)
C(1)-C(2)-C(3)	92.3(7)	92.5(10)	90.3(12)
O(1)-C(4)-C(3)	136.2(8)	137.7(10)	137.2(12)
O(2)-C(3)-C(4)	136.6(8)	139.7(12)	136.0(13)
O(1)-C(4)-C(1)	136.5(8)	132.8(12)	135.8(14)
O(2)-C(3)-C(2)	136.4(8)	133.1(13)	135.9(14)
C(1)-C(4)-C(3)	87.2(7)	89.5(10)	86.9(12)
C(2)-C(3)-C(4)	86.9(7)	87.2(10)	88.0(12)

[a] The atom numbers are given for ligand 1. The atom numbers for ligands 2 and 3 are as shown in Figure 2 or can be derived by adding 2 to the oxygen and sulfur numbers for ligand 2 and adding 4 to the numbers for ligand 3. The atom numbers of the carbon atoms can be derived by adding 4 to the numbers shown to get labels for ligand 2 or adding 8 to get the labels for ligand 3.

Table VIII. Distances and Angles in the Tetraphenylphosphonium Cations

	Distances (Å)[a]		
P(1)-*C(13)	1.791	P(2)-*C(37)	1.778
P(1)-*C(19)	1.783	P(2)-*C(43)	1.781
P(1)-*C(25)	1.773	P(2)-*C(49)	1.776
P(1)-*C(31)	1.787	P(2)-*C(55)	1.794
	Av P-C = 1.783(3)[b]		
	Angles (deg)[a]		
*C(13)-P(1)-*C(19)	110.3	*C(37)-P(2)-*C(43)	111.4
*C(13)-P(1)-*C(25)	111.2	*C(37)-P(2)-*C(49)	109.4
*C(13)-P(1)-*C(31)	107.9	*C(37)-P(2)-*C(55)	108.2
*C(19)-P(1)-*C(25)	108.0	*C(43)-P(2)-*C(49)	106.2
*C(19)-P(1)-*C(31)	110.6	*C(43)-P(2)-*C(55)	112.6
*C(25)-P(1)-*C(31)	108.8	*C(49)-P(2)-*C(55)	108.9
	Av C-P-C = 109.5(5)[b]		

[a] Because the phenyl rings were refined as rigid groups, no esd is available for the individual bond distances or angles. [b] Estimated standard deviation calculated from scatter of values around mean.

The three crystallographically independent ligands take the twist-planar configuration found in other complexes of this ligand.[34,35] The labeling of the three ligands consistent with the orientations of the "planar" and twisted $COOC_2H_5$ groups is shown in Figure 6. The actual torsion angles for the "planar" carboethoxy groups around C(1)-C(2), C(9)-C(10), and C(17)-C(18) (Figure 6) are 22.6, 8.5, and 4.8° for ligands 1, 2 and 3, respectively. The torsion angles for the "twisted" carboethoxy groups are 78.2, 87.6, and 85.2°. The individual S_2CCC_2 and CCO_2 planes are all planar to within four standard deviations of the atomic positions. The S_2CCC_2 "backbone" planes are all close to orthogonality with respect to the Cu_4 planes forming the cube, with the maximum deviation from orthogonality being for ligand 2 which passes 0.29 Å from the center of the cube and shows angular deviations of almost 6° with respect to the Cu_4 planes. The other two ligand planes pass less than 0.10 Å from the center of the cube and deviate from orthogonality by less than 2.5° with respect to the Cu_4 planes.

One interesting point is the extreme pseudo-symmetry displayed by the cluster well out toward the periphery of the molecule. Though the "twist-planar" configuration of the ligand destroys the twofold symmetry elements in T_h symmetry, the cluster as a whole retains a threefold inversion axis to a reasonable approximation (ignoring the C_2H_5 groups of the DED ligands). This can be seen clearly in Figure 7 where the view direction is approximately down the pseudo threefold axis. (The cations, of course, break the "threefold" symmetry.)

Table XI gives bond distances and angles in the DED ligands. Given the large esd's of the distances, there are no systematic differences between ligands observable other than the changes in the torsion angles around the C-C single bonds,

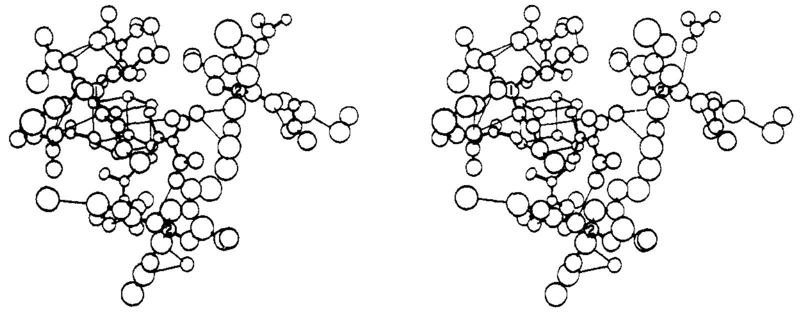

Figure 8. Stereographic pair showing packing of the cations and anions in the crystal. Thermal ellipsoids have been scaled to represent the 40% probability surfaces. Intermolecular contacts of less than 3.5 Å have been indicated by light lines between the atoms. The labels indicate N(1) and N(2) of the two independent cations.

