Phosphine and Olefin Complexes of Copper(I) Trifluoroacetate

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The preparation and characterization of several phenylphosphine and unsaturated eight-membered-ring complexes of copper(I) trifluoroacetate are presented. Evidence is offered which indicates that of the series of compounds under discussion, bis[bis(diphenylphosphino)ethano]copper(I) trifluoroacetate alone does not involve the anion in the inner coordination sphere of the metal ion.

Only brief attention has been focused on the copper-(I) salt of trifluoroacetic acid in the period since its first fleeting mention by Swarts.[1] Other than a description of the preparation of a carbon monoxide adduct,[2] a patent concerning the utilization of the salt as an olefin separations agent,[3] and a recent report including a method of preparing two complexes of the salt from copper(II) trifluoroacetate,[4] no information dealing with the coordination chemistry of the compound has appeared. Some current studies on phosphine complexes of copper(I) salts have indicated that steric factors play a decisive role in dictating the configuration of the coordination sphere about the copper-(I) ion.[5] Another critical factor is, of course, the donating properties and size of the anionic ligand. Thus, tetrakis(triphenylphosphine) complexes are only known for those copper(I) salts of the strongest acids, *e.g.*, fluoroboric and perchloric.[6] In virtually every other case the limiting ratio of triphenylphosphine to copper is 3. Seemingly, a modest free energy gain is realized only in those situations in which relegation of a nominally basic anion to the outer coordination sphere can be forced by the fourth triphenylphosphine crowding into the inner sphere. Much less sterically inhibiting is diphenylmethylphosphine, and bis(diphenylphosphino)ethane has even the further advantage of the entropy of a chelating ligand. We have found that only in the last case is the anion trifluoroacetate apparently "bumped" to an outer-sphere role, and we present evidence of this effect.

Analogously, bidentating polyolefins form complexes with the copper(I) ion in which one, two, or four sites about the metal are occupied by the olefinic moiety. Steric restrictions may again be operable, both between the polyolefins and between polyolefin and anionic ligand. Thus, only copper(I) salts of the above-mentioned strong acids will accept two mole-

cules of 1,5-cyclooctadiene to form ionic products.[7] Copper(I) salts of halogen and other weaker acids accept but one molecule of a bidentating ligand.[8]

Discussion and Results

Preparation of the Complexes.—The starting material in our preparations was simply the bare salt, isolated as a stable white crystalline material, melting at 204–206°, and acutely sensitive to moisture and oxygen.

Complexes with triphenylphosphine having one, two, and three molecules of phosphine per copper are readily prepared by admixture of the above material and the appropriate quantity of the ligand. Any attempts to prepare a 4:1 complex failed, including treatment of copper(II) trifluoroacetate with excesses of phosphine. This method, which yields only the 3:1 complex, has been found in some other cases to yield 4:1 complexes when simply adding excess phosphine to the copper(I) salt failed.[9]

Further indication of the unwillingness of the copper to part with trifluoroacetate was the limiting ratio of 3:1 even in the case of diphenylmethylphosphine, a ligand of substantially less steric demand and greater donating ability than triphenylphosphine.

Only in the case of bis(diphenylphosphine)ethane was there evidence of tetracoordination about copper by phosphorus. The fact that a compound containing two molecules of the bidentating ligand per copper is formed was not in itself sufficient evidence of this fact, nor was substantiation found in solution molecular weight data. Certain conclusions drawn from the solid-state (mineral oil mull) infrared spectrum of the complex were, however, considered to be indicative of this behavior. The insolubility in benzene of this compound alone in the series is further evidence of high charge separation. In addition, the measured conductivity in methylene dichloride corroborated the argument for ionicity.

Very similar behavior—that is, formation of an ionic

(1) F. Swarts, *Bull. Soc. Chim. Belg.*, **48**, 176 (1939).

(2) A. F. Scott, L. L. Wilkening, and B. Rubin, *Inorg. Chem.*, **8**, 2533 (1969).

(3) A. K. Dunlop, Shell Oil Co., U. S. Patent 3,401,112 (1968).

(4) B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nucl. Chem.*, **33**, 1017 (1971).

(5) See, for instance, S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, **10**, 1322 (1971).

