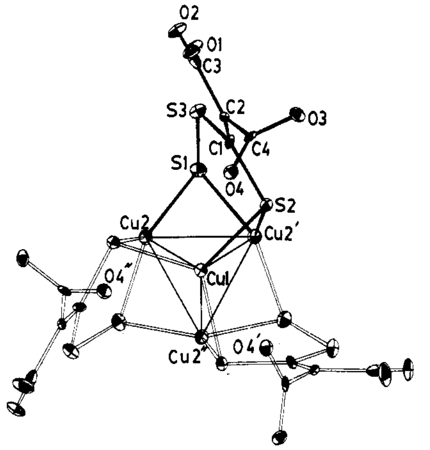

Figure 10. Molecular structure of the $(Ph_4P)KCu_4(S\text{-}t\text{-}Bu_2DED)_3$ cluster. The K^+ ion is located exactly above Cu1 on a crystallographic 3-fold axis perpendicular to the paper. The K^+ ion is octahedrally coordinated by the three acetone molecules of solvation and the ligand carbonyl oxygens O4, O4', and O4''. The *t*-Bu groups have been omitted for clarity.

Summary

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

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

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

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

Acknowledgment. We thank Professor W. Bennett for the provision of the computer program used in the determination of structural isomers. Financial support of this work by a grant from the National Science Foundation (CHE-79-0389) also is gratefully acknowledged.

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

Contribution from Departamento de Química, Universidad Autónoma de Guadalajara, A. P. 1-440, Guadalajara, Jal., México, and and the Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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

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

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

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

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(1) (a) Universidad Autónoma de Guadalajara. (b) University of Arizona.

(2) Gilliland, E. R.; Seebold, J. E.; FitzHugh, J. R.; Morgan, P. S. *J. Am. Chem. Soc.* **1939**, *61*, 1960. Gilliland, E. R.; Bliss, H. L.; Kip, C. E. *Ibid.* **1941**, *63*, 2088.

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best characterized.[9,10] Rodesiler and Amma[9] have shown by a crystallographic study that the complex is tetrameric, $(CuCF_3CO_2)_4(C_6H_6)_2$. These authors have also reported that the tetramer dissolved in benzene undergoes partial dissociation to a dimeric species.[10] Similar complexes with π-donor ligands such as carbon monoxide[11] and alkenes[6,12] have been synthesized. It has also been demonstrated that the molecular weights of these complexes are concentration and solvent dependent.[12]

Copper(I) trifluoroacetate (CuT) has been synthesized by the use of various reactions such as $CuO + CF_3CO_2H + (CF_3CO)_2O$[6] and $Cu + Cu(CF_3COO)_2$.[13] Copper(I) trifluoroacetate is also formed when the carbonyl[11] or benzene[10] complexes are heated in vacuo. CuT has a relatively high vapor pressure, 0.3 mmHg (100 °C).[13] The compound has been shown to exist as a dimeric species[13,14] in the gas phase. A structure similar to a carboxylic acid dimer has been proposed[13] for CuT in the vapor phase on the basis of its infrared spectrum and the resemblance of its structure to the moleculalr structure of copper(I) acetate.[15,16]

In this work we have elucidated the composition of the molecular species that are formed in the solid phase or liquid phase when copper(I) trifluoroacetate is brought into contact with alkenes or benzene. The experimental techniques that have been employed consist mainly of (1) manometric vapor pressure for the determination of the equilibrium vapor pressures of the ligands benzene, ethylene, and cyclohexene over solid copper(I) trifluoroacetate, (2) a recently developed method, vacuum vapor pressure osmometry,[17] for molecular weight determinations, and (3) a gas chromatographic method for the determination of the vapor phase composition with the aid of an internal standard.

