Copper(I) Carboxylates: Preparations and Infrared and Mass Spectral Features

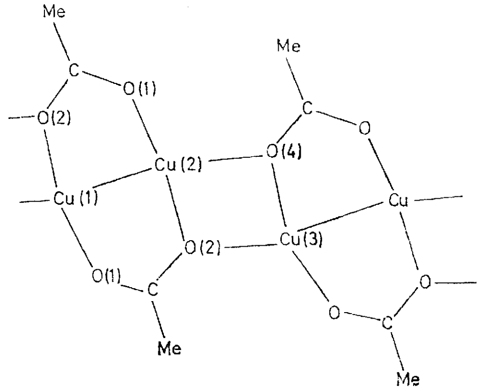
By **Dennis A. Edwards** * and **Roger Richards**, School of Chemistry and Chemical Engineering, University of Bath, Bath BA2 7AY

Procedures for the high-yield preparations of a range of copper(I) carboxylates, CuO_2CR (R = H, Me, CH_2Cl, $CHCl_2$, CF_3, CH_2CN, CH_2SH, Et, Pr^n, Ph, o-$NO_2{\cdot}C_6H_4$, CH=CHPh, and $CH{=}CH{\cdot}CO_2H$) are reported. The i.r. spectra of these compounds are briefly discussed. The mass spectra of a selection of the copper(I) carboxylates show the presence of dimeric ions in high abundance in the vapour, together with very low abundances of trimeric and tetrameric ions. The alkanecarboxylates initially lose $RCO_2^{\bullet}$ from the radical ion $Cu_2(O_2CR)_2^{+\bullet}$, whereas the arenecarboxylates also easily lose CO_2 from this radical ion leading to the formation of many ions containing Cu–C bonds. The monochloroacetate and o-nitrobenzoate also fragment to give ions possessing Cu–Cl and Cu–NO_2 bonds respectively.

ALTHOUGH copper(II) carboxylates have been extensively studied[1] in recent years, much less is known of the preparation and structural features of copper(I) carboxylates. This may in part be due to the ease of disproportionation, hydrolysis, and oxidation of these compounds. Impure copper(I) formate and acetate were isolated[2,3] in very low yields in the opening decade of this century, further methods[4,5] for the preparation of the acetate being subsequently reported. The trifluoroacetate[6] and some phosphine and olefin complexes[7] of this carboxylate have been reported. The rather exotic reaction between *m*-(trifluoromethyl)phenylcopper octamer and carboxylic acids[8] gives excellent yields of some copper(I) carboxylates, and the acetate has also been prepared[9] from phenylcopper and acetic acid. Tetrahedral copper(I) carboxylate complexes are the products of the reduction of copper(II) carboxylates by triphenylphosphine,[10] and $Cu(OAc)(PPh_3)_2$ is produced[11] by insertion of carbon dioxide into the Cu–C bond of $MeCu(PPh_3)_2{,}0{\cdot}5Et_2O$.

The interest in copper(I) carboxylates centres on two topics, namely catalysis[4,12] and organic synthesis. From a synthetic standpoint, there is much interest in the role played by copper(I) carboxylates in the decarboxylation of organic acids.[13] Organic acids which are less easily decarboxylated react with alkyl halides in the presence of copper(I) oxide to give esters, a reaction assumed[14] to proceed *via* the formation of a copper(I) carboxylate. Indeed, it has been shown[15] that copper(I) acetate, benzoate, and pivalate react with many organic halides and tosylates to give esters.

This interest in copper(I) carboxylates stimulated our determination[16] of the crystal structure of the acetate (Figure). This compound provides the first example of planar copper(I) stereochemistry. Almost simultaneously other workers independently reported[17] the crystal structure of the acetate, and there is gratifying agreement between the two sets of results. The crystal structure of a copper(I) complex of 2,5-dithiahexane-1,6-dicarboxylic acid has also been reported[18] but involves only copper–sulphur bonds.



Solid-state structure of copper(I) acetate

Although the use of copper(I) carboxylates is increasing little effort has been made to improve the preparations or even systematically to study these compounds. This paper therefore gives details of some simple methods which can be used to prepare a range of copper(I)

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carboxylates pointing out those which give good yields, and also reports i.r. and mass spectral results which can now be correlated with the established structure of the acetate.

