Complexes of Copper(I) Acetate. Part I. Complexes with σ-Donor Ligands

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Reactions of copper(I) acetate with various nitrogen-, phosphorus-, arsenic-, sulphur-, and selenium-donor ligands have been studied. With unidentate donors, either $[Cu(O_2CMe)L_3]$ (L = thiourea or selenourea) or $[Cu(O_2CMe)L_2]$ (L = Ph_3P or imidazoline-2-thione) are formed. With the bidentate donors, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$ (dppe), or $Ph_2AsCH_2CH_2AsPh_2$ (dpae) complexes of the type $[Cu(O_2CMe)(bidentate)]$ can be isolated. With dppe and dpae further complexes may be produced by varying the reaction conditions, *viz.* $[\{Cu(O_2CMe)\}_2(dppe)_3]$ and its benzene solvate, and $[Cu(O_2CMe)(dpae)_2]$. A further type, $[\{Cu(O_2CMe)\}_2(bidentate)]$, thought to involve bridging ligand molecules, has been isolated using 2,5-dithiahexane or 2,2′-bipyridyl.

COPPER(I) acetate was first prepared [1,2] over seventy years ago, but its structure and reactions have only recently been effectively explored. Two independent crystal-structure determinations [3,4] show the acetate to be a polymeric planar molecule. Although the involvement of copper(I) acetate in organic reactions such as decarboxylations [5] and dehalogenations [6] is established, little is known of its complexes with σ-donor ligands. All such complexes isolated to date have been indirectly prepared. The complexes $[Cu(O_2CMe)(PPh_3)_3]$ and $[Cu(O_2CMe)(PPh_3)_2]$ result from the reduction of copper(II) acetate in methanol using an excess of the phosphine,[7] the bis complex also having been produced [8] by CO_2 insertion into the Cu–Me bond of $[MeCu(PPh_3)_2]{\cdot}0{\cdot}5OEt_2$; $[Cu(O_2CMe)\{P(C_6H_{11})_3\}_2]$ has been prepared analogously.[9] The reaction of acetic acid with copper(I) oxide in the presence of the appropriate ligand leads to the formation of $[Cu(O_2CMe)(CNBu^t)]$ [10] or $[Cu(O_2CMe)(tu)_3]$ (tu = thiourea).[11] The substituted tu complexes $[Cu(O_2CMe)(RHN{\cdot}CS{\cdot}NHR')_x]$ (R = Ph, R′ = H, x = 1; R = R′ = Ph, x = 1; R = MeCO, R′ = H, x = 1 and 2; R = R′ = MeCO, x = 4), prepared by reduction of copper(II) acetate, have also been briefly reported.[12] Finally, bis[acetato(2,9-dimethyl-1,10-phenanthroline)-copper(I)] has been produced [7] by displacement of the phosphine ligands of $[Cu(O_2CMe)(PPh_3)_2]$.

The present work extends the range of such complexes, reporting the direct reactions of a selection of σ-donors with copper(I) acetate itself.

EXPERIMENTAL

Materials.—Copper(I) acetate was prepared as before [13] by reducing copper(II) acetate with copper foil in an acetonitrile–acetic acid–acetic anhydride solvent mixture under nitrogen. Ligands were generally recrystallised and vacuum dried before use. All solvents were dried and deoxygenated by standard methods before use.

Physical Measurements.—I.r. spectra were recorded on Perkin-Elmer 621 and Hilger and Watts Infrascan spectrophotometers. Far-i.r. spectra of samples dispersed in Polythene were obtained on a R.I.I.C. FS 720 interferometer. N.m.r. spectra were obtained using Varian A60 and Jeol 100 MHz spectrometers with an internal $SiMe_4$ standard. Conductance measurements at 25 °C were carried out using a Wayne–Kerr Autobalance universal bridge and a dip-type cell with platinum electrodes. Molecular-weight determinations were carried out either cryoscopically or osmometrically in benzene, bromoform, or 1,2-dibromoethane. Mass spectra were recorded on A.E.I. MS 12 and 902 spectrometers using direct-insertion probes. Spectra were normally recorded at *ca.* 200 °C using an ionising energy of 70 eV.† Ion abundances were obtained by summation of the isotope contributions of a particular ion and expressed relative to a copper-containing base peak of 100 units.

Reactions.—As copper(I) acetate and a number of complexes were sensitive to both moisture and oxygen, all preparations and manipulations were carried out under dry nitrogen or in a closed vacuum system.

Acetatobis(triphenylphosphine)copper(I). Copper(I) acetate (0·67 g) was added to triphenylphosphine (6·13 g) dissolved in toluene (30 cm^3). After stirring under nitrogen for 30 min, the colourless *solid* was filtered off, washed with toluene and diethyl ether, and dried *in vacuo* (yield 40%) (Found: C, 70·3; H, 5·10; Cu, 9·80. Calc. for $C_{38}H_{33}CuO_2P_2$: C, 70·5; H, 5·15; Cu, 9·80%).

Acetato[bis(diphenylphosphino)methane]copper(I). Copper(I) acetate (0·29 g) was added to the phosphine (1·13 g) dissolved in a mixture of diethyl ether (25 cm^3) and benzene (10 cm^3). The acetate dissolved, but on stirring for 20 min a colourless solid began to form. After 16 h the *product* was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 60%) (Found: C, 63·8; H, 4·70; Cu, 12·7. Calc. for $C_{27}H_{25}CuO_2P_2$: C, 64·0; H, 4·97; Cu, 12·5%).

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† $1\ eV \approx 1{\cdot}60 \times 10^{-19}$ J.