(6) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960), first prepared the copper(I) perchlorate complex from copper(II) perchlorate. It was subsequently prepared by F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965), by adding excess triphenylphosphine to the bis(phosphine)-copper(I) complex. E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **91**, 4114 (1970), have observed the tetrakis(triphenylphosphine) complex of copper(I) hexafluorophosphate. We have prepared (from the copper(II) salt) the corresponding complex of copper(I) fluoroborate and, from it, the tetraphenylborate analog.

(7) Perchlorate complex: S. E. Manahan, *Inorg. Chem.*, **5**, 2063 (1966). Fluoroborate complex: S. E. Manahan, *Inorg. Nucl. Chem. Lett.*, **3**, 363 (1967).

(8) For examples, see (a) J. H. Van den Hende and W. C. Baird, Jr., *J. Amer. Chem. Soc.*, **85**, 1009 (1963); (b) B. W. Cook, R. G. J. Miller and P. F. Todd, *J. Organometal. Chem.*, **19**, 421 (1969); (c) also see N. C. Baenziger in "Characterization of Organometallic Compounds," Part I, M. Tsutsui, Ed., Interscience, New York, N. Y., 1969.

(9) Although this behavior is not understood, we have found at least two cases in our laboratory in which a tetrakis(triphenylphosphine)copper(I) complex was isolable only *via* the copper(II) salt; addition of excessive triphenylphosphine to the tris(phosphine)copper(I) complex led only to starting materials. Copper(I) fluoroborate is an example. See W. A. Anderson, A. J. Carty, G. J. Palenik, and G. Schreiber, *Can. J. Chem.*, **49**, 761 (1971), for further discussion of the method.

complex of a copper(I) salt only with the chelating bis-(diphenylphosphino)ethane—has recently been observed for copper(I) nitrate.[10] Measurements of conductivity in acetic acid have shown that nitric and trifluoroacetic acids are of equal strength,[11] implying that donor abilities of an anion can in some cases be inferred directly from acid strength of the derived anion.

Infrared Spectra.—Mull spectra were run since both potassium bromide disks and solution spectra can be ambiguous; the former have been known to perturb solid-state crystals, and the latter are subject to complications due to dissociation–association phenomena characteristic of phosphine complexes of copper(I)[12] and due to solvation effects as well.

It was decided that a suitable model for a "free" trifluoroacetate group was not to be found in the alkali metal or group Ib metal salts, or even in the ammonium salt, for reasons to be discussed. Instead, tetra-*n*-butylammonium trifluoroacetate was chosen. Furthermore, it was found that the most helpful band arising from the anion was carbon–carbon stretching absorption[13] which occurs in the 800–870-cm^{-1} region. The other regions of absorption, 1600–1700 cm^{-1} (attributable to asymmetric carbonyl stretching bands) and 1100–1200 cm^{-1} (carbon–fluorine absorptions), were found to be less desirable probes of the nature of the anion and its coordination.[14]

Listed in Table I is the position of this carbon–carbon stretching band for the compounds under discussion. It is obvious from the data that the band for the tetra-*n*-butylammonium compound—the best model for the least perturbed trifluoroacetate ion and therefore for an outer-sphere ligand—falls substantially lower in energy than those for the metal and ammonium ion compounds. This means that in its least bound state, the carbon–carbon bond in the trifluoroacetate anion is of relatively low bond order.[15] A simplistic explanation is that contributions to the ground state by valence-bond structure II are more operative with a free anion, and any bonding of the carboxyl to an acceptor will stabilize structure I. Electrostatic dispersion forces between the carboxyl and trifluoromethyl groups undoubtedly also contribute to diminution of the bond order in the free or most free anion, and this situation is also somewhat mitigated by bonding to an acceptor.

It is felt that a detailed interpretation of the position and shifting of the C–C bond is unwarranted due to insufficient knowledge of the structures of the complexes in the solid state and an imprecise understanding of the individual oscillator contributions to the absorption.[13] Nevertheless, the coincidence of the position of this band for the tetraalkylammonium salt and the bis-(diphenylphosphino)ethane complex reinforces the contention that an essentially free ionic trifluoroacetate species occurs in both compounds.

