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Synproportionation reactions between copper(II) trihalogenoacetates $Cu(CX_3CO_2)_2$, X = F, Cl or Br, and copper in the presence of carbon monoxide

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Received 8th March 2000, Accepted 19th May 2000
Published on the Web 14th June 2000

The trichloro- and tribromo-acetato derivatives of copper(II) of general formula $Cu_2(CX_3CO_2)_4(CX_3CO_2H)_2$ have been prepared by exchange reactions from $Cu(CF_3CO_2)_2$ and CX_3CO_2H (X = Cl or Br) in a hydrocarbon solvent. The chloro derivative, which has also been obtained from CuO in the presence of $CCl_3CO_2H/(CCl_3CO)_2O$, has been characterized by variable-temperature magnetic measurements and by X-ray diffraction. The trifluoroacetato carbonyl derivative of copper(I), $Cu(CF_3CO_2)(CO)$, has been prepared: (a) by reaction of Cu_2O with $CF_3CO_2H/(CF_3CO)_2O$ in the presence of CO; (b) by direct carbonylation of $Cu(CF_3CO_2)$ in toluene or in the solid state; (c) by synproportionation of $Cu(CF_3CO_2)_2$ and copper in the presence of CO in MeOH, DME, THF or toluene at room temperature. Solutions of $Cu(CCl_3CO_2)(CO)$ have been obtained by the synproportionation of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ and copper under a CO atmosphere in toluene. No carbonyl derivative was observed in solution with $Cu_2(CBr_3CO_2)_4(CBr_3CO_2H)_2$ under similar conditions. On standing, hydrocarbon solutions of $Cu(CCl_3CO_2)(CO)$ slowly gave CuCl(CO) and a mixed-valence, polynuclear carbonyl derivative of formula $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ which has fully been characterized by variable temperature magnetic measurements and by X-ray diffraction.

Carbonyl complexes of copper(I) are important chemical species from both industrial and academic points of view as they are involved in the synthesis of methanol,[1] and in the removal of CO from industrial streams.[2] The first evidence of copper carbonyls dates back to two centuries ago when Leblanc[3] and Berthelot[4] observed that acidic solutions of copper(I) absorbed CO up to a CO : Cu molar ratio of 1 : 1. Since then, the chemistry of copper carbonyls has extensively been studied.[5] Most of the known carbonyl derivatives are stabilized by additional (mainly nitrogen donors) ligands. Only a limited number of unsupported CuX(CO) complexes have been prepared, examples of structurally characterized derivatives being $[CuCl(CO)]_n$,[6] $Cu(EtSO_3)(CO)$,[7] $[Cu(OBu^t)(CO)]_4$,[8] $[Cu(OC_6H_2Bu^t_3\text{-}2,4,6)(CO)]_2\cdot THF$,[9] $[Cu(OC_6H_2Me_3\text{-}2,4,6)(CO)]_2$,[9] $[Cu(CO)]_2[Pt(CN)_6]$,[10] $[Cu(R)(CO)]_4$ (R = 2-methylquinolin-8-olato),[11] and Cu(L)(CO), $L = [CpCo\{P(O)Me_2\}_3]^-$.[12] Carboxylato carbonyl complexes of copper(I) are rare: a literature survey at the Cambridge Crystallographic Data Centre has shown that two examples only of copper(I) (both containing bridging carboxylato groups and bridging carbon monoxide) have been structurally characterized: $[Cu_2(NN)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)][BPh_4]$, NN = *N,N,N′N′*-tetramethylpropylenediamine or *N,N,N′N′*-tetramethylethylenediamine.[13] In addition, a preliminary X-ray structural study (cell constants) of $Cu_4(CF_{3-x}Cl_xCO_2)_4(CO)_4$, $x = 0$ or 1, has been reported.[14]

These observations prompted us to investigate synthetic pathways to carboxylato/carbonyl derivatives of copper(I) without supporting ligands and this paper describes the results of a study concerning carbonyl derivatives of trihalogenoacetatocopper(I) and a comparative study of the synproportionation reactions between $Cu(CX_3CO_2)_2$ and copper in the presence of carbon monoxide. Moreover, the crystal and molecular structure of a mixed-valence, polynuclear trichloroacetato carbonyl derivative is presented.

Results and discussion

Trihalogenocarboxylates of copper(II)

The trifluoroacetato derivative of copper(I), $Cu(CF_3CO_2)$,[15] was obtained as a microcrystalline compound by reaction of copper(I) oxide with a mixture of trifluoroacetic acid and trifluoroacetic anhydride in heptane, eqn. (1a). The copper(I)

$$Cu_2O + 2CF_3CO_2H \longrightarrow 2Cu(CF_3CO_2) + H_2O \qquad (1a)$$

derivative is transformed into $Cu(CF_3CO_2)_2$ by bubbling dioxygen into the reaction mixture, eqn. (1b), the water produced in the reaction being subtracted by the anhydride.

$$Cu_2O + 4CF_3CO_2H \xrightarrow{O_2} 2Cu(CF_3CO_2)_2 + 2H_2O \qquad (1b)$$

The same reaction procedure cannot be used for the preparation of the trichloro- or the tribromo-acetates of mono- or bi-valent copper due to the formation of halogenoacetato-substituted copper halides arising from the oxidation of copper(I) by the CX_3 fragment.† The lower C–X bond strength with increasing atomic number of the halide may be responsible for the observed reactivity. In this connection, it is interesting that less halogenated carboxylato derivatives $Cu(CH_nCl_{3-n}CO_2)$, $n = 1$ or 2, are considerably more stable and are obtained in good yields from Cu_2O and the corresponding carboxylic acid.[16]

The availability of $Cu(CF_3CO_2)_2$ prompted us to use this compound as starting material to the heavier halogenoacetato

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† A GC-MS analysis of the solution obtained after the reaction of Cu_2O with $CCl_3CO_2H/(CCl_3CO)_2O$ revealed the presence of dichloroacetic acid.

DOI: 10.1039/b001889i

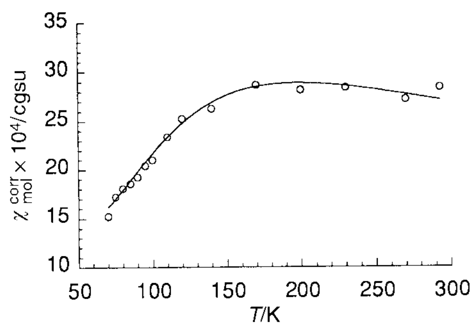


Fig. 1 Plot of the molar susceptibility of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$, as a function of temperature.

derivatives by exchange reactions. A suspension of it in heptane reacts with CCl_3CO_2H in the presence of $(CCl_3CO)_2O$, or with CBr_3CO_2H, to give an almost quantitative yield of the corresponding trichloro- or tribromo-acetate, see eqn. (2) (X = Cl or

$$2Cu(CF_3CO_2)_2 + 6CX_3CO_2H \longrightarrow Cu_2(CX_3CO_2)_4(CX_3CO_2H)_2 + 4CF_3CO_2H \quad (2)$$

Br). Reaction (2) is shifted to the right as shown by the amount of CF_3CO_2H (96% of the theoretical value) found (^{19}F NMR analysis) in the mother liquor, see Experimental section. As an alternative route, the dinuclear trichlorocarboxylato derivative, $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$, has been prepared in satisfactory yields from CuO in refluxing heptane in the presence of an excess of $CCl_3CO_2H/(CCl_3CO)_2O$, see eqn. (3), water being eliminated by the anhydride.

$$2CuO + 6CCl_3CO_2H \longrightarrow Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2 + 2H_2O \quad (3)$$

On the basis of analytical and spectroscopic data, magnetic measurements and, in the case of the trichloroacetato derivative, of an X-ray crystallographic study, the products are dinuclear with bridging trihalogenoacetates and axially bonded monodentate RCO_2H.