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Acetato[1,2-*bis*(*diphenylphosphino*)*ethane*]*copper*(I). Copper(I) acetate (0·57 g) was suspended in benzene (30 cm^3) and the phosphine (1·68 g) dissolved in benzene (20 cm^3) added slowly with stirring under nitrogen. After 18 h the colourless *product* was filtered off, recrystallised from benzene, washed with diethyl ether, and dried *in vacuo* (yield 75%) (Found: C, 64·1; H, 5·15; Cu, 12·3. Calc. for $C_{28}H_{27}CuO_2P_2$: C, 64·6; H, 5·25; Cu, 12·2%).

Bis(*acetato*)*tris*[1,2-*bis*(*diphenylphosphino*)*ethane*]*dicopper*(I)–*benzene* (1/1). Copper(I) acetate (0·30 g) was added to a solution of the phosphine (2·63 g) in benzene (30 cm^3). The acetate dissolved and, on stirring under nitrogen, a colourless solid slowly formed. After 16 h the *product* was filtered off, washed with benzene and diethyl ether, and dried at room temperature *in vacuo* (yield 92%) (Found: C, 69·7; H, 5·60; Cu, 8·25. Calc. for $C_{88}H_{84}Cu_2O_4P_6$: C, 69·6; H, 5·60; Cu, 8·35%).

Bis(*acetato*)*tris*[1,2-*bis*(*diphenylphosphino*)*ethane*]*dicopper*(I). The benzene solvate was heated *in vacuo* at 110 °C for 24 h (Found: C, 68·2; H, 5·45; Cu, 8·70. Calc. for $C_{82}H_{78}Cu_2O_4P_6$: C, 68·4; H, 5·45; Cu, 8·80%).

Acetato[1,2-*bis*(*diphenylarsino*)*ethane*]*copper*(I). Copper(I) acetate (0·40 g) was added to a solution of the arsine (1·58 g) in diethyl ether (40 cm^3). After stirring under nitrogen for 18 h, the colourless *solid* was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 94%) (Found: C, 55·1; H, 4·50; Cu, 10·5. Calc. for $C_{28}H_{27}As_2CuO_2$: C, 55·2; H, 4·45; Cu, 10·4%).

Acetatobis[1,2-*bis*(*diphenylarsino*)*ethane*]*copper*(I). A similar method to that above using copper(I) acetate (0·19 g) and arsine (1·79 g) in diethyl ether (30 cm^3) gave a colourless *solid* (yield 87%) (Found: C, 59·2; H, 4·80; Cu, 6·05. Calc. for $C_{54}H_{51}As_4CuO_2$: C, 59·2; H, 4·70; Cu, 5·80%).

Acetatotris(*thiourea*)*copper*(I). (a) Anhydrous copper(II) acetate (5·0 g) was added to a saturated solution of thiourea (8·6 g) in ethanol (180 cm^3) and 2,2-dimethoxypropane (40 cm^3). Decolourisation of the solution was complete after stirring for 1 h under nitrogen. After filtration, diethyl ether (100 cm^3) was added to the filtrate to give a colourless *solid* which was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 85%) (Found: C, 17·3; H, 4·40; Cu, 18·1; N, 23·9; S, 27·1. Calc. for $C_5H_{15}CuN_6O_2S_3$: C, 17·1; H, 4·30; Cu, 18·1; N, 23·9; S, 27·4%).

(b) Copper(I) acetate (0·39 g) was added to a solution of thiourea (2·24 g) in 2,2-dimethoxypropane (40 cm^3). The resulting solution was filtered and diethyl ether (100 cm^3) added to the filtrate to give a colourless *solid* subsequently treated as in (a), (yield 87%) (Found: C, 17·0; H, 4·40; Cu, 17·9; N, 24·2%).

Acetatobis(*imidazolidine-2-thione*)*copper*(I). Copper(I) acetate (0·26 g) was added to a stirred solution of the thione (0·82 g) in *NN*-dimethylformamide (30 cm^3) under nitrogen. After the initial grey colouration cleared a colourless solid slowly formed. This was filtered off, washed with diethyl ether, and dried *in vacuo*. Copper analysis and an i.r. spectrum suggested that this solid was not the expected product, but may have been impure acetato(*NN*-dimethylformamide)copper(I) (Found: Cu, 33·6. Calc. for $C_5H_{10}CuNO_3$: Cu, 32·5%). It was not examined further. Diethyl ether (40 cm^3) was added to the filtrate and the resulting colourless *precipitate* filtered off, washed with diethyl ether, and dried *in vacuo* (Found: C, 29·1; H, 4·70; Cu, 19·3; N, 17·2. Calc. for $C_6H_{15}CuN_4O_2S_2$: C, 29·4; H, 4·65; Cu, 19·4; N 17·1%).

Bis(*acetato*)(2,5-*dithiahexane*)*dicopper*(I). Copper(I) acetate (0·36 g) was added to 2,5-dithiahexane (1·24 g) in diethyl ether (20 cm^3) and benzene (5 cm^3). After stirring under nitrogen for 1 h the very air-sensitive colourless *precipitate* was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 70%) (Found: C, 26·5; H, 5·10; Cu, 34·8; S, 17·5. Calc. for $C_8H_{16}Cu_2O_4S_2$: C, 26·2; H, 4·40; Cu, 34·6; S, 17·5%).

Acetatotris(*selenourea*)*copper*(I). Copper(I) acetate (0·31 g) was added to a solution of selenourea (1·26 g) in ethanol (100 cm^3), with the exclusion of light. The acetate dissolved and a light-sensitive colourless *solid* slowly precipitated. This was then filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* with the exclusion of light (yield 83%) (Found: C, 12·3; H, 3·10; Cu, 13·0; N, 16·4. Calc. for $C_5H_{15}CuN_6O_2Se_3$: C, 12·2; H, 3·10; Cu, 12·9; N, 17·1%).

