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COMPLEXES OF COPPER(I) ACETATE

II*. OLEFIN COMPLEXES

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Summary

Copper(I) acetate reacts with the olefins, 1,5-hexadiene, 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene to give complexes of the type $(CuO_2CCH_3)_2$(olefin), whereas with 2,5-bicyclo[2.2.1]heptadiene a complex CuO_2CCH_3(olefin) is formed. Although readily hydrolysed and oxidised, the complexes are of reasonable thermal stability.

Introduction

Solutions of copper(I) salts have long been used for the extraction of olefins from gaseous mixtures. However, because of their instability at room temperature complexes of monoolefins with copper(I) salts have been characterised mainly by distribution studies in solution or by measurements of the pressure of olefin in equilibrium with the solid complex. Polyolefin complexes of copper(I) salts [2] are of moderate stability in the solid state, most of these complexes isolated to date involving coordinated halide.

Some recent interest has centred around the isolation of copper(I)—olefin complexes that do not involve coordinated halide. $(Cod)_2CuClO_4$** and $(Cod)_2CuBF_4$ have been prepared [3, 4] by electrolytic reduction of copper(II) salts in the presence of the olefin, and reduction by triphenyl phosphite [5] has also been employed. The trifluoromethane sulphonate $(CuOSO_2CF_3)_2C_6H_6$ [6] has been used to prepare other alkylaromatic complexes by displacement of the more weakly coordinated benzene [7], and a variety of cationic olefin—

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* For part I see ref. 1.

** The abbreviations Hd, 1,5-hexadiene; Chd, 1,4-cyclohexadiene; Cod, 1,5-cyclooctadiene; Cot, 1,3,5,7-cyclooctatetraene and Nbd, 2,5-bicyclo[2.2.1]heptadiene (norbornadiene) will be used in formulae throughout the text and tables.

—trifluoromethane sulphonate complexes have been similarly prepared [8] and are found to be of high thermal stability and soluble in polar organic solvents, in contrast to the low thermal stability and insolubility of the corresponding halide complexes.

Whilst the present work was in progress, three copper(I) trifluoroacetate—olefin complexes, $(CuO_2CCF_3)_2(Cot)$, $(CuO_2CCF_3)_2(Cod)$ and $CuO_2CCF_3(Cod)$ were reported [9]. Very recently the preparation and crystal structure of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ was reported [10]. The copper atoms form a planar parallelogram and are held together by bridging trifluoroacetate groups alternating above and below the Cu_4 plane. Each benzene is very weakly bonded to two copper atoms and may easily be displaced by indene to form $CuO_2CCF_3(C_9H_8)$ or by 1,4-cyclohexadiene or 1,3-cyclohexadiene to give $(CuO_2CCF_3)_2$(olefin) complexes. We report here the isolation of five copper(I) acetate—olefin complexes and note that the stoichiometry of copper(I)—olefin complexes appears to be very dependent upon the coordinating ability of the anionic group present.

Experimental

Copper(I) acetate was prepared [11] by reducing copper(II) acetate with copper foil in an acetonitrile/acetic acid/acetic anhydride solvent mixture under nitrogen. Since the acetate itself and more particularly the olefin complexes were sensitive to both moisture and oxygen, all preparations and manipulations were carried out under dry nitrogen, in a vacuum system, or dry box. All solvents were deoxygenated and dried before use.

Infrared spectra were recorded using Perkin—Elmer 621 and Hilger and Watts Infrascan spectrophotometers. Mass spectra were recorded using an A.E.I. MS 12 spectrometer, samples being introduced into the ionisation chamber on direct-insertion probes.