Equivalent Conductivities.—Solutions 10^{-3} M in methylene dichloride of the phosphine complexes were subjected to a conductivity bridge and the results, summarized in Table II, clearly imply that in the case

TABLE I
POSITION OF THE C–C BAND FOR VARIOUS
TRIFLUOROACETATE COMPOUNDS (M–O$_2$CCF$_3$), RUN
AS MINERAL OIL MULLS

M$^+$	Band energy, cm^{-1}	M$^+$	Band energy, cm^{-1}
Na	845	((C$_6$H$_5$)$_2$PCH$_3$)$_3$Cu	830
K	840	$\left(\begin{smallmatrix}P(C_6H_5)_2\\ P(C_6H_5)_2\end{smallmatrix}\right)_2$Cu	822
NH$_4$^{a}	840	(C$_2$H$_4$)Cu	848
N(C$_4$H$_9$)$_4$	820	(C$_8$H$_{12}$)Cu	845
Cu	860	(C$_8$H$_{12}$)$_{0.5}$Cu	850
(P(C$_6$H$_5$)$_3$)Cu	845	(C$_8$H$_8$)Cu	845
(P(C$_6$H$_5$)$_3$)$_2$Cu	838	(CO)Cu	855
(P(C$_6$H$_5$)$_3$)$_3$Cu	828		

^{a} Recently a crystal structure of this salt has been reported[16] in which a melting point of 156° is given. We have prepared the salt, with a satisfactory analysis, having mp 124–125°.

TABLE II
EQUIVALENT CONDUCTIVITIES OF THE PHOSPHINE
COMPLEXES OF COPPER(I) TRIFLUOROACETATE^a

Complex	$\Lambda_{25}°$, cm^2/ ohm equiv
((C$_6$H$_5$)$_3$P)$_2$CuTFA	0.473
((C$_6$H$_5$)$_3$P)$_3$CuTFA	1.33
((C$_6$H$_5$)$_2$PCH$_3$)$_3$CuTFA	1.78
((C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_2$CuTFA	57.1
((C$_6$H$_5$)$_3$P)$_2$CuBH$_4$	0.12
((C$_6$H$_5$)$_3$P)$_4$CuBF$_4$	61.6
((C$_6$H$_5$)$_3$P)$_4$CuClO$_4$	89.3^b
((C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_2$CuNO$_3$	30.0^c

^{a} All run 10^{-3} M in CH$_2$Cl$_2$, except the last two, run in nitromethane and nitrobenzene, respectively. ^{b} F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960). ^{c} Reference 10.

of the bis(phosphino)ethane complex there is significantly greater charge mobility. Bis(triphenylphosphino)copper(I) borohydride is included as a reference. The tetrakis(triphenylphosphino)copper(I) fluoroborate complex will be discussed elsewhere.

Olefin Complexes.—At atmospheric pressure, solutions of copper(I) trifluoroacetate absorb 1 mol of

(10) See Anderson, *et al.,*[9] and F. H. Jardine, A. G. Vohra and F. J. Young, *J. Inorg. Nucl. Chem.,* **33**, 2941 (1971).
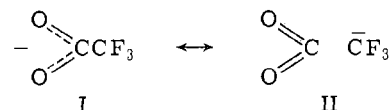
(11) T. Gramstad, *Tidsskr. Kjemi, Bergv. Met.,* **19**, 62 (1959).

(12) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.,* **91**, 4114 (1970), and references within. It may also be commented that solution spectra were run in benzene and chloroform, and the bands under discussion, particularly the 800–860-cm^{-1} band, remained in nearly constant position in going from the mono- to the bis- to the tris-phosphine complex.

(13) This assignment was first made by N. Fuson, *et al., J. Chem. Phys.,* **20**, 1627 (1952), then by R. E. Kagarise, *ibid.,* **27**, 519 (1957), and again by R. E. Robinson and R. C. Taylor, *Spectrochim. Acta,* **18**, 1093 (1962). It is understood that rather than being a "pure" carbon–carbon stretch band, there are doubtless contributions to this absorption from other low-energy bands such as asymmetric carbonyl stretches. E. Spinner, *J. Chem. Soc.,* 4217 (1964), has called this band "a pseudo-symmetric stretching motion of all four CF and CC bonds." Orrell[14] stated, "The formally assigned C–C stretching mode is better described as a mixture of symmetric and antisymmetric –O–C–C stretching modes. . . ."