Bis(*acetato*)(2,2′-*bipyridyl*)*dicopper*(I). Anhydrous 2,2′-bipyridyl (1·0 g) was dissolved in diethyl ether (25 cm^3) and copper(I) acetate (0·29 g) added. A black solid formed immediately and the mixture was stirred for 16 h. The air-sensitive *solid*, by this time dark brown in colour, was filtered off under nitrogen, washed with diethyl ether, and dried *in vacuo* (yield 80%) (Found: C, 41·3; H, 3·70; Cu, 29·3; N, 7·20. Calc. for $C_{14}H_{14}Cu_2N_2O_4$: C, 41·9; H, 3·50; Cu, 31·7; N, 7·00%).

Acetato(1,10-*phenanthroline*)*copper*(I). A suspension of copper(I) acetate (0·45 g) in benzene (10 cm^3) was added to a solution of anhydrous 1,10-phenanthroline (2·40 g) in benzene (30 cm^3). A dark purple solid formed immediately and the reaction mixture was then stirred for 6 d under nitrogen. After 3 d the colour of the solid had changed to brick-red. The air-sensitive *solid* was filtered off, washed with benzene, and dried *in vacuo* (yield 90%) (Found: C, 55·4; H, 3·65; Cu, 20·0; N, 9·20. Calc. for $C_{14}H_{11}CuN_2O_2$: C, 55·5; H, 3·65; Cu, 21·0; N, 9·25%).

Acetato(2,9-*dimethyl*-1,10-*phenanthroline*)*copper*(I). Copper(I) acetate (0·26 g) was added to a solution of 2,9-dimethyl-1,10-phenanthroline (0·97 g) in benzene (25 cm^3). After stirring under nitrogen for 18 h the air-stable bright red solid was filtered off, recrystallised from benzene, and dried *in vacuo* (yield 70%) (Found: C, 57·6; H, 5·35; N, 8·55. Calc. for $C_{16}H_{15}CuN_2O_2$: C, 58·1; H, 4·55; N, 8·45%).

RESULTS AND DISCUSSION

Several types of complexes of copper(I) acetate with σ-donor ligands were isolated. With unidentate ligands the types $[Cu(O_2CMe)L_2]$ (L = PPh_3 and etu *) and $[Cu(O_2CMe)L_3]$ (L = tu and su) were found. With potentially bidentate ligands the types $[Cu(O_2CMe)B]$ (B = dppm, dppe, dpae, phen, and 2,9-Me_2phen), $[Cu(O_2CMe)(dpae)_2]$, $[\{Cu(O_2CMe)\}_2B_3]$ (B = dppe and its benzene solvate), and $[\{Cu(O_2CMe)\}B]$ (B = dth and bipy) were found. All the complexes are diamagnetic and also colourless except for the bidentate nitrogen-donor complexes which are deeply coloured, presumably due to copper→ligand π* or ligand π→π* transitions appearing in the visible region. A few other reactions of copper(I) acetate with σ-donor ligands were attempted, but did not

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* etu = Imidazolidine-2-thione (ethylenethiourea); tu = thiourea; su = selenourea; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; 1,2-dpae = 1,2-bis(diphenylarsino)ethane; phen = 1,10-phenanthroline; 2,9-Me_2phen = 2,9-dimethyl-1,10-phenanthroline; dth = 2,5-dithiahexane; and bipy = 2,2′-bipyridyl.

lead to desired products. With bis(diethylphosphino) disulphide the major product appeared to be copper(I) sulphide, with triphenylphosphine oxide oxidation to copper(II) occurred, and little or no reaction was evident with triphenylantimony, dimethyl sulphoxide, or 1,2-dicyanoethane.

TABLE 1

Molecular-weight and conductivity results

Complex	*M* Found	*M* Calc. for monomer	Conductivity Λ/S cm^2 mol^{-1} (10^{-3}M-solutions, 25 °C) ^{a}
$[Cu(O_2CMe)(PPh_3)_2]$	623,^{b} 686 ^{c}	647	3·9 ^{d}
$[Cu(O_2CMe)(etu)_2]$			<1 ^{e}
$[Cu(O_2CMe)(tu)_3]$			<1 ^{e}
$[Cu(O_2CMe)(su)_3]$			<1 ^{e}
$[Cu(O_2CMe)(dppm)]$	740,^{b} 541 ^{c}	507	22·5,^{d} 57·5,^{f} 26·5 ^{g}
$[Cu(O_2CMe)(dppe)]$	1 008,^{c} 973 ^{h}	521	15·8,^{d} 17·2 ^{g}
$[Cu(O_2CMe)(dpae)]$	1 263,^{c} 1 355 ^{h}	609	10·5,^{d} 10·1,^{f} 0·4 ^{g}
$[Cu(O_2CMe)(dpae)_2]$	1 135,^{c} 979 ^{h}	1 095	16·5,^{d} 13·1,^{f} 0·5 ^{g}
$[\{Cu(O_2CMe)\}_2(dppe)_3]$	910 ^{h}	1 440	75·5,^{d} 153·0,^{f,i} 64·5 ^{g}

^{a} Ranges for 1 : 1 electrolytes: MeCN 120—160; $MeNO_2$ 75—95; dmf 65—90; and dmso 25—65 S cm^2 mol^{-1} at 10^{-3}M concentration. ^{b} In C_6H_6. ^{c} In 1,2-dibromoethane. ^{d} In $MeNO_2$. ^{e} In dmso. ^{f} In MeCN. ^{g} In dmf. ^{h} In $CHBr_3$. ^{i} 6·0 × 10^{-4}M-Solution.

