Acknowledgment. The work was supported by a grant from the Public Health Services (AM-17806) and partially by the UH-Biomedical program. G. Leong and C. Yen provided technical assistance at different stages of this work. We gratefully acknowledge a generous sample of C_{18} ketone from Dr. J. Kok of Philips Duphar.

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(5) The six known isomers all contain the 7-trans geometry: all-trans, 9-cis, 11-cis, 13-cis, 9,13-dicis, 11,13-dicis. For their synthesis, see U. Schwieter, G. Saucy, M. Montavon, C. Planta, R. Rüegg, and O. Isler, *Helv. Chim. Acta*, **45**, 517, 528, 541 (1962). See also U. Schwieter and O. Isler in "The Vitamins", Vol. 1, Academic Press, New York, N.Y., 1967, p 1.

(6) In a paper on the photochemistry of the regular C_{18} ketone, which was reported to give only the 9-cis, 11-cis, 9,11-dicis isomers, the photochemistry of II was described as being similar to the dihydro analogue: M. Mousseron-Canet and J. Olive, *Bull. Soc. Chim. Fr.*, **7**, 3242 (1969).

(7) Prepared by bromination with NBS of the C_{18} ketone followed by dehydrobromination. The product mixture contained the trans and the 9-cis isomers in a 6:1 ratio. They were readily separated on silica gel columns.

(8) Irradiation was carried out either with a high-pressure Hg arc lamp coupled with a Schoeffel monochromator, bandwidth 25 nm (analytical scale), or with a 550-W Hanovia medium-pressure Hg lamp with appropriate cutoff filter plates (preparative).

(9) All of the HPLC work were done on a $\frac{1}{2}$ in. Altex 5-μ Lichrosorb column. Hexane containing 5–10% of ether was the solvent.

(10) Two minor peaks of shorter retention time were also observed. In analogy to the parent C_{18} ketone,[6] we tentatively assigned these to the 11-cis and 9,11-cis isomers.

(11) The retention time of a small peak in the HPLC chromatogram of the aldehyde mixture was identical with that of 7-*cis*-I (see text).

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(13) The ^{1}H NMR signals in the dehydro series generally follow the parent retinal isomers. Therefore, the 7,8 and 11,12 geometry can be deduced from their coupling constants and the chemical shifts of CH_3-5, CH_3-13, and H-8 reliably indicate, respectively, the 7,8, 13,14, and 9,10 geometry. See, e.g., D. Patel, *Nature*, **221**, 825 (1969), and R. Rowan III, A. Warshel, B. D. Sykes, and M. Karplus, *Biochemistry*, **13**, 970 (1974).

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Acid–Base Reactions of the Metallocubanes. Synthesis and Structural Characterization of $Cu_{10}[S_2CCH(COO\text{-}t\text{-}C_4H_9)_2]_6[S_2CC(COO\text{-}t\text{-}C_4H_9)_2]_2$, a Ten Copper Atom Aggregate

Sir:

The pronounced tendency of Cu^I ions toward the formation of clusters with sulfur ligands is well established. A remarkable variety in composition and structures occurs in these clusters where the molecular architecture is based on the existence of cores such as Cu_4S_6,[1] Cu_4S_8,[2] Cu_5S_6,[3] Cu_5S_7,[4] and Cu_8S_{12}.[5] With the exception of the Cu^I, Cu^{II} mixed valence clusters obtained with β,β-dimethylcysteamine,[6] $[Cu_{14}L_{12}Cl]^{7+}$ ($L = [SC(CH_3)_2CH_2NH_2]^-$), and D-penicillamine,[7] $[Cu_{14}L_{12}Cl]^{5-}$ ($L = [SC(CH_3)_2CHCOO]^{2-}$), there exist no other copper cluster compounds which contain more than eight copper atoms in a molecular unit.