EXPERIMENTAL

Materials.—Anhydrous sodium carboxylates were prepared from the carbonate and appropriate acid, followed by recrystallisation and dehydration *in vacuo* at 130 °C. To avoid rapid uptake of moisture these compounds were stored and subsequently handled in an efficient dry-box. Anhydrous copper(II) carboxylates were normally prepared from the carbonate and acid followed by dehydration *in vacuo* at 110 °C.

Physical Measurements.—I.r. spectra of Nujol and hexachlorobutadiene mulls were recorded on Perkin-Elmer 621 and Hilger and Watts Infrascan spectrophotometers. Some far-i.r. spectra of samples dispersed in polyethylene were obtained on a R.I.I.C. FS 720 interferometer. Mass spectra were recorded on A.E.I. MS 12 and MS 902 mass spectrometers, some spectra being recorded at the Physicochemical Measurements Unit, Harwell. Samples were introduced into the ionisation chamber on direct-insertion probes and spectra normally recorded at 200—220 °C with an ionising energy of 70 eV and a trap current of 100 μA. Ion abundances were obtained by summation of the isotope contributions observed for a particular ion and these abundances expressed relative to a metal-containing base peak of 100 units. To aid interpretation of the copper(I) monochloroacetate spectrum a computer programme was written to calculate the isotope-intensity ratios of any copper and chlorine combination from 0 to 6. The masses of ions at high mass were occasionally verified by the introduction of heptacosafluorotributylamine as a reference.

TABLE 1

Analytical results *

$\mathrm{Cu^{I}}$ carboxylate	Cu (%)		C (%)		H (%)		N (%)	
	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.
Formate	58·1	58·5	11·5	11·1	0·95	0·95		
Acetate	51·7	51·8	19·5	19·6	2·50	2·45		
Propionate	46·4	46·5	26·3	26·4	3·75	3·70		
n-Butyrate	42·4	42·4	31·8	31·9	4·70	4·70		
Benzoate	34·7	34·4	44·4	45·5	2·85	2·75		
o-Nitrobenzoate	27·9	27·7	36·3	36·6	1·75	1·75	6·1	6·1
Cinnamate	29·8	30·1	50·9	51·3	3·30	3·30		
Monochloracetate	40·7	40·5	15·2	15·3	1·40	1·30		
Dichloroacetate	32·9	33·2	12·9	12·5	0·70	0·55		
Trifluoroacetate	36·3	36·0	13·0	13·6	0·00	0·00		
Cyanoacetate	43·4	43·1	25·6	24·4	1·80	1·35	9·8	9·5
Hydrogen fumarate	35·4	35·6	27·2	26·9	1·50	1·70		
Thioglycollate	40·4	41·1	15·7	15·5	2·05	1·95	19·9 †	20·7 †

* Representative results from method giving highest yield. † S Analysis.

Reactions.—Owing to the sensitivity of the products to both moisture and oxygen, all preparations, filtrations, and subsequent manipulations were carried out under dry nitrogen or in a closed vacuum system. Samples for spectroscopic measurements were prepared in an efficient dry-box. The copper content of the carboxylates was determined by oxidation to copper(II) and estimation with edta. Typical analyses are in Table 1.

Copper(I) *formate*. (*a*) Anhydrous copper(II) formate (3 g) was carefully heated to 180 °C *in vacuo* in a sublimation apparatus. Extensive decomposition occurred but a very low yield (*ca.* 2%) of copper(I) formate could be collected from the cold surfaces of the sublimation apparatus.

(*b*) Anhydrous copper(II) formate (2·22 g), 98% formic acid (2·20 g), and copper foil (5·7 g) were added to anhydrous acetonitrile (40 ml). The reactants were stirred under dry nitrogen for 48 h by which time the solution had become colourless. The solution was then decanted from the remaining foil into stirred anhydrous, deoxygenated ether (200 ml). The product was filtered off, washed with ether, and dried *in vacuo* (yield 90%).

(*c*) Copper(I) n-butyrate (1·55 g) was stirred for 45 min under nitrogen in triethyl orthoformate (40 ml) to which had been added 98% formic acid (0·97 g). The colourless product was filtered off, washed with triethyl orthoformate and ether, and then re-treated at least twice with further portions of 98% formic acid in triethyl orthoformate to remove last traces of the n-butyrate. The product was finally dried *in vacuo* (yield 80%).

Copper(I) *acetate*. (*a*) An analogous method to method (*a*) for copper(I) formate with anhydrous copper(II) acetate gave a low yield (*ca.* 5%) of the desired product.