TABLE 2

I.r. spectra (cm^{-1})

Complex	Medium	$\nu_{asym}(CO_2)$ ^{a}	$\nu_{sym}(CO_2)$ ^{a}	Δ	ν(CuO)	ν (CuL)
$[Cu(O_2CMe)(PPh_3)_2]$	Mull	1 552	1 421	131	256m, 217m	144ms, 139ms
	$C_2H_4Br_2$	1 556	1 413	143		
	C_6H_6	1 554	1 418	136		
$[Cu(O_2CMe)(etu)_2]$ ^{b}	Mull	1 556	1 402	154		210(sh), 190vs, 186vs
$[Cu(O_2CMe)(tu)_3]$ ^{c}	Mull	1 541	1 395	146	248w	208s, 198, 193s, d
$[Cu(O_2CMe)(su)_3]$ ^{d}	Mull	1 548	1 392	156		186, 181s, d
$[Cu(O_2CMe)(dppm)]$	Mull	1 594	1 394	200	273m, 220m	149s, 125m
	$CHCl_3$	1 574, 1 554	1 395	179, 159		
	C_6H_6	1 581, 1 566	1 410	171, 156		
$[Cu(O_2CMe)(dppe)]$	Mull	1 598	1 411	187	286m, 254s	166m, 132s
	$CHCl_3$	1 584	1 417	167		
	$C_2H_4Br_2$	1 582	1 412	170		
$[Cu(O_2CMe)(dpae)]$	Mull	1 590	1 414	176	269m, 237m	139s, 114s
	$CHCl_3$	1 582	1 417	165		
$[Cu(O_2CMe)(2,9\text{-}Me_2phen)]$	Mull	1 556	1 395	161	237(sh)	278w
$[Cu(O_2CMe)(phen)]$	Mull	1 574	1 380	194	265w, 215(sh)	283m
$[Cu(O_2CMe)(dpae)_2]$	Mull	1 592	1 375	217	273s, 244m	112s
	$CHCl_3$	1 582	1 382	200		
$[\{Cu(O_2CMe)\}_2(dppe)_3]$	Mull	1 606	1 372	234	256m	144m, 127s
	$CHCl_3$	1 577	1 415	162		
$[\{Cu(O_2CMe)\}_2(dppe)_3]\cdot C_6H_6$	Mull	1 598	1 373	225		
$[\{Cu(O_2CMe)\}_2(dth)]$	Mull	1 567	1 380	187	261m	207w
$[\{Cu(O_2CMe)\}_2(bipy)]$	Mull	1 573	1 372	201	251m, 241m	276w

^{a} Very strong bands. ^{b} $\delta(CuS_2)$ at 120m cm^{-1}. ^{c} δ(CuSC) at 168s, $\delta(CuS_2)$ at 127s cm^{-1}. ^{d} δ(CuSeC) at 142mw, $\delta(CuSe_2)$ at 105w and 98w cm^{-1}.

Unidentate Ligands.—The complex $[Cu(O_2CMe)(PPh_3)_2]$, prepared in this work by direct reaction of the acetate with the phosphine in toluene, has previously been prepared [7,8] by two indirect routes. It is monomeric and non-ionic both in the solid state and in a range of organic solvents, as shown (Table 1) by molecular-weight determinations in benzene and 1,2-dibromoethane and a conductivity measurement in nitromethane. The solid-state i.r. spectrum (Table 2) shows the separation, Δ, of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ to be 131 cm^{-1}, a reasonable value for the presence of a chelating acetate group [*cf.* Δ 120 cm^{-1} for the symmetrically chelating acetates in $Zn(O_2CMe)_2\cdot 2H_2O$]. Retention of this structure in solution is also indicated by the positions of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ in benzene and 1,2-dibromoethane solution spectra. The absence of dissociation–association phenomena so characteristic [14,15] of solutions of phosphine complexes of copper(I) is further indicated by the simple ^1H n.m.r. spectrum obtained in $CDCl_3$. The complex $[Cu(O_2CMe)(PPh_3)_2]$ is a further example of a well-established series of distorted tetrahedral $[CuX(PPh_3)_2]$ complexes where X is a chelating monoanion. Using the generalisations of Lippard and Palenik,[16] it is to be expected that the P–Cu–P angle will be greater than 109·5° due to the packing of unequally bulky ligands around the spherical copper(I) ion, and should be similar to that of $[Cu(NO_3)(PPh_3)_2]$ (131·2°),[17] this angle being the largest found in the series investigated. This prediction is based on the concept that the angles are largest for planar X groups and decrease as the non-planarity and general crowding of the X ligand increases. In order to test this postulate we intend to determine the crystal structure of the acetato-complex. [Preliminary results show the crystals to be monoclinic, $M = 647\cdot1$, $a = 18\cdot092$, $b = 11\cdot099$, $c = 19\cdot378$ Å, $\beta = 122\cdot43°$, $U = 3279\cdot7$ Å^3, $Z = 4$. Systematic absences: $h0l$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$), space group $P2_1/a$.]

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Discussion of the far-i.r. spectrum is difficult since any discussion based on local C_{2v} symmetry ignores both the distortion suggested above and the possible coupling of ν(Cu–O) modes with both internal carboxylate modes and with ν(Cu–P) modes. There is a lack of information on such vibrations apart from ν(Cu–P) of $[\{MeC(CH_2O)_3P\}_4Cu][ClO_4]$ [18] found at 132 cm^{-1}, and the skeletal frequencies of copper(I) acetate itself observed [19] at 381, 374(sh), 242, 190, 178, and 122 cm^{-1}. The ν(Cu–O) and ν(Cu–L) assignments in Table 2 for this and all other complexes should therefore be regarded as no more than tentative, but reasonable in the light of the above and similar comparisons and considerations.