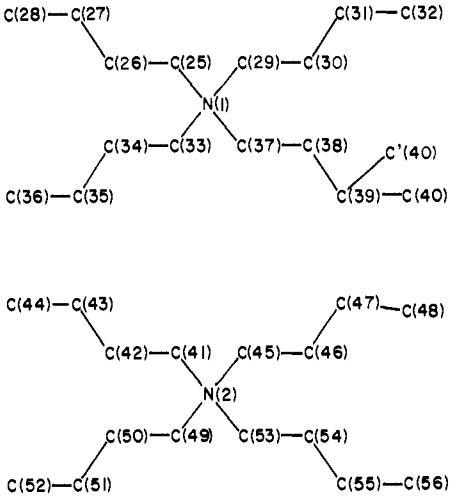

Figure 9. Labeling of the cations. Each *n*-butyl group was refined as a whole with the exception of C′(40) and C(48), which were refined individually.

Table IX. Nonbonded Contacts between Nonhydrogen Atoms Shorter than 3.5 Å

O(1)-C(33)	3.15	O(3)-C(40)	3.44
O(1)-C(34)	3.39	O(3)-C(34)	3.47
O(1)-C(57)	3.48	O(4)-C(20)	3.15
O(2)-O′(2)	3.22(1)[a]	O(5)-C(51)	3.16
O(2)-C(56)	3.32	O(5)-C(35)	3.22
O(3)-C(33)	3.30	O(5)-C(36)	3.22
O(3)-C(32)	3.34	O(6)-C(60)	3.32
O(3)-C(30)	3.37		
C(4)-C(39)	3.43	C(8)-C(30)	3.50

[a] Since all but this contact are between dithiosquarate atoms and those in the phenyl rings refined as groups, there are no esd's reported for the other distances. O′(2) is related to O(2) by the transformation $-x, y, \frac{1}{2} - z$.

which can be easily attributed to packing forces (see below).

The distances in the DED ligands can be compared to those observed in $Ni(DED)_2^{2-}$, $Cu(DED)_2^{-}$,[35] and $Fe(DED)_3^{2-}$,[34] within the limitations of the present structure. Major differences which can be noted are in the torsion angles of the "twisted" carboethoxy groups and in the bite distance of the ligand. In the present study the S-S "bite" distance is 3.04 Å, rather long compared to corresponding distances in the other DED complexes[35,34] (2.74-2.79 Å). The average S-C-S bond angle of 121° suggests that the ligand in the copper cluster is in a rather unstrained environment.

Table X. Distances (Å) and Angles (deg) in the Cu_8S_{12} Core of $Cu_8(DED)_6^{4-}$ [a]

Distances		Angles	
Cu(1)-Cu(2)	2.763(6)	Cu(2)-Cu(1)-Cu′(3)	91.5(2)
Cu(1)-Cu′(3)	2.814(7)	Cu(2)-Cu(1)-Cu(4)	89.8(2)
Cu(1)-Cu(4)	2.797(6)	Cu′(3)-Cu(1)-Cu(4)	88.1(2)
Cu(2)-Cu(3)	2.782(5)	Cu(1)-Cu(2)-Cu(3)	91.4(2)
Cu(2)-Cu′(4)	2.759(6)	Cu(1)-Cu(2)-Cu′(4)	89.6(2)
Cu(3)-Cu(4)	2.822(6)	Cu(3)-Cu(2)-Cu′(4)	89.5(2)
Cu(1)-Cu′(2)	3.982(6)	Cu′(1)-Cu(3)-Cu(2)	90.8(2)
Cu(1)-Cu(3)	3.969(5)	Cu′(1)-Cu(3)-Cu(4)	87.4(2)
Cu(1)-Cu′(4)	3.893(6)	Cu(2)-Cu(3)-Cu(4)	88.9(2)
Cu(2)-Cu′(3)	3.996(6)	Cu(1)-Cu(4)-Cu′(2)	91.6(2)
Cu(2)-Cu(4)	3.925(5)	Cu(1)-Cu(4)-Cu(3)	89.9(2)
Cu(3)-Cu′(4)	3.902(6)	Cu′(2)-Cu(4)-Cu(3)	91.4(2)
S(1)-S(3)	3.918(12)	S(1)-Cu(1)-S(3)	120.0(5)
S(1)-S′(5)	3.864(13)	S(1)-Cu(1)-S′(5)	117.5(4)
S(3)-S′(5)	3.844(13)	S(3)-Cu(1)-S′(5)	117.2(5)
S(2)-S(3)	3.881(13)	S(2)-Cu(2)-S(3)	118.8(5)
S(2)-S(6)	3.843(12)	S(2)-Cu(2)-S(6)	117.0(4)
S(3)-S(6)	3.915(13)	S(3)-Cu(2)-S(6)	119.5(4)
S(2)-S′(4)	3.858(12)	S(2)-Cu(3)-S′(4)	117.6(4)
S(2)-S(5)	3.942(12)	S(2)-Cu(3)-S(5)	122.4(5)
S′(4)-S(5)	3.824(12)	S′(4)-Cu(3)-S(5)	116.1(4)
S(1)-S′(4)	3.852(12)	S(1)-Cu(4)-S′(4)	116.7(5)
S(1)-S′(6)	3.865(14)	S(1)-Cu(4)-S′(6)	116.8(4)
S′(4)-S′(6)	3.930(13)	S′(4)-Cu(4)-S′(6)	120.8(4)
S(1)-S(2)[b]	3.043(13)		
S(3)-S(4)[b]	3.042(12)	Cu(1)-S(1)-Cu(4)	76.0(3)
S(5)-S(6)[b]	3.044(12)	Cu(2)-S(2)-Cu(3)	76.5(3)
		Cu(1)-S(3)-Cu(2)	75.4(3)
Cu(1)-S(1)	2.271(10)	Cu′(3)-S(4)-Cu′(4)	77.4(3)
Cu(1)-S(3)	2.253(10)	Cu′(1)-S(5)-Cu(3)	77.5(3)
Cu(1)-S′(5)	2.250(11)	Cu(2)-S(6)-Cu′(4)	75.0(3)
Cu(2)-S(2)	2.242(10)		
Cu(2)-S(3)	2.268(10)	Cu(1)-S(1)-C(4)	108.0(11)
Cu(2)-S(6)	2.264(11)	Cu(4)-S(1)-C(4)	110.3(11)
Cu(3)-S(2)	2.252(10)	Cu(2)-S(2)-C(4)	109.2(12)
Cu(3)-S′(4)	2.260(10)	Cu(3)-S(2)-C(4)	110.4(11)
Cu(3)-S(5)	2.246(10)	Cu(1)-S(3)-C(12)	106.1(10)
Cu(4)-S(1)	2.272(11)	Cu(2)-S(3)-C(12)	110.2(11)
Cu(4)-S′(4)	2.252(10)	Cu′(3)-S(4)-C(12)	108.8(10)
Cu(4)-S′(6)	2.267(11)	Cu′(4)-S(4)-C(12)	110.4(11)
		Cu′(1)-S(5)-C(20)	108.8(11)
		Cu(3)-S(5)-C(20)	109.6(11)
		Cu(2)-S(6)-C(20)	114.5(11)
		Cu′(4)-S(6)-C(20)	109.0(11)

