fore, that the metal center in NiTCPP is not bonded to axial ligands in aqueous solution. This conclusion is consistent with the observation that as the basicity of porphyrin nitrogen atoms increases, the donation of electron density to the nickel atom increases and that this is reflected in a decreased tendency for the nickel atom to bind axial ligands.[24,25] TCPP is considerably more basic than TMPyP and therefore NiTCPP should have less tendency to add water molecules in the axial positions than does NiTMPyP. Therefore, we conclude that the two metallo derivatives of TCPP which dimerize have the metal in the plane and no bonds to axial ligands whereas ZnTCPP has the metal out of the porphyrin plane and bonded to an axial water molecule. These two conditions, that the metal ion is out of the plane with the resulting influence on the π-electron density and that axial ligands are present to interfere with the close approach of the porphyrin planes, lead, we suggest, to ZnTCPP remaining monomeric in solution.

A summary of thermodynamic and kinetic results of a number of porphyrins is shown in Table II. There is very little variation in the forward rate constants for the porphyrin materials (5×10^7-$2 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$) although there is considerable variation in solvent system and nature of the porphyrin material (substitution at meso positions and at pyrrole rings). The dimerization rate constant for $(V^{II}O)$-TSP has been studied at $\mu = 0.006\ M$[19] and it has been shown that association rate constants for phthalocyanines increase with increasing ionic strength.[20] The activation energy for dimerization of (VO)TSP is 4.9 kcal/mol as compared to 4.1 kcal/mol obtained for TEP IX.[14] Therefore, we conclude that the dimerization of (VO)TSP as well as that for the porphyrin materials is a nearly diffusion-controlled process. That the rate constants are somewhat less than limiting values may reflect solvent structural rearrangement, electrostatic repulsion, and geometric requirements for effective collisions. It is believed that these dimers are of a stacking type[4,15] and the porphyrin ring systems must encounter one another in a proper orientation for dimer formation. This should be reflected in unfavorable entropies of activation and these have been observed.[14,15,19]

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Registry No. NiTMPyP, 41699-90-5; CuTMPyP, 41667-72-5; ZnTMPyP, 41699-91-6; NiTCPP, 41699-92-7; CuTCPP, 41699-93-8; ZnTCPP, 26747-84-3.

(24) B. D. McLees and W. S. Caughey, *Biochemistry*, **7**, 642 (1968).

(25) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, *J. Amer. Chem. Soc.*, **84**, 1735 (1962).

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Mass Spectrometry and Structures of Copper(I) Carboxylates in the Vapor Phase

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The copper(I) complexes of the saturated monocarboxylic, acetic, trimethylacetic, and trifluoroacetic acids as well as the complexes of the unsaturated monocarboxylic, acrylic, vinylacetic, and benzoic acids have been synthesized. Vapor pressure measurements, mass spectra, and vapor-phase infrared spectra have shown that all the copper(I) carboxylates are dimeric in the vapor phase. The ease of sublimation of these carboxylates suggests that there is a similarity between the structures of these complexes in the vapor phase and in the solid state. The presence of dimeric units in the crystal structure of copper(I) acetate lends additional support to this hypothesis.

Introduction

The simple aliphatic monocarboxylic acids such as formic acid and acetic acid react with numerous metal ions to form metal carboxylates. One of the most interesting metal carboxylates is copper(II) acetate. Its dimeric structure[1] and its novel magnetic properties[2] have provided a fresh impetus to the investigation of metal carboxylates. The corresponding copper(I) carboxylates however seem to have attracted little attention probably because they are difficult to obtain free of copper(II) contamination and because they are extremely sensitive to oxygen and water. Despite these difficulties, we have initiated a systematic study of the copper(I) carboxylates as a result of our observation that they have a relatively high vapor pressure and are stable in the vapor phase at temperatures up to about 100°.

The syntheses of several copper(I) carboxylates have been reported many years ago: copper(I) formate was prepared by the dissolution of copper(I) oxide in formic acid;[3] copper(I) acetate was obtained in low yields by the thermal decomposition of copper(II) acetate *in vacuo*[4] or by the reduction of copper(II) acetate with hydroxylamine;[5] copper(I) benzoate was isolated as an intermediate in the reduction of copper(II) benzoate with hot benzaldehyde,[6] and copper(I) trifluoroacetate was obtained in the course of the synthesis of the carbonyl complexes.[7] With the exception

(1) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

(2) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

(3) A. Angel, *J. Chem. Soc.*, **89**, 345 (1906).