Experimental Section

$Cu(CF_3CO_2)(OH)(H_2O_2)_2$ and $Cu(CF_3CO_2)$. Trifluoroacetic acid (30 g, 0.26 mol) was added to copper(II) hydroxide (10 g, 0.10 mol) suspended in 50 mL of water at room temperature, while the suspension was stirred continuously with a magnetic stirrer. The reaction mixture was filtered, and the filtrate was kept under vacuum in a desiccator that contained calcium sulfate as the desiccant. The crystals that were obtained were dissolved in 100 mL of tetrahydrofuran, and the solution was poured into 1 L of water at room temperature. The precipitate that was formed was extracted with ether. The solid that was obtained from the ether extract was analyzed as follows: The percentage of copper in the solid was determined by an EDTA titration. Sulfuric acid was added to an aqueous solution of the complex, and the resulting solution was distilled. The trifluoroacetic acid in the distillate was determined by titration with a standard solution of NaOH. Anal. Calcd for $CuC_2F_3O_6H_7$: Cu, 25.67; $CF_3CO_2^-$, 45.66. Found: Cu, 25.51; $CF_3CO_2^-$, 47.02. When the complex was heated at 130 °C for 15 h, two molecules of water were lost. This was confirmed by obtaining the infrared spectrum of the condensed vapor phase. Weight loss: calcd, 14.54%; found, 14.65%.

The identical complex was obtained when crystalline copper(II) trifluoroacetate that was obtained from the aqueous solution, as described above, was dried at 100 °C for 5 h. The complex is sparingly soluble in water but has a considerable solubility in oxygenated organic solvents such as ethers, esters, and alcohols. The complex is also readily soluble in trifluoroacetic anhydride; anhydrous copper(II) trifluoroacetate remained as a residue upon evaporation of the solvent. Anal. Calcd for $CuC_4F_6O_4$: Cu, 21.94. Found: Cu, 21.47. The copper(II) basic trifluoroacetate, $Cu(CF_3CO_2)(OH)(H_2O)_2$, was employed as the starting material for the synthesis of copper(I) trifluoroacetate complexes.

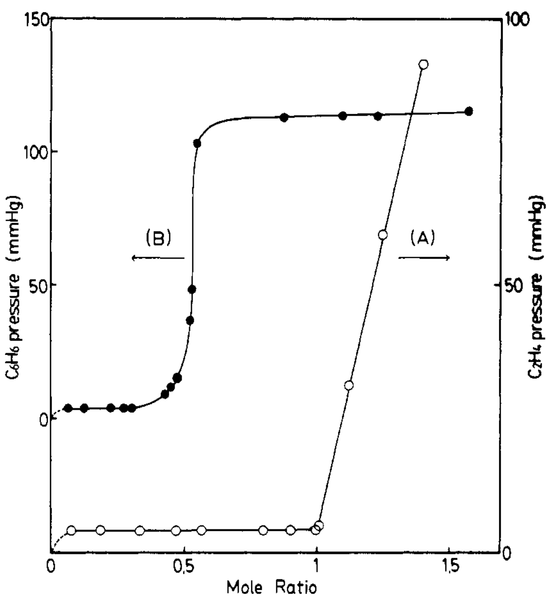

Figure 1. Equilibrium ligand pressures over solid CuT: (A) ethene at 50.0 °C; (B) benzene at 30.0 °C.

$CuCF_3CO_2$. An ampule containing 1.0 mmol of $Cu(CF_3CO_2)(OH)(H_2O)_2$ and copper metal in excess, together with a magnetic stirring bar, was placed in a vacuum system and evacuated. Five milliliters of trifluoroacetic anhydride was introduced into the ampule by vacuum distillation, and the mixture was stirred for 1 h before the solvent was removed by vacuum distillation. A mixture of benzene (5 mL), trifluoroacetic acid (0.5 mL), and trifluoroacetic anhydride (0.5 mL) was transferred into the same ampule. A colorless solution resulted within 1 h. This solution was filtered through a sintered-glass filter, and upon removal of the solvent, $Cu(CF_3CO_2)$, i.e., CuT, was formed and was dried at 80 °C for 1 h in vacuo.

Ligand Vapor Pressure–Composition Measurements. An apparatus similar to that previously described[18] was employed for these measurements. It consisted of a mercury manometer, a buret or a gas reservoir, and a reaction vessel. An adequate amount of CuT was synthesized in the reaction vessel, and aliquots of ligand (benzene, ethene, or cyclohexene) were introduced successively into the vessel containing the CuT at a constant temperature. The resultant equilibrium pressure was measured with the aid of the mercury manometer.

Molecular Weight Determination. Molecular weights were determined by the use of a vacuum vapor pressure osmometer as described previously.[17] $CuCF_3CO_2$ was synthesized in the apparatus for molecular weight determination, and benzene and cyclohexene were introduced into the apparatus by vacuum distillation.