(14) Although other workers (*e.g.,* M. J. Baillie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc. A,* 3110 (1968); C. A. Agambar and K. G. Orrell, *ibid.,* 897 (1969)) have found useful correlations in these bands, we were unable to find consistent, meaningful trends or relationships among the compounds under consideration.

(15) This conclusion follows from the finding that in a recent crystal structure study of ammonium trifluoroacetate (D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J. Chem. Soc.,* 1303 (1964)) a long bond length was measured between the two carbons (1.542 Å). The shift by 20 cm^{-1} toward lower energy for the tetra-*n*-butyl salt is supposed to reflect an even longer bond, although it is realized that the presence of hydrogen bonding in the former case can have effects manifested in this band (see ref 13).

ethylene. 1,5-Cyclooctadiene will form both a 1:1 or a 1:2 complex (hydrocarbon to copper salt), depending on the amounts initially present. Both compounds are isolated as white solids, sensitive to the atmosphere and insoluble in low polar solvents. Solid-state infrared spectra failed to yield any clues of the structures and were virtually identical.

Cyclooctatetraene forms a complex containing two ions of copper per ring. The most likely structure contains a core as indicated in III, with bridging (polymeric) or chelating trifluoroacetate groups.

III
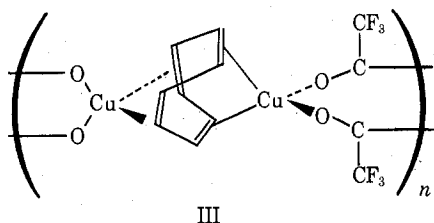
The absence of uncomplexed carbon double-bond stretches in the infrared spectrum is usually cited as evidence of structures such as that depicted; however, overlapping of the intense carboxyl band in the region prevented definitive conclusions. No other "core" type cyclooctatetraene–copper(I) complexes have been reported, the only other mention of a COT complex being a 1:1 compound of copper(I) chloride in which only one of the double bonds involves itself with the metal.

The complex with cyclooctatetraene is somewhat more atmosphere stable than the cyclooctadiene adducts, but it, too, is insoluble in most common solvents. In trifluoroacetic acid, a red solution results; this red color is also apparent in the reaction during formation of the complex, disappearing as the reaction proceeds or if more olefin is added. Interestingly, the benzene-insoluble 1:2 complex dissolves upon addition of more tetraolefin; however, precipitation with pentane affords only the original complex. It may be concluded that a benzene-soluble complex(es) arises in excess cyclooctatetraene, but crystallization favors the structure shown.

Summary

Ligated with copper(I), trifluoroacetate ion appears to behave much like nitrate. The two anions are of very similar basicity and can, under appropriate circumstances, behave as a mono- or bidentate or as an outer-sphere anion.[16] The infrared interpretation of the trifluoroacetate group is less straightforward, however, and a complete normal-coordinate analysis remains to be performed. Only when a more complete understanding of the contributions and dependencies of the "carbon–carbon" band are available can such intriguing effects as back-bonding into the group by transition metals and the shifting of the band with various coordinative situations about the metal be meaningfully explored. Investigation of the solution-phase behavior of such complexes, including colligative and fluorine or phosphorus nuclear magnetic spectral properties, will furthermore enhance such understanding.

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(16) For a recent comprehensive review of coordinated nitrate see C. C. Addison, N. Logan, S. W. Wallwork, and C. D. Garner, *Quart. Rev., Chem. Soc.*, **25**, 289 (1971).

A mass spectral study of the compounds under discussion will be reported elsewhere.

Experimental Section

Infrared spectra were run on a Beckman IR-20 instrument. Melting points are corrected and were determined on a Mel-Temp apparatus in sealed capillary tubes. All preparations were carried out under a blanket of dry nitrogen, using distilled solvents. Other chemicals, however, were used as received from suppliers. Molecular weights were measured osmometrically at concentrations *ca.* 10^{-2} *M* unless otherwise specified. A Barnstead Model PM-70CB bridge was used to measure the equivalent conductivities listed in Table II.