TABLE 3

^1H N.m.r. spectra (τ values)

Complex	Solvent	$MeCO_2$ Protons	Ph Protons *	Other resonances
$[Cu(O_2CMe)(PPh_3)_2]$	$CDCl_3$	7·87	2·77	
$[Cu(O_2CMe)(etu)_2]$	$(D_3C)_2SO$	7·92		6·42(CH_2), 1·53(NH)
$[Cu(O_2CMe)(tu)_3]$	$(D_3C)_2SO$	8·25		2·20(NH_2)
$[Cu(O_2CMe)(su)_3]$	$(D_3C)_2SO$	8·19		1·99(NH_2)
$[Cu(O_2CMe)(dppm)]$	$CDCl_3$	7·90	2·90	6·82(CH_2)
$[Cu(O_3CMe)(dppe)]$	$CDCl_3$	n.o.	2·69, 2·78	7·69(C_2H_4)
	CS_2	8·15	2·80, 2·97	7·81(C_2H_4)
$[Cu(O_2CMe)(dpae)]$	$CDCl_3$	n.o.	2·78, 2·83	7·75(C_2H_4)
	CS_2	8·16	2·87	7·96(C_2H_4)
$[Cu(O_2CMe)(dpae)_2]$	$CDCl_3$	n.o.	2·80	7·68(C_2H_4)
	CS_2	8·15	2·86	8·00(C_2H_4)
$[\{Cu(O_2CMe)\}_2(dppe)_3]$	$CDCl_3$	8·06	2·74, 2·78, 2·83	7·64(C_2H_4)
$[\{Cu(O_2CMe)\}_2(dppe)_3]\cdot C_6H_6$	$CDCl_3$	8·06	2·75, 2·78, 2·85	7·66(C_2H_4), 2·68(C_6H_6)

* Often a complex splitting; absorption maxima only given. n.o. = Not observed.

Investigation of the vapour phase of $[Cu(O_2CMe)(PPh_3)_2]$ by mass spectrometry required a high source temperature and this led to some thermal decomposition with the appearance of ions originating from both copper(I) acetate [13] and triphenylphosphine.[20] However, the copper-containing base peak was $[Cu(PPh_3)]^+$ (*m/e* 325 based on ^{63}Cu). Although the molecular ion was not detected, the observation of a monocopper ion at *m/e* 567 (relative intensity 0·1) indicates that $[Cu(O_2CMe)(PPh_3)_2]$ fragments to $[Cu(O_2CMe)(PPh_3)\{P(C_6H_4)_2\}]^+$, presumably containing a co-ordinated 9-phosphafluorenylium cation.[20] Other copper-containing ions of relative intensities of 1 and above detected include $[Cu(PPh_3)_2]^+$, $[Cu(O_2CMe)(PPh_3)]^+$, and $[Cu(OPPh_3)]^+$. Fragmentation of acetate and triphenylphosphine groups appear to be competitive processes.

It is likely that $[Cu(O_2CMe)(etu)_2]$ is similarly four-co-ordinate, the i.r. Δ value being reasonable for a chelating acetate group, although the presence of strong ligand bands in the same region as $\nu_{asym}(CO_2)$ makes this assignment less certain than for the phosphine complex. The very low solubility of the complex in a variety of organic solvents limited its characterisation to showing non-electrolyte behaviour in dimethyl sulphoxide. The far-i.r. spectrum was assigned by analogy with the results of Adams and Cornell,[21] the 340 cm^{-1} ligand band being observed as a well resolved doublet at 364 and 356 cm^{-1} in the complex. A ligand band is also likely to be found in the region of the bands assigned to ν(Cu–S).

The complexes $[Cu(O_2CMe)(tu)_3]$ and $[Cu(O_2CMe)(su)_3]$ would also be expected to be four-co-ordinate, but the i.r. Δ values of 146 and 156 cm^{-1} respectively are remarkably small for unidentate acetato-groups {*cf.* $[Cu(O_2CMe)(PPh_3)_3]$,[7] Δ 202 cm^{-1}}. Intramolecular hydrogen bonding between the oxygen of the unco-ordinated carbonyl group and the ligand amino-groups is probably responsible for these small Δ values, intermolecular hydrogen bonding also being possible. A similar effect has been observed for $[Ni(O_2CMe)_2(H_2O)_4]$ [22] (Δ 125 cm^{-1}). Co-ordination of the ligands through the Group 6 donor atom is indicated [23] by a lowering of the frequency of the thiourea band [mainly ν(C=S)] from 732 to 717 cm^{-1} and a similar effect on the 645 and 394 cm^{-1} bands of selenourea, these bands being shifted to 635 and 630 (doublet) and 389 cm^{-1}. The assignments of ν(Cu–E), δ(Cu–E–C), and δ(CuE_2) (E = S or Se) are in the ranges previously suggested for metal–thiourea [21] and metal–selenourea [23] complexes, but there is little directly comparable information available on other copper(I)–thiourea or –selenourea [24] complexes. Lack of solubility of the two complexes restricted measurements to dimethyl sulphoxide solutions in which the complexes were non-electrolytes and by n.m.r. showed no evidence of dissociation. Attempts to obtain mass spectra of these, or indeed of all copper(I) acetate–sulphur- or –nitrogen-donor complexes isolated, failed to give spectra showing copper-containing ions.