(4) A. Pechard, *C. R. Acad. Sci.*, **131**, 504 (1903).

(5) A. Angel and A. V. Harcourt, *J. Chem. Soc.*, **81**, 1385 (1902).

(6) T. L. Davis and W. P. Green, Jr., *J. Amer. Chem. Soc.*, **62**, 3014 (1946).

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

of the elemental analyses that have been reported for these compounds, none of them has been characterized and no information on their structures is available. We report below a vapor-phase study of a series of copper(I) complexes of simple saturated and unsaturated carboxylic acids.

Experimental Section

Materials. Acetonitrile and benzonitrile were dried over phosphorus pentoxide and used after distillation. Pyridine was dried over calcium hydride and used after distillation. Copper wire and granules were treated with methanolic hydrogen chloride, washed with acetonitrile and ether, and dried in a nitrogen stream. Copper(II) acetate monohydrate (Mallinckrodt) was recrystallized from acetonitrile and the coordinated solvent was removed in a stream of dry nitrogen until there was no evidence of the C≡N stretching frequency in the infrared spectrum. Anhydrous copper(II) trideuterioacetate was prepared from copper(II) hydroxide and trideuterioacetic acid in acetonitrile and purified in the same manner as the acetate. Copper(II) trifluoroacetate, trimethylacetate, acrylate, vinylacetate, and benzoate were prepared from copper(II) hydroxide and acetonitrile solutions of each of the respective carboxylic acids. Any water present in these copper(II) carboxylates was removed by recrystallization from acetonitrile as described above.

Synthesis of the Copper(I) Carboxylates. Because all the copper(I) complexes employed in this study are highly sensitive to moisture and air, they were handled in a vacuum line.

Copper(I) Acetate. A pyridine solution of anhydrous copper(II) acetate was reduced by copper wire for a few hours until the color of the copper(II) disappeared completely. The yellowish solution was filtered through a sintered-glass funnel and evaporated to dryness. The residue consisted of a white powder which sublimed at 120° under vacuum. This complex was also obtained when copper(II) acetate in benzonitrile was reduced with copper metal at 150° and the hot filtrate was cooled to room temperature. Copper(I) trideuterioacetate was synthesized in a similar manner. *Anal.* Calcd for CH_3CO_2Cu: Cu, 51.84; C, 19.59; H, 2.47. Found: Cu, 52.21; C, 19.71; H, 2.75.

Copper(I) Trimethylacetate. A pyridine solution of anhydrous copper(II) trimethylacetate was reduced by copper; the solution was filtered, evaporated to dryness, and sublimed under vacuum. *Anal.* Calcd for $(CH_3)_3CCO_2Cu$: Cu, 41.55; C, 31.47; H, 3.33. Found: Cu, 42.34; C, 30.90; H, 3.10.

Copper(I) Trifluoroacetate. An ampoule that contained the anhydrous copper(II) trifluoroacetate (0.5 g), copper granules (2 g), and trifluoroacetic acid vapor (10-20 Torr) was heated to 140°. Within 1 hr, the copper(II) was reduced and a yellowish liquid was obtained. The reaction mixture was cooled to 100°. After the vapor phase was removed, the complex distilled over and condensed on the cool glass walls of the reaction vessel and formed colorless, transparent crystals of copper(I) trifluoroacetate. These crystals did not melt when heated up to 150°, but above this temperature, considerable decomposition occurred with the deposition of copper metal. *Anal.* Calcd for CF_3CO_2Cu: Cu, 35.99; C, 13.60; F, 32.28. Found: Cu, 35.86; C, 13.30; F, 30.75.

Copper(I) Acrylate. Copper(II) acrylate in pyridine was stirred for several hours at room temperature in the presence of copper metal. The resultant pale yellow solution was filtered and evaporation yielded a crystalline material which was rinsed with a small amount of pyridine. The crystals were desolvated under vacuum at 100° for 6 hr with vigorous stirring. Sublimation of this compound was accompanied by a great deal of decomposition. The complex is practically insoluble in nitriles. *Anal.* Calcd for CH_2CHCO_2Cu: Cu, 47.21; C, 26.77; H, 2.25. Found: Cu, 48.35; C, 27.11; H, 2.67.