Gas Chromatography. A Perkin-Elmer 990 gas chromatograph equipped with a thermal conductivity detector was employed for the determination of vapor-phase composition. A mixture of carbon tetrachloride and benzene was separated and quantitated with the aid of helium as a carrier gas, in a 6-ft column of silylated Celite coated with diethylene glycol succinate and maintained at 80 °C. A mixture of chloroform and cyclohexene was separated and quantitated by the use of helium as the carrier gas and a silylated Celite column coated with Apiezon H and maintained at 80 °C.

Results

Equilibrium Ligand Pressure vs. Complex Composition Diagram. Figure 1 shows the equilibrium pressures of ethene

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and benzene in the reversible reaction (1) as a function of the

$$\mathrm{CuT{\cdot}L}_n(\mathrm{s}) \rightleftharpoons n\mathrm{L(g)} + \mathrm{CuT(s)} \qquad (1)$$

mole ratio ethene/CuT or benzene/CuT. The presence of a single plateau at a mole ratio $0 < \text{ethene/CuT} < 1$ in Figure 1A proves the existence of a single equilibrium in which $n = 1$, at 50.0 °C. Studies at lower (0 °C) and higher (60 °C) temperatures support the existence of the same equilibrium. The successive addition of ethene in small increments resulted in a linear increase of the C_2H_4 pressure up to 600 mmHg at temperatures of 50 °C as well as at 0 °C. This indicated that there was no further absorption of C_2H_4 under these conditions. No evidence was obtained for the formation of cyclohexene complexes in which n was greater than 1.

The temperature dependence of the ethene pressure is represented by eq 2 in the temperature range 30–60 °C. The

$$\ln\,[P\ (\mathrm{atm})] = 6.704 \times 10^3/T + 16.08 \pm 8.6 \times 10^{-2} \qquad (2)$$

uncertainty term is the standard deviation. Thus, the enthalpy and entropy changes for the decomposition of the complex into gaseous ethene are $\Delta H = -55.7$ kJ·mol^{-1} and $\Delta S = 134$ J·mol^{-1}·K^{-1}, respectively. These changes for the liquid alkene[19] are $\Delta H = -78.4$ kJ·mol^{-1} and $\Delta S = 191$ J·mol^{-1}·K^{-1}. Equilibrium benzene pressures at various mol ratios at 30.0 °C that are plotted in Figure 1B show the formation of a complex in which $n = {}^1/_2$. It is clear that other complexes, e.g., where $n = 1$, are not formed in the reaction system.

The equilibrium pressure–temperature relationship of $(\mathrm{CuT})_2\mathrm{C}_6\mathrm{H}_6$ is expressed as $\ln\,[P\ (\mathrm{atm})] = 6.110 \times 10^3/T + 15.03 \pm 3.7 \times 10^{-2}$. Thus, the enthalpy and entropy changes for the decomposition of the complex into gaseous or liquid benzene[19] are $\Delta H(\mathrm{g}) = -50.8$ kJ·mol^{-1}, $\Delta S(\mathrm{g}) = 125$ J·mol^{-1}·K^{-1}, $\Delta H(\mathrm{l}) = -24.5$ kJ·mol^{-1}, and $\Delta S(\mathrm{l}) = 62$ J·mol^{-1}·K^{-1}.

The cyclohexene complex decomposed on heating to temperature above 50 °C. At temperatures less than 50 °C, reliable values for the equilibrium vapor pressures could not be obtained because they were too low to measure.

Molecular Weight Determination of CuT in Benzene and Cyclohexene. A plot of the bridge potential difference, ΔE, which is proportional to the temperature difference between a pure solvent and a solution, vs. various concentrations of 1,4-bis(trichloromethyl)benzene, $C_8H_4Cl_6$, is shown in curve 1 of Figure 2.. Surprisingly, a linear relationship persists up to 1 M. A least-squares treatment shows that $\Delta E\ (\mathrm{mV}) = 20.49[\mathrm{C_8H_4Cl_6}] \pm 2.0 \times 10^{-4}$. On the other hand, a plot of ΔE vs. f, the analytical concentration of CuT (mol of CuT/kg of benzene), is not linear (curve 2, Figure 2) and lies below curve 1. This indicates the formation of a species that has a higher molecular weight than CuT. The data obtained by Rodesiler and Amma[10] that are also plotted on the same curve (curve 2 in Figure 2) agree well with the values obtained in this work.