Bis(acetato)(1,5-hexadiene)dicopper(I)

Copper(I) acetate (0.36 g) was dissolved in 1,5-hexadiene (5 g) by stirring under nitrogen. After dissolution a colourless solid slowly formed and was filtered off after 1 h. Dry nitrogen was briefly passed over the solid on the filter to remove excess olefin. Yield 90%. (Found: Cu, 39.0. $C_{10}H_{16}Cu_2O_4$ calcd.: Cu, 38.8%.) Samples submitted in sealed tubes to a commercial analyst gave low results for carbon and hydrogen analyses. Since at least four days elapsed between preparation and analysis partial dissociation of the complex had presumably occurred. The stoichiometry of the complex was confirmed by removing the coordinated olefin of a freshly prepared sample by pumping the solid under high vaccum for at least one hour and weighing the solid before and after pumping. (Weight loss found: 24.1%. Weight loss calcd. for $(CuO_2CCH_3)_2Hd \rightarrow 2\ CuO_2CCH_3 + Hd$: 25.1%.)

Bis(acetato)(1,4-cyclohexadiene)dicopper(I)

Copper(I) acetate (0.31 g) was added to 1,4-cyclohexadiene (5 g), anhydrous ether (20 ml) added, and the mixture stirred for 17 h under dry nitrogen. The colourless solid was filtered off, washed twice with ether (15 ml) and the product dried by passage of a slow stream of dry nitrogen over the solid. Yield 82%. (Found: C, 37.0; H, 4.62; Cu, 39.1. $C_{10}H_{14}Cu_2O_4$ calcd.: C, 36.9; H, 4.34; Cu, 39.1%.)

Bis(acetato)(1,5-cyclooctadiene)dicopper(I)

Copper(I) acetate (0.78 g) was added to a deoxygenated solution of 1,5-cyclooctadiene (5 g) in anhydrous ether (40 ml). After stirring under nitrogen for 1 h the colourless solid was filtered off, washed with ether and dried by pumping in vacuo for 5 min. Yield 76%. (Found: C, 39.4; H, 5.12; Cu, 36.4. $C_{12}H_{18}Cu_2O_4$ calcd.: C, 40.8; H, 5.14; Cu, 36.0%.)

Bis(acetato)(1,3,5,7-cyclooctatetraene)dicopper(I)

Copper(I) acetate (0.35 g) was added to a deoxygenated solution of 1,3,5,7-cyclooctetraene (4.4 g) in anhydrous ether (15 ml). After stirring under nitrogen for 1 h, the colourless solid was filtered off, washed with ether and dried in vacuo for 5 min, followed by storage under dry nitrogen. Yield 60%. (Found: C, 40.9; H, 4.13; Cu, 36.4. $C_{12}H_{14}Cu_2O_4$ calcd.: C, 41.3; H, 4.04; Cu, 36.4%.)

Acetato(2,5-bicyclo[2.2.1]heptadiene)copper(I)

Copper(I) acetate (1.8 g) was completely dissolved in the olefin (40 ml) by stirring under dry nitrogen for 15 min. 40-60 petroleum spirit (40 ml) was added and a colourless solid slowly precipitated with further stirring. After 15 min the product was filtered off, washed with petroleum spirit and dried in vacuo for 10 min. Yield 90%. (Found: C, 49.3; H, 4.86; Cu, 30.0. $C_9H_{11}CuO_2$ calcd.: C, 50.4; H, 4.70; Cu, 29.6%.)

Results and discussion

Before this work the only known copper(I) carboxylate—olefin complexes were some recently reported [9, 10] trifluoroacetates. We report here the isolation of five copper(I) acetate—olefin complexes, four of the type $(CuO_2CCH_3)_2$(olefin) where olefin is 1,5-hexadiene, 1,4-cyclohexadiene, 1,5-cyclooctadiene or 1,3,5,7-cyclooctatetraene, as well as CuO_2CCH_3(norbornadiene). All five complexes were simply prepared by reaction of the acetate with an excess of olefin at room temperature under nitrogen, usually with the addition of ether or 40-60 petroleum spirit to effect precipitation of the product. Several attempts to prepare a complex using 1,3-pentadiene by a similar method were unsuccessful even though reaction times of up to 20 h were employed. Copper(I) acetate was always recovered unchanged.