Copper(I) Vinylacetate-Monopyridine Adduct. The copper(I) vinylacetate was synthesized by reduction of a pyridine solution of copper(II) vinylacetate with copper metal. The solution was filtered and evaporated to dryness, and the residue was washed with acetonitrile and dried overnight at room temperature. The complex is very soluble in pyridine. It is partially decomposed around 100°. Before the copper(I) vinylacetate was subjected to electron impact it was maintained at about 80° and 10^{-7} Torr for 10 min, in which time most of the pyridine was removed from the monopyridine adduct. *Anal.* Calcd for $CH_2CHCH_2CO_2CuC_5H_5N$: Cu, 27.90; C, 47.46; H, 4.43; N, 6.15. Found: Cu, 27.86; C, 47.70; H, 4.33; N, 6.28.

Copper(I) Benzoate. The copper(I) benzoate was synthesized in a manner similar to that described above for the acrylate. The complex was recrystallized from a hot anhydrous benzonitrile solution and separated as unsolvated colorless transparent crystals. *Anal.* Calcd for $C_6H_5CO_2Cu$: Cu, 34.36; C, 45.53; H, 2.73. Found: Cu, 34.57; C, 46.08; H, 3.09.

All the copper(I) carboxylates were analyzed for their copper content by atomic absorption spectrophotometry.

Vapor Pressure Measurements. The Knudsen method[8] was used to measure the vapor pressure of copper(I) trifluoroacetate. The measurements were carried out in a Pyrex cell in which the size of the orifice including the Clausing factor[9] was calibrated by measuring the loss in weight of mercury. The copper complex was assumed to be dimeric in the vapor phase. Attempts to confirm vapor pressure measurements by the quasistatic method[10] or by vapor density measurements gave nonreproducible results.

In the temperature range between 333.8 and 347.8°K the vapor pressure of P (in Torr) of copper(I) trifluoroacetate is given by

$$\log P = \frac{-8.092 \times 10^3}{T} + 21.17$$

in which the error limits of the measured pressure values are ±7.5%.

Vapor-Phase Infrared Spectra. The infrared spectrum of copper(I) trifluoroacetate was measured in the cell described below. The cell consisted of a 90 mm long Pyrex tube (15-mm o.d.) with its ends sealed with silver chloride windows. Two side arms in the cell enabled the complex to be prepared in a vacuum line and distilled into the cell. The side arms were sealed off at constrictions and the cell was placed in a close-fitting Pyrex jacket which was wrapped with nichrome wire. Copper-constantan thermocouples were placed between the cell wall and the outer jacket in order to measure the cell temperature. Two short lengths of aluminum tubing (15-mm o.d.) were placed adjacent to the cell windows to maintain the silver chloride plates at a higher temperature than that of the cell. The cell temperature was 130° and the cell windows were maintained at 145° during the measurement of the infrared spectra. At this temperature the equilibrium vapor pressure of the copper(I) complex was estimated to be about 10 Torr which is about twice the value of the vapor pressure of the complex when it was introduced *via* the side arm into the cell. A Perkin-Elmer Model 337 infrared spectrophotometer was used for all the measurements.

Mass Spectra. All mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer with an electron energy of 70 eV and an ionizing current of 80 μA. The compounds were introduced into the ionization chamber by the direct insertion method and temperatures varying between 100 and 150° were used to obtain the spectra.

Results

The natural abundances of ^{63}Cu and ^{65}Cu are in a ratio of approximately 7:3 and their atomic weights which are 62.93 and 64.93, respectively, differ significantly from integral values. Hence, the copper-containing fragments with molecular weights that are less than 200 give rise to peaks that are distinct doublets. If the fragment contains one copper atom, the M:(M + 2) peak has an intensity ratio of about 7:3 and if it contains two copper atoms the M:(M + 2):(M + 4) peaks are in the ratio 1:0.9:0.2. All the copper-containing peaks therefore are readily identifiable and are collected in Table I.