The IR spectra of $Cu_2(CX_3CO_2)_4(CX_3CO_2H)_2$, X = Cl or Br, show the presence of both co-ordinated carboxylato- and carboxylic acid ligands, as evidenced by the absorptions of 1730 (X = Cl) and 1718 cm^{-1} (X = Br) (assigned to the C=O stretching vibration of the co-ordinated carboxylic acid), and at 1671, 1382 and 1664, 1365 cm^{-1} (due to the asymmetric and symmetric stretching vibrations of the trichloro- and tribromo-acetato groups, respectively[17]). In addition, strong bands due to the CX_3 groups in the 900–600 cm^{-1} region were observed.

The trihalogenoacetato derivatives of copper(II), $Cu_2(CX_3CO_2)_4(CX_3CO_2H)_2$, X = Cl or Br, are paramagnetic with magnetic moments of 2.59 (X = Cl) and 2.22 (X = Br) μ_B per dinuclear unit at 293 K. The magnetic study of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ at temperatures between 70 and 293 K has shown some interactions between the copper centres, as usually observed in other carboxylato derivatives of copper(II) of general formula $Cu_2(CX_3CO_2)_4L_2$, L = Lewis base.[18] The effective magnetic moment of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ gradually increases with temperature between 0.93 (70 K) and 2.59 μ_B (293 K) suggesting that the ground state is a singlet and the observed paramagnetism is due to the thermal population of a triplet state. Fitting of the magnetic data[19] (Fig. 1) gave values of $g = 1.99$, $-2J = 239.6$ cm^{-1}, in good agreement with the values found for $Cu_2(CCl_3CO_2)_4(2\text{-}ClPy)_2$ ($g = 2.26$ and $-2J = 217$ cm^{-1}).[20] Owing to the fact that the trihalogenoacetato derivatives of the present study represent examples of the still restricted family of co-ordination compounds containing the carboxylato and the conjugated acid as ligands,[21] we decided to study the molecular structure of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ obtained as a crystalline material by slowly cooling a hot heptane solution.

Table 1 Selection of bond distances (Å) and angles (°) of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$

Cu···Cu	2.648(1)	C12–O13	1.245(5)
Cu–O11	1.995(3)	C12–C14	1.555(7)
Cu–O13	1.949(3)	O21–C22	1.265(6)
Cu–O21	1.956(4)	C22–O23	1.240(6)
Cu–O23	1.945(3)	C22–C24	1.522(9)
Cu–O31	2.143(3)	O31–C32	1.202(6)
O11–C12	1.244(5)	C32–O33	1.300(6)
		C32–C34	1.524(7)
Cu–Cu–O11	82.0(1)	Cu–O11–C12	123.4(3)
Cu–Cu–O13	85.9(1)	O11–C12–O13	127.5(5)
Cu–Cu–O21	83.0(1)	O11–C12–C14	115.8(4)
Cu–Cu–O23	85.6(1)	O13–C12–C14	116.7(4)
Cu–Cu–O31	170.7(1)	Cu–O13–C12	121.1(3)
O11–Cu–O13	167.9(1)	Cu–O21–C22	122.2(3)
O11–Cu–O21	87.5(2)	O21–C22–O23	128.8(5)
O11–Cu–O23	90.5(2)	O21–C22–C24	114.2(5)
O11–Cu–O31	90.1(1)	O23–C22–C24	116.8(5)
O13–Cu–O21	90.1(2)	Cu–O23–C22	120.2(3)
O13–Cu–O23	89.5(2)	Cu–O31–C32	129.2(3)
O13–Cu–O31	101.8(1)	O31–C32–O33	127.4(5)
O21–Cu–O23	168.5(1)	O31–C32–C34	120.4(5)
O21–Cu–O31	91.8(1)	O33–C32–C34	112.1(4)
O23–Cu–O31	99.5(1)		

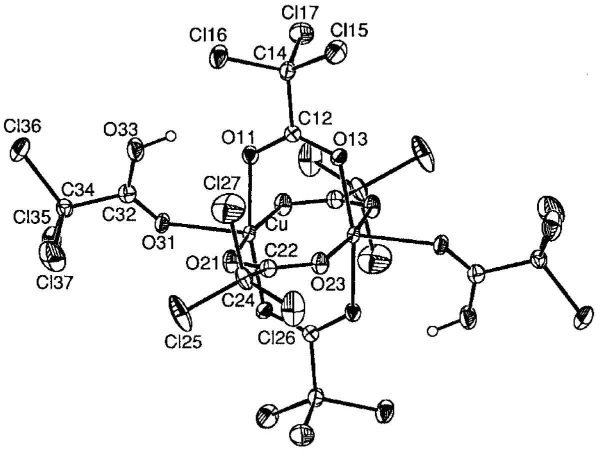


Fig. 2 View of the molecular structure of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$.

The structure consists of discrete centrosymmetric dinuclear units, see Fig. 2. Table 1 lists a selection of bond distances and angles. The copper–copper distance of 2.648(1) Å and the rather weak magnetic interactions between the copper centres suggest that the copper atoms can be regarded as five-co-ordinate with approximately square-pyramidal geometry. A Cu···Cu distance of 2.766(3) Å has been found[20] in $Cu_2(CCl_3CO_2)_4(2\text{-}ClPy)_2$ which to the best of our knowledge, is the only trichloroacetato derivative of copper(II) in the literature. The copper centres are co-ordinated to four oxygen atoms of four bridging trichloroacetato groups (mean value of the Cu–O bond distance: 1.98 Å) and to the carbonyl oxygen of the monodentate trichloroacetic ligand [Cu–O31: 2.143(3) Å]. The Cu···Cu separation and the displacement (0.193 Å) of the copper atom from the best plane containing the four oxygen atoms of the trichlorocarboxylato bridging groups are well within the range of values observed in $Cu_2(RCO_2)_4L_2$ derivatives (2.6–2.9 and 0.18–0.32 Å, respectively), see Table 2.[22]

In the axially co-ordinated CCl_3CO_2H ligand two different C–O bond distances are present: a shorter one [C32–O31 1.202(6) Å] and a longer one corresponding to the C32–O33 single bond [1.300(6) Å]. The hydroxyl oxygen O33 is involved in an intramolecular hydrogen bond to the trichloroacetato