(*b*) Copper(I) oxide (3 g) was treated for 12 h with refluxing acetic acid (15 ml) containing sufficient acetic anhydride to remove all water produced in the reaction. The reaction rate was slow and the product obtained after cooling, filtration, and vacuum drying always contained some oxide. The pure acetate was obtained by sublimation as in (*a*) (yield 25%).

(*c*) The method of Angel [3] was slightly modified. Copper(I) oxide (4·5 g) was added to a solution of ammonium acetate (15 g) in ammonium hydroxide (0·880 g ml^{-1}) (5·5 ml) and water (5·0 ml). Unchanged oxide was filtered off and to the blue filtrate acetic acid–acetic anhydride (5 : 1) was added dropwise. The solution became green and a colourless precipitate formed. This was filtered off, and washed with acetic acid–acetic anhydride and then ether before vacuum drying. The yields from several experiments, some involving minor modifications, were consistently poor (*ca.* 5%).

(*d*) Ammonium hydroxide (0·880 g ml^{-1}) (20 ml) was slowly added to anhydrous copper(II) acetate (4·0 g) and hydroxylammonium acetate (2·0 g) under nitrogen. The blue solution was stirred and heated at 70 °C under nitrogen until all gas evolution ceased. The solution was cooled in ice and diluted with an equal volume of ethanol. Acetic acid–acetic anhydride (4 : 1) was added dropwise until no further colourless precipitate formed. The product was filtered off, washed, and dried as in (*c*) (yield 61%).

(*e*) Hydrazine hydrate was added dropwise to a stirred saturated solution of anhydrous copper(II) acetate in acetic acid–acetic anhydride (4 : 1) under nitrogen. Stirring was continued until a colourless precipitate appeared, which was then filtered off and treated as in (*c*) (yield 25%).

(*f*) Anhydrous copper(II) acetate (4·0 g) was added to a stirred solution of ammonium hydroxide (0·880 g ml^{-1}) (15 ml) and hydrazine hydrate, as a 10% solution in ammonium hydroxide (0·880 g ml^{-1}), added dropwise until it was apparent that the formation of a precipitate was imminent. The solution was heated under nitrogen at 60 °C until effervescence ceased. The solution was cooled, then diluted with an equal volume of ethanol and the precipitated product treated as in (*c*) (yield 30%).

(*g*) Anhydrous acetonitrile (100 ml) was added to anhydrous copper(II) acetate (4·0 g) and copper foil (10 g). Acetic acid–acetic anhydride (4 : 1, 25 ml) was then added and the reactants stirred for 48 h under nitrogen. After removal of excess of copper the product was obtained by adding the solution to stirred, anhydrous, de-oxygenated ether (300 ml). The product was finally washed with anhydrous ether and dried *in vacuo* (yield 85%).

Copper(I) *propionate*. Hydrazine hydrate was added to a concentrated solution of anhydrous copper(II) propionate in propionic acid. The colourless precipitate which formed was washed with propionic acid, then anhydrous ether, before being dried *in vacuo* (yield 55%).

Copper(I) *n-butyrate*. This compound was prepared either by an analogous method to the propionate (yield 70%) or by method (*g*) for the acetate (yield 82%).

Copper(I) *benzoate*. Benzoic acid (10 g) was heated under nitrogen for 2 h in refluxing sodium-dried xylene (125 ml) in a Dean and Stark apparatus. After cooling, copper(I) oxide (0·8 g) was added and refluxing repeated until all the oxide had reacted (*ca.* 12 h). The Dean and Stark apparatus allows the continuous removal of water by azeotropic distillation. After cooling the product was filtered off, washed with xylene, then ether, and dried *in vacuo* (yield 85%). Samples (1·0 g) could be recrystallised from xylene (150 ml) containing benzoic acid (2·0 g).

Copper(I) o-*nitrobenzoate*. This compound was prepared in an analogous manner to the benzoate, but with avoidance of the use of a large excess of *o*-nitrobenzoic acid (yield 65%).

Copper(I) *cinnamate*. Cinnamic acid (16·6 g) and copper(I) oxide (4·34 g) were heated in refluxing xylene (125 ml) for 24 h in a Dean and Stark apparatus. After cooling, the product was filtered off, washed with xylene and ether, and dried *in vacuo* (yield 80%).

Copper(I) *monochloroacetate*. This compound was prepared in an analogous manner to the benzoate, except that refluxing toluene was used as the reaction medium (yield 84%).

