Synthesis, Spectroscopic Characterization, and Magnetic Properties of a Mixed-valence Copper(I,II) Acetato Complex with Triphenylphosphine. Crystal Structure of Hexa-μ-acetato-tetrakis(triphenylphosphine)tetracopper(I,II)†

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Copper(II) acetate reacts with triphenylphosphine, in ethanol solution, in a manner depending on the concentration of $Cu(O_2CMe)_2$, the molar ratio of PPh_3 to Cu^{II}, and temperature, to form the copper(I) complex $[Cu(O_2CMe)(PPh_3)_n]$ (*n* = 2 or 3), the copper(II) complex $[Cu_2(O_2CMe)_4(PPh_3)_2]$, and the mixed-valence copper(I,II) complex $[Cu_4(O_2CMe)_6(PPh_3)_4]$. The pale blue-green complex $[Cu_4(O_2CMe)_6(PPh_3)_4]$ has been characterized by microanalysis, electronic, i.r., and e.s.r. spectra, and magnetic susceptibility measurements. The crystal and molecular structure of $[Cu_4(O_2CMe)_6(PPh_3)_4]$ has been determined from *X*-ray diffractometer data by the heavy-atom method and refined by full-matrix least-squares methods to $R = 0.0565$ for 2 227 reflections. Crystals are triclinic, space group $P\bar{1}$, with $a = 10.898(8)$, $b = 12.850(4)$, $c = 19.877(8)$ Å, $\alpha = 121.03(2)$, $\beta = 90.14(5)$, $\gamma = 117.98(4)°$, and $Z = 1$. The crystal structure comprises centrosymmetrical molecules of $[Cu_4(O_2CMe)_6(PPh_3)_4]$. Each molecule consists of a $Cu_2(O_2CMe)_4$ dimeric unit in the axial positions to which two molecular $Cu(O_2CMe)(PPh_3)_2$ ligands are co-ordinated through the oxygen atom of each acetate group.

Reduction of copper(II) to copper(I) by triphenyphosphine[1–6] leading to the formation of relatively stable complexes has been used frequently for the synthesis of copper(I) triphenylphosphine complexes.[1] The copper(I) complexes $[CuY(PPh_3)_n]$ (*n* = 2 or 3, Y = carboxylate anion or half dicarboxylate anion) were prepared in accordance with that procedure.[2] In spite of the reducing influence of PPh_3 the copper(II) complexes $[Cu(O_2CR)_2(PPh_3)]$ [R = CH_2CHCH_2,[7] $CH_2CH(CH_2)_2$,[7] Bu^t,[8] or Me[9]] and $[CuY(PPh_3)]$ [Y = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioate(2−)[10]] could also be prepared.

By reaction of copper(II) acetate with PPh_3 under various reaction conditions we have recently synthesized[11] acetato copper(II) and mixed-valence acetato copper(I,II) complexes with PPh_3: $[Cu_2(O_2CMe)_4(PPh_3)_2]$ and $[Cu_4(O_2CMe)_6(PPh_3)_4]$, respectively. Both the conditions of their syntheses[11] and their properties[9,12] showed a significant role of the dimeric structure of copper(II) acetate in solution and in solid state in the prevention of reduction and in the stabilization[13] of copper(II) relative to copper(I). The properties of other previously described[7,8,11] copper(II) carboxylate complexes with PPh_3 are consistent also with this observation.[13]

Since the dimeric structure unit of copper(II) carboxylates exhibits interesting chemical and structural features, we decided to solve the crystal and molecular structure of both complexes $[Cu_2(O_2CMe)_4(PPh_3)_2]$ and $[Cu_4(O_2CMe)_6(PPh_3)_4]$. The results of the *X*-ray structure determination of the latter complex together with its synthesis, spectroscopic characterization, and magnetic properties are presented in this paper. A brief preliminary report of this structure has appeared.[14]

Results and Discussion

Structure of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—The final fractional positional co-ordinates of the non-hydrogen atoms are listed in Table 1. The crystal structure of $[Cu_4(O_2CMe)_6(PPh_3)_4]$ (**1**) consists of molecules held together by van der Waals interactions and weak hydrogen bonds. The molecular packing of (**1**) in the crystal structure is shown in Figure 1.

The structure of a molecule of (**1**) and the atomic numbering are shown in Figure 2 while the relevant interatomic distances and angles are presented in Table 2. The molecule of (**1**) is centrosymmetrical with the symmetry centre between the two copper(II) atoms Cu(1) and Cu(1′). Each molecule of (**1**) contains two copper atoms in oxidation state II, Cu(1) and Cu(1′), and two copper atoms Cu(2) and Cu(2′) in oxidation state I. The copper(II) atoms are bonded together by four bridging acetate groups thus forming the dimeric $Cu_2(O_2CMe)_4$ unit as in copper(II) acetate monohydrate.[15,16] Two molecules of triphenylphosphine and one acetate group are bonded to each copper(I) atom thus forming two molecular $Cu(O_2CMe)(PPh_3)_2$ ligands, which are bonded to the copper(II) atoms in the $Cu_2(O_2CMe)_4$ unit through the oxygen atoms O(1) and O(1′).