In an attempt to evaluate the importance of various ligand characteristics that may affect the structural and chemical properties of copper clusters with sulfur ligands, we have undertaken a study of the $[Cu_8L_6]^{4-}$ cubanes.[5b,8] The coordinated 1,1-dithiolate ligands in these clusters undergo facile protonation and sulfur addition[9] reactions that make it possible to alter the electronic and structural properties of the ligands.

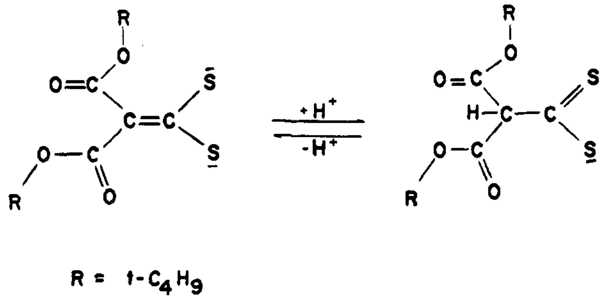

Figure 1. Structure and acid–base behavior of the *t*-Bu-DED, $[S_2CC(COO\text{-}t\text{-}C_4H_9)_2]^{2-}$, ligand.

In this communication we report on the acid–base behavior of the $[Cu_8(t\text{-Bu-DED})_6]^{4-}$ cluster (I) (*t*-Bu-DED = $S_2CC(COO\text{-}t\text{-}C_4H_9)_2$) (Figure 1) and the crystal and molecular structure of one of the proton addition products, $Cu_{10}(t\text{-Bu-DEDH})_6(t\text{-Bu-DED})_2$.

The reaction of $K_2(t\text{-Bu-DED})$[10] with $Cu(CH_3CN)_4ClO_4$[11] in acetonitrile in 1:1 molar ratio affords I as a potassium salt which upon recrystallization from an acetone–pentane mixture is obtained as orange crystals, mp 180 °C dec. Anal. Calcd for $K_4Cu_8S_{12}O_{24}C_{72}H_{108}$: C, 35.91; H, 4.52. Found: C, 35.70; H, 4.88. Cation exchange in I is accomplished readily in warm acetonitrile, CH_3CN, upon the addition of tetraalkylammonium or tetraarylphosphonium chlorides. The apparent molecular weight of the $BzPh_3P$ salt of I in 1,2-dichloroethane solution varies as a function of concentration. At concentrations >0.08 M, however, the apparent molecular weight is 3600 ± 70 and stays constant. This value indicates complete ionic association at higher concentrations and agrees well with the calculated molecular weight of 3666 for the $(BzPh_3P)_2Cu_8(t\text{-Bu-DED})_6$ cluster.

A potentiometric titration of I with $HClO_4$ in CH_3CN shows inflections at 1 and 6 equiv of acid/mol of I. Addition of 1 equiv of HCl (0.1 M in CH_3CN) to a solution of I (0.5 mmol in a minimum amount of CH_3CN) results in the formation of a dark green solution. Addition of 3 equiv of Ph_4PCl[12] to this solution, followed by solvent removal, results in the formation of a dark green crude solid contaminated with KCl. The solid mixture is extracted with $CHCl_3$. The green $CHCl_3$ solution upon addition of CS_2 gives dark green crystals of $(Ph_4P)_3Cu_8(t\text{-Bu-DED})_5(t\text{-Bu-DEDH})$ (II), mp 164 °C dec, in 83% yield. Anal. Calcd for $Cu_8S_{12}P_3O_{24}C_{144}H_{169}$: C, 52.90; H, 5.21; Cu, 15.6. Found: C, 52.10; H, 5.25; Cu, 15.5. Addition of a standard Bu_4NOH solution to a solution of II results in the formation of the cluster anion of I in a quantitative yield. A preliminary structure determination of the Bu_4N^+ "salt" of II clearly shows the Cu_8 cube in a Cu_8S_{12} core similar to those observed previously in other structures.[5b,8] Additions of 2 or 1 equiv of acid to I or II, respectively, result in violet solutions. Following a procedure similar to the one described previously, and employing $BzPh_3P^+$ [12] as a counterion, purple crystals of $(BzPh_3P)_2Cu_8(t\text{-Bu-DED})_4(t\text{-Bu-DEDH})_2$ (III), mp 125 °C dec, can be isolated in 54% yield. Anal. Calcd for $Cu_8S_{12}P_2O_{24}C_{122}H_{154}$: C, 49.51; H, 5.25; S, 13.00; P, 2.09; Cu, 17.2. Found: C, 49.51; H, 5.19; S, 13.8; P, 2.13; Cu, 17.0. Quantitative conversion of the anion in III to the cluster anions of II or I is accomplished by the addition of 1 or 2 equiv of base, respectively.