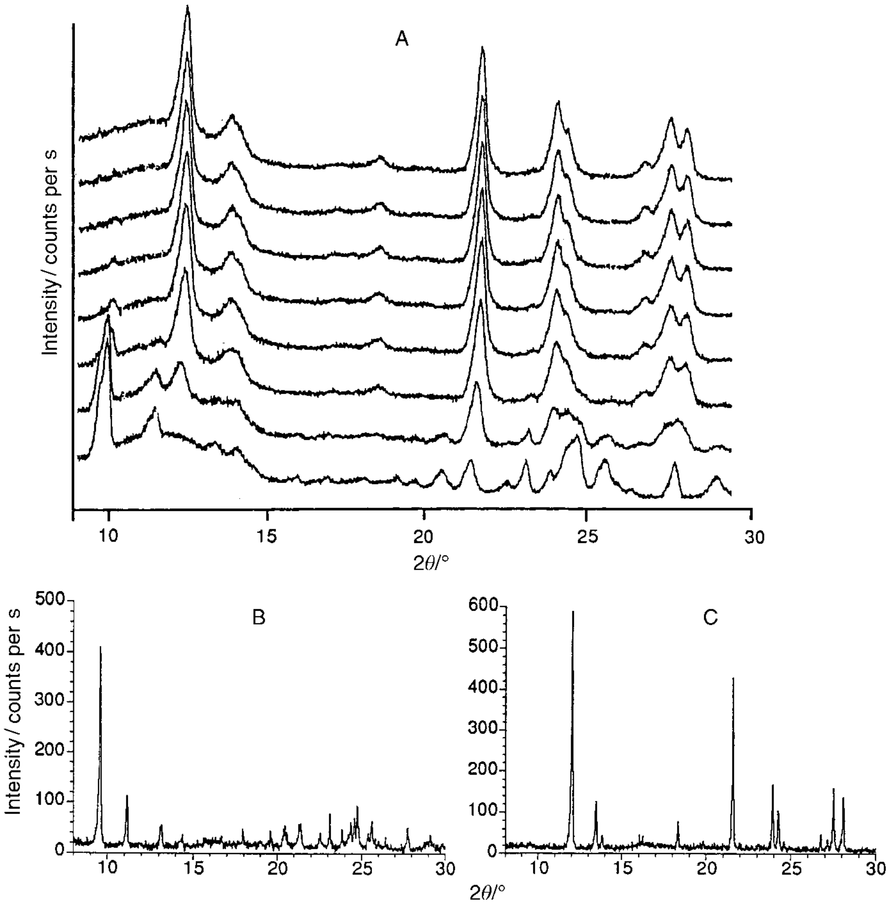


Fig. 3 X-Ray powder diffractograms: (**A**) carbonylation reaction of $Cu(CF_3CO_2)$ to $Cu(CF_3CO_2)(CO)$ as a function of time; (**B**) $Cu(CF_3CO_2)$; (**C**) $Cu(CF_3CO_2)(CO)$.

Table 2 Cu · · · Cu separations and displacements of the copper atoms from the basal plane defined by the four oxygen atoms of the carboxylato bridging groups in some selected copper(II) carboxylato complexes

Compound	Cu · · · Cu/ Å	Deviation[a]/ Å	Ref.
$Cu_2(CH_3CO_2)_4(CH_3CO_2H)_2$	2.581(1)	0.18	21(*g*)
$Cu_2(CH_3CO_2)_4(CH_3OH)_2$	2.596(1)	0.18	21(*g*)
$Cu_2(CH_3CO_2)_4(H_2O)_2$	2.616(1)	0.19	23
$Cu_2(CH_2ClCO_2)_4(C_9H_7N)_2$	2.724(2)	0.248	24
$Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$	2.648(1)	0.193	This work
$Cu_2(CCl_3CO_2)_4(2\text{-}ClPy)_2$	2.766(3)	0.28	20
$Cu_2(CBr_3CO_2)_4(2\text{-}ClPy)_2$	2.766(3)	—	25
$Cu_2(CH_2FCO_2)_4(C_9H_7N)_2$	2.725(1)	0.239	26
$Cu_2(CF_3CO_2)_4(C_9H_7N)_2$	2.886(2)	0.32	27

[a] From the best plane passing through the four basal oxygen atoms.

oxygen O11 (O11 · · · O33; 2.734 Å); similar distances [2.62, 2.642(5), 2.614 and 2.632(4) Å] have been observed in $Cu(CH_3CO_2)_4(CH_3CO_2H)_2$,[21g] $M(RCO_2)_4(RCO_2H)_2$, M = Cr, R = CH_3,[21f] Ph,[21c] M = Ru, R = Ph,[21c] respectively. The elongation of Cu–O11 [1.995(3) Å] with respect to Cu–O21 [1.956(4 Å] is probably a consequence of the hydrogen bond. The axial ligand is tilted towards O11 as is evident from the O31–Cu–O11 and O31–Cu–O13 angles which amount to 90.1(1) and 101.8(1)°, respectively. Consequently, the angle Cu–O11–C12 [123.4(3)°] is slightly larger with respect to Cu–O21–C22 [122.2(3)°].

Carbonyl derivatives

Several years ago, two research groups reported[14,28] the carbonyl adduct of $Cu(CF_3CO_2)$ to be stable *in vacuo* in the solid state even over an extended period of time. One of the research groups[28] also reported an X-ray structural study (cell constants only) of $Cu_4(CF_{3-x}Cl_xCO_2)_4(CO)_4$, $x = 0$ or 1. In re-examining the $Cu(CF_3CO_2)$/CO system we discovered that the carbonylation of $Cu(CF_3CO_2)$ occurs in the solid state ultimately and exclusively to give a 1 : 1 adduct at atmospheric pressure of carbon monoxide, as shown by the gas-volumetric determination. The carbonylation is fast and complete (about 30 min). Monitoring by X-ray powder diffractometry, see Fig. 3, shows that microcrystalline $Cu(CF_3CO_2)$ (Fig. 3A) is gradually converting into $Cu(CF_3CO_2)(CO)$ (Fig. 3B), a diagram of the carbonylated product being shown in Fig. 3C. During the carbonylation, no peaks due to other crystal phases were detected, thus suggesting that only one product is obtained, namely the 1 : 1 adduct. An attempt was made to solve the structure of $Cu(CF_3CO_2)(CO)$ from the powder diagram of a microcrystalline sample on the basis of the known[14] cell constants of $Cu_4(CF_2ClCO_2)_4(CO)_4$, which was reported[14] to be isotypical with $Cu_4(CF_3CO_2)_4(CO)_4$. However, a reasonable solution of the structure was not found. Since the structure of $Cu(CF_3CO_2)$ is unknown, only hypotheses can be proposed for the solid-state structures of both $Cu(CF_3CO_2)$ and $Cu(CF_3CO_2)(CO)$, on the basis of the spectroscopic data, and by similarity with the structurally characterized $Cu_4(PhCO_2)_4$[29] and the corresponding benzene adduct[30] $Cu_4(CF_3CO_2)_4(C_6H_6)_2$. These tetranuclear compounds have a substantially planar arrangement of the copper atoms, with the carboxylato ligands being alternately above and below this plane. The carbonyl derivative $Cu(CF_3CO_2)(CO)$ shows a strong IR absorption at 2122 (toluene) or 2130 cm^{-1} (solid state, Nujol mull), in agreement with the data reported by Rodesiler and Amma (2120 cm^{-1}, unspecified medium),[30] slightly different rom the wavenumber value (2155 cm^{-1}) reported by Scott *et al.*[28] for both $Cu(CF_3CO_2)(CO)$ and $Cu(CF_3CO_2)(CF_3CO_2H)(CO)$. The carbonyl group is therefore terminally bonded to copper. Moreover, the difference of

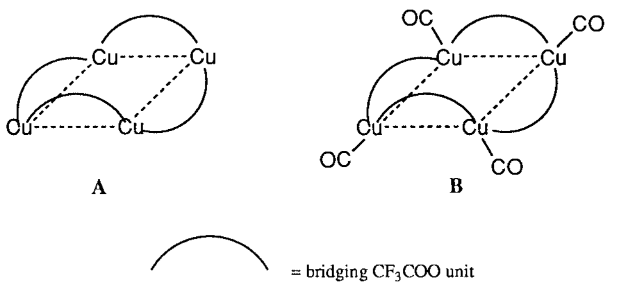


Fig. 4 Structural arrangements proposed for (**A**) $Cu(CF_3CO_2)$, (**B**) $Cu(CF_3CO_2)(CO)$.