[a] For labeling, see Figure 5. [b] Ligand "bite" distance.

Because of the group refinement of the *n*-butyl groups of the cations, the only independent bond lengths and angles are those to the nitrogens, to C(48), which was refined individually because of the nonplanarity of the group, and to C′(40), the additional half-atom of the disorder at the end of one butyl group

Table XI. Intraligand Distances (Å) and Angles (deg) in $Cu_8(DED)_6^{4-}$

Distance[a]	Ligand 1	Ligand 2	Ligand 3
S(1)-C(4)	1.72(4)	1.76(4)	1.77(3)
S(2)-C(4)	1.76(3)	1.70(3)	1.76(3)
C(4)-C(2)	1.39(4)	1.38(3)	1.30(4)
C(2)-C(1)	1.46(5)	1.46(4)	1.37(5)
C(2)-C(3)	1.54(4)	1.52(4)	1.65(4)
C(1)-O(1)	1.15(5)	1.18(4)	1.25(4)
C(1)-O(2)	1.41(5)	1.39(4)	1.38(4)
C(3)-O(3)	1.16(4)	1.18(4)	1.33(4)
C(3)-O(4)	1.36(4)	1.32(4)	1.17(4)
O(2)-C(5)	1.58(4)	1.57(5)	1.58(4)
C(5)-C(6)	1.53(5)	1.36(7)	1.59(6)
O(4)-C(7)	1.57(6)	1.62(5)	1.58(5)
C(7)-C(8)	1.43(7)	1.37(6)	1.31(8)
S(1)- - -S(2)	3.04(1)	3.04(1)	3.04(1)
S(1)- - -O(1)	3.05(3)	2.97(2)	3.03(2)
S(2)- - -O(3)	3.36(3)	3.40(2)	3.34(2)
S(2)- - -O(4)	3.63(3)	3.50(2)	3.49(3)
	Angle[a]		
S(1)-C(4)-S(2)	121.7(13)	122.8(12)	118.7(13)
S(1)-C(4)-C(2)	120.2(19)	119.7(19)	122.5(20)
S(2)-C(4)-C(2)	117.9(20)	117.5(18)	118.0(18)
C(4)-C(2)-C(1)	123(5)	125(4)	130(5)
C(4)-C(2)-C(3)	120(3)	122(4)	124(3)
C(1)-C(2)-C(3)	117(4)	113(4)	106(4)
C(2)-C(1)-O(1)	135(4)	132(3)	130(4)
C(2)-C(1)-O(2)	103(3)	109(3)	119(3)
O(1)-C(1)-O(2)	120(4)	119(3)	111(3)
C(2)-C(3)-O(3)	132(3)	119(3)	105(3)
C(2)-C(3)-O(4)	106(3)	115(3)	118(4)
O(3)-C(3)-O(4)	122(4)	126(3)	135(3)
C(1)-O(2)-C(5)	113(5)	116(4)	126(4)
O(2)-C(5)-C(6)	103(3)	98(4)	91(3)
C(3)-O(4)-C(7)	115(4)	106(4)	111(5)
O(4)-C(7)-C(8)	103(4)	94(4)	95(4)

[a] Atom labels are shown for ligand 1. To generate labels for ligand 2, add 2 to the numerals for sulfur, 4 to the numerals for oxygen, and 8 to the numerals for carbon. To generate the labels for ligand 3 add 4, 8, and 16 to the numerals for sulfur, oxygen, and carbon, respectively. See also Figure 6.

(see Figure 9). Because of the rigid body refinement no esd's could be calculated for these distances, but it is likely that they would be similar to those calculated for the ethyl groups of the DED ligands, in view of the thermal behavior of the cations (see Table XI). Thus while the C-C distances in Table XII are not particularly close to the ideal value of 1.54 Å, variations of 3σ or 4σ with σ on the order of 0.08 Å bring them into line. The angles to C'(40) and C(48) are especially convincing that the proposed model is at least chemically reasonable. The torsion angles for the two independent carbon atoms have absolute values of 50° for C'(40) and 142° for C(48).