Copper(I) *dichloroacetate*. Dichloroacetic acid (3·3 g) was added to anhydrous, degassed n-heptane (40 ml). Copper(I) n-butyrate (0·8 g) was added and the reactants stirred under nitrogen for 1 h. The impure product was filtered off and treated with further dichloroacetic acid in n-heptane. The product was finally filtered off, washed with n-heptane, and dried *in vacuo* (yield 80%).

Copper(I) *trifluoroacetate*. Copper(I) n-butyrate (1·5 g) was added to trifluoroacetic acid (30 ml) containing a little trifluoroacetic anhydride. As soon as the n-butyrate had dissolved, the solution was rapidly cooled by a short immersion in liquid nitrogen. The precipitate which formed was quickly filtered off, washed with a little trifluoroacetic acid, and dried by pumping on a vacuum line for at least 30 min. The final stage is necessary to decompose any 1 : 1 copper(I) trifluoroacetate–trifluoroacetic acid adduct which may have been formed (yield 30%).

Copper(I) *cyanoacetate*. Cyanoacetic acid (0·57 g) was dried *in vacuo* at 50 °C before dissolution in degassed triethyl orthoformate (40 ml). Copper(I) n-butyrate (1·0 g) was added and the reactants stirred under nitrogen for 1 h. The product was filtered off, washed with triethyl orthoformate, then ether, and dried *in vacuo* (yield 95%). An excess of cyanoacetic acid must be avoided to prevent the formation of an acid adduct.

Copper(I) *hydrogen fumarate*. Fumaric acid (6·7 g) and copper(I) oxide (4·1 g) were heated in refluxing xylene (125 ml) for 48 h in a Dean and Stark apparatus under nitrogen. The finely dispersed suspension of the buff-coloured product in xylene was carefully decanted from any unchanged oxide, filtered off, and washed with xylene, then ether. The product was stirred after suspension in tetrahydrofuran and after gentle centrifugation any remaining oxide was collected at the bottom of the centrifuge tube. The solid still suspended in the tetrahydrofuran was finally filtered off and dried *in vacuo*.

Copper(I) *thioglycollate*. Hydrated copper(II) acetate (5 g) was stirred in thioglycollic acid (25 ml) for 6 h. The product was filtered off, washed with several portions of boiling ether, and dried *in vacuo* (yield 100%).

RESULTS AND DISCUSSION

Preparations.—Apart from the preparations of copper(I) *o*- and *p*-nitrobenzoates [13c,19] from copper(I) oxide and the carboxylic acid in toluene, the only high-yield preparative methods reported for copper(I) carboxylates use inconvenient organocopper starting materials.[8] We give details here of some much simpler methods for preparing a range of these carboxylates in high yield. Copper(I) carboxylates are susceptible to attack by oxygen and moisture and these features have probably limited the study of these compounds. This reactivity is to be expected since copper(I) has a low affinity for oxygen donors and oxoanions, being regarded as a typical 'soft' acid. Indeed, it has been reported [9] that copper(I) acetate could not be analysed owing to its extreme sensitivity to moist air. We have found, however, that all the carboxylates prepared can be successfully handled in dry nitrogen and satisfactory analyses have been obtained (Table 1).

The earliest methods [2,20] for the preparation of the formate and acetate made use of the reduction of copper(II) in aqueous solution by sulphur dioxide or hydroxylammonium sulphate. Only low yields of products contaminated by sulphite and sulphate were obtained. We have found that the use of an aqueous preparative medium (ammonium hydroxide solution) does not lead to very satisfactory yields of the acetate [methods (*c*) and (*f*)], although reduction of anhydrous copper(II)

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acetate by hydroxylammonium acetate in ammonium hydroxide (0·880 g ml^{-1}) [method (*d*)] is satisfactory.

We favour the use of non-aqueous solvents if the reduction of copper(II) carboxylates is to be used to give the copper(I) analogues since disproportionation problems are eliminated. Hydrazine hydrate, hydroxylammonium carboxylates, and copper itself are useful reducing agents since no foreign ion remains in solution after reduction, the oxidation product of the first two reagents being nitrogen. Thus, copper(I) propionate and n-butyrate have been prepared by adding hydrazine hydrate to the copper(II) carboxylate dissolved in the parent carboxylic acid.

Another report [3a] mentions the isolation of copper(I) acetate from the thermal decomposition of copper(II) acetate. We confirm [method (*a*)] that a sublimate of the acetate is produced by heating copper(I) acetate *in vacuo* at 180 °C and the formate can similarly be prepared. Unfortunately the yields in both cases are extremely low and organic decomposition products are extensively produced, ruling out such decompositions as useful preparative methods. The mass spectra of copper(I) acetate and benzoate have been obtained [21] in this manner.