223 cm^{-1} between the asymmetric and symmetric stretching vibrations of the carboxylato groups in the carbonyl derivative $Cu(CF_3CO_2)(CO)$, 1674 and 1451 cm^{-1}, respectively, suggests a bidentate co-ordination of the CF_3CO_2 group.

A reasonable structural suggestion is therefore that the trifluoroacetato derivative $Cu(CF_3CO_2)$ is tetranuclear with a structure similar to those reported for both the benzoato and the trifluoroacetato-benzene derivatives, as shown in Fig. 4. Its ready conversion into the carbonyl derivative in the solid state may be rationalized by the addition of one CO to each of the four copper centres.

It is interesting that the copper(I) derivative $CuAsF_6$ was reported[31] to undergo carbonylation in the solid state yielding three carbonylation products, the dicarbonyl and the tricarbonyl derivatives, $Cu(CO)_2^+$ and $Cu(CO)_3^+$, being suggested to have $D_{\infty h}$ and D_{3h} symmetry, respectively, on the basis of the unique IR carbonyl stretching vibration.

Copper(I) is known to disproportionate in water, see eqn. (4),

$$2Cu^+(aq) \rightleftharpoons Cu + Cu^{2+}(aq) \qquad (4)$$

with an equilibrium constant of the order of 10^6 at 298 K.[32] Disproportionation of Cu^I is also observed in non-aqueous, polar solvents.[33] In media solvating copper(I) more effectively than water (acetonitrile,[34] liquid ammonia,[35] or molten $AlCl_3$–NaCl–KCl mixture[36]) or in the presence of ligands such as CO or tertiary phosphine,[5] copper(I) is stable and metallic copper can be used to reduce copper(II) derivatives to copper(I). In conclusion, the synproportionation reaction of copper(II) with copper to copper(I) may be a useful procedure for the preparation of carbonyl derivatives of copper(I). To the best of our knowledge, the application of this procedure to the synthesis of copper(I) carbonyls has been reported in a few cases only, namely carbonyl(hexafluoroacetylacetonato)copper,[7] $Cu_2SO_4\cdot 2CO\cdot H_2O$,[37] $Cu(ClO_4)(CO)$,[38] and Cu(L)(CO), $L = [CpCo\{P(O)Me_2\}_3]^-$ or $[Cp^*Rh\{P(O)Me_2\}_3]^-$.[12,39]

We have found that the reaction between copper(II) trifluoroacetate and copper in the presence of carbon monoxide, see eqn. (5), proceeds in methanol, DME, THF or toluene. In

$$Cu(CF_3CO_2)_2 + Cu + CO \longrightarrow 2Cu(CF_3CO_2)(CO) \qquad (5)$$

toluene, the reaction is complete (molar ratio $Co:Cu^{II} = 2:1$ by gas volumetry) in *ca.* 5 h at 295 K at atmospheric pressure and the carbonyl derivative may be isolated by filtration from the excess of copper. The synproportionation reaction in the absence of CO does not proceed in MeOH or in toluene at room temperature but is fast at *ca.* 80 °C in toluene affording $Cu(CF_3CO_2)(C_6H_5Me)_{0.5}$ in 90% yield. The toluene adduct is probably similar to the tetranuclear benzene adduct of formula $Cu_4(CF_3CO_2)_4(C_6H_6)_2$ isolated and structurally characterized by Rodesiler and Amma.[30]

Owing to the fact that all the attempts to prepare the trichloracetato and the tribromoacetato derivatives of copper(I) were unsuccessful, we reckoned that the synproportionation reaction between $Cu_2(CX_3CO_2)_4(CX_3CO_2H)_2$, X = Cl or Br, and copper under a CO atmosphere could be a valid alternative procedure to prepare $Cu(CX_3CO_2)(CO)$. The reaction of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ with copper in toluene in the presence of CO proceeds with fast absorption of CO up to a $CO:Cu^{II}$ molar ratio of about 2:1 to give a pale green solution (about 120 min) showing a strong carbonyl absorption at 2122 cm^{-1} suggesting the formation of the trichloracetato carbonyl derivative of copper(I) according to eqn. (6). (No carbon

$$Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2 + 2Cu + 4CO \longrightarrow 4Cu(CCl_3CO_2)(CO) + 2CCl_3CO_2H \qquad (6)$$

monoxide absorption is observed in the case of the tribromoacetate.) The solutions of $Cu(CCl_3CO_2)(CO)$ thus obtained are not stable and slowly deposit the colourless CuCl(CO) identified by infrared spectroscopy in the solid state. The solution shows a strong absorption at 2128 cm^{-1} assigned to a CO stretching vibration of a new carbonyl compound. Owing to the high solubility in toluene and to the formation of copper metal on reducing the CO partial pressure, all attempts to isolate the chloroacetato carbonyl derivative of copper(I) failed.

On the other hand, during attempts to precipitate $Cu(CCl_3CO_2)(CO)$ by addition of heptane under an atmosphere of carbon monoxide pale green crystals were slowly obtained which were characterized by X-ray diffraction methods to be the polynuclear derivative $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$. The IR spectrum in the solid state (Nujol mull) shows a strong carbonyl absorption at 2135 cm^{-1} (2128 cm^{-1} in toluene). The compound shows IR bands at 1674 and 1626 and 1379 cm^{-1} due to vibrations associated with the carboxylato groups. As two copper(II) centres are present in the tetranuclear unit the compound is paramagnetic with an effective magnetic moment at room temperature of 2.62 μ_B per tetranuclear unit. Variable-temperature magnetic measurements have shown that $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ follows the Curie–Weiss law in the range 70–293 K with a Weiss temperature of −59 K.

As anticipated, the compound is a polynuclear, $Cu^{II}Cu^I$ mixed-valence derivative, containing trichloracetato, dichloroacetic acid and carbon monoxide as ligands. Fig. 5A shows a view of the polynuclear chain while the repeating tetranuclear unit is in Fig. 5B. Table 3 lists a selection of bond distances and angles. The molecular structure of the repeating unit $Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2$ shows bridging bidentate and bridging tridentate trichlorocarboxylato ligands. Moreover, one dichloroacetic acid group bridges two copper(II) atoms through one oxygen atom (the carbonylic one), a situation rarely observed before in carboxylato systems.

The repeating unit consists of two dinuclear sections one containing two copper(II) and the other two copper(I) metal centres. The copper(II) metal centres (Cu3 and Cu4) are co-ordinated to five oxygen atoms: two of them (O33, O63 and O31, O61, respectively) belong to two bridging trichloroacetato groups in *syn-syn* configuration,[40] while O23, O43 and O13, O53 bridge two dinuclear units, containing both copper(II) and copper(I). The five-co-ordination of copper(II) is completed by one oxygen atom (O71) of one dichloroacetic acid unit bridging two copper(II) centres. The copper(II)–copper(II) separation is 3.447 Å, much larger than in typical dinuclear copper(II) carboxylates. The mean values of the Cu^{II}–O bond distances are 1.92 and 1.93 Å at Cu3 and Cu4, respectively, with the copper atoms slightly displaced out of the least-squares plane defined by the basal oxygen atoms (Cu3, 0.127; Cu4, 0.146 Å).