The analogous fragmentation patterns of the copper(I) acetate and copper(I) trideuterioacetate were used as a basis for the assignment of all the copper-containing peaks. The mass spectra of the copper(I) acetate and trideuterioacetate had peaks that could be attributed to the dimeric molecular ions $Cu_2(CH_3CO_2)_2^+$ and $Cu_2(CD_3CO_2)_2^+$. Corresponding peaks for dimeric species were found in the spectra of all seven copper(I) complexes but no peaks that corresponded to the monomers were observed in the spectra of any of the complexes that were investigated. The assignments of the rest of the copper-containing peaks are shown in Figures 1-5 and are summarized in Table I. The peaks assigned to the ions Cu_2OH^+, Cu_2H^+, and Cu_2^+ are of relatively low intensity and are found in almost all the compounds.

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(8) M. Knudsen, *Ann. Phys. (Leipzig)*, [4] 29, 179 (1909).
(9) P. Clausing, *Ann. Phys. (Leipzig)*, [5] 12, 961 (1932).
(10) W. H. Rodebush and A. L. Dixon, *Phys. Rev.*, 26, 851 (1925).

Table I. Relative Intensities[a] of Copper-Containing Ions in the Mass Spectra at an Electron Energy of 70 eV

	Saturated R groups				Unsaturated R groups		
Cation	CH_3	CD_3	$(CH_3)_3C$	CF_3	$CH_2{=}CH$	$CH_2{=}CHCH_2$	C_6H_5
$Cu_2(RCO_2)_2^+$	89.0	47.2	16.0	34.2	29.5	4.2	37.6
$Cu_2(R)(RCO_2)^+$					5.0	4.1	13.1
$Cu_2(CO_2)(RCO_2)^+$	15.0	5.4	0.6	5.0			
$Cu_2(RCO_2)^+$	100.0	60.5	76.5	100.0	30.5	18.3	3.48
$Cu_2R_2^+$					5.3		11.5
Cu_2R^+	18.6	<7.4[b]	6.8		21.1	5.3	37.4
Cu_2OH^+	7.5	<7.4[b]	1.5		2.9	1.0	
Cu_2O^+	12.1	5.7	0.6	4.7	4.7	1.2	
Cu_2H^+	0.6		2.0		8.4	2.5	1.2
Cu_2F^+				17.9			
Cu_2^+	9.8	4.5	1.2	6.5	7.8	2.0	1.3
$Cu_2(CO_2)(HCO_2)^+$	0.8						
$Cu_2(F_2CO)(CF_3CO_2)^+$				0.9			
CuR_2^+					39.6	1.7	23.7
CuR^+							6.4
$CuCO_2^+$	17.9	8.6		4.13	6.0	1.3	1.4
Cu^+	15.3	7.0	1.4	11.9	18.4	3.3	12.4

[a] Only the ^{63}Cu peak intensities are given. [b] $Cu_2OD^+ + Cu_2CD_3^+ = 7.4$.

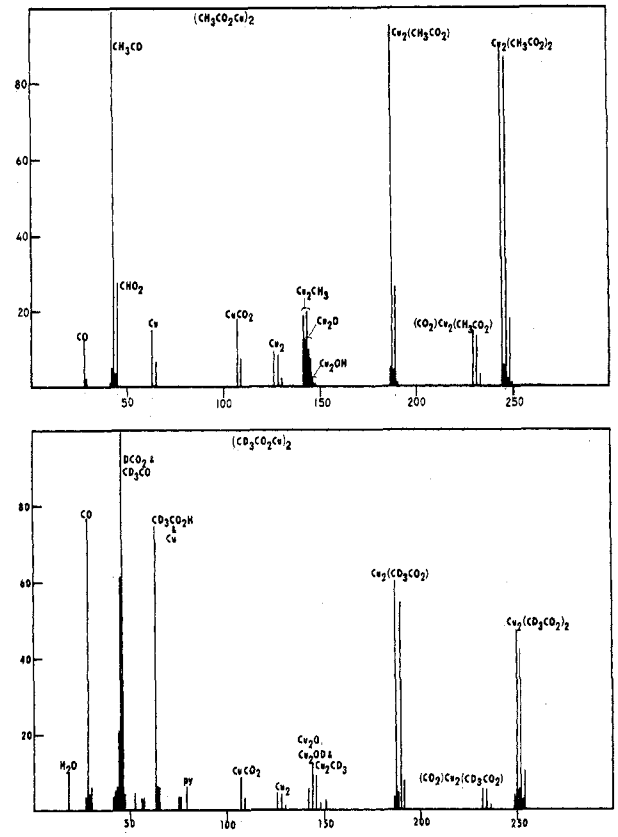


Figure 1. Mass spectra of copper(I) acetate and copper(I) trideuterioacetate: relative intensity *vs. m/e*.