A satisfactory method for the preparation of copper(I) formate has not been reported before, the most recent attempt,[5a] by reducing copper(II) formate in acetonitrile–formic acid with hydrazine hydrate, resulting in total reduction to copper. We have found however [method (*b*)] that in acetonitrile containing only a little formic acid, copper(II) formate can be smoothly reduced with copper to give an excellent yield of the formate. The same method is also an acceptable way of preparing both copper(I) acetate [method (*g*)] and n-butyrate.

The n-butyrate has subsequently been used to prepare good yields of the dichloroacetate, trifluoroacetate, cyanoacetate, and also the formate, by exchange reactions with use of the appropriate carboxylic acid.

The benzoate, *o*-nitrobenzoate, cinnamate, monochloroacetate, and hydrogen fumarate have been prepared in good yield by the reaction of copper(I) oxide with the carboxylic acid in refluxing xylene or toluene whilst continuously removing the water produced in the reaction by azeotropic distillation. The hydrogen fumarate was difficult to purify owing to incomplete reaction of the oxide and the insolubility of the carboxylate in inert solvents.

The thioglycollate was readily prepared by reducing copper(II) acetate with an excess of thioglycollic acid.

I.r. Spectra.—The i.r. spectra of the carboxylates have been measured and in each case a comparison has been made with the corresponding sodium salt which is taken to typify an ionic situation. Reasonably complete carboxylate assignments can be arrived at in each case and this point is illustrated for the relatively simple formate, acetate, and trifluoroacetate in Supplementary Publication No. 20819 (3 pp.).* The crystal structure of copper(I) acetate [16,17] provides, to our knowledge, the sole example of bridging carboxylate co-ordination where one oxygen forms a further bridge to another metal atom, although the structure of molybdenum(II) trifluoroacetate [22] can be held to be related if intermolecular contacts shorter than the sum of the van der Waals radii are considered. The Figure shows that the basic unit of the structure is an eight-membered ring formed by two planar acetates in the *syn–syn* configuration bridging two copper atoms, Cu(1) and Cu(2). One of the oxygen atoms, O(2), of the acetate group further bonds to the next copper, Cu(3), in the chain, the eight-membered rings thereby being held together by alternating four-membered Cu_2O_2 planar rings. Unexpectedly, the C–O(1) and C–O(2) bond lengths within the eight-membered rings are virtually identical (1·26 and 1·27 Å), as are the Cu–O(1) and Cu–O(2) bond lengths (1·90 and 1·89 Å). It might have been expected that an asymmetric bridge would be formed since O(2) also bonds to Cu(3) at 2·31 Å. The most surprising feature is the planar arrangement around each copper atom, comprising three oxygen atoms and the other copper atom of the eight-membered ring. Four-co-ordinate copper(I) has always previously exhibited tetrahedral geometry.

We believe that the remaining carboxylates, except the thioglycollate, possess the same structural features as the acetate, particularly because they show similar mass spectral fragmentations (see later). The i.r. spectra, listed in Supplementary Publication No. SUP 20819 (3 pp.)* particularly the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ positions, tend to support this view. For example, monodentate co-ordination will shift $\nu_{sym}(CO_2)$ to higher and $\nu_{sym}(CO_2)$ to lower frequencies than in the free ion, giving an increased separation, Δ, between these modes. An examination of the deposited data shows that this type of co-ordination is not present in any of the copper(I) carboxylates.

Apart from the trifluoroacetate where no significant change is observed, Δ for the copper(I) carboxylates is smaller than that of the corresponding sodium salt, in accord with the known co-ordination of the acetate.[16,17] This reduction in Δ is due largely to a lowering of $\nu_{asym}(CO_2)$ for the copper(I) compounds, $\nu_{sym}(CO_2)$ showing very little change when compared with $\nu_{sym}(CO_2)$ of the sodium salts.

Since the i.r. spectra of some complexes of copper(I) carboxylates have been measured,[10] comparisons can be made with the carboxylates themselves and the results in Table 2 indicate that consistent trends in the variation of Δ with co-ordination type are observed when closely related compounds are studied. The spectra also show, for example, that the cyano-group in copper(I) cyanoacetate, and the second carboxylate group of the hydrogen fumarate, are not co-ordinated.

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* For details of the Supplementary Publications scheme see Notice to Authors No. 7, *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full size copies.