Curves 3 and 4 in Figure 2 are similar plots for $C_8H_4Cl_6$ and CuT in cyclohexene. Again, the plot of ΔE vs. $C_8H_4Cl_6$ concentration is linear up to a concentration as high as 1 M and is expressed as $\Delta E\ (\mathrm{mV}) = 25.76[\mathrm{C_8H_4Cl_6}] \pm 2.8 \times 10^{-4}$. A plot of the ΔE values for CuT vs. f, the concentration of CuT in cyclohexene, shows the same behavior that was observed in benzene solution; the data obtained by Rodesiler and Amma[10] are also shown.

Determination of the Number of Molecules of Benzene or Cyclohexene Coordinated at Relatively High Concentrations of CuT. Consider a liquid phase that contains $m_S{}^\circ$ moles of solvent, S, and a small amount, $m_A{}^\circ$ moles, of an inert compound A; the gas phase in equilibrium with the liquid phase consists of their vapor with partial pressures of $P_S{}^\circ$ and $P_A{}^\circ$ at a constant temperature. If m_c moles of CuT is dissolved in this liquid phase, it results in a change in the vapor-phase composition and a change in the partial pressures to P_S and P_A, respectively, at the same temperature. If the copper(I) compound is coordinated to N moles and if the relation $(P_A{}^\circ/m_A{}^\circ)/(P_S{}^\circ/m_S{}^\circ) = (P_A/m_A{}^\circ)/(P_S/m_S)$[20] holds in both systems, the number of coordinated solvent molecules, N, can be determined from $N = [1 - (P_A{}^\circ/P_S{}^\circ)(P_S/P_A)](m_S{}^\circ/m_c)$.

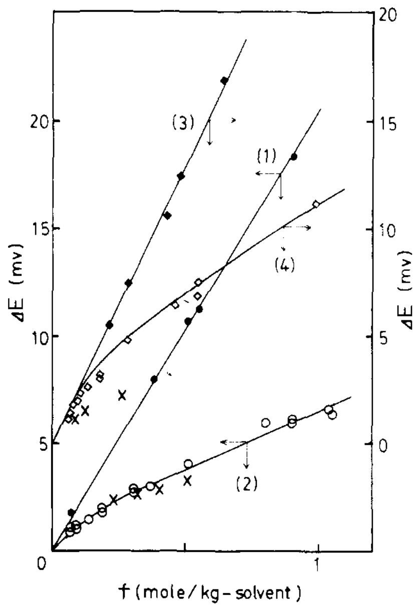

Figure 2. Plots of ΔE vs. f at 29.0 °C: (1) $1,4\text{-}(\mathrm{CCl_3})_2\mathrm{C_6H_4}$ in benzene; (2) CuT in benzene; (3) $1,4\text{-}(\mathrm{CCl_3})_2\mathrm{C_6H_4}$ in cyclohexene; (4) CuT in cyclohexene. The points marked × have been calculated from data published in ref 10.

Thus, for the determination of $P_A{}^\circ/P_S{}^\circ$ and P_A/P_S, various mixtures of CCl_4 and C_6H_6 were analyzed gas chromatographically. It was found that the peak height ratio of CCl_4 to C_6H_6, R_p, is proportional to the mole ratio, R_m, when R_m is less than 2×10^{-2}. The relation between R_p and R_m is represented by $R_p = 1.690R_m \pm 2.0 \times 10^{-4}$. An ampule containing 9.023 g of C_6H_6 and 0.1859 g of CCl_4 was kept at 29.0 °C in a vacuum system, and 3 μL of the vaporized liquid was condensed from the resultant vapor phase (5 mL) into a capillary vessel and sealed. The R_p values of the condensate were 2.079×10^{-2} and 2.073×10^{-2} (average 2.076×10^{-2}).

An 11.69-mmol amount of CuT was dissolved in the same mixture, and the condensed vapor (3 μL) was analyzed. The R_p values were 2.215×10^{-2} and 2.194×10^{-2} (average 2.205×10^{-2}). Hence, N was found to be 0.566.