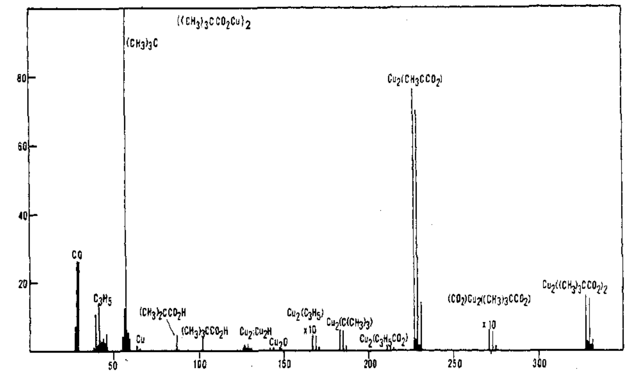


Figure 2. Mass spectrum of copper(I) trimethylacetate: relative intensity *vs. m/e*.

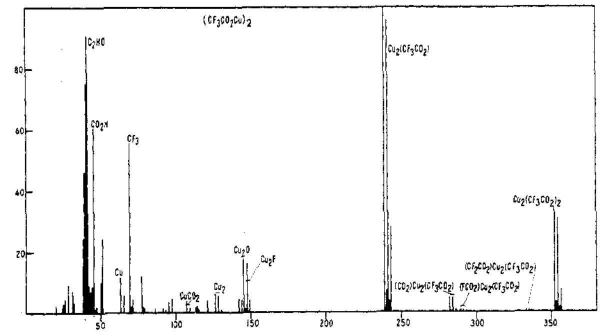


Figure 3. Mass spectrum of copper(I) trifluoroacetate: relative intensity *vs. m/e*.

In the mass spectrum of copper(I) trimethylacetate, Figure 2, a peak corresponding to the ion $(M - 117)^+$ was obtained. This must arise from either $Cu_2((CH_3)_3CC{=}O)^+$ or $Cu_2(CH_2{=}C(CH_3)COO)^+$. No fragments that correspond to the former species were found in any of the copper(I) complexes investigated. The assignment of the $(M - 117)^+$ peak to the latter species is confirmed by the presence of a small $(M - 161)^+$ peak that arises from the loss of CO_2. This assignment is substantiated further by the presence of $Cu_2(CH_2{=}CH)^+$ and $Cu_2(CH_2{=}CHCO_2)^+$ peaks in the mass spectrum of copper(I) acrylate (Figure 4).

Discussion

The most significant difference in the mass spectra of the saturated carboxylates and the unsaturated carboxylates of copper(I) is that the former give the ionic species $Cu_2(CO_2)(RCO_2)^+$ while the latter give $Cu_2(R)(RCO_2)^+$. The saturated carboxylates are stable and can sublime without appreciable decomposition whereas the unsaturated carboxylates of copper(I) are unstable and are difficult to sublime.

Some possible courses of fragmentation are shown in Scheme I. The fragmentations that give metastable peaks are indicated by numbered arrows. A metastable peak corresponding to the fragmentation

$$Cu_2(RCO_2)_2^+ \xrightarrow{1} Cu_2(RCO_2)(CO_2)^+ + R\cdot$$

was observed with the acetate, trideuterioacetate, and trifluoroacetate complexes. Copper(I) acrylate and benzoate