Noteworthy is the presence of one dichloroacetic acid $CHCl_2CO_2H$ unit which is bonded through the O71 atom to Cu3 and Cu4 in a monodentate bridging mode, *i.e.* O71 constitutes the common vertex of the two square-pyramidal co-ordination polyhedra of copper(II). The Cu3–O71 and Cu4–O71 bond distances and the Cu3–O71–Cu4 bond angle are

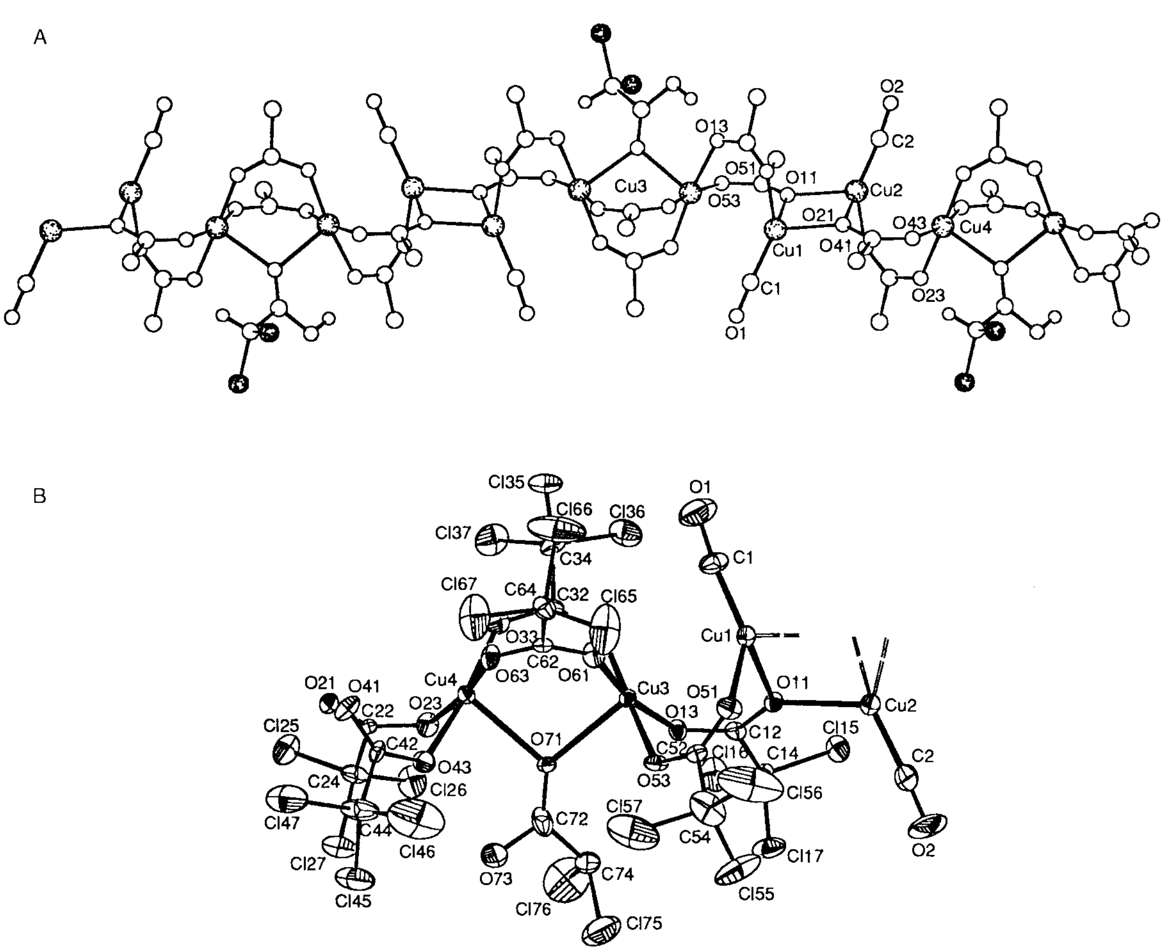


Fig. 5 View of the polynuclear chain (A) and of the repeating tetranuclear units (B) of $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$.

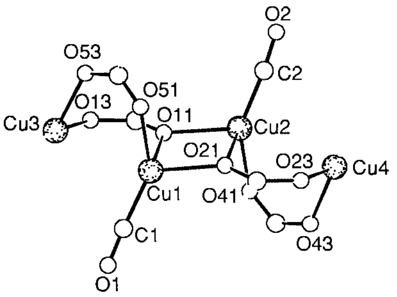


Fig. 6 View of the copper(I)-containing dinuclear unit in $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$.

2.27(1), 2.29(1) Å and 98.3(3)°, respectively. Consistent with the monodentate co-ordination of the carboxyl the C72–O71 bond [1.21(3) Å] is significantly different from that between C72 and the protonated oxygen atom O73 [1.34(3) Å], similar to those found in CH_3CO_2H (1.32 Å),[41] CF_3CO_2H/CH_3CO_2H (1.31 Å)[42] and $PhCO_2H$ (1.30 Å).[43]

As in the case of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$, the O73 ··· O43 distance of 2.628 Å indicates the presence of a hydrogen bond between the O73 and O43 atoms of the dichloroacetic acid ligand and the trichloroacetato group, respectively. A similar distance [2.516(7) Å] has been observed in a tetranuclear nickel(II) derivative containing a bridging acetic acid molecule.[44]

Fig. 6 shows a view of the copper(I)-containing section of the tetranuclear unit. The copper(I) centres are bonded in a distorted tetrahedral co-ordination to the oxygen atoms of the bridging tridentate trichlorocarboxylato groups (O11 and O21), to the oxygen atom of the bridging bidentate trichloroacetate (O51 and O41) and to the carbon atom of carbon monoxide. The O11, Cu1, O21 and Cu2 atoms form a slightly distorted rectangle (Fig. 6) with angles at oxygen [96.6(4) and 95.5(4)°] larger than that at copper [83.3(4) and 84.5(4)°]. The Cu^{I}–O bond distances (mean value: 2.115 Å) are longer than the Cu^{II}–O bond distances (mean value: 1.931 Å) involving the same trichlorocarboxylato groups, in agreement with increasing dimensions on decreasing the oxidation state of copper (0.72 *vs.* 0.96 Å).[45]

As further evidence of the co-ordination flexibility of the carboxylato group,[40] two trichlorocarboxylato groups assume a tridentate, bridging disposition, while the third one is bridging bidentate with a *syn-syn* conformation.

As far as the Cu–CO fragment is concerned, the Cu–C and C–O bond distances (mean values: 1.785 and 1.13 Å, respectively) and the Cu–C–O bond angles (mean value: 171°) are in the range generally observed in copper(I) carbonyl derivatives.[5b,c,6–10]

Conclusion

Trichloroacetato and tribromoacetato derivatives of copper(II) have been obtained in high yields through a carboxylato-exchange reaction starting from the readily available trifluoroacetato complex $Cu(CF_3CO_2)_2$. At variance with the trifluoroacetato system, trichloro- and tribromo-acetato derivatives of copper(I) cannot be prepared due to the reactivity of the CX_3 fragment of the CX_3CO_2 group which probably produces halogenoacetato-substituted copper halides.[46] According to the lower C–X bond strength on increasing the atomic number of the halogen, the reactivity of the CX bond is more pronounced with tribromoacetic acid than with trichloro- and trifluoroacetic acid.