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[22] F. A. Cotton and J. G. Norman, *J. Co-ordination Chem.*, 1971, **1**, 161.

The type of bonding present in copper(I) thioglycollate is not clear. There is some evidence to suggest that copper–sulphur bonds may be formed and $-CO_2H$ groups retained since a strong, broad band which can be assigned to hydrogen-bonded ν(OH) is found at 3060 cm^{-1} and $\nu_{asym}(CO_2)$ is found at 1690 cm^{-1}, a value which may be compared with $\nu_{asym}(CO_2)$ of thioglycollic acid (1715 cm^{-1}) and with $\nu_{sym}(CO_2)$ of sodium thioglycollate (1574 cm^{-1}). The far-i.r. spectrum is not helpful in elucidating the mode of bonding (bands at 317s, 295m, 208s, 171m, 142w, and 127w), since both Cu–S and Cu–O modes could occur over this wide range. The mass spectrum of the compound was recorded in an attempt to observe ions containing Cu–S or Cu–O units, but no copper-containing fragment was detected.

TABLE 2

Variation of Δ/cm^{-1} with carboxylate co-ordination type

R	$Cu(O_2CR)$-$(PPh_3)_3$ [a] Monodentate	$Cu(O_2CR)$-$(PPh_3)_2$ [a] Chelating	$Cu(O_2CR)$ Bridging [b]
H	225	201	197
Me	202	160	111
CF_3	280		234
CH_2Cl	230		173
Ph	190	143	130
o-$NO_2\cdot C_6H_4$	260		195

[a] Ref. 10. [b] See Figure.

Mass Spectra.—The mass spectra of eight of the carboxylates were examined. Westmore and his co-workers have studied [21] the thermal decomposition of copper(II) acetate and benzoate in a mass spectrometer and shown that the copper(I) carboxylates are amongst the products. We have given a preliminary account [23] of the mass spectra of four of the carboxylates, without fully discussing the significance of the results. The only other mass spectra reported for metal carboxylates concern thallium(III),[24] molybdenum(II),[22,25] and rhodium(II).[26]

TABLE 3

Copper-containing ions in the mass spectra of copper(I) carboxylates [a]

Monochloroacetate

(R = CH_2Cl) [b]

Ion	*m/e*	R.I.
Cu^+	63	6
$Cu(O_2C)^+$	107	14
Cu_2^+	126	5
Cu_2O^+	142	5
Cu_2Cl^+	161	41
$CuCl(O_2CR)^+$	191	6
$Cu_2Cl_2^+$	196	3
$Cu(O_2CR)(O_2C\cdot CH_2)^+$	214	2
$Cu_2(O_2CR)^+$	219	45
$Cu_3Cl_2^+$	259	100
$Cu_2(O_2CR)(CH_2Cl)^+$	268	2
$Cu_2(O_2CR)(O_2C\cdot CH_2)^+$	277	14
$Cu_3Cl_3^+$	294	31
$Cu_3(O_2C)Cl_2^+$	303	8
$Cu_2(O_2CR)_2^+$	312	29
$Cu_3Cl_2(O_2CR)^+$	352	48
$Cu_3(O_2CR)_2^+$	375	1
$Cu_4Cl_4^+$	392	6
$Cu_3(O_2CR)_2Cl^+$	410	4
$Cu_5Cl_4^+$	455	0·4
$Cu_3(O_2CR)_3^+$	468	0·4
$Cu_4(O_2CR)_2Cl^+$	473	0·3
$Cu_5(O_2CR)Cl_3^+$	513	0·7
$Cu_3(O_2CR)_3(O_2C\cdot CH_2)^+$	526	0·04
$Cu_4(O_2CR)_3^+$	531	0·12
$Cu_6Cl_5^+$	553	0·4
$Cu_5(O_2CR)_2Cl_2^+$	571	0·2
$Cu_4(O_2CR)_3(O_2C\cdot CH_2)^+$	589	0·03
$Cu_6(O_2CR)Cl_4^+$	611	0·07

o-Nitrobenzoate

(R = $C_6H_4NO_2$) [c]

Ion	*m/e*	R.I.
Cu^+	63	100
$Cu_2(NO_2)_2^+$	218	33
$Cu(NO_2)R^+$	231	39
$Cu_2(NO_2)R^+$	294	21
$Cu_2(O_2CR)R^+$	414	64
$Cu_2(O_2CR)_2^+$	458	88

n-Butyrate

(R = Pr^n) [c]