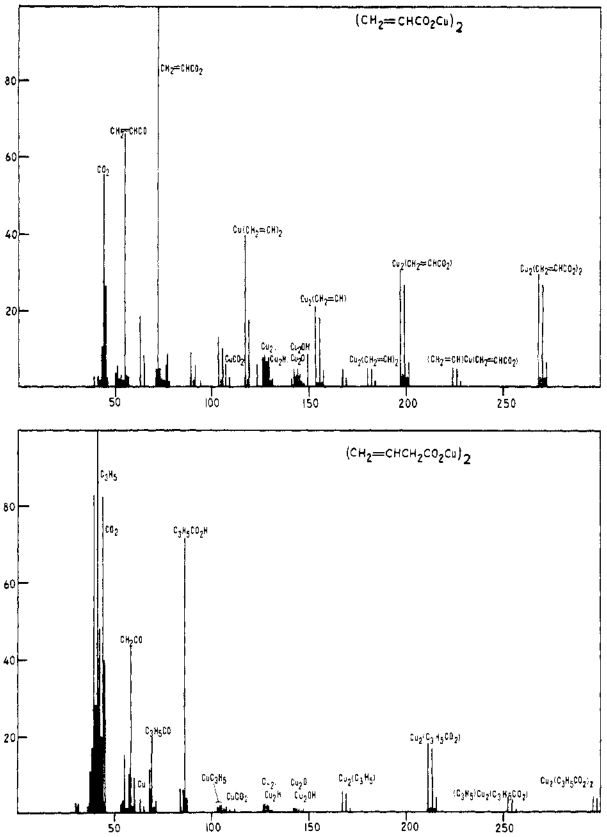


Figure 4. Mass spectra of copper(I) acrylate and copper(I) vinylacetate: relative intensity *vs. m/e*.

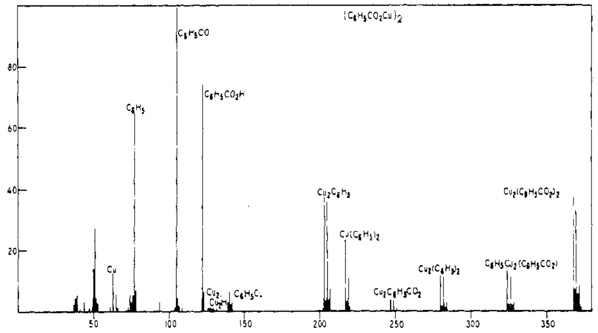


Figure 5. Mass spectrum of copper(I) benzoate: relative intensity *vs. m/e*.

gave metastable peaks corresponding to

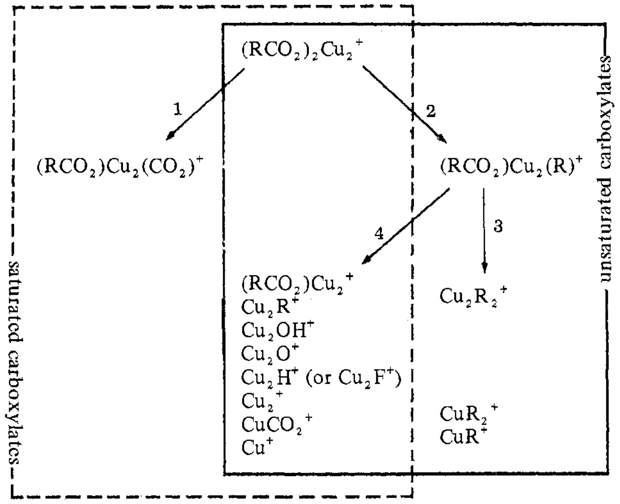
$$Cu_2(RCO_2)_2^+ \xrightarrow{2} Cu_2(RCO_2)(R)^+ + CO_2$$

Hence the first step in the rearrangement reaction after electron impact is the homolytic fission of the C-C bond adjacent to the carboxylate group (reaction 1). In the saturated carboxylates, the CO_2 group remains on the copper atom, whereas in the case of the unsaturated carboxylates, an alkene group migrates to the copper atom (reaction 2). The latter reaction is the reverse of the CO_2 insertion reaction. Elimination of the CO_2 group and the elimination of the phenyl group from $Cu_2(C_6H_5)(C_6H_5CO_2)^+$ (reactions 3 and 4—see Scheme I and Table II) gave two more metastable peaks in the mass spectrum of copper(I) benzoate.