The distances to the nitrogens from the α carbons of the n-butyl chains are all quite regular, and normal for N-C single bonds, and the angles at the nitrogen, though obviously distorted from ideal tetrahedral values, are not so much so that other than packing considerations need to be involved. That there are strong packing forces involved can be seen from the distortion of the planes in the cations from the normal configuration wherein two pairs of butyl groups lie in two mutually perpendicular planes parallel to the $S_4(\bar{4})$ axis of the ideal cation. Both cations show strong deviation from this behavior.

The reasons for this deviation can be seen by examination of the close intermolecular contact distances in the structure. These are listed in Table XIII, and it can be seen that all but two of them are between atoms in the complex anion, in particular the oxygen atoms, and atoms in the cations.

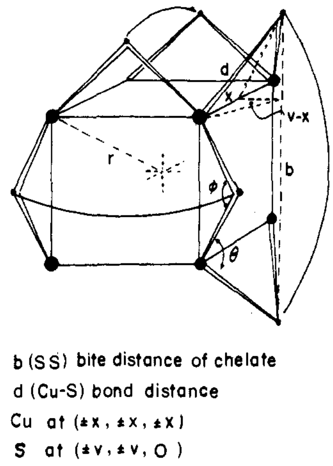

Figure 10. Cu_8S_{12} core calculations based on idealized T_h symmetry. Given b the bite distance of the chelating ligand and d the Cu–S bond distance, and assuming a Cu–Cu distance = $2x$, then: $v = b/2$; $u = x + (d^2 - x^2 - (v - x)^2)^{1/2}$; S–S (inter) = $(2(u^2 - uv + v^2)^{1/2}$; S–Cu–S = θ, $\sin \theta/2$ = S–S (inter)/$2d$; Cu–S–Cu = ϕ, $\sin \phi/2 = x/d$; distance from origin to S_3 plane is $(u + v)/\sqrt{3}$; distance from Cu to S_3 plane is $(u + v)/\sqrt{3} - \sqrt{3}x$.

Table XII. Distances (Å) and Angles (deg) in the $(n\text{-}C_4H_9)_4N^+$ Cations of $((n\text{-}C_4H_9)_4N)_4Cu_8(DED)_6$[a,b]

Distance		Distance	
N(1)-C(25)	1.505	N(2)-C(41)	1.477
N(1)-C(29)	1.513	N(2)-C(45)	1.502
N(1)-C(33)	1.521	N(2)-C(49)	1.525
N(1)-C(37)	1.486	N(2)-C(53)	1.489
C(39)-C'(40)[c]	1.844	C(47)-C(48)[c]	1.317
Angle		Angle	
C(25)-N(1)-C(29)	103.3	C(41)-N(2)-C(45)	101.8
C(25)-N(1)-C(33)	113.0	C(41)-N(2)-C(49)	118.7
C(25)-N(1)-C(37)	113.2	C(41)-N(2)-C(53)	95.6
C(29)-N(1)-C(33)	109.8	C(45)-N(2)-C(49)	118.3
C(29)-N(1)-C(37)	112.8	C(45)-N(2)-C(53)	116.2
C(33)-N(1)-C(37)	104.9	C(49)-N(2)-C(53)	104.6
N(1)-C(25)-C(26)	116.6	N(2)-C(41)-C(42)	116.5
N(1)-C(29)-C(30)	116.4	N(2)-C(45)-C(46)	111.1
N(1)-C(33)-C(34)	119.0	N(2)-C(49)-C(50)	123.1
N(1)-C(37)-C(38)	113.3	N(2)-C(53)-C(54)	113.6
C(38)-C(39)-C'(40)[c]	110.8	C(46)-C(47)-C(48)[c]	107.2
C(40)-C(39)-C'(40)[c]	116.8		

[a] Carbon-carbon distances in the butyl groups were fixed at 1.540 Å and carbon-carbon-carbon angles at 109.5° with the exceptions noted in the text. [b] Owing to the group refinement procedures, no esd's are available for these quantities. [c] Carbon atoms C'(40) and C(48) were refined independently of the rigid body refinement. See text for details.

Table XIII. Intermolecular Contact Distances Less Than 3.50 Å[a]

Distance		Distance	
O(1)-C(39)	3.20	O(8)-C(34)	3.46
O(1)-C(38)	3.21	O(11)-C(33)	3.32
O(1)-C(26)	3.48	O(11)-C(30)	3.35
O(3)-C(50)	3.19	O(11)-C(37)	3.36
O(4)-C(28)	3.33	C(24)-C(52)	3.46
O(5)-C(49)	3.27	C'(40)-C(56)	3.42
O(7)-C(41)	3.17	C(40)-C(40)[b]	2.43
O(7)-C(43)	3.36		

[a] Because of rigid-body refinement, no esd's are available for these quantities. For C'(40) see Figure 9. [b] Related by crystallographic twofold axis.

Table XIV. Selected Molecular Parameters of the Cu_8S_{12} Core of $Cu_8(DTS)_6$, $Cu_8(i\text{-}MNT)_6$, and $Cu_8(DED)_6$ (distances in Å, angles in degrees)