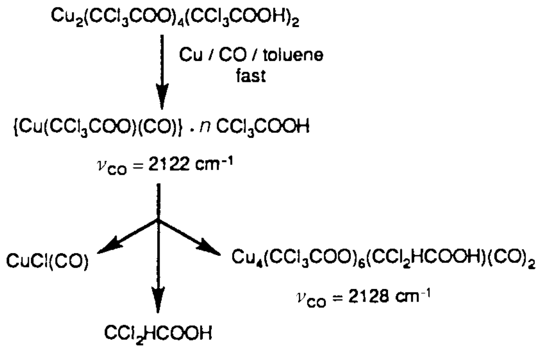
The trifluoroacetato carbonyl derivative of copper(I), $Cu(CF_3CO_2)(CO)$, has been prepared by synproportionation

Table 3 Selection of bond distances (Å) and angles (°) of $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$

Cu1–O11	2.233(9)	O23–C22	1.27(2)
Cu1–O21	2.13(1)	O31–C32	1.19(2)
Cu1–O51	1.99(1)	O33–C32	1.27(2)
Cu1–C1	1.76(2)	O41–C42	1.14(2)
Cu2–O11	2.09(1)	O43–C42	1.23(2)
Cu2–O21	2.23(1)	O51–C52	1.19(2)
Cu2–O41	2.02(1)	O53–C52	1.23(2)
Cu2–C2	1.81(3)	O61–C62	1.23(2)
Cu3–O13	1.914(9)	O63–C62	1.23(2)
Cu3–O31	1.92(1)	O71–C72	1.21(3)
Cu3–O53	1.92(1)	O73–C72	1.34(3)
Cu3–O61	1.940(9)	C12–C14	1.54(2)
Cu3–O71	2.27(1)	O1–C1	1.14(3)
Cu4–O23	1.92(1)	O2–C2	1.12(4)
Cu4–O33	1.92(1)	O11–C12	1.26(2)
Cu4–O43	1.97(1)	O13–C12	1.24(2)
Cu4–O63	1.92(1)	O21–C22	1.19(2)
Cu4–O71	2.29(1)		
O11–Cu1–O21	83.3(4)	O13–Cu3–O31	88.0(5)
O11–Cu1–O51	90.9(4)	O13–Cu3–O53	91.6(5)
O11–Cu1–C1	116.9(7)	O13–Cu3–O61	166.6(5)
O21–Cu1–O51	92.4(5)	O13–Cu3–O71	94.9(4)
O21–Cu1–C1	116.5(8)	O31–Cu3–O53	178.3(5)
O11–Cu2–O21	84.5(4)	O31–Cu3–O61	91.6(6)
O11–Cu2–O41	91.1(5)	O31–Cu3–O71	97.2(4)
O11–Cu2–C2	119.7(8)	O53–Cu3–O61	88.3(5)
O21–Cu2–O41	89.2(5)	O53–Cu3–O71	84.5(4)
O21–Cu2–C2	117.0(9)	O23–Cu4–O33	88.5(6)
O41–Cu2–C2	139.8(9)	O23–Cu4–O43	88.8(5)
O51–Cu1–C1	140.7(8)	O23–Cu4–O63	169.4(5)
O61–Cu3–O71	98.4(4)	O23–Cu4–O71	89.3(4)
Cu1–O11–Cu2	96.6(4)	O33–Cu4–O43	172.8(6)
Cu1–O11–C12	124.1(9)	O33–Cu4–O63	92.4(6)
Cu1–O21–Cu2	95.5(4)	O33–Cu4–O71	100.0(5)
Cu1–O21–C22	135.3(9)	O43–Cu4–O63	89.1(5)
Cu1–O51–C52	132.0(1)	O43–Cu4–O71	86.5(4)
Cu2–O41–C42	129.0(1)	O63–Cu4–O71	100.9(4)
Cu2–O11–C12	139.0(1)	Cu4–O23–C22	126.1(9)
Cu2–O21–C22	129.1(9)	Cu4–O33–C32	133.0(1)
Cu3–O13–C12	126.7(8)	Cu4–O43–C42	122.0(1)
Cu3–O31–C32	135.0(1)	Cu4–O63–C62	131.0(1)
Cu3–O53–C52	122.0(1)	Cu4–O71–C72	126.0(1)
Cu3–O61–C62	138.4(9)	Cu1–C1–O1	172.0(2)
Cu3–O71–Cu4	98.3(3)	Cu2–C2–O2	170.0(3)
Cu3–O71–C72	133.0(1)		

between the trifluoroacetate of copper(II) and copper in the presence of CO. On the other hand, evidence has been collected of the existence of the trichloroacetato compound, $Cu(CCl_3CO_2)(CO)$. The compound forms *via* the synproportionation reaction (as evidenced by the consumption of copper and by gas-volumetric data) but it is not stable and slowly decomposes to give the copper(I) carbonyl chloride, CuCl(CO), and a polynuclear, mixed-valence carbonyl derivative of formula $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$. Although the decomposition reaction is slow, all attempts to isolate the intermediate carbonyl trichloroacetato derivative failed. Noteworthy is the observation that the reaction of $Cu_2(CBr_3CO_2)_4(CBr_3CO_2H)_2$ with copper does not proceed with CO absorption and no evidence has been collected of a carbonyl compound in such a system. Our data suggest that CuCl(CO) and $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ are formed through a C–Cl activation process promoted by copper(I), as in Scheme 1. The compound $CHCl_2CO_2H$ is found as a product of the reaction both as a ligand in the polynuclear copper derivative and in solution (see Experimental section). Moreover, $CHCl_2CO_2H$ is the product of the reaction of copper metal with CCl_3CO_2H.[46]

The new carbonyl derivative $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ shows several peculiarities such as: (a) it is a rare example of a transition metal derivative containing a monodentate bridging carboxylic acid; (b) it belongs to the elusive family of compounds containing both RCO_2 and RCO_2H ligands; (c) it is the first example‡ of a carboxylato compound of copper containing terminal carbonyl groups.



Scheme 1

Experimental

All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified nitrogen or carbon monoxide. The reduction vessels were oven-dried prior to use. Solvents were dried by conventional methods. Elemental analyses were performed with a C. Erba elemental analyzer Model 1106. IR spectra were recorded with a Perkin-Elmer model FT 1725X instrument on solutions or Nujol or polychlorotrifluorethylene mulls prepared under exclusion of moisture and oxygen. Magnetic susceptibilities were measured with a magnetic balance (balance Sartorius 4104, electromagnet Varian V 2900) according to the Faraday method (using $CuSO_4 \cdot 5H_2O$ as calibrating substance). Diamagnetic corrections were calculated by using Pascal[47] contributions and the diamagnetic correction for the glass tube was determined experimentally. Powder diffractograms of $Cu(CF_3CO_2)$ and of $Cu(CF_3CO_2)(CO)$ were recorded at room temperature at the Institut für Anorganische Chemie der Universität Tübingen (Germany) with a D5000 Siemens diffractometer using Cu-Kα radiation and a Braun OED 50 M detector. In the carbonylation experiments diagrams were collected at 8 min intervals.