Addition of 3 equiv of acid to I results in the formation of a red-brown solution which contains III and a red by-product. This by-product becomes the major product in the reaction of

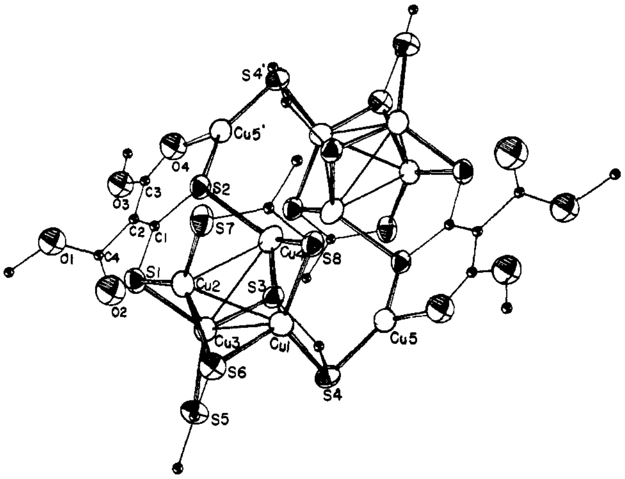

Figure 2. Structure and labeling of the Cu_{10}(*t*-Bu-DED)$_8$ cluster. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces. For clarity (a) the carbon atoms have been assigned very low temperature factors, (b) for three of the ligands the carbo-*tert*-butoxy groups have been left out, and (c) the *tert*-butyl groups on the bridging ligand have been omitted.

Table I. Selected Structural Parameters of the Cu_{10} Core

	Distances, Å		
Cu(1)-Cu(2)	2.656 (2)	Cu(2)-Cu(3)	2.686 (2)
Cu(1)-Cu(3)	2.888 (2)	Cu(2)-Cu(4)	3.056 (2)
Cu(1)-Cu(4)	2.664 (2)	Cu(3)-Cu(4)	2.968 (2)
Cu(1)-Cu(5)	3.438 (2)	Cu(4)-Cu(4)'	2.872 (2)
	Angles, degree		
Cu(2)-Cu(1)-Cu(3)	57.79 (5)	Cu(1)-Cu(3)-Cu(2)	56.77 (5)
Cu(2)-Cu(1)-Cu(4)	70.12 (6)	Cu(1)-Cu(3)-Cu(4)	54.11 (5)
Cu(2)-Cu(1)-Cu(5)	141.37 (6)	Cu(1)-Cu(4)-Cu(2)	54.81 (5)
Cu(1)-Cu(2)-Cu(3)	65.44 (5)	Cu(1)-Cu(4)-Cu(3)	61.40 (5)
Cu(1)-Cu(2)-Cu(4)	55.07 (5)	Cu(1)-Cu(4)-Cu(4)'	128.18 (6)

I with 4 equiv of acid and can be isolated as red crystals in 80% yield, by recrystallization of the crude material from a chloroform-pentane mixture, Cu_{10}(*t*-Bu-DED)$_2$(*t*-Bu-DEDH)$_6$ (IV), mp 128 °C dec. Anal. Calcd for $Cu_{10}S_{16}O_{32}C_{96}H_{150}$: C, 38.90; H, 5.06; S, 17.29; Cu, 21.44. Found: C, 39.13; H, 5.29; S, 17.05; Cu, 21.2.