Ion	*m/e*	R.I.
Cu^+	63	6
$Cu(O_2C)^+$	107	17
$Cu(OAc)^+$	122	3
Cu_2^+	126	6
Cu_2H^+	127	9
Cu_2Me^+	141	6
Cu_2O^+	142	6
Cu_2OH^+	143	10
CuR_2^+	149	17
$Cu(O_2CR)^+$	150	26
$Cu(O_2C)_2^+$	151	19
Cu_2R^+	169	18
$Cu_2(OAc)^+$	185	5
$Cu(O_2CR)R^+$	193	5
$Cu(O_2CR)(O_2C)^+$	194	7
$Cu_2R_2^+$	212	2
$Cu_2(O_2CR)^+$	213	100
$Cu(O_2CR)_2^+$	237	5
$Cu_2(O_2CR)(OAc)^+$	272	4
$Cu_2(O_2CR)_2^+$	300	85
$Cu_3(O_2CR)_2^+$	363	0·5
$Cu_2(O_2CR)_3^+$	387	0·7
$Cu_3(O_2CR)_3^+$	450	0·1
$Cu_4(O_2CR)_3^+$	513	0·1
$Cu_3(O_2CR)_4^+$	537	0·3
$Cu_3(O_2CR)_5^+$	624	1·3

Metastables

Process	Fragment lost
$300 \longrightarrow 272$	C_2H_4
$194 \longrightarrow 150$	CO_2

Cinnamate

(R = CH=CHPh) [c]

Ion	*m/e*	R.I.
Cu^+	63	8
Cu_2H^+	127	15
Cu_2Ph^+	203	5
$Cu(O_2CR)H^+$	211	5
Cu_2R^+	229	24
$CuRPh^+$	243	6
CuR_2^+	269	27
$Cu_2(O_2CR)^+$	273	14
$Cu(O_2CR)Ph^+$	287	2
$Cu_2R(O_2C\cdot CH{=}CH)^+$	299	1
Cu_2RPh^+	306	5
$Cu(O_2CR)R^+$	313	6
$Cu_2R_2^+$	332	3
$Cu_2(O_2CR)Ph^+$	350	5
$Cu_2(O_2CR)R^+$	376	42
$Cu_4Ph_2^+$	406	1·5
$Cu_2(O_2CR)_2^+$	420	100
$Cu_4(O_2CPh)Ph^+$	450	1
$Cu_4(O_2CR)Ph^+$	476	0·6
$Cu_4(O_2CR)RO^+$	518	0·8
$Cu_3(O_2CR)_2Ph^+$	550	0·2

Metastables

Process	Fragment lost
$420 \longrightarrow 376$	CO_2
$420 \longrightarrow 350$	$CO_2 + C_2H_2$
$376 \longrightarrow 332$	CO_2

[a] Data for the acetate, formate, benzoate, and trifluoroacetate are in ref. 23. [b] Based on ^{63}Cu and ^{35}Cl. [c] Based on ^{63} Cu.

Table 3 lists only the observed copper-containing

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[23] D. A. Edwards and R. Richards, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 783.

[24] A. T. T. Hsieh, A. G. Lee, and P. L. Sears, *J. Org. Chem.*, 1972, **37**, 2637.

[25] G. Holste and H. Schafer, *Z. anorg. Chem.*, 1972, **391**, 263.

[26] J. Kitchens and J. L. Bear, *Thermochim. Acta*, 1970, **1**, 537.

ions of the carboxylates not mentioned in the preliminary account.[23] Intensities are given relative to a copper-containing base peak of 100 units. These ions can be clearly distinguished by a consideration of the isotopic abundances ^{63}Cu 69·1% and ^{65}Cu 30·9% and where appropriate ^{35}Cl 75·8% and ^{37}Cl 24·2%. Approximate data for the formate, acetate, trifluoroacetate, and benzoate can be obtained from the figures in ref. 23. We have not considered the organic ions produced so the individual ion abundances will not approximate to the percentage of total ion current carried.

The major fragments for each carboxylate contain two copper atoms, and this observation can be related to the solid-state structure of the acetate.[16,17] We suggest that the eight-membered ring of the acetate is retained as the principal species in the vapour, the longer Cu(2)–O(4) and Cu(3)–O(2) bonds being broken on volatilisation. The mass-spectral results also provide support to our contention that all the carboxylates possess analogous structures in the solid state. However, it appears that the solid polymer does not fragment solely into dimeric units, since ions of very low intensity containing three or four copper atoms are detected in the mass spectra of the carboxylates, showing that more highly associated molecules are present in the vapour, albeit in low concentrations. Similar low-intensity polymeric ions have been observed [27] in the mass spectra of some metal acetylacetonates, where the principal vapour-phase species is the monomer.