Trifluoroacetic acid, CF_3CO_2H (Aldrich) was stored in the presence of 15% (v/v) $(CF_3CO)_2O$. Trichloroacetic acid, CCl_3CO_2H, was used as a 2 M solution in trichloroacetic anhydride, $(CCl_3CO)_2O$. Tribromoacetic acid, CBr_3CO_2H, was dried *in vacuo* at room temperature in the presence of P_4O_{10} and stored in a dinitrogen atmosphere. The compounds Cu_2O (Aldrich), CuO (Merck) and finely divided copper (Merck) were used as received.

The trifluoroacetates of copper(I) and copper(II) were prepared by a slight modification of the published procedures.[15] A solution of $(CF_3CO)_2O$ (15 ml), CF_3CO_2H (8 ml) and heptane (50 ml) was treated with Cu_2O (3.18 g, 22.2 mmol). The suspension was refluxed for 15 h and the colourless solid filtered off, washed with heptane (4 × 10 ml) and dried *in vacuo* affording 7.52 g (96% yield) of $Cu(CF_3CO_2)$ in the form of a microcrystalline solid. Found: C, 12.8; Cu, 36.0. $C_2CuF_3O_2$ requires: C, 13.6; Cu, 36.0%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 1633s, 1589s, 1462s, 1217s, 1155s, 862s, 806sh, 784s, 635w, 525m and 500m. A solution of $(CF_3CO)_2O$ (7 ml), CF_3CO_2H (15 ml) and hexane (400 ml) was treated with Cu_2O (4.57 g, 31.1 ml). The suspension was refluxed for 8 h. During the first 4 h O_2 was passed for 5 min through the suspension every 30 min; afterwards the mixture was treated with sporadic oxygen bubbling. The light blue solid was filtered off, washed with heptane (5 × 15 ml) and dried *in vacuo* affording 16.98 g (94%) of $Cu(CF_3CO_2)_2$ in the form of a microcrystalline light blue solid. Found: Cu, 20.8. $C_2CuF_3O_2$

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‡ Some years ago a tetranuclear carbonyl trifluoroacetato derivative was said to be structurally characterized by Rodesiler and Amma,[14] but the details of the crystal structure determination have never appeared.

requires: Cu, 21.9%. IR (Nujol): ṽ/cm^{-1} 1675s, 1619s, 1461s, 1206s, 1175s, 867m, 794s, 628w, 528m, 479w, 446w, 437w and 420w.

Syntheses

$Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$. *(a) From $Cu(CF_3CO_2)_2$.* A pale blue suspension of $Cu(CF_3CO_2)_2$ (3.21 g, 11.1 mmol) in heptane (75 ml) was treated with 16 ml of a 2 M solution of $CCl_3CO_2H/(CCl_2CO)_2O$ (32.0 mmol of CCl_3CO_2H). The suspension rapidly turned blue-green. After 5 h stirring at room temperature, the volatiles were evaporated *in vacuo* at room temperature§ and heptane (50 ml) was added to the residue. The solid was filtered off and dried *in vacuo* at room temperature affording 5.13 g (84% yield) of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ as a green-blue microcrystalline solid. Found: C, 12.9; H, 0.1; Cu, 11.1. $C_6HCl_9CuO_6$ requires: C, 13.1; H, 0.2; Cu, 11.5%. IR (Nujol): ṽ/cm^{-1} 1730s, 1671s, 1382s, 1223s, 1170 ms, 975ms, 957m, 854s, 830s, 756s and 690s. $\chi^{corr}_{mol} = 2.83 \times 10^{-3}$ cgsu, diamagnetic correction = -495.3×10^{-6} cgsu, μ_{eff} (293 K) = 2.59 μ_B.

^{19}F NMR control of the reaction. A solution of 1.36 g (8.31 mmol) of CCl_3CO_2H in heptane (25 ml) was treated with $Cu(CF_3CO_2)_2$ (0.802 g, 2.77 mmol). After 4 h stirring at room temperature the reaction mixture was filtered and the solid dried *in vacuo* at room temperature affording 1.398 g (91% yield) of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ identified by IR spectroscopy. To the filtrate was added C_6H_5F as an internal standard. A ^{19}F NMR spectrum of the filtrate showed the presence of 5.32 mmol of CF_3CO_2H (96% of the theoretical amount).

(b) From CuO. A solution of CCl_3CO_2H (10 g, 61.4 mmol) in $(CCl_3CO)_2O$ (20 ml) was diluted with heptane (50 ml) and treated with CuO (1.84 g, 23 mmol). After being refluxed for 12 h the mixture was filtered still hot and allowed to cool slowly, giving well formed deep green crystals of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ (6.792 g, 53% yield, identified by IR and copper analysis).

Data collection and processing for $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$. Crystal data, collection and refinement parameters are compiled in Table 4. No significant variation in intensities of three standard reflections was observed during data collection. An empirical absorption correction based on ψ scans was applied. The structure was solved by Patterson and difference Fourier syntheses. Full-matrix least-squares refinement[48] on F was carried out with anisotropic displacement parameters for all non-hydrogen atoms. Refinement converged with 2748 observations for 215 variables with a goodness of fit of 1.952.

$Cu_2(CBr_3CO_2)_4(CBr_3CO_2H)_2$. A pale blue suspension of $Cu(CF_3CO_2)_2$ (3.09 g, 10.7 mmol) in heptane (100 ml) was treated with CBr_3CO_2H (11.24 g, 37.9 mmol), rapidly turning blue-green. After 5 h stirring at room temperature the volatiles were evaporated *in vacuo* at room temperature.¶ After addition of heptane (25 ml) the blue solid was filtered off, washed with heptane (4 × 3 ml) and dried *in vacuo* at room temperature, affording 9.219 g (90% yield) of $Cu_2(CBr_3CO_2)_4(CBr_3CO_2H)_2$ as a green-blue microcrystalline solid. Found: C, 7.6; H, 0.1; Cu, 6.3. $C_6HBr_9CuO_6$ requires: C, 7.6; H, 0.1; Cu, 6.7%. IR (Nujol): ṽ/cm^{-1} 1718s, 1664ms, 1365ms, 1244vs, 1213m, 839ms, 803ms, 781vs, 734vs, 683s, 614vs and 442s. $\chi^{corr}_{mol} = 2.09 \times 10^{-3}$ cgsu, diamagnetic correction = -626×10^{-6} cgsu, μ_{eff} (293 K) = 2.22 μ_B.

Carbonylation of $Cu(CF_3CO_2)$ in the solid state to give $Cu(CF_3CO_2)(CO)$. In a gas volumetric apparatus, solid $Cu(CF_3CO_2)$ (0.23 g, 1.3 mmol) was treated with CO at 297 K. Absorption of CO up to a CO : Cu molar ratio of 2 : 1 was observed within 30 min. The IR spectrum of the solid (Nujol mull) was superimposable on that obtained by the synproportionation reaction described below.

$Cu(CF_3CO_2)(CO)$ from $Cu(CF_3CO_2)_2$ and Cu. A copper platelet (1.5 g, 23.6 mgatom) in MeOH (25 ml) was treated at room temperature with $Cu(CF_3CO_2)_2$ (1.23 g, 4.25 mmol) under an atmosphere of carbon monoxide. A fast CO absorption was noticed. After 12 h stirring at room temperature the unchanged copper was removed mechanically and the colourless solid filtered off, washed with hexane (2 × 10 ml) and dried *in vacuo* at room temperature affording 0.71 g (40% yield) of $Cu(CF_3CO_2)(CO)$ as a microcrystalline colourless solid. Found: C, 17.1; H, 0.0; Cu, 31.6. $C_3CuF_3O_3$ requires: C, 17.6; H, 0.0; Cu, 31.1%. IR (Nujol): ṽ/cm^{-1} 2130. The reaction proceeds analogously in THF or DME as medium.