Bidentate Ligands.—(a) 1 : 1 *Complexes*. The molecular weight of $[Cu(O_2CMe)(dppm)]$ in benzene is somewhat less than that of a dimer, whilst that in 1,2-dibromoethane is only slightly above that of a monomer. Conductivity results in three solvents were indicative of the presence of ions, but were very much lower than those expected for a 1 : 1 electrolyte. These features suggest that $[Cu(O_2CMe)(dppm)]$ is at least dimeric but undergoes solvent-dependent dissociation in solution. This is in line with the solution behaviour of many discrete solid copper(I)–phosphine complexes,[14,15] several solution species often being simultaneously formed in solvents of low polarity. Dissociation usually results in the liberation of ligand, but for $[Cu(O_2CMe)(dppm)]$ the conductivity results imply the formation of at least some acetate ions in solution. The 1 : 1 copper(I) halide–dppm com-

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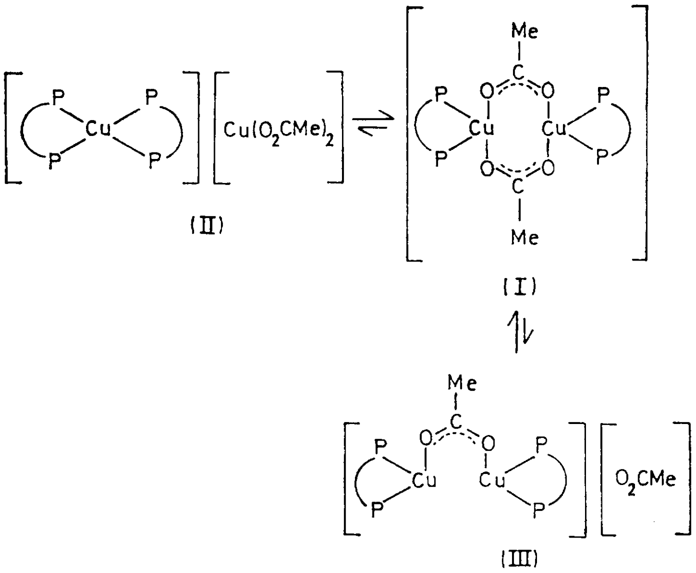
plexes are thought[25] to ionise in dichloroethane by process (1).

$$[\mathrm{CuX(dppm)}]_4 \rightleftharpoons 2[\mathrm{Cu(dppm)_2}][\mathrm{CuX_2}] \quad (1)$$

The high-i.r. $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ position of the solid and larger Δ value compared to that of $[\mathrm{Cu(O_2CMe)(PPh_3)_2}]$ suggests[26] that the solid complex contains bridging acetate, structure (I) being reasonable. Solution i.r. spectra in benzene and chloroform had two bands in the $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ region, again indicative of dissociation, but the n.m.r. spectrum in $\mathrm{CDCl_3}$ showed only one environment for the acetate groups, perhaps favouring the formation of an equilibrium concentration of (II) even though migration of a dppm molecule is required. Alternatively rapid exchange may prevent the detection of individual acetate-proton signals in which case (III) is a further possible dissociation product, the three-co-ordinate copper atoms probably being further solvated in the polar solvents used for conductance studies. The n.m.r. spectrum indicated that the dppm ligands are bidentate, but, as for the copper(I) halide–dppm complexes,[25] the splitting of the methylene-protons signal by interaction with the two equivalent ^{31}P nuclei was not evident. The presence of bridging acetate rests only on i.r. evidence and the alternative formulation of chelating acetate and bridging dppm {as found[27] for $[(\mathrm{CuI})_2(\mathrm{dppm})]$ and $[(\mathrm{CuCl})_2(\mathrm{dppm})]\cdot 0\cdot 25\mathrm{C_2H_4Cl_2}$}, which would relieve the strained $\overline{\mathrm{CuPCP}}$ rings, should not be conclusively ruled out.



(II)

(I)

(III)

The molecular-weight results for $[\mathrm{Cu(O_2CMe)(dppe)}]$ in bromoform and 1,2-dibromoethane were slightly below those required for a dimer, the conductivity results suggesting slight ionic dissociation of such a dimer. The $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ frequencies changed but slightly from the solid state to solution, suggesting no major change of structure in solution. The Δ values are reasonable for a structure of type (I). A resonance peak for the acetate protons was not found in the n.m.r. spectrum in $\mathrm{CDCl_3}$, there merely being a gradual increase in absorption between τ 7 and 9, apart from the observation of the $\mathrm{CH_2CH_2}$ peak. A similar effect was found for both $[\mathrm{Cu(O_2CMe)(dpae)}]$ and $[\mathrm{Cu(O_2CMe)(dpae)_2}]$ in $\mathrm{CDCl_3}$, yet in $\mathrm{CS_2}$ the precise resonance position of the acetate protons was easily found. The mass spectrum of $[\mathrm{Cu(O_2CMe)(dppe)}]$ provided some evidence in favour of a dimeric structure. The spectrum showed many ions due to ligand[28] and copper(I) acetate fragmentations, so thermal decomposition may accompany fragmentation by electron bombardment in the spectrometer. However, as the ratio of copper–phosphorus to other copper-fragment ions was reasonably constant for several runs carried out under different conditions, we believe some vaporisation of the discrete complex can occur. Considering only copper-containing ions, the base peak is $[\mathrm{Cu_2(O_2CMe)}]^+$ (*m/e* 185) and the most significant ion detected favouring a dimeric formulation was $[\mathrm{Cu_2(O_2CMe)_2(dppe)}]^+$ (*m/e* 642, rel. intensity 1·1). Other copper–phosphorus-containing ions detected with relative intensities greater than 5 include $[\mathrm{Cu(dppe)(Ph_2P{=}CH_2)}]^+$, $[\mathrm{Cu(O_2CMe)(dppe)}]^+$, $[\mathrm{Cu(O_2CMe)(PPh_2)_2}]^+$, $[\mathrm{Cu(dppe)}]^+$, $[\mathrm{Cu(PPh_2)_2}]^+$, $[\mathrm{Cu(PPh_3)}]^+$, $[\mathrm{Cu(O_2CMe)(PPh_2)}]^+$, $[\mathrm{Cu(PPh_2)}]^+$, and $[\mathrm{CuP}]^+$. The detection of $[\mathrm{Cu(PPh_3)}]^+$ shows that a 1,3-phenyl migration can occur on fragmentation, a process previously observed for the free ligand.[28] The fragmentations (2) and (3) are