The principal species in the vapour is the dimer and the radical ion $Cu_2(O_2CR)_2^{+\cdot}$ is a dominant ion in all of the spectra, being the base peak for the formate and cinnamate. The base peak for the acetate, trifluoroacetate, and n-butyrate is the even-electron ion $Cu_2(O_2CR)^+$, whereas for the benzoate it is Cu_2Ph^+ and for the monochloroacetate it is $Cu_3Cl_2^+$.

The cyclic radical ion $Cu_2(O_2CR)_2^{+\cdot}$ can be described with either the odd electron residing on a carbon atom or by suggesting that one of the copper atoms is oxidised to copper(II). However, since the carboxylate groups possess delocalised π-orbital systems and the copper atoms can also make available π-orbitals, the unpaired electron may reside in an orbital delocalised over the eight-membered ring. This may explain the unexpected stability of the radical ion. The $Cu_2(O_2CR)^+$ ions, formed by elimination of $RCO_2\cdot$, or $R\cdot$ and CO_2, could also be cyclic if a copper–copper bond is envisaged. The loss of $R\cdot$ from the dimer radical ion is obviously not favoured since $Cu_2(O_2CR)(O_2C)^+$ is only observed, and then of low intensity, for the acetate.

Decarboxylation of the dimeric radical ion is also a dominant fragmentation process particularly for the arenecarboxylates where the radical ions $Cu_2R_2^{+\cdot}$ and $Cu_2(O_2CR)R^{+\cdot}$, and the ion Cu_2R^+ are present in high abundance. Such fragmentations are supported by the observation of metastable peaks. Decarboxylation results in the formation of copper–alkyl and copper–aryl species by migration of R, and the high abundance of copper–aryl species in the arenecarboxylate spectra (15 such species for the benzoate, only one for the acetate) parallels the known greater stability of arylcopper compounds compared with alkylcopper compounds.

The mass spectra of the formate and *o*-nitrobenzoate were difficult to obtain, the proportion of ion current carried by copper-containing ions being low. Decarboxylation of the formate dimer radical ion giving the radical ion $Cu_2(O_2CH)H^{+\cdot}$ is a significant fragmentation and is supported by observation of the appropriate metastable peak. The *o*-nitrobenzoate gives several ions possessing $Cu{-}NO_2$ groups.

The spectrum of the monochloroacetate is rather complex, many ions containing copper–chlorine bonds being observed. Ions containing only copper and chlorine up to $Cu_6Cl_5^+$ have been detected, their relative intensities being reminiscent of the ions found [28] in the mass spectrum of copper(I) chloride. An important fragmentation must be the elimination of a chlorine radical from the parent dimer radical ion, as evidenced by the detection of $Cu_2(O_2C{\cdot}CH_2Cl)(O_2C{\cdot}CH_2)^+$. The electropositive nature of the copper makes it the preferred point of attack for chlorine radicals, giving, for example, $CuCl(O_2C{\cdot}CH_2Cl)^+$.

The spectrum of the n-butyrate is also complex since, as well as elimination of $RCO_2\cdot$ and CO_2 from the dimer radical ion, a further fragmentation process in which ethylene is eliminated (supported by the observation of a metastable peak), presumably by a McLafferty rearrangement, leads to the detection of ions such as $Cu_2(OAc)^+$ which then decarboxylates to Cu_2Me^+.

For the cinnamate, elimination of both $-CH{=}CHPh$ and $-O_2C{\cdot}CH{=}CHPh$ groups is observed, together with a fragmentation process where simultaneous loss of acetylene and carbon dioxide leads to the detection of several ions possessing copper–phenyl bonds. A metastable peak supporting the process has been observed.

$$Cu_2(O_2C{\cdot}CH{=}CHPh)_2^{+\cdot} \longrightarrow Cu_2(O_2C{\cdot}CH{=}CHPh)Ph^{+\cdot} + CO_2 + C_2H_2 \quad (1)$$

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[27] C. G. MacDonald and J. S. Shannon, *Austral. J. Chem.*, 1966, **19**, 1545.

[28] H. M. Rosenstock, J. R. Sites, J. R. Walton, and R. Baldock, *J. Chem. Phys.*, 1955, **23**, 2442.