The complexes appear to be more thermally stable than the corresponding chloride complexes. Thus, for example, $(CuCl)_2$(Hd) is of no more than marginal stability at room temperature [12], olefin being continuously evolved. Loss of olefin from the acetate complex is evidently slow since removal of the stoichiometric amount of 1,5-hexadiene from 0.5 g of the complex required continuous high vacuum pumping for about 1 hour. $(CuO_2CCH_3)_2$(Chd) loses its coordinated olefin at a slightly slower rate than $(CuO_2CCH_3)_2$(Hd) but the other three olefin complexes retain significant amounts of olefin even after high vacuum pumping for 24 h. As expected, all five complexes are readily hydrolysed and oxidised in normal laboratory moist atmospheric conditions. Attempts to obtain mass spectra of the complexes were unsuccessful. At the temperatures below 80° only fragment ions of the olefins were observed. At higher temperatures copper-containing ions were observed but since none contained bonded olefin fragments they undoubtedly arise from copper(I) acetate itself [11] formed by thermal decomposition of the complexes.

From observations of their insolubilities in organic solvents with which they do not react, it is suspected that the complexes are polymeric. Some of the complexes appeared to dissolve to a limited extent in chlorohydrocarbon solvents such as chloroform, but dissolution was followed almost immediately by precipitation of a solid, probably a copper(I) chloride—olefin complex. ^{1}H NMR spectra which may have been useful in structural characterisation could not therefore be obtained. Characterisation rests with evidence obtained from solid state IR spectroscopy.

Table 1 lists the IR bands assigned to the carboxylate modes of the complexes, after elimination of the coordinated olefin bands found in the 1600-400 cm^{-1} region. Comparisons are made with the analogous bands of copper(I) acetate, and with sodium acetate which is taken to typify an ionic situation. An acetate group can act as a ligand in a variety of ways [13], but since the acetate ion is of low symmetry no great differences in the vibrational spectra can be expected for the various types of coordination. At best frequency shifts may occur which can be used as a guide to the coordination type present. For example, unidentate coordination will shift $\nu_{asym}(CO_2)$ to higher and $\nu_{sym}(CO_2)$ to lower frequencies than in the free ion, giving an increased separation, Δ, between these modes. It is evident from Table 1 that unidentate acetate coordination is not present in any of the olefin complexes. (Unidentate coordination is thought to be present in $(CuO_2CCH_3)_2(Ph_2PCH_2CH_2PPh_2)_3$ [1], for which Δ = 234 cm^{-1}). There is no such basis for expecting a distinction in the IR spectra between bridging and chelating acetates, Δ often being similar to or smaller than that of the free acetate ion. A decrease in Δ on coordination may be indicative of bridging or chelation, but failure to observe this effect does not exclude such coordinations since the band position will be sensitive to the other ligands present. The Δ values of the olefin complexes are slightly lower than that of sodium acetate, the acetate groups in each complex therefore being either bridging or chelating.

The basic structural unit of polymeric copper(I) acetate [14] is an eight-membered ring formed by two planar acetate groups bridging two copper atoms. One of the oxygen atoms of each acetate group in addition forms a long bond (2.31 Å) to the next copper in the polymer chain, the eight-membered rings thereby being linked by alternating four-membered Cu_2O_2 planar rings. If the olefin complexes contain chelating acetate groups a fundamental rearrangement of this structure must occur with at least one strong copper—oxygen bond, as well as the weaker copper—oxygen bonds, being broken. If bridging acetate groups are retained in the olefin complexes only the weak copper—oxygen bonds between the eight-membered rings need to be broken. We therfore favour the latter arrangement in which the $(CuO_2CCH_3)_2$ unit is retained.