An analysis of the ^{13}C NMR spectra of I, II, III, and IV suggests[13] that protonation occurs at the ethylenic, "methane" carbons of the 1,1-dithiolate ligands, $S_2C{=}C(COOR)_2{}^{2-}$ which are converted to the dithioacids, $S_2CCH(COOR)_2{}^-$ (Figure 1). An x-ray crystal structure determination was undertaken for IV, to establish the site of protonation as well as the molecularity and structure of this molecule.

The crystals of IV are triclinic with cell dimensions of a = 14.435 (3), b = 16.979 (3), c = 14.843 (3) Å; α = 98.16 (4), β = 108.09 (2), γ = 85.24 (4)°. The calculated density of 1.53 g·cm^{-3} (Z = 1) compares favorably to 1.51 g·cm^{-3} found by flotation in a hexachlorobutadiene-pentane mixture. The centrosymmetric space group $P\bar{1}$ was confirmed by successful refinement. Intensity data on a crystal (0.44 × 0.13 × 0.25 mm) were obtained on a Picker FACS I automatic diffractometer using a θ-2θ scan technique employing graphite monochromatized Mo Kα radiation (λ 0.7107 Å, $2\theta m$ = 12.2°).

Of the 6409 unique reflections measured ($\sin\theta/\lambda \leq 0.48$), and following an absorption correction (μ = 18.8), 4284 had $F^2 > 3\sigma(F^2)$ and were used in refinement. The structure was solved by conventional Patterson and Fourier techniques. The least-squares refinement of 77 nonhydrogen atoms, with the 75 hydrogen atoms included but not refined, resulted in a final R_1 value of 0.067. The five copper and eight sulfur atoms were refined with anisotropic temperature factors. The carbon and oxygen were refined with isotropic temperature factors.

The copper framework within IV consists of two Cu_4 distorted tetrahedra related by a crystallographic center of symmetry. The orientation of the two units is such that only one copper is close to the center of symmetry and 2.80 Å away from its symmetry related counterpart (Figure 2). The remaining two copper atoms are coordinated by ligand donor atoms on both tetrahedral units and thus bridge the two units.

The coordination geometry of the two Cu_4(*t*-Bu-DEDH)$_3$(*t*-Bu-DED) fragments of IV is a distorted version of the one observed in the structures of the $[Cu(Dtc)]_4$[2a] and $[Cu(Dtp)]_4$[2b] clusters. The four ligands are centered above and more or less bisect each of the four faces of the distorted Cu_4 tetrahedron. On each face two of the copper atoms are bridged by one of the sulfur atoms, while the third copper is coordinated by the other sulfur atom of the chelating ligand. Of the four ligands surrounding each of the Cu_4 units three are protonated at the ethylenic carbon adjacent to the CS_2 unit and can be considered dithio acid monoanions.[14] The fourth ligand is an ethylene dithiolate dianion. This unique ligand connects the Cu_4L_4 fragment to the "bridging" copper atom by coordination via an oxygen and sulfur atoms. A third coordination site on the bridging copper is occupied by a dithio acid sulfur on the adjacent Cu_4L_4 fragment (Figure 2).

The coordination geometry about each of the copper atoms in the Cu_4S_8 unit is distorted trigonal and nearly planar. The S-Cu-S angles range from 106.0 (1) to 131.8 (1)°. The deviation of the copper atoms from the appropriate S3 planes in the Cu_4S_8 fragment ranges from 0.02 to 0.19 Å. A more pronounced distortion from trigonal coordination is found for the "bridging" copper atoms. In the CuS_2O unit the two S-Cu-O and the S-Cu-S angles are 99.6 (3), 110.8 (3), and 148.9 (2)°, respectively. The copper is found 0.29 Å out of the S_2O plane. Values of selected bond distances and bond angles in the Cu_4S_8 unit are presented in Table I. Variations among the 12 individual Cu-S distances in this unit are rather large with a range of 2.230 (3) to 2.322 (3) Å. The average (2.269 (29) Å), however, is comparable with values reported[2] for the $[Cu(Dtc)]_4$ and $[Cu(Dtp)]_4$ clusters. Quite short Cu-S bond lengths of 2.187 (3) and 2.209 (3) Å are found in the CuS_2O unit that contains the "bridging" copper, and the Cu-O bond length is 1.898 (8) Å. The C-S-Cu angles range from 98.5 (4) to 110.0 (4)°. The C-O-Cu angle is 128.9 (6)° with a C-O bond length of 1.23 (1) Å.