The species CuR^+, CuR_2^+, Cu_2R^+, and $Cu_2R_2^+$ may be regarded as fragments that arise from organocopper(I), and Cu_2H^+ is from copper(I) hydride. Methyl-[11] and phenylcopper(I)[12] as well as copper(I) hydride[13] have been synthesized and characterized. Methylcopper(I) decomposes vigorously at room temperature into metallic copper and the methyl radical. Phenylcopper(I) and copper(I) hydride are somewhat more stable but decompose slowly at room temperature. The cation Cu_2R^+ is found in the mass spectra of the saturated as well as the unsaturated copper(I) carboxylates whereas the cations CuR^+ and CuR_2^+ are found only in the spectra of the unsaturated compounds. Unsaturated alkyl groups are therefore more strongly coordinated to the copper atom than saturated alkyl groups are. A similar conclusion could be drawn from the experimental observation that the saturated carboxylates form $Cu_2(CO_2)(RCO_2)^+$ (metastable reaction 1) and the unsaturated carboxylates form $Cu_2(R)(RCO_2)^+$ (metastable reaction 2).

The fragmentation pattern of copper(I) vinylacetate is similar to that of the acrylate and the benzoate. A peak corresponding to $(M - 117)^+$ was observed in the fragmentation pattern of copper(I) trimethylacetate. This implies that either the fragments $[(CH_3)_3CCOCu_2]_2^+ + O + (CH_3)_3CCO_2$ or $CH_3(CH)_2CCO_2Cu_2^+ + CH_4 + (CH_3)_3CCO_2$ are formed. The presence of an additional low-intensity peak

Scheme I. Fragmentation of Copper(I) Carboxylates



reaction 1: $R = CH_3, CD_3, CF_3$
reaction 2: $R = CH_2{=}CH, C_6H_5$
reaction 3: $R = C_6H_5$
reaction 4: $R = C_6H_5$

Table II. Calculated and Observed Values for the Metastable Peaks

	Calcd[a]	Obsd
Reaction 1		
$(CH_3CO_2)_2Cu_2^+ \rightarrow (CH_3CO_2)Cu_2(CO_2)^+$	214.9	215.0
$(CD_3CO_2)_2Cu_2^+ \rightarrow CD_3CO_2Cu_2(CO_2)^+$	215.3	216.5
$(CF_3CO_2)_2Cu_2^+ \rightarrow CF_3CO_2Cu_2(CO_2)^+$	227.5	227.0
Reaction 2		
$(CH_2{=}CHCO_2)_2Cu_2^+ \rightarrow CH_2{=}CHCO_2Cu_2CH{=}CH_2^+$	187.2	187.0
$(C_6H_5CO_2)_2Cu_2^+ \rightarrow C_6H_5CO_2Cu_2C_6H_5^+$	285.3	286.5
Reaction 3		
$(C_6H_5CO_2)Cu_2C_6H_5^+ \rightarrow Cu_2(C_6H_5)_2^+$	242.0	242.5
Reaction 4		
$(C_6H_5CO_2)Cu_2C_6H_5^+ \rightarrow C_6H_5CO_2Cu_2^+$	188.3	189.0

[a] Calculated only for ^{63}Cu: $m^* = m_f^2/m_i$.

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(11) G. Costa, G. deAlti, L. Stefani, and G. Boscarato, *Ann. Chim. (Rome)*, **52**, 289 (1962).

(12) G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometal. Chem.*, **5**, 568 (1966).

(13) M. H. L. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

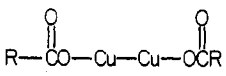
corresponding to $Cu_2(C_3H_5)^+$ supports the formation of the latter fragments in which the $(CH_3)_3CCO_2$ group can be considered to be an acrylate derivative rather than an acyl derivative. It is noteworthy that no analogous acyl derivatives were obtained in any of the other copper(I) complexes that were investigated. Therefore, the hydrocarbon moiety of the vinylacetate group must have undergone a rearrangement after CO_2 elimination to form $CH_2{=}C(CH_3)$- or $CH_3CH{=}CH$-.

Organosilver(I) complexes have been more extensively studied[14] than organocopper(I) complexes. The stability order of the silver(I) complexes is phenylsilver ≫ vinylsilver > alkylsilver. This stability sequence agrees with the experimental observation that vinylcopper(I) complexes are more stable than the alkylcopper(I) compounds and suggests that the electrons in the p_z orbitals of the carbon atoms are involved in π-bond formation between the copper and the carbon atoms.