Parameter	$Cu_8(DTS)_6$	Cu_8-)(i-MNT)$_6$[a]	$Cu_8(DED)_6$
Cu-Cu (min)	2.787(2)[b]	2.782(3)	2.759(6)
(max)	2.906(2)	2.870(3)	2.882(6)
(av)	2.844(20)	2.829(14)	2.790(11)
Cu-S (min)	2.229(3)	2.239(4)	2.242(10)
(max)	2.268(3)	2.261(4)	2.272(10)
(av)	2.247(10)	2.250(4)	2.258(10)
S-S (av) (bite)	3.922(10)	3.080(5)	3.043(12)
S-S (min)	3.715(4)	3.820(5)	3.82(1)
(max)	3.866(4)	3.917(5)	3.94(1)
(av) (other)	3.814(12)	3.870(7)	3.88(1)
Cu-Cu-Cu (min)	88.75(5)	87.4(1)	88.1(2)
(max)	91.26(6)	92.2(1)	91.6(2)
(av)	90.0(2)	90.0(5)	90.0(4)
S-Cu-S (min)	111.37(12)	116.7(2)	116.1(5)
(max)	118.61(12)	120.5(2)	122.4(5)
(av)	116.2(6)	118.6(4)	118.4(5)
Cu-S-Cu (min)	76.43(7)	76.4[c]	75.0(3)
(max)	80.83(8)	79.4[c]	77.5(3)
(av)	78.6(8)	77.9(5)	76.3(4)
S_3 plane 1 2[d]	2.90 2.90	2.72 2.69	2.72 2.71
to cube 3 4	2.91 2.94	2.73 2.72	2.70 2.67
center (av)	2.91(1)	2.72(1)	2.70(1)
Cu 1 2	2.45 2.46	2.47 2.39	2.42 2.43
to cube 3 4	2.49 2.44	2.43 2.50	2.44 2.37
center (av)	2.46(1)	2.45(2)	2.42(2)

[a] Parameters taken from ref 36 after further refinement from those reported in ref 3. [b] Estimated standard deviations of the least significant digit(s) (max) and (min) entries. The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation of the mean. [c] Esd's were not available for this parameter. [d] The numbering of the plane and Cu distances for a given column correspond. No correspondence is implied between columns.

As shown in Figure 8, which shows part of the packing of the cations and anions, the two are linked together by the very close contacts between the carboethoxy carbonyl and ether oxygens and the cation carbons, as the oxygens insert themselves into the open "cracks" in the cation structure. The carbonyl oxygens can do this better than the ether oxygens, of course, since they do not have any steric interaction from their attached ethyl groups, and it can be seen from Table XIII that all of the contacts less than 3.30 Å are to carbonyl oxygens. These close contacts connect the structure in a three-dimensional fashion in the crystal lattice.

Copper-Copper Interactions in the Cu_8S_{12} Cores. The rather long Cu-Cu distances observed in the Cu_8 clusters are intermediate between extremes reported for other copper cluster compounds. Distances as short as 2.38 Å in the (4-methyl-2-cupribenzyl)dimethylamine tetramer[37] and as long as 3.45 Å in the "step" conformation of $(Ph_3PCuBr)_4$[38] have been observed. In Cu(I) clusters with sulfur ligands, Cu-Cu distances are found within the upper part of the this range. In the diethyl dithiocarbamate copper(I) tetramer, distances between 2.76 Å and 2.66 Å have been reported.[28] In the $Cu_5(\mu\text{-}S(t\text{-}C_4H_9))_6^-$,[30] $Cu_5(SC_6H_5)_7^{2-}$,[31] $Cu_4(\mu\text{-}SC_6H_5)_6^{2-}$,[39] and $Cu_4(SC(NH_2)_2)_6^{4+}$,[40] the Cu-Cu distances vary between 2.65 and 3.12 Å.

The nearly equal dimensions of the three Cu_8 cubes in the DTS, DED, and i-MNT clusters pose an interesting problem regarding the nature of the Cu-Cu interactions in these compounds. The similarity of the three Cu_8 cubes in the octanuclear copper clusters is striking in view of the fact that the ligand geometry and steric requirements change drastically from the i-MNT and DED ligands to the DTS ligand (Table XIV). Outstanding among the ligand geometry differences is the difference in the S- - -S "bite". For the DTS ligand this distance is 0.9 Å greater than that observed in the 1,1-dithiolate ligands. The only structural feature that seems to be affected by ligand "bite" size differences, in the Cu_8S_{12} cores, is the coordination geometry about the copper atoms.

In the structure of the $Cu_8(DED)_6{}^{4-}$ cluster the copper coordination geometry is nearly trigonal planar. To maintain this type of coordination geometry around the copper atoms in the $Cu_8(DTS)_6{}^{4-}$ cluster, an expansion of the Cu_8 cube would be necessary because of the larger DTS ligand bite. This expansion is not observed, however, and instead the coordination geometry about the copper atoms in the DTS cluster changes to quasi-trigonal pyramidal.

The fact that the copper cube has varied insignificantly compared to the change in the ligand geometry is even clearer if we look (Table XIV) at the distances from the center of the cube to the planes of the sulfur atoms which coordinate to each copper (e.g., S1, S3, and S6 in Figure 1). In the $Cu_8(DTS)_6$ cluster these planes are 0.2 Å further from the center of the cube than they are for the other two clusters. The copper atoms of the $Cu_8(DTS)_6$ cluster, however, are an average of only 0.01 Å further from the center than they are in the $Cu_8(i\text{-}MNT)_6$ cluster and only 0.04 Å further from the center than they are in the $Cu_8(DED)_6$ cluster. The fact that the copper atoms in $Cu_8(DTS)_6$ could move further away from the center of the cube without seriously changing any of the molecular parameters other than the Cu-Cu distances may suggest that there is an attractive interaction between the copper atoms of the cube.