$$[\mathrm{Cu(O_2CMe)(dppe)}]^+ \longrightarrow [\mathrm{Cu(O_2CMe)(PPh_2)_2}]^+ + \mathrm{C_2H_4} \quad (2)$$

$$[\mathrm{Cu(dppe)}]^+ \longrightarrow [\mathrm{Cu(PPh_2)_2}]^+ + \mathrm{C_2H_4} \quad (3)$$

supported by the detection of the appropriate metastable peaks. The complex $[\mathrm{Cu(O_2CMe)(dpae)}]$ was the least stable of all the arsenic- and phosphorus-donor complexes towards oxidation and hydrolysis. However, the evidence available (see Tables) points to an analogous structure to that suggested for $[\mathrm{Cu(O_2CMe)(dppe)}]$.

The complex $[\mathrm{Cu(O_2CMe)(2,9\text{-}Me_2phen)}]$ has previously been prepared[7] by ligand exchange from $[\mathrm{Cu(O_2CMe)(PPh_3)_2}]$ and was assigned a dimeric structure of type (I). The $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ was reported at 1 363 cm^{-1} leading to a Δ value of 199 cm^{-1}, but we find this mode at 1 395 cm^{-1} with Δ 161 cm^{-1}. Whilst this complex is quite air stable, we find $[\mathrm{Cu(O_2CMe)(phen)}]$, isolated for the first time in this work, to be extremely air sensitive. Although a dark purple solid formed immediately on treating the acetate with phen in benzene, a stoicheiometric product was only reached after at least 3 d reaction time. The air sensitivity and insolubility of the complex hindered its full characterisation, but an analogous structure to that of $[\mathrm{Cu(O_2CMe)(2,9\text{-}Me_2phen)}]$ seems reasonable.

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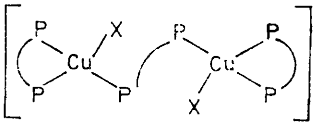
(b) 1 : 2 *Complexes.* Only [Cu(O_2CMe)(dpae)$_2$] of this stoicheiometry was isolated and the evidence available does not allow a unique structural assignment. The molecular-weight determinations were indicative of the presence of a monomer, and the conductivity results suggest only a slight tendency towards ionic dissociation in polar solvents. The mull-i.r. Δ value was significantly greater than that found for either [Cu(O_2CMe)(dpae)] or even [Cu(O_2CMe)(PPh$_3$)$_3$],[7] suggesting the presence of a unidentate acetate group. The formation of a four-co-ordinate monomer would thus require the presence of one bidentate and one unidentate dpae ligand; alternatively, a three-co-ordinate monomer would have both dpae ligands unidentate. However, no splitting of the methylene-proton signal could be found in the ^{1}H n.m.r. spectra of the complex in either $CDCl_3$ or CS_2. Perhaps rapid interchange of bonded and non-bonded arsenic atoms on the n.m.r. time scale at room temperature prevents the observation of separate methylene-proton signals.

(c) 2 : 3 *Complexes.* This stoicheiometry, found in this work for [{Cu(O_2CMe)}$_2$(dppe)$_3$] and its benzene solvate, is quite common for copper(I)–dppe complexes. Marsich *et al.*[25] have prepared several [(CuX)$_2$(dppe)$_3$] complexes (X = halogen), such complexes often retaining solvent of crystallisation. Crystal-structure determinations have shown that where X = azido,[29] 5-perfluoromethyltetrazolato,[30] and chloro[31] the centrosymmetric structure (IV) is present.



(IV)

The complex [{Cu(O_2CMe)}$_2$(dppe)$_3$] was precipitated from benzene solution as a 1 : 1 benzene solvate, the benzene only being completely removed by pumping *in vacuo* for 24 h at 110 °C. The large mull-i.r. Δ value of 234 cm^{-1} (225 cm^{-1} for the solvate) is good evidence for the presence of only unidentate acetate groups and so this complex is thought to be a further example of type (IV). The complexes [(CuX)$_2$(dppa)$_3$] [X = uninegative unidentate group; dppa = 1,2-bis(diphenylphosphino)-acetylene] are thought to possess an alternative structure in which all three dppa ligands are bridging.[32] However, this is a consequence of the linear P–C≡C–P skeleton which precludes the possibility of chelation for this ligand. The solution-i.r. spectrum of [{Cu(O_2CMe)}$_2$-(dppe)$_3$] in chloroform indicates that structure (IV) does not persist in solution, Δ being reduced to 162 cm^{-1}. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ positions are very close to those of [Cu(O_2CMe)(dppe)], suggesting that the dissociation (4) occurs. Supporting evidence for such a dissociation is given by the molecular-weight determination in bromoform, an apparent molecular weight below that of the formula weight being obtained. However, the conductance results obtained in more polar solvents are in the ranges expected for 1 : 1 electrolytes, so alternative dissociation modes in these solutions may be (5) or, less likely since it involves migration of one acetate to the other copper atom, (6). Similar solvent-dependent dissociations have been noted before. For example,[33] conductance measurements show that [Cu(o-Et$_2$PC$_6$H$_4$-AsEt$_2$)Cl] is almost completely ionised in nitrobenzene, yet a molecular-weight determination in methyl ethyl ketone indicated that the complex was present as a dimer.