A gas-volumetric control of the reaction showed that a suspension of $Cu(CF_3CO_2)_2$ (0.862 g, 2.54 mmol) and finely divided copper (0.176 g, 2.77 mgatom) in toluene (50 ml) absorbed CO at 296 K up to CO : Cu molar ratio of 2.0 : 1 within 5 h. The volume of the filtrate was reduced to *ca.* 5 ml *in vacuo* at room temperature, obtaining a colourless solution which gave a colourless solid upon treatment with CO. The suspension was filtered and the solid washed with heptane and dried *in vacuo* affording $Cu(CF_3CO_2)(CO)$ (0.74 g, 71% yield) by analytical (Cu and C analysis) and spectroscopic methods ($\tilde{\nu}_{CO}$ 2122 cm^{-1}, toluene).

$Cu(CF_3CO_2)(C_6H_5Me)_{0.5}$ from $Cu(CF_3CO_2)_2$ and Cu. Finely divided copper (0.695 g, 10.9 mgatom) in toluene (50 ml) was treated at room temperature with $Cu(CF_3CO_2)_2$ (1.622 g, 5.2 mmol). No reaction was observed after 24 h stirring at room temperature. The suspension was heated at 80 °C for 30 min obtaining a colourless solution in the presence of unchanged copper. After filtration, the volume of the solution was reduced to *ca.* 2 ml (no solid formed) and heptane (15 ml) was added which caused the formation of a colourless solid which was filtered off and dried *in vacuo* at room temperature affording 2.022 g (87% yield) of $Cu(CF_3CO_2)(C_6H_5Me)_{0.5}$ as a microcrystalline colourless solid. Found: C, 29.0; H, 1.6; Cu, 28.4. $C_{5.5}H_4CuF_3O_2$ requires: C, 29.7; H, 1.8; Cu, 28.5%. IR (Nujol): ṽ/cm^{-1} 3107w, 3093w, 3031w, 1655vs, 1495m, 1436s, 1201vs, 1147vs, 842s, 798s, 729s, 636mw, 619mw and 522m.

Reaction of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ with copper and CO giving $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$. *Method (a).* To a suspension of copper (0.11 g, 1.74 mgatom) in toluene (25 ml) was added $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ (0.915 g, 0.8 mmol). Fast absorption of CO was observed and the deep green solution turned pale green. An infrared spectrum of the solution (recorded 100 min from mixing the reagents) showed a strong absorption at 2122 cm^{-1}; copper metal had almost disappeared. After 12 h stirring at room temperature the solution showed a strong absorption at 2128 cm^{-1}: a colourless solid was present which was separated by filtration. The volume of the solution was reduced to 5 ml *in vacuo* at room temperature. Formation of a colourless solid and of copper metal was observed. An infrared spectrum of the solution did not reveal any carbonyl absorption. Upon stirring under carbon monoxide copper metal disappeared. By operating under a CO atmosphere, to the green solution was added heptane (25 ml): some colourless solid formed which was removed by filtration. The solution was left standing at room temperature overnight giving well formed pale green crystals of $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ which were filtered off and briefly dried in a stream of carbon monoxide (0.193 g, 19% based on copper). Found: C, 12.8; H, 0.0; Cu, 18.7. $C_8HCl_{10}Cu_2O_8$ requires: C, 13.6; H, 0.1; Cu, 18.0%. IR (Nujol): ṽ/cm^{-1} 2135s, 1674s, 1626s, 1606s, 852s, 836s,

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§ The volatiles collected in a cold trap (−196 °C) were extracted with water. The aqueous layer contained 22.0 mmol of acidity (titration with NaOH) corresponding to a acid : Cu molar ratio of 1.99 : 1.

¶ The volatiles collected in a cold trap (−196 °C) were extracted with water. The aqueous layer contained 19.3 mmol of acidity (titration with NaOH) corresponding to a acid : Cu molar ratio of 1.8 : 1.

Table 4 Crystallographic data and details of the structure refinement of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ and $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$

	$Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$	$[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$
M	1103.38	1413.40
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
a/Å	9.354(4)	11.695(4)
b/Å	9.650(1)	17.566(7)
c/Å	10.875(5)	22.437(6)
α/°	79.00(2)	
β/°	67.62(3)	
γ/°	73.08(2)	
V/Å^3	864.9(6)	4610(3)
Z	1	4
μ/cm^{-1}	26.87	30.56
T/K	203	203
Reflections collected	6832	8809
Reflections unique	3384	8076
Observations in refinement	2748 ($I > 1.0\sigma(I)$)	8071
R	0.069	0.091
R_w	0.075	
$wR2$	—	0.226

754m-s and 691s. $\chi_{mol}^{corr} = 2.90 \times 10^{-3}$ cgsu, diamagnetic correction $= -567 \times 10^{-6}$ cgsu. The compound is stable in air for short periods of time and dissolves in toluene; it is almost insoluble in saturated hydrocarbons and decomposes with formation of copper metal in THF, acetone and acetonitrile.

Method (b). In a gas volumetric system, 2.85 mgatom of finely divided copper and 1.2 mmol of $Cu_2(CCl_3CO_2)_4(CCl_3CO_2H)_2$ in toluene (25 ml) at 296 K absorbed 4.66 mmol of CO corresponding to a $CO:Cu^{II}$ molar ratio of 1.93 : 1 within 2 h to give a pale green solution showing a strong absorption at 2128 cm^{-1}. The reaction was repeated three times and the amount of absorbed CO was reproducible. By operating as described in method (a), 0.315 g (19.3% yield, IR spectroscopy in toluene and Nujol) of $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$ was isolated.

Method (c). By operating as described in method (a) the green suspension was evaporated to dryness at 10^{-2} mmHg/*ca.* 100 °C. The distillate, collected in a trap cooled at liquid nitrogen temperature, was examined by GC-MS which showed the presence of appreciable amounts of $CHCl_2CO_2H$ only.

Method (d). By operating as above, the green suspension after carbonylation was filtered and the solid examined by infrared spectroscopy after a short drying in a stream of carbon monoxide. It showed a strong absorption at 2125 cm^{-1} (Nujol mull), typical[49] of CuCl(CO).

Data collection and processing for $[Cu_4(CCl_3CO_2)_6(CHCl_2CO_2H)(CO)_2]_n$. Crystal data, collection and refinement parameters are compiled in Table 4. A significant loss of intensity (*ca.* 46%) during data collection was indicated by three regularly checked standard reflections and corrected by scaling the intensities to the closest standards. The structure was solved by direct methods.[50] Full-matrix least-squares refinement on intensities[51] was carried out with anisotropic displacement parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions. Refinement converged with 8071 data for 506 refined variables.

CCDC reference number 186/1994.

See http://www.rsc.org/suppdata/dt/b0/b001889i/ for crystallographic files in .cif format.

Acknowledgements

The authors wish to thank the Consiglio Nazionale delle Ricerche, Progetto Finalizzato per Materiali Speciali II for financial support, and the Programma Vigoni for an exchange programme between the Università di Pisa and the RWTH Aachen. Thanks are due to Professor J. Strähle, Universität Tübingen, for the collection and the discussion of the X-ray powder diffractograms of $Cu(CF_3CO_2)$ and of $Cu(CF_3CO_2)(CO)$.

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