Recently, we and others[39] have determined the structure of the $Cu_4(\mu\text{-}SC_6H_5)_6{}^{2-}$ tetranuclear copper cluster where the six SPh^- ligands in a distorted octahedral arrangement bridge the edges of a tetrahedron defined by the four copper atoms. In this molecule the Cu_4S_6 core has the same stoichiometry,

Table XV. T_h Cluster Calculation[a]

Obsd parameters	$Cu_8(DED)_6{}^{4-}$[b]				$Cu_8(DTS)_6{}^{4-}$[c]				"$(Cu_8PhS_{12})^{4-}$"[d]			
Assumed												
Cu-Cu	2.714	2.794	2.829	3.141	2.714	2.794	2.841	3.406	2.60	2.77	3.00	3.40
Calculated												
S-S (interligand)	3.864	3.879	3.885	3.911	3.778	3.802	3.814	3.892	3.80	3.84	3.90	3.96
S-Cu-S	117.7	118.4	118.7	120.0	114.4	115.5	116.1	120.0	112	114	117	120
Cu-S-Cu	73.9	76.5	77.6	88.1	74.3	76.9	78.4	98.6	69	74	182	96
Origin to S_3 plane	2.699	2.706	2.709	2.721	2.889	2.901	2.908	2.948	2.90	2.92	2.96	2.99
Cu to S_3 plane	0.349	0.296	0.259	0.00	0.539	0.481	0.448	0.00	0.65	0.54	0.36	0.0

[a] See also Figure 10. [b] d = Cu-S = 2.258 Å; b = S-S (bite) = 3.922 Å; Cu-Cu = 2.790 Å. [c] d = Cu-S = 2.247 Å; b = S-S (bite) = 3.922 Å; Cu-Cu = 2.844 Å. [d] d = Cu-S = 2.29 Å; b = S-S = 3.94 Å; Cu-Cu = 2.77 Å.

and the Cu-Cu distances are similar to those observed in the Cu_8S_{12} unit. Furthermore the coordination geometry about the copper atoms is trigonal and deviates from planarity with the copper atoms slightly *out of the S_3 planes and away from the tetrahedral Cu_4 center.* It appears that a shortening of all Cu-Cu distances in the Cu_4 tetrahedron, which could result in planar CuS_3 units, is not favorable either.

The basic "adamantane" type of structure of the $M_4(SR)_6$ unit also has been found[41] in the structure of the $Co_4(SR)_{10}{}^{2-}$ cluster. It is important to note that the Co-S-Co angle in this structure, which contains tetrahedrally coordinated Co(II) ions, is 113 ± 1°, and the Co-Co distances vary from 3.85 to 3.89 Å.

These data illustrate the flexibility of the M-S-M angle in bridging mercaptide ligands and suggest that the M-S-M angle cannot be a major limitation on the dimensions of the M_4 tetrahedral core. In the $Cu_4(\mu\text{-}SC_6H_5)_6{}^{2-}$ cluster, if the Cu-Cu interactions at 2.77 Å were repulsive in nature one might expect a further increase of the Cu-Cu distances with a concomitant, and apparently feasible, "opening up" of the Cu-S-Cu angle. An elevation of the copper atoms from the appropriate S3 planes, which also would occur, is acceptable in view of the quasi-pyramidal structure of the CuS_3 units in the $Cu_8(DTS)_6{}^{4-}$ cluster.

A calculation was carried out to examine the effects of cube expansion or contraction on the overall structural features of the Cu_8S_{12} cores. In this calculation the observed Cu-S bond length and S- - -S "bite" and Cu-Cu distances were used to derive other structural parameters of a Cu_8S_{12} core with idealized T_h symmetry (Figure 10). The results for various Cu-Cu distances are shown in Table XV. On the basis of this calculation, it becomes evident that (a) expansion of the Cu_8 cube, in the DTS cluster, does not affect any of the structural parameters in a serious way, and (b) a small contraction of the Cu_8 cube in the DED or i-MNT clusters also does not seem to cause a drastic change. A reasonable expansion of the Cu_8 cube in the DTS cluster will be accompanied by an increase of the Cu-S-Cu angle, a decrease of the copper distance from the trigonal plane of the sulfur ligands, and a slight increase of the C-S-Cu angles. All of these changes are expected to result in a less strained configuration of the sulfur lone pairs (opening of the acute Cu-S-Cu angle in particular) and a more reasonable coordination geometry (trigonal planar) about the copper atoms. It should be noted that the coordination geometry of the copper atoms in the monomeric $Cu(SPh)_3{}^{2-}$ complex anion is triangular and the anion is strictly planar.[39a]

These findings suggest that the *Cu-Cu distances in the Cu_8S_{12} cores represent the optimum conditions where the attractive interactions prevail, with repulsion arising at closer distances; i.e., these distances are close to the minimum in the interatomic potential energy curve.* The interesting fact that the Cu_8S_{12} core is not obtained with monodentate ligands, where instead the Cu_4S_6 is formed, suggests the following. (a) The Cu_4S_6 is probably the preferred structure for the cores in clusters with the Cu_2S_3 stoichiometry.[42] (b) The long S- - -S distances (3.94 Å) in the Cu_4S_6 core preclude the formation of such cores with the bidentate 1,1-dithiolate ligands. With such ligands the small S- - -S bite dictates the formation of the Cu_8S_{12} core. In such a core, with approximate T_h symmetry, the Cu-Cu distances and copper coordination geometries are very similar to those in Cu_4S_6. For the DTS ligand, the S- - -S bite is large enough to allow the formation of a $Cu_4(DTS)_3{}^{2-}$ cluster. An examination of the molecular model, however, shows that this type of structure can be obtained only with a severe distortion of the sulfur donor lone pairs, if they are to be directed at the copper atoms.