The peak height ratios of chloroform to cyclohexene, R_p, were also proportional to their mol ratios R_m ($R_m \leq 4 \times 10^{-2}$), and the linear relationship between R_p and R_m could be expressed as $R_p = 1.674R_m \pm 4.8 \times 10^{-4}$.

An ampule containing 9.085 g of C_6H_{10} and 0.0950 g of $CHCl_3$ was kept in a constant-temperature bath maintained at 29.0 °C. A small portion (3 μL) was condensed fromt the vapor phase (5 mL). The R_p values of the condensate were 2.035×10^{-2} and 1.968×10^{-2} (average 2.002×10^{-2}). Then, 11.53 mmol of CuT was dissolved in the same mixture and a small portion of the condensed vapor phase was analyzed gas chromatographically: $R_p = 2.298 \times 10^{-2}$ and 2.300×10^{-2} (average 2.299×10^{-2}). Hence, the value of N was found to be 1.24.

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(20) This relation is obtained if the solution obeys Raoult's law; P_A and P_S represent the vapor pressures of pure A and S, respectively.

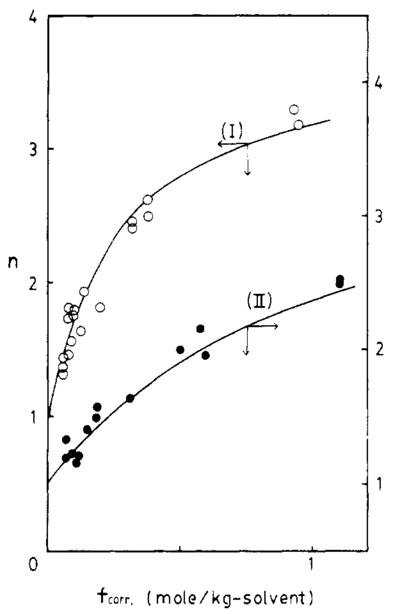

Figure 3. Average association number, n, vs. f_{cor} for CuT at 29.0 °C: (I) in benzene; (II) in cyclohexene.

Discussion

From the experimental data in Figure 2, a quantity c can be defined by the expression c = (ΔE values of CuT)/(slope of ΔE vs. concentration of $C_8H_4Cl_6$); hence, c = (ΔE of CuT in mV)/(20.49 for benzene) and c = (ΔE of CuT in mV)/(25.76 for cyclohexene). Here $c = [\mathrm{CuT}] + [(\mathrm{CuT})_2] + ... + [(\mathrm{CuT})_n]$; $c = \sum_{n=1}{}^{n}[(\mathrm{CuT})_n]$. On the other hand, the analytical concentration, f_{cor}, of CuT is given by $f_{cor} = [\mathrm{CuT}] + 2[(\mathrm{CuT})_2] + ... + n[(\mathrm{CuT})_n]$; $f_{cor} = \sum_{n=1}{}^{n}n[(\mathrm{CuT})_n]$. Thus, the ratio f_{cor}/c corresponds to the average association number n. Plots of n vs. f_{cor} with the values in Figure 2 give curve I shown in Figure 3.

Two features are apparent in Figure 3: when f_{cor} approaches zero, n approaches 1, from which it may be deduced that monomeric CuT is the predominant species at extremely low concentrations; when the value of f_{cor} increases, the value of n exceeds 3, which indicates that the pedominant molecular species under these conditions is the trimer or tetramer. The values of the abscissa in Figure 2 have been expressed as (mol of CuT)/(kg of solvent). When solid CuT is dissolved in benzene or cyclohexene, a series of solvent-coordinated species $(\mathrm{CuT})_n\mathrm{L}_l$ is formed and exists in equilibrium with the solvent. Hence, the weight of the free solvent decreases and causes an increase in the real concentrations of the complexes.

The gas chromatographic study showed that the average number of benzene molecules coordinated is 0.57 at f = 1.296 mol/kg of solvent. On the other hand, Figure 2(1) shows that c = 8.55/20.5 = 0.417 mol/kg of solvent at the same concentration, and threfore, $n' = f/c = 3.14$. These values are consistent with the assumption that there are two molecular species, $\mathrm{CuT(C_6H_6)_2}$ and $\mathrm{(CuT)_4(C_6H_6)_2}$, in solution.