The copper-containing peaks (Table I) can be divided into two groups on the basis of their relative intensities. The more intense peaks correspond to the species $Cu_2(RCO_2)(CO_2)^+$, $Cu_2(RCO_2)^+$, Cu_2OH^+, Cu_2H^+, Cu_2F^+, CuR_2^+, $CuCO_2^+$, and Cu^+, which contain an even number of electrons. The less intense peaks arise from the odd-electron species $Cu_2(RCO_2)_2^+$, $Cu(R)(RCO_2)^+$, $Cu_2R_2^+$, Cu_2O^+, Cu_2^+, and CuR^+, all of which are destabilized with respect to the species with an even number of electrons. This can account for the observation that peaks corresponding to radicals $Cu_2(CO_2)_2^+$ and $Cu(CO_2)^+$ with an odd number of electrons were not found, whereas the species $CuCO_2^+$ was identified in the mass spectra of the copper(I) carboxylates.

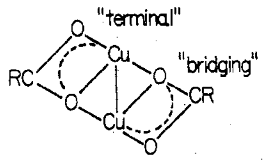
Most of the copper-containing fragments are dimers from which the organic groups are eliminated in a stepwise manner to give Cu_2^+. Metal carbonyls in which metal-metal bonds are present have been found to behave in a similar manner,[15] and therefore, copper-copper bonds must be present in any structure that is postulated for the copper(I) dimers in the vapor phase.

Four possible dimeric structures for the copper(I) carboxylates in the vapor phase are I-IV.

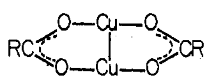


$R-\overset{O}{\overset{\|}{C}}O-Cu-Cu-O\overset{O}{\overset{\|}{C}}R$

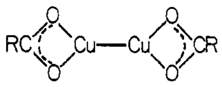
I



II



III



IV

It should be possible to decide which of the four structures is the best representation of the copper(I) carboxylates in the vapor phase from their infrared spectra. It was found that copper(I) trifluoroacetate in the vapor phase had a well defined C=O stretching frequency at 1700 cm^{-1}. Structure I should give at least one C=O stretching frequency in the vicinity of 1820 cm^{-1}, which is the value for the stretching frequency of an uncoordinated carbonyl group. In II there are two different oxygen atoms bonded to a carbon atom, a "bridging" oxygen and a "terminal" oxygen atom. Hence, more than two different carbonyl stretching frequencies, in addition to the symmetric and asymmetric modes, are expected in the carbonyl stretching region of this compound. Structures I and II are therefore invalid on the basis of the infrared spectra.

Carboxylic acids exist in the vapor phase as an equilibrium mixture of the monomer and dimer. For example, trifluoroacetic acid exists mainly in the dimeric form at 25° and at 135° it is primarily a monomer. The carbonyl stretching frequency of the monomer is at 1820 cm^{-1} and that of the dimer is at 1760 cm^{-1}. The structure of the hydrogen-bonded dimer resembles III. The infrared spectra therefore indicate that the copper(I) carboxylates in the vapor phase are best represented by III, although there is no *a priori* reason for excluding IV. The relative ease of sublimation of these carboxylates suggests that there is little structural difference between the vapor phase and solid phase in these copper(I) complexes. It has been shown that copper(I) acetate is a polymer which consists of infinite sheets of planar dimeric units that resemble III.[16] It is reasonable to infer, therefore, that the structure of copper(I) acetate in the vapor phase is the dimer represented by III.

Registry No. Copper(I) acetate, dimer, 41367-42-4; copper(I) trimethylacetate, dimer, 41367-43-5; copper(I) trifluoroacetate, dimer, 41367-44-6; copper(I) acrylate, dimer, 41367-45-7; copper(I) vinylacetate–monopyridine adduct, dimer, 41367-46-8; copper(I) benzoate, dimer, 41367-47-9; copper(I) trideuterioacetate, dimer, 41367-48-0; copper(I) acetate, 598-54-9; copper(I) trimethylacetate, 35389-37-8; copper(I) trifluoroacetate, 25535-55-1; copper(I) acrylate, 41380-06-7; copper(I) benzoate, 14604-51-4; copper(I) trideuterioacetate, 41380-07-8.

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