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Supplementary Material Available: Listings of observed structure factor amplitudes, their estimated standard deviations, and the difference $|F_o| - |F_c|$, as well as the equivalent coordinates of the phenyl group carbon atoms in $[(PhyP)_4][Cu_8(DTS)]\cdot CH_3CN$ (34 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Alfred P. Sloan Fellow, 1972–1974, to whom correspondence should be addressed.

(2) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

(3) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Am. Chem. Soc.*, **90**, 7357 (1968).

(4) Throughout this paper the following abbreviations will be used: i-MNT, = 1,1-dicyanoethylene-2,2-dithiolate, $S_2CC(CN)_2{}^{2-}$; DED = 1,1-dicarboethoxy-2,2-ethylenedithiolate, $(S_2CC(COOC_2H_5)_2)^{2-}$; DTS = dithiosquarate; Ph_4P = tetraphenylphosphonium; Bu_4N = tetrabutylammonium.

(5) (a) A. Avdeef, Ph.D. Thesis, Case Western Reserve University, 1973; (b) J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **21**, 55 (1976).

(6) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 247 (1971).

(7) (a) E. Soderback, *Acta Chem. Scand.*, **24**, 228 (1970); (b) D. Coucouvanis and M. O'Connor, submitted for publication.

(8) F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 5646 (1974).

(9) L. D. Lower and L. F. Dahl, *J. Am. Chem. Soc.*, **98**, 5046 (1976).

(10) M. Boudart, Proceedings of the Robert A. Welch Foundation Conference on Chemical Research. XIV. Solid State Chemistry, W. O. Milligan, Ed., The Robert A. Welch Foundation, Houston, Texas, 1970, p 299.

(11) J. C. Slater and K. H. Johnson, *Phys. Today*, 34 (Oct 1974).

(12) D. Coucouvanis, F. J. Hollander, R. West, and D. Eggerding, *J. Am. Chem. Soc.*, **96**, 3006 (1974).

(13) (a) M. L. Caffery, Ph.D. Thesis, University of Iowa, 1973; (b) M. L. Caffery, R. Pedelty, and D. Coucouvanis, manuscript in preparation.

(14) P. Hemmerich and C. Sigwart, *Experientia*, **19**, 488 (1963).

(15) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(17) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(18) These residuals are defined as $\Sigma(Q_i - Q_{av})/\Sigma Q_i$ where Q_i represents either F or F^2 and Q_{av} is the average value of Q for two or more equivalent reflections.

(19) L. K. Templeton and D. H. Templeton, American Crystallographers Association Summer Meetings, June 1973, Storrs, Conn., Abstract E10.

(20) J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(21) This corresponds to a resolution of 1.4 Å. Larger, better quality crystals could not be obtained. It was felt that the information obtainable from even a low-resolution data set would be worthwhile. Most of the problems encountered in the solution and refinement of the structure can be traced to the low resolution of the data.

(22) Programs for the IBM 360/65 used were MAGPIK, INCOR, and ORDER, general data reduction programs.

(23) F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, **13**, 2381 (1974).

(24) "International Tables for X-Ray Crystallography", Vol. III, Sect. 4, "Interatomic and Interionic Distances", Kynoch Press, Birmingham, 1968, p 275.

(25) R. B. K. Dewar, Ph.D. Thesis, 1968, University of Chicago.

(26) The *n*-butyl groups were defined as follows. All atoms were taken to lie in the *x*-*y* plane. The center two of the four carbon atoms lie on the *y* axis, and the origin of the group coordinate system is midway between them. The coordinates in this group coordinate system (Å) were as follows: C(*n*), $x = -1.452$, $y = -1.283$; C($n + 1$), $x = 0.0$, $y = -0.770$; C($n + 2$), $x = 0.0$, $y = 0.770$; C($n + 3$), $x = 1.452$, $y = 1.283$. This corresponds to carbon-carbon distances of 1.540 Å and C-C-C angles of 109.5°. The program refines the coordinates of the center of the group system, the orientational angles Φ, θ, and ρ and the individual isotropic thermal parameters of the atoms in the group.[27]

(27) C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

(28) R. Hesse, *Ark. Kemi*, **20**, 481 (1962).

(29) R. Hesse and U. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970).

(30) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 103 (1976).

(31) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976).

(32) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(33) D. Coucouvanis, D. G. Holah, and F. J. Hollander, *Inorg. Chem.*, **14**, 2657 (1975).

(34) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4032 (1974).

(35) (a) F. J. Hollander, M. L. Caffery, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4682 (1974); (b) D. Coucouvanis, F. J. Hollander, and M. L. Caffery, *Inorg. Chem.*, **15**, 1853 (1976).

(36) E. C. Bissell, Ph.D. Thesis, Case Western Reserve University, 1970.

(37) J. M. Guss, R. Mason, I. Sotofte, G. Van Koten, and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 446 (1972).

(38) M. R. Churchill and K. L. Kalra, *J. Am. Chem. Soc.*, **95**, 5772 (1973); *Inorg. Chem.*, **13**, 1065 (1974).

(39) (a) D. Coucouvanis, D. G. Holah, C. Murphy, and S. Kanodia, paper presented at the 172nd National Meeting of the American Chemical Society, San

Francisco, Calif., Sept. 1976; (b) J. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, **19**, L41 (1976).

(40) E. H. Griffith, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 432 (1976).

(41) I. G. Dance and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.* 762 (1975).

(42) The possibility exists, as pointed out by a referee, that a $Cu_8(SPh)_{12}^{4-}$ cluster does not form because of nonbonding repulsions of the phenyl groups. The validity of this argument can be tested by employing less bulky R groups on the bridging mercaptide ligands.