$$[\{Cu(O_2CMe)\}_2(dppe)_3] \rightleftharpoons [\{Cu(O_2CMe)(dppe)\}_2] + dppe \quad (4)$$

$$[\{Cu(O_2CMe)\}_2(dppe)_3] \rightleftharpoons [Cu_2(O_2CMe)(dppe)_3]^+ + MeCO_2^- \quad (5)$$

$$[\{Cu(O_2CMe)\}_2(dppe)_3] \rightleftharpoons [Cu(dppe)_2]^+ + [Cu(O_2CMe)_2]^- + dppe \quad (6)$$

The ^{1}H n.m.r. spectrum of the benzene solvate showed a very sharp resonance peak at τ 2·68 assignable to the benzene protons. Since the spectra of the complex and its benzene solvate were both recorded in $CDCl_3$, dissociation of the complex giving free dppe must have occurred, but no splitting of the CH_2CH_2 proton-resonance signal was observed. Perhaps rapid exchange of free and complexed dppe at room temperature is responsible. The mass spectrum of the unsolvated complex has [CuP]$^+$ as base peak and many of the ions detected for [Cu(O_2CMe)(dppe)] were observed again. In addition peaks due to [Cu(dppe)$_2$]$^+$, [{Cu(O_2CMe)}$_2$(dppe)(Ph$_2$P=CH$_2$)]$^+$, [Cu(PPh$_2$)$_2$(Ph$_2$PCH=CH$_2$)]$^+$, and [Cu$_2$(PPh$_2$)$_2$]$^+$ were also detected in relative intensities between 2·0 and 53. The two metastable peaks associated with the two fragmentations involving loss of CH_2CH_2 mentioned for [Cu(O_2CMe)(dppe)] were also observed for [{Cu(O_2CMe)}$_2$-(dppe)$_3$].

(d) 2 : 1 *Complexes.* The complexes [{Cu(O_2CMe)}$_2$-(dth)] and [{Cu(O_2CMe)}$_2$(bipy)] were prepared and, although readily formed, both proved to be very difficult to handle, being rapidly oxidised on exposure to air. Reliable solution measurements could not be obtained, assignment of reasonable structures resting with an interpretation of solid-state i.r. data.

In the gaseous and liquid states 2,5-dithiahexane exists as a mixture of *trans*- and *gauche*-conformers (considering only free rotation about the C–C bond; if the C–S bonds are also considered ten isomers are possible). In a complex, 2,5-dithiahexane usually assumes the *gauche*-form since this enables chelation to occur. More rarely, the ligand assumes the *trans*-form to allow a bridging arrange-

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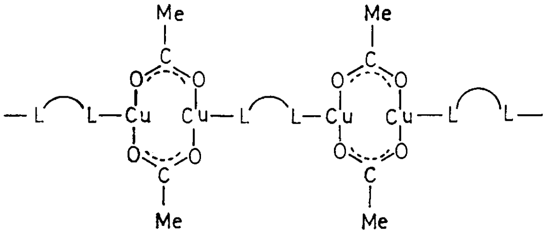
ment, for example [34] in $[Re_3Cl_9(dth)_{1\cdot5}]$. I.r. spectroscopy can be used [34] to detect the presence of a particular conformer in a complex. Bands at 1 206 [CH_2(wag)], 1 134 [CH_2(twist)], 738 (C–S stretch and CH_2 rock), and 686 cm^{-1} (C–S stretch) in the free ligand have been assigned [35] to vibrational modes exclusively associated with the *trans*-conformer. The complex $[\{Cu(O_2CMe)\}_2(dth)]$ exhibited these bands at 1 215, 1 138, 734, 718, and 681 cm^{-1}, so the *trans*-conformer is certainly stabilised in this complex. The Δ value is of a magnitude to suggest the presence of bridging acetate groups, so the polymeric structure (V) is in agreement with these features.



(V)

Although bipy conventionally acts as a chelating ligand, rotation about the ring-linking C–C bond enables the ligand to adopt a bridging co-ordination. Although no crystal-structure determinations have shown such a role for this ligand in a complex, the free ligand adopts this *trans*-planar conformation,[36] and a bridging function has been suggested in several complexes, for example [37] $[\{ZrCl_3\}_2(bipy)_3]$. We suggest structure (V) is therefore also appropriate for $[\{Cu(O_2CMe)\}_2(bipy)]$. Even using a large excess of bipy and a reaction time of 10 d this stoicheiometry is not exceeded. It is interesting to note that phen and 2,9-Me_2phen, which are unable to act in a bridging manner, only form 1 : 1 complexes with copper(I) acetate. Assignment of $\nu_{asym}(CO_2)$ for $[\{Cu(O_2CMe)\}_2(bipy)]$ is made difficult by the presence of ligand bands in the same region. The free ligand has bands at 1 582 and 1 555 but on co-ordination these shift to higher frequencies. In the present complex the ligand bands were found at 1 615 and 1 597 cm^{-1} leaving the band at 1 573 cm^{-1} to be assigned to $\nu_{asym}(CO_2)$.

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