The corrected analytical concentration of CuT in benzene, f_{cor} [(number of moles of CuT)/(number of moles of free solvent)], is assumed to be given[21] by $f_{cor} = f(1 + 0.156c)$ and the average number of coordinated benzene molecules, n, by $n = f_{cor}/c$. In Figure 3(I) these values of n have been plotted against the corresponding values of f_{cor}.

Table I. Calculated N Values for Various Sets of m and t Values in $(\mathrm{CuT})_m\mathrm{L}_t$ for the Cyclohexene Complexes

m	1	2	3	4	2	3	4
t	4	4	4	4	6	6	6
N_{calcd}	1.00	1.21	1.42	1.63	1.61	1.82	2.03

The best fit for curve I in Figure 3 was obtained on the assumption that the equilibrium constants are defined by $K_2 = [(\mathrm{CuT})_2]/[\mathrm{CuT}]^2$, $K_3 = [(\mathrm{CuT})_3]/[\mathrm{CuT}]^3$, and $K_4 = [(\mathrm{CuT})_4]/[\mathrm{CuT}]^4$ and that the contribution of dimer and trimer to the equilibrium is minimal since the sum $[(\mathrm{CuT})_2] + [(\mathrm{CuT})_3]$ does not exceed 10% of c. [22] Therefore, taking into account only the last equilibrium, we applied a least-squares treatment to the set of c vs. f_{cor} data in order to minimize $\sum(c_{obsd} - c_{calcd})^2$. The K_4 value was found to be 4.03×10^3 with a standard deviation 0.049.[23] Curve 2 in Figure 2 has been calculated on the basis of the K_4 value, and curve I in Figure 3 was obtained in the same manner except that values of $f_{cor}/(1 + 0.156c)$ were used instead of the f_{cor} values. The standard deviation of f_{cor} was estimated to be 0.14 mV from $[(\Delta E_{calcd} - \Delta E_{obsd})^2/(n - 2)]^{1/2}$.

The values $c = 0.416$, $f_{cor} = 1.380$, and $n = 3.32$ have been obtained from the gas chromatographic data. On the assumption that the molecular species in the solution are $\mathrm{CuT(C_6H_6)}_m$ and $\mathrm{(CuT)_4(C_6H_6)}_t$, the observed value[24] of N was 0.57. The value of t, however, must be equal to or greater than 2, because $\mathrm{(CuT)_4(C_6H_6)_2}$ is formed in the reaction between solid CuT and gaseous benzene, as shown above. Moreover, the monomer species is formed as a result of Cu–Cu bond rupture and the number of molecules of benzene that are coordinated to each copper atom in the monomer should not be less than that in the tetramer; i.e., $m \geq (t/4)$. The N values obtained for various combinations of m and t are as follows: $N = 0.534$ for $m = 1$ and $t = 2$; $N = 0.603$ for $m = 2$ and $t = 2$; $N = 0.673$ for $m = 3$ and $t = 2$; $N > 1$ for $t = 4$. Thus, the observed value $N = 0.57$ shows conclusively that the composition of the tetrameric species is $\mathrm{(CuT)_4(C_6H_6)_2}$. On the other hand, the monomeric species may be represented by $\mathrm{CuT(C_6H_6)_2}$, although the existence of the species $\mathrm{CuT(C_6H_6)}$ cannot be discounted. Since the tetrameric species in benzene solution retains that stoichiometry of the complex in the crystalline state, it is conceivable that the molecular structure of the tetramer may be the same as that in the crystalline state.[9]

The average association number, $n = f_{cor}/c$, vs. analytical concentration of CuT, f_{cor} (vide infra), in cyclohexene[24] is plotted in curve II of Figure 3. As before, n approaches 1 as f_{cor} approaches 0; however, n does not exceed a value of 3 even at $f_{cor} = 2$. Again, the best fit for the curve was obtained on the assumption that the only important equilibrium was that between the monomer and tetramer and that the contribution from a dimer or trimer was negligible. A least-squares treatment[25] gave $K_4 = 33.8$, with a standard deviation of 0.055. The solid curves in Figure 3(II) and Figure 2(4) have been calculated with aid of this K_4 value; the values of abscissa in Figure 2 have been expressed as $f_{cor}/(1 + 4cM_r/3000 +$