Copper(I) Trifluoroacetate.—Since no satisfactory preparations of this salt are reported, we will detail our method. Into a 100-ml three-necked flask equipped with a reflux condenser and stirrer was first added 20 ml of trifluoroacetic acid; then, with fast stirring, 14.5 g of cuprous oxide was added and finally 30 ml of trifluoroacetic anhydride was dribbled in using a dropping funnel. There was developed enough heat to bring the mixture to a vigorous reflux, after which the reaction was maintained at reflux for 1 hr. On cooling and filtering, a bluish white crystalline solid was isolated. This substance appears, on the basis of repeatable copper analyses, to be copper(I) trifluoroacetate containing 0.25 mol of trifluoroacetic acid per mole of salt. This solid is dissolved in deoxygenated methylene chloride (*ca.* 75 ml) and on pouring into 200 ml of pentane, 24.0 g of white solid is afforded, mp (sealed capillary tube) 204–206°. *Anal.* Calcd for $CuC_2O_2F_3$ (186.56): Cu, 35.99; C, 13.60; F, 32.28. Found: Cu, 35.66; C, 13.47; F, 30.44. This material is quite sensitive to attack by water and oxygen, yielding green or blue products or solutions. In ether an apparently spontaneous disproportionation occurs.

(Triphenylphosphino)copper(I) Trifluoroacetate.—A solution of 5.2 g of the phosphine in 20 ml of ethylene chloride was added to 3.6 g of copper(I) salt in 30 ml of the same solvent. After stirring a short while, the resultant clear solution was poured into 200 ml of pentane and the solution was cooled. A faint green crystalline solid (6.6 g, mp 160.5–162.5°) was recovered by filtration. *Anal.* Calcd for $C_{20}H_{15}PCuO_2F_2$: C, 54.86; H, 3.46; P, 7.07; Cu, 14.51 (mol wt 437.9). Found: C, 54.59; H, 3.29; P, 7.02; Cu, 14.26 [mol wt (CHCl₃) 860, 584 (dichlorobenzene)].

Bis(triphenylphosphino)copper(I) Trifluoroacetate.—To a solution of 2.0 g of copper(I) salt in 25 ml of benzene was added a solution of 5.3 g of phosphine in 15 ml of the same solvent. After stirring 3 hr the reaction was poured into 150 ml of pentane, resulting in the precipitation of 6.2 g of white crystalline solid, mp 178.9°. This material needed no further purification. *Anal.* Calcd for $C_{39}H_{30}P_2CuO_2F_3$: C, 65.09; H, 4.31; P, 8.84; Cu, 9.06 (mol wt 701.2). Found: C, 65.62; H, 4.35; P, 8.96; Cu, 9.12 [mol wt 765 (CHCl₃), 656 (C₆H₆, cryoscopic), 400 (dichlorobenzene)].

Tris(triphenylphosphino)copper(I) Trifluoroacetate. (A) From Copper(I) Trifluoroacetate.—A solution of 1.0 g of copper(I) salt in 15 ml of benzene was treated with 25 ml of a benzene solution containing 6.0 g of the phosphine. After being stirred 0.5 hr the reaction mixture was poured into 150 ml of pentane, yielding 5.1 g of white powder, mp 136°. White crystals, mp 148.5–149.5°, were isolated after recrystallizing from absolute ethanol. *Anal.* Calcd for $C_{56}H_{45}P_3CuO_2F_3$: C, 69.81; H, 4.71; Cu, 6.59 (mol wt 963.5). Found: C, 69.36; H, 5.00; Cu, 6.60 [mol wt 562 (CHCl₃), 548 (dichlorobenzene)].

(B) From Copper(II) Trifluoroacetate.—A solution was made of 1.0 g of copper(II) trifluoroacetate in 60 ml of absolute methanol to which 8.0 g of triphenylphosphine was added. After refluxing 1.5 hr the clear colorless liquid was stripped on a rotary evaporator, leaving a faint yellow oil which was extracted with 150 ml of hexane, resulting in the isolation of 4.5 g of white solid, mp 126–130°. Recrystallization from ethanol afforded white crystals, mp 147.5–148.5°. The melting point was not depressed on mixing this solid with that from above, and their infrared spectra matched. This method is similar to that of ref 4.