TABLE 1

IR CARBOXYLATE FREQUENCIES (cm^{-1})

Assignment	NaO_2CCH_3	CuO_2CCH_3	$(CuO_2CCH_3)_2Hd$	$(CuO_2CCH_3)_2Chd$	$(CuO_2CCH_3)_2Cod$	$(CuO_2CCH_3)_2Cot$	$CuO_2CCH_3(Nbd)$
$\nu_{asym}(CO_2)$	1578 vs	1525 vs	1578 vs	1569 vs	1586 vs	1562 vs	1575 vs
$\delta(CH_3)$	1443 ms	1452 s 1429 s	1448 s	1438 s	1430 s	1439 vs	1443 ms
$\nu_{sym}(CO_2)$	1414 s	1414 s	1426 s	1412 s	1422 s	1413 s	1414 s
$\delta(CH_3)$	1333 m	1347 m	1346 m	1340 m	1347 mw	1354 m	1333 m
$\rho(CH_3)$	1043 ms	1050 m	1043 m	1045 mw	1041 mw	1049 mw	1043 ms
$\rho(CH_3)$	1012 m	1039 ms	1022 m	1019 m	1025 mw	1034 mw	1012 m
$\nu(CC)$	924 m	937 m	931 m	924 w	936 w	920 w	924 w
$\delta(CO_2)$	648 m	692 ms	692 m	677 s	675 m	691 m	648 m
$\pi(CO_2)$	625 mw	620 m 612 m	606 m	622 m 613 m	624 m 619 (sh)	627 m 622 m	625 mw
$\rho(CO_2)$	462 m		417 m	463 vw	441 w	443 m	462 m
Δ^a	164	111	152	147	164	149	155

[a] $\Delta = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$.

TABLE 2

IR FREQUENCIES OF COPPER(I)—OLEFIN COMPLEXES (cm^{-1})

Compound	ν(C=C)	π(C=C—H)	ν(Cu—O)	ν(Cu—olefin)
CuO_2CCH_3			381 m, 374 (sh), 242 s	
Hd	1643 s	647 ms		
$(CuO_2CCH_3)_2Hd$	1553 m	724 ms	366 m, 255 m	319 w
$(CuCl)_2Hd$[c]	1545 m	764 m		
Chd	1639 s	680 ms, 672 ms		
$(CuO_2CCH_3)_2Chd$	1529 s	751 s, 710 s	350 vw, 235 s (br)	298 m, 267 m
$(CuCl)_2Chd$[b]	1573	720, 710		
Cod	1654 s	720 ms, 707 s		
$(CuO_2CCH_3)_2Cod$	1543 m	755 mw	367 mw, 240 w, (br)	317 m, 287 m
CuCl(Cod)[c]	1620, 1550	750, 720		
Cot	1634 ms	798 vs, 670 vs, 630 s		
$(CuO_2CCH_3)_2Cot$	1589 ms, 1543 m	811 ms, 753 mw, 725 s	384 mw, 254 mw	332 mw, 315 m, (br) 297 mw
$(CuCl)_2Cot$[c]	1540, 1515	730		
Nbd	1540 s	798 s, 773 vw, 727 vs[d], 656 s[d]		
$CuO_2CCH_3(Nbd)$	1462 w	822 mw, 789 m 738 s[d], 671 s[d]	367 w, 247 w	315m, (br), 296 mw
$(CuCl)_2Nbd$[c]	1470			

[a] Ref. 12. [b] Ref. 17. [c] Ref. 5 [d] $\geqslant$CH deformation.

As evidence in favour of this arrangement we find that bands are present in the far IR spectra of the olefin complexes at similar frequencies to those of copper(I) acetate itself, (Table 2). These bands must involve considerable copper—oxygen stretching character. It is unlikely that the complete chain polymeric structure of the acetate is retained in the complex with the olefins merely bonding above and below the acetate polymer, since the acetate initially dissolves in the olefins, the products subsequently being precipitated by the addition of ether or petroleum spirit.

Other IR bands observed below 350 cm^{-1}, (Table 2), may be associated with copper—olefin stretching modes. Such bands for d^8 complexes are found in the 600-350 cm^{-1} region [15], so the metal—olefin bonds of the copper complexes are weaker than those of d^8 complexes in accord with the lower chemical stability of the copper complexes.