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(21) If f mol of CuT was dissolved in 1 kg of benzene and resulted in the formation of two molecular species $\mathrm{CuT(C_6H_6)_2}$ and $\mathrm{(CuT)_4(C_6H_6)_2}$, $c = [\mathrm{CuT(C_6H_6)_2}] + [\mathrm{(CuT)_4(C_6H_6)_2}]$. If the remaining free benzene weighs W kg, the following relation must hold: $1000/M_r = 1000W/M_r + 2[\mathrm{CuT(C_6H_6)_2}]W + 2[\mathrm{(CuT)_4(C_6H_6)_2}]W = 1000W/M_r + 2cW$. Since $f_{cor} = f/W$, $f_{cor} = f(1 + 2cM_r/1000)$ where M_r represents the molecular weight of benzene.

(22) It has been assumed that $f = [\mathrm{CuT}] + 2K_2[\mathrm{CuT}]^2 + 3K_3[\mathrm{CuT}]^3 + 4K_4[\mathrm{CuT}]^4$ and $c = [\mathrm{CuT}] + K_2[\mathrm{CuT}]^2 + K_3[\mathrm{CuT}]^3 + K_4\mathrm{CuT}]^4$. Then, if an initial set of K_2, K_3, and K_4 values are employed, f and c values can be calculated for each of the specific [CuT] values. Thus, $\sum(c_{obsd} - c_{calcd})^2$ values for corresponding f values were obtained upon changing the K_2, K_3, and K_4 values.

(23) $K_4 = 27[\sum_i(4c_i - f_i)^4(f_i - c_i)]/[\sum_i(4c_i - f_i)^8]$.

(24) Since $n = 3.32 = \{[\mathrm{CuT(C_6H_6)}_m] + 4[\mathrm{(CuT)_4(C_6H_6)}_t]\}/\{[\mathrm{CuT(C_6H_6)}_m] + [\mathrm{(CuT)_4(C_6H_6)}_t]\}$, $K_4 = 4.03 \times 10^3 = [\mathrm{(CuT)_4(C_6H_6)}_t]/[\mathrm{CuT(C_6H_6)}_m]^4$ and $f_{cor} = 1.380 = [\mathrm{CuT(C_6H_6)}_m] + 4[\mathrm{(CuT)_4(C_6H_6)}_t]$, $[\mathrm{CuT(C_6H_6)}_m] = 0.0945$, and $[\mathrm{(CuT)_4(C_6H_6)}_t] = 0.321$ are obtained. therefore, N is calculated from $N = \{m[\mathrm{CuT(C_6H_6)}_m + t[\mathrm{CuT})_4\mathrm{(C_6H_6)}_t]\}/f_{cor} = (0.0945\ m + 0.321t)/1.380$.

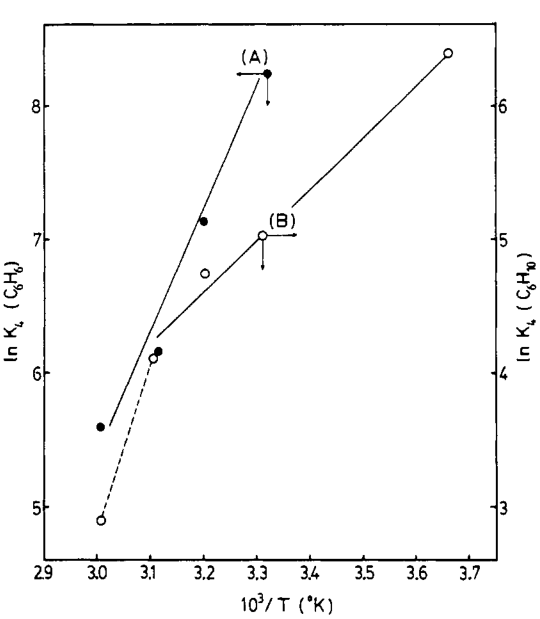

Figure 4. Plots of ln K_4 vs. $1/T$: (A) in benzene ($f = 0.3273$); (B) in cyclohexene ($f = 0.4480$).

$2f_{cor}M_r/3000$),[25] with an estimated standard deviation of 0.32 mV.