Tris(methyldiphenylphosphino)copper(I) Trifluoroacetate.—Two solutions of 15 ml of benzene were mixed together; the first contained 2.0 g of copper(I) trifluoroacetate; the second, 9.0 g of methyldiphenylphosphine. There were dramatic color changes resulting in a yellowish solution which became colorless after 5 min. It was stirred another 45 min and then poured into 100 ml of hexane. A white crystalline solid precipitated which, on

filtering, washing (hexane), and drying weighed 7.0 g. This solid was found to be satisfactory without recrystallization, mp 116°. *Anal.* Calcd for $C_{41}H_{39}P_3CuO_2F_3$: C, 63.36; H, 5.06; P, 11.96; Cu, 8.17 (mol wt 777.24). Found: C, 63.20; H, 5.00; P, 11.69; Cu, 7.66 [mol wt 539 (dichlorobenzene)].

Bis[bis(diphenylphosphino)ethano]copper(I) Trifluoroacetate. —With stirring, a solution of 8.10 g of bis(diphenylphosphinoethane) in 50 ml of benzene was added to 1.8 g of copper(I) trifluoroacetate dissolved in 25 ml of benzene. After 30 sec a white solid appeared, but stirring was maintained 1 hr. Filtration gave 9.9 g of white powder. Recrystallization from ethanol-heptane yielded white crystals, mp 199–200° dec (effeverscence). It appeared that a molecule of ethanol was included in the crystal from the analysis. *Anal.* Calcd for $C_{56}H_{54}P_4$-CuO_2F_3: C, 65.97; H, 5.34; P, 12.15; Cu, 6.23 (mol wt 1018.51). Found: C, 65.81; H, 5.20; P, 12.04; Cu, 6.26 [mol wt 1440 ($CHCl_3$), 1045 (dichlorobenzene)].

Tetra-*n*-butylammonium Trifluoroacetate.—Two methanolic solutions were added together in a flask; the first contained 4.5 g (0.0204 mol) of silver trifluoroacetate in 5 ml; the second, 7.52 g (0.0204 mol) of tetra-*n*-butylammonium iodide also in 5 ml. After stirring several minutes, the yellow silver iodide was filtered (4.7 g). From the filtrate, 7.9 g of clear oil was obtained by flashing the alcohol. White crystals (6.2 g, mp 45°) were obtained from ethanol-ether-pentane. The solid was quite hygroscopic. After pumping at 55°, 0.01 Torr overnight, satisfactory analysis on the white crystals, mp 85.5–86°, was obtained. *Anal.* Calcd for $C_{18}H_{36}NO_2F_3$: C, 60.81; H, 10.21; N, 3.94 (mol wt 355.49). Found: C, 60.48; H, 9.85; N, 4.15.

(1,5-Cyclooctadiene)copper(I) Trifluoroacetate.—A solution composed of 2.16 g (0.02 mol) of 1,5-cyclooctadiene in 5 ml of pentane was added dropwise to a well-stirred slurry of 1.77 g (0.01 mol) of copper(I) trifluoroacetate in 50 ml of pentane. There was a slight temperature rise, and the solution took on a green cast. After stirring 2 hr the solid was filtered and washed with two 15-ml portions of pentane in a drybox, resulting in 1.7 g

of a white solid, mp 188–190°. *Anal.* Calcd for $C_{10}H_{12}CuO_2F_3$: C, 42.18; H, 4.25; Cu, 22.31 (mol wt 284.75). Found: C, 41.64; H, 4.35; Cu, 22.75. Infrared spectrum (cm^{-1}): in KBr: ν_{CO_2} 1680 (vb); ν_{C-C} 1545 (w); ν_{CF_3} 1200, 1140 (vb); $\nu_{O_2C-CF_3}$ 840; in Nujol mull: ν_{CO_2} 1670 (b); ν_{CF_3} 1200, 1150 (b); $\nu_{O_2C-CF_3}$ 845.

(1,5-Cyclooctadiene)dicopper(I) Trifluoroacetate.—To a solution of 3.5 g of copper(I) trifluoroacetate (0.02 mol) in 25 ml of benzene, 1.0 g of 1,5-cyclooctadiene (0.0094 mol) was added dropwise, and the reaction was stirred at ambient temperature 3 days. A precipitate appeared which was then filtered, washed with pentane, and dried, resulting in the isolation of 2.75 g of light yellow solid, mp 192° dec. *Anal.* Calcd for $C_{12}H_{12}$-$Cu_2O_4F_6$: Cu, 27.55 (mol wt 461.31). Found: Cu, 27.61. Infrared spectrum (cm^{-1}) (Nujol mull): ν_{CO_2} 1675; ν_{CF_3} 1145, 1205; $\nu_{O_2C-CF_3}$ 850.