Disproportionation of Saturated Alkali Metal Ketyls to Give Enolates and Alcoholates: a General Reaction That Has Been Overlooked[1a]

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Abstract: The reactions between 2,2-dimethylcyclohexanone-*6*-d_2 (**3**-*6*-d_2) and lithium, sodium, and potassium in THF and in liquid ammonia/THF at ca. −75 °C are investigated. The corresponding ketyls (**3**-*6*-d_2)$^-$·M$^+$ are formed in high yield, are transient, and decay, by disproportionation to give the enolate of **3**-*6*-d_2 and the alcoholate of 2,2-dimethylcyclohexanol-*1*-*d*-*6*-d_2 (**4**-*1*-*d*-*6*-d_2), by dimerization to give the dialcoholates of the pinacols **5**-*6*-d_2-*6′*-d_2, and by abstraction of a proton or a hydrogen atom from the medium to give the alcoholate of **4**-*6*-d_2. Partitioning between these decay modes differs somewhat for the lithium, sodium, and potassium ketyls, but is in each case unaffected when the concentration of the ketone precursor is changed drastically. This suggests that the ion pairs [(**3**-*6*-d_2)$^-$·M$^+$]$_1$, the primary products, rapidly associate, and that the decay reactions then proceed within an associated species, probably within the ion quadruplets [(**3**-*6*-d_2)$^-$·M$^+$]$_2$. The dissolving metal reductions of **3**-*6*-d_2 using lithium, sodium, and potassium in liquid ammonia/THF containing excess *tert*-butyl alcohol or ethanol at ca. −75 °C are investigated. Disproportionation of the ketyls strongly competes with the protonation of the ketyls, the key step of the general mechanism proposed by House. Protonation of the enolate formed by disproportionation regenerates the ketone, which is then rereduced.

Evaluation of the large body of published experimental results led House to propose[2] that the dissolving metal reduction of saturated ketones proceeds via the main sequence: (1) reduction, ketone → ketyl; (2) protonation, ketyl → ketyl radical; (3) reduction, ketyl radical → α-hydroxycarbanion; and (4) protonation, α-hydroxycarbanion → alcohol. To account for the empirical rule that the more stable diastereomeric alcohol is often the predominant product, he proposed that diastereomeric ketyl radicals and/or α-hydroxycarbanions equilibrate via inversion, and that the stabilities of these pyramidal species parallel those of the corresponding alcohols. Furthermore, he suggested that these species dimerize[3] in part, concurrently with steps 2 and/or 3, to give the pinacolates and/or the pinacols. He stressed that the association[3] of the ketyls may be playing a crucial role, but left open its extent and timing.

We find[4] that saturated ketyls with a hydrogen atom in an α position disproportionate[5] readily to give the enolates and the alcoholates. We hypothesize that this reaction takes place via the branched sequence (1) reduction, ketone → ketyl ion pair; (2) association, ketyl ion pair → ketyl ion quadruplet; (3) quasi-intramolecular decay via (a) disproportionation, ketyl ion quadruplet → enolate + alcoholate, (b) dimerization, ketyl ion quadruplet → pinacolates; (4) protonations, (a) enolate → ketone, (b) alcoholate → alcohol, (c) pinacolates → pinacols. We suggest that this sequence is kinetically favorable and that protonations of the ketyl ion pair and the ketyl ion quadruplet according to House's general mechanism compete, often inefficiently, with steps 2 and 3a, 3b, respectively. The ketone which is liberated through protonation of the enolate (4a) is reduced in turn. In the absence of a proton source, the new reaction dominates and the enolate survives and can be trapped. Under these conditions a third decay mode, a reaction with the THF and the liquid ammonia, which we also ascribe to the ketyl ion quadruplet, comes to light.

Unlabeled Substrate, Lithium, THF. We have recently shown[6] that the reaction of 2,2,6,6-tetramethylcyclohexanone (**1**) with metallic lithium in THF at ca. −75 °C gives the corresponding, persistent ketyl, **1**$^-$·Li$^+$,[7] in high yield. This ketyl was characterized by its typical rigid medium ESR spectrum and was shown to undergo characteristic chemical reactions such as, in particular, that with water or deuterium oxide: deuteronation produces the corresponding O-deuterated ketyl radical, which cleanly disproportionates[5] to give back the ketone **1**, and the corresponding alcohol, 2,2,6,6-tetramethylcyclohexanol, with deuterium atoms in the 1-position and in the hydroxyl group, **2**-*1*-*d*-*O*-*d*. On workup with water the hydroxylic deuterium atom is exchanged and the alcohol with one deuterium atom in the 1-position, **2**-*1*-*d*, is isolated.

When saturated ketones such as 2,2-dimethylcyclohexanone (**3**), with a hydrogen atom in an α position are treated with lithium in the same manner, a metal-consuming reaction again takes place, but the resulting solutions do not exhibit an ESR signal. Hydrolysis with deuterium oxide and workup with water again predominantly gives ca. 1:1 mixtures of the ketone and the corresponding alcohol, but now the ketone contains ca. one deuterium atom, in the α position, and the alcohol is unlabeled. These results, contrasted with that for the persistent ketyl (**1**$^-$·Li$^+$), demonstrate that the lithium ketyls with an α-hydrogen atom are formed as expected, apparently again in high yield, that they are transient under the conditions of their formation, and that decay mainly leads, overall, to the formation of 1:1 enolate/alcoholate mixtures. ESR experiments (see below) support the conclusion that these ketyls are transient. Overall, the main decay reaction (→ enolate/alcoholate) seemingly brings about a transfer of the hydrogen