On the basis of the available structural information,[2] it appears that 1,1-dithio acid ligands favor formation of the Cu_4L_4 neutral clusters. The octanuclear $Cu_8L_6{}^{4-}$ cubanes are obtained with a number of 1,1-dithiolate ligands.[13] A structural study of copper(I) clusters that contain both dithio acid and dithiolate ligands in various ratios may provide data for an evaluation of effects that may determine the stoichiometries and structures of copper-sulfur clusters. Structure determinations of II and III, currently in progress, are aimed at this goal.

Acknowledgment. This research was supported by grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: A listing of observed structure factor amplitudes, their estimated standard deviations, and the difference $|F_o| - |F_c|$ (14 pages). Ordering information is given on any current masthead page.

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(9) (a) D. Coucouvanis and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **89,** 1346 (1967). (b) The sulfur addition reaction to 1,1-dithiolate ligands in cluster complexes has been observed in our laboratory in the reactions of $Cu_8(t\text{-}Bu\text{-}DED)_6$ with elemental sulfur. The crystal structure of one of the reaction products, $BzPh_3PCu_5(t\text{-}Bu\text{-}DEDS)_4^-$, unequivocally shows the presence of perthiolate ligands.

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(12) The following abbreviations are used: Ph_4P = tetraphenolphosphonium, $BzPh_3P$ = benzyltriphenylphosphonium, Bu_4N = tetrabutylammonium, Dtc = diethyldithiocarbamate, Dtp = diethyl dithiophosphate.

(13) D. Coucouvanis, M. O'Connor, R. Pedelty, and W. Richardson, unpublished work.

(14) Clear evidence for protonation of the methine carbon of the ligand is provided by the C–C–C angles around the three sp^3-hybridized methine carbons. For the three protonated ligands these angles are (a) 112.8 (9), 108.8 (9), 112.0 (9)°; (b) 114.2 (9), 108.1 (9), 110.0 (9)°; and (c) 113.2 (9), 111.2 (9), 111.0 (9)°. For the 1,1-dithiolate ligand the C–C–C angles found at the corresponding, sp^2-hybridized carbon atom are 125 (1), 120 (1), and 115 (1)°.

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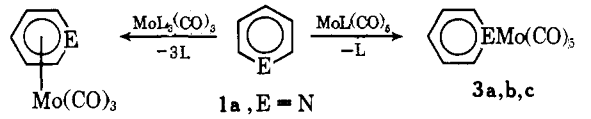
Molybdenum-Carbonyl Complexes of the Group 5 Heterobenzenes

Sir:

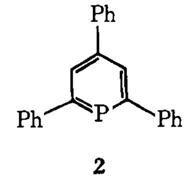
A variety of heteroaromatic compounds are known to act as both two-electron σ ligands and six-electron π ligands toward transition metals.[1-4] For example, pyridine (**1a**) readily forms σ-metal complexes while apparently only the 2,6-disubstituted pyridines easily give π complexes.[2] The highly substituted pyridine analogue 2,4,6-triphenylphosphabenzene (**2**) also gives both σ-[3] and π-[4]metal–carbonyl complexes. The recent availability of the complete series of pyridine homologues **1b**,[5] **1c**,[5] **1d**,[6] and **1e**[7] has prompted us to undertake a comparative study of their σ- and π-coordination chemistry.