The assignment of ν(C=C) for the complexes (Table 2) proved difficult since this band shifted on complexing into the carboxylate stretching region. However, the tabulated frequencies are reasonable by comparison with those of analogous copper(I) chloride complexes. The observation of two ν(C=C) bands for $(CuO_2CCH_3)_2$(Cot) may indicate that although all the olefinic linkages of the olefin are bonded to copper, two bonds are weaker than two others. The IR spectrum of $(CuCl)_2$(Cot), on the other hand, shows the presence of both coordinated and uncoordinated olefinic linkages [16]. The ν(C=C) frequency of CuO_2CCF_3(Cod) [9], 1545 cm^{-1}, is very close to that found for $(CuO_2CCH_3)_2$(Cod). IR evidence for the coordination of an olefin to a metal has also been obtained from observation of the shifts of the out-of-plane olefinic C—H deformation frequencies [5]. Such modes are likely to show an increase in frequency on coordination of the olefin. These bands, (Table 2),

TABLE 3

STOICHIOMETRIES OF COPPER(I)—OLEFIN COMPLEXES (Cu/OLEFIN RATIOS)

Copper(I) compound	Hd	Chd	Cod	Cot	Nbd
ClO_4			1/2 [a]		
BF_4			1/2 [b]		
O_3SCF_3			1/2 [c]	1/1 [c]	2/1 [c, d]
Cl	2/1 [e]	2/1 [f]	1/1 [g]	1/1 [h], 2/1 [i]	1/1 [j], 2/1 [k]
Br			1/1 [l]	1/1 [l]	1/1 [l], 2/1 [k]
O_2CCF_3		2/1 [m]	1/1 [n], 2/1 [n]	2/1 [n]	
O_2CCH_3	2/1 [o]	2/1 [o]	2/1 [o]	2/1 [o]	1/1 [o]

[a] Ref. 3. [b] Ref. 4. [c] Ref. 8. [d] Solution study, solid not isolated. [e] Ref. 12. [f] Ref. 17. [g] Ref. 18. [h] Ref. 19. [i] Ref. 16. [j] Ref. 20. [k] Ref. 5. [l] Ref. 21. [m] Ref. 10. [n] Ref. 9. [o] This work.

are less likely than ν(C=C) to be confused with carboxylate bands for the acetate complexes.

Taking the view that the complexes contain $(CuO_2CCH_3)_2$ units reasonable structures can be postulated. One diene molecule is presumably coordinated to each copper of a $(CuO_2CCH_3)_2$ unit in CuO_2CCH_3(Nbd), since norbornadiene is a chelating diene. The other olefins are capable of bridging $(CuO_2CCH_3)_2$ units, so the other acetate complexes may be polymeric, in agreement with their insolubilities in organic solvents. Since $(CuO_2CCH_3)_2$·(Cot) appears from its IR spectrum to have a structure with the olefin forming two strong and two weak bonds to copper, the tetraene may be bridging, forming two bonds of unequal strength to each of two copper atoms from adjacent $(CuO_2CCH_3)_2$ units. However, structures similar to that of $(CuO_2CCF_3)_4(C_6H_6)_2$ [10] cannot be ruled out.

Finally it is instructive to examine the stoichiometries of copper(I)—olefin complexes, (Table 3), since it is apparent that the anions compete with the olefins for available coordination sites on copper. 1,5-Cyclooctadiene complexes form the most complete series. As expected, anions of low coordinating ability, (ClO_4^-, BF_4^- and $O_3SCF_3^-$), are ineffective in competing with the olefin and complexes of stoichiometry $[Cu(Cod)_2]X$ result. Chloride and bromide however, compete successfully to give $[Cu(Cod)X]_n$ complexes and the carboxylates form complexes of the type $(CuO_2CR)_2$(Cod), (R = Me or CF_3), the carboxylate group probably acting in a bridging manner.

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