The number of coordinated cyclohexene molecules, N, determined by the gas chromatographic technique was 1.24 at $f = 1.264$. The values $c = 0.589$ and $f_{cor} = 1.446$ were calculated on the basis that $K_4 = 33.8$, and the value of n that was obtained was 2.46. The value of N was calculated on the assumption that the molecular species that were formed were $CuTL_m$ and $(CuT)_4L_t$, where L represents cyclohexene.[26] The following restrictions apply to the integers m and t: (1) $(t/4) \geq 1$ since solid CuT absorbs one cyclohexene molecule to form a solid complex; (2) $m \geq (t/4)$ because the cyclohexene molecules in the monomer occupy, at least partially, the Cu–Cu bonding sites in the tetramer. Table I shows N values that correspond to some possible values of m and t.

The observed value of N agrees well with the calculated value for $m = 2$ and $t = 4$, which is also the basis on which f_{cor} was evaluated. The maximum error in the experimentally determined value of N is about 10%.

Figure 4(A) shows the temperature dependence of K_4, the tetramer formation constant of the benzene complex. The linear relation is expressed as $\ln K_4 = 9.2887 \times 10^3/T - 22.50 \pm 0.14$. Therefore, the calculated enthalpy and entropy changes for tetramer formation are $\Delta H = 77.2$ kJ·mol^{-1} and $\Delta S = 187$ J·mol^{-1}·K^{-1}, respectively. Tetramer formation is accompanied by an increase in the number of molecules, which explains the positive entropy change: $4CuT(C_6H_6)_2 \rightarrow Cu_4T_4(C_6H_6)_2 + 6C_6H_6$.

A plot of ln K_4 (for cyclohexene) vs. $1/T$ is nonlinear, and the deviations from linearity are more evident at higher temperatures as shown in Figure 4(B). This indicates that, at high temperatures, species other than the monomer and tetramer play an important role. The dimeric species is probably formed at the higher temperatures. If the first four points at low temperature can be attributed to the formation of a tetramer from the monomer and if ln K_4 vs. $1/T$ is linear in this region, a least-squares treatment gives $\ln K_4 = 3.9525 \times 10^3/T - 8.051 \pm 0.099$. The enthalpy and entropy changes that accompanied tetramer formation are $\Delta H = 32.9$ kJ·mol^{-1} and $\Delta S = 66.9$ J·mol^{-1}·K^{-1}. The increase of entropy in tetramer formation is reasonable if the number of coordinating ligands is taken into account in the reaction $4CuT(C_6H_{10})_2 \rightarrow Cu_4T_4(C_6H_{10})_4 + 4C_6H_{10}$.

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Registry No. CuT, 25535-55-1; C_6H_6, 71-43-2; C_2H_4, 74-85-1; C_6H_{10}, 110-83-8; $Cu(CF_3CO_2)(OH)(H_2O)_2$, 79898-44-5; $Cu(CF_3CO_2)_2$, 16712-25-7.

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(25) If f mol of CuT is dissolved in 1 kg of cyclohexene and yields $[CuTL_2]$ and $[(CuT)_4L_4]$, leaving behind W kg of free cyclohexene, where L represents the cyclohexene molecule, the following mass balance equation for cyclohexene can be written: $1000/M_r = 1000W/M_r + 2W\cdot[CuTL_2] + 4W[(CuT)_4L_4]$. On the other hand, $c = [CuTL_2] + [(CuT)_4L_4]$ and $f_{cor} = [CuTL_2] + 4[(CuT)_4L_4)$; therefore, $1/W = 1 + (2f_{cor} + 4c)M_r/3000 = 1 + (2f_{cor}/W + 4c)M_r/3000$. Since $f_{cor} = f/W$, $f_{cor} = f(1 + 4cM_r/3000)/(1 - 2fM_r/3000)$ or $f = f_{cor}/(1 + 4cM_r/3000 + 2f_{cor}M_r/3000)$.

(26) Since $c = [CuTL_m] + [(CuT)_4L_t]$, $f_{cor} = [CuTL_m] + 4[(CuT)_4L_t]$, $f_{cor} = f(1 + 0.1095c)/(1 - 0.0548f)$, and $[(CuT)_4L_t] = 33.8[CuTL_m]^4$, $[CuTL_m] = 0.3032$ and $[(CuT)_4L_t] = 0.2856$ are obtained by a trial and error method. Hence, $c = 0.589$, $f_{cor} = 1.446$, and $N = (0.303m + 0.286t)/1.446$.