4c,d

1a, E = N
b, E = P
c, E = As
d, E = Sb
e, E = Bi

3a,b,c



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The σ complex, phosphabenzenemolybdenum pentacarbonyl (**3b**), may be readily prepared by ligand displacement from THF·$Mo(CO)_5$. The complex is obtained as air-sensitive yellow crystals:[8] mp 76–77 °C; IR ($CHCl_3$) 2078 (m), 1962 (s) cm^{-1} (CO); mass spectral parent peak at *m/e* 334 for $C_5H_5P^{98}Mo(CO)_5$. Both the ^1H and ^{13}C-nmr chemical shift lues of σ complex **3b** are very similar to those of free phosphabenzene (Tables I and II). However, the marked divergence of the J_{PH} and J_{PC} values of **1b** and **3b** is an expected consequence of the difference in coordination at phosphorus.[3,9] Unlike the analogous complex of **2**,[3,4] **3b** was thermally stable to 200 °C and did not lose CO to form the expected π complex **4b**.

A similar reaction of arsabenzene (**1c**) with pyridine·$Mo(CO)_5$ and boron trifluoride etherate gave the σ complex arsabenzenemolybdenum pentacarbonyl (**3c**) as yellow air-sensitive crystals: mp 64–65 °C; IR ($CHCl_3$) 2079 (w), 1986 (s) cm^{-1} (CO); mass spectral parent ion at *m/e* 378 for $C_5H_5As^{98}Mo(CO)_5$. Like the phosphabenzene complex, the proton and carbon NMR spectra are almost identical with those of the free ligand. Pyrolysis of **3c** at 120 °C destroyed the complex, eventually leading to small quantities of arsabenzenemolybdenum tricarbonyl (**4c**). This π complex is more conveniently prepared by heating $Mo(CO)_6$ with arsabenzene in diglyme or by the boron trifluoride etherate catalyzed ligand displacement from tris(pyridine)molybdenum tricarbonyl.

Table I. The Proton Chemical Shift Values[a] of the Heterobenzenemolybdenum Carbonyl Complexes[b] (with the Values for the Free Heterobenzenes in Parentheses[c])

Position	3b	3c	4c	4d
H_α (H_2,H_6)	8.5, $^2J_{PH}$ = 26 (8.6, $^2J_{PH}$ = 38)	9.6 (9.7)	5.9 (9.7)	6.1 (10.9)
H_β (H_3,H_5)	7.7, $^3J_{PH}$ = 20 (7.7, $^3J_{PH}$ = 8)	7.8 (7.8)	5.4 (7.8)	5.7 (8.2)
H_γ (H_4)	7.4, $^4J_{PH}$ = 6 (7.4, $^4J_{PH}$ = 3.5)	7.5 (7.5)	5.9 (7.5)	6.1 (7.8)

[a] The chemical shift values are quoted to the nearest 0.1 ppm and are measured downfield from internal TMS in $CDCl_3$. Phosphorus-proton coupling constants are in hertz. [b] The apparent chemical shift values have been taken as the centers of multiplets. [c] Reference 12.

Table II. The Carbon-13 Chemical Shift Values[a] of the Heterobenzenemolybdenum Carbonyl Complexes (with the Values for the Free Heterobenzenes in Parentheses[b])

Position	3b	3c	4c	4d
C_α (C_2,C_6)	151.0, $^1J_{PC}$ = 12.7 (154.1, $^1J_{PC}$ = 53)	164.5 (167.7)	110.8 (167.7)	114.6 (178.3)
C_β (C_3,C_5)	137.2, $^2J_{PC}$ = 16.8 (133.6, $^2J_{PC}$ = 14)	136.1 (133.2)	94.2 (133.2)	95.5 (134.4)
C_γ (C_4)	127.2, $^3J_{PC}$ = 32.0 (128.8, $^3J_{PC}$ = 22)	126.4 (128.2)	87.5 (128.2)	88.0 (127.4)

[a] The chemical shift values are measured in parts per million downfield from internal TMS in $CDCl_3$. J_{PC} values are in hertz. [b] Reference 12.