(Cyclooctatetraene)dicopper(I) Trifluoroacetate.—Cyclooctatetraene (1.04 g; 0.01 mol) in 5 ml of benzene was mixed dropwise with a solution of 25 ml of benzene containing 3.54 g (0.02 mol) of copper(I) salt. A dark red solution resulted concommtant with a temperature rise of 10°. After overnight stirring, a light green solution over a precipitate was evident. Filtration, washing (pentane), and drying yielded 3.0 g of faintly yellow solid (mp *ca.* 235°, some dec 170°). *Anal.* Calcd for $C_{12}H_8Cu_2O_4F_6$: C, 31.52; H, 1.76; Cu, 27.79 (mol wt 457.28). Found: C, 31.85; H, 1.89; Cu, 27.67. Infrared spectrum (cm^{-1}) (Nujol mull): ν_{CO_2} 1670 (b); ν_{CF_3} 1140, 1200 (vb); $\nu_{O_2C-CF_3}$ 845. Addition of excess cyclooctatetraene to slurries of the above complex in benzene dissolves the solid; however, isolation of the product by precipitation with pentane led to the starting complex (27.67% Cu), with an identical ir spectrum.

Amino Acid Catalysis of the Transfer of Copper(II) from Oligopeptide Complexes to Ethylenediaminetetraacetate
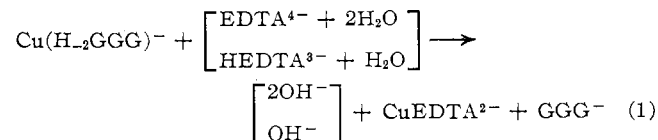
BY GARY R. DUKES AND DALE W. MARGERUM*

The reactions of the copper(II)–oligopeptide complexes of triglycine ($Cu(H_{-2}GGG)^-$), tetraglycine ($Cu(H_{-3}GGGG)^{2-}$), and L-alanyl-L-alanyl-L-alanine ($Cu(H_{-2}AAA)^-$) with EDTA are catalyzed by amino acids. Under conditions of excess EDTA and low amino acid concentrations the experimentally observed rates are first order in the copper–oligopeptide and pseudo first order in the amino acid. The resolved second-order rate constants for the amino acid catalysis exhibit a direct dependence on the stability of their corresponding copper(II) complexes. Steric hindrance prevents EDTA from being an effective nucleophile with the copper(II)–oligopeptide complexes and the postulated role of the amino acid catalyst is to facilitate the formation of a species with only one Cu–N(peptide) bond. This complex, $Cu(H_{-1}L)(aa)^-$ (where L = oligopeptide and aa is the amino acid), allows nucleophilic attack by a tertiary nitrogen of EDTA on a planar copper site. A general mechanism for catalysis of the transfer of copper ion from oligopeptide complexes to EDTA is proposed.

Introduction

Recent work in this laboratory has shown that the transfer of copper(II) from its triglycine complex to ethylenediaminetetraacetate ion (EDTA) is catalyzed by the released triglycine above pH 8.[1] The exchange reaction is given in eq 1 where GGG$^-$ is the glycylglycylglycinate ion and $Cu(H_{-2}GGG)^-$ is the complex in which two protons are ionized from the peptide nitrogens. Steric factors are important in controlling which ligands are able to react *via* a nucleophilic path with $Cu(H_{-2}GGG)^-$. EDTA and other ligands with only

$$Cu(H_{-2}GGG)^- + \begin{bmatrix} EDTA^{4-} + 2H_2O \\ HEDTA^{3-} + H_2O \end{bmatrix} \longrightarrow$$
$$\begin{bmatrix} 2OH^- \\ OH^- \end{bmatrix} + CuEDTA^{2-} + GGG^- \quad (1)$$

tertiary nitrogens are sterically hindered in their reactions with this complex.[2] The proposed path of autocatalysis involves the formation of a bis(triglycine) complex which is more readily attacked by EDTA.

In the present work amino acids are shown to be remarkably effective catalysts for the transfer of copper

(1) G. R. Dukes, G. K. Pagenkopf, and D. W. Margerum, *Inorg. Chem.*, **10**, 2419 (1971).

(2) G. K. Pagenkopf and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2683 (1970).