The copper(II) atoms in the structure of (**1**) have distorted square-pyramidal geometry. The basal plane of the copper(II) polyhedron is formed by four oxygen atoms O(3), O(4′), O(5), and O(6′) of the acetate groups of the $Cu_2(O_2CMe)_4$ unit. The copper(II) atom is displaced from the basal plane towards the apical oxygen atom by 0.211(2) Å. The apical oxygen atom O(1) is slightly displaced from the regular axial position and the Cu(1′)–Cu(1)–O(1) angle is 171.6(1)° (see also the torsion angles in Table 2).

The copper(I) atoms in the two $Cu(O_2CMe)(PPh_3)_2$ fragments serving as ligands in the structure of (**1**) have distorted tetrahedral co-ordination similar to that found[17] in the $[Cu(O_2CMe)(PPh_3)_2]$ complex. The Cu(2)–P and Cu(2)–O

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† *Supplementary data available* (No. SUP 56616, 8 pp.): H-atom co-ordinates, thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	984(1)	531(1)	666(1)	C(31)	1 561(8)	9 314(7)	4 709(4)
Cu(2)	1 549(1)	952(1)	2 686(1)	C(32)	794(7)	8 776(6)	3 891(4)
P(1)	804(2)	8 834(2)	2 490(1)	C(33)	1 445(6)	7 761(6)	1 758(3)
P(2)	1 118(2)	2 627(2)	3 555(1)	C(34)	1 850(7)	6 996(6)	1 898(4)
O(1)	2 314(4)	1 154(4)	1 752(2)	C(35)	2 348(8)	6 171(7)	1 311(4)
O(2)	3 963(4)	1 573(4)	2 638(2)	C(36)	2 424(8)	6 156(8)	611(4)
O(3)	338(4)	1 872(4)	1 250(2)	C(37)	2 030(8)	6 917(8)	479(4)
O(4)	8 666(4)	970(4)	137(2)	C(38)	1 502(7)	7 724(6)	1 046(3)
O(5)	2 384(4)	1 873(4)	420(2)	C(39)	9 166(6)	1 829(5)	3 320(3)
O(6)	714(4)	961(4)	9 300(2)	C(40)	8 324(6)	987(6)	2 474(3)
C(1)	3 568(6)	1 407(6)	1 978(3)	C(41)	6 823(7)	288(7)	2 220(4)
C(2)	4 560(6)	1 499(8)	1 465(4)	C(42)	6 063(7)	379(7)	2 793(4)
C(3)	9 374(6)	1 826(6)	902(3)	C(43)	6 885(7)	1 204(7)	3 626(4)
C(4)	8 964(8)	2 941(7)	1 434(4)	C(44)	8 402(6)	1 930(6)	3 896(4)
C(5)	1 981(6)	1 826(6)	9 803(3)	C(45)	1 816(6)	4 174(6)	3 504(3)
C(6)	3 150(6)	2 902(6)	9 677(4)	C(46)	1 016(7)	4 837(6)	3 654(4)
C(21)	8 865(6)	7 546(6)	2 225(3)	C(47)	1 639(8)	6 087(7)	3 645(4)
C(22)	8 253(6)	6 021(6)	1 723(3)	C(48)	2 950(8)	6 579(7)	3 484(4)
C(23)	6 782(7)	5 052(7)	1 516(4)	C(49)	3 749(8)	5 922(7)	3 340(4)
C(24)	5 856(7)	5 530(6)	1 806(4)	C(50)	3 165(7)	4 696(6)	3 350(4)
C(25)	6 454(6)	7 044(8)	2 304(4)	C(51)	1 810(6)	3 458(6)	4 663(3)
C(26)	7 946(6)	8 049(6)	2 515(3)	C(52)	2 216(8)	4 899(7)	5 273(4)
C(27)	1 643(6)	9 279(5)	3 477(3)	C(53)	2 754(9)	5 515(7)	6 121(4)
C(28)	3 148(6)	287(7)	3 828(3)	C(54)	2 857(7)	4 699(7)	6 339(4)
C(29)	3 883(7)	783(8)	4 623(4)	C(55)	2 458(8)	3 299(8)	5 748(4)
C(30)	3 043(7)	270(7)	5 047(4)	C(56)	1 905(8)	2 661(7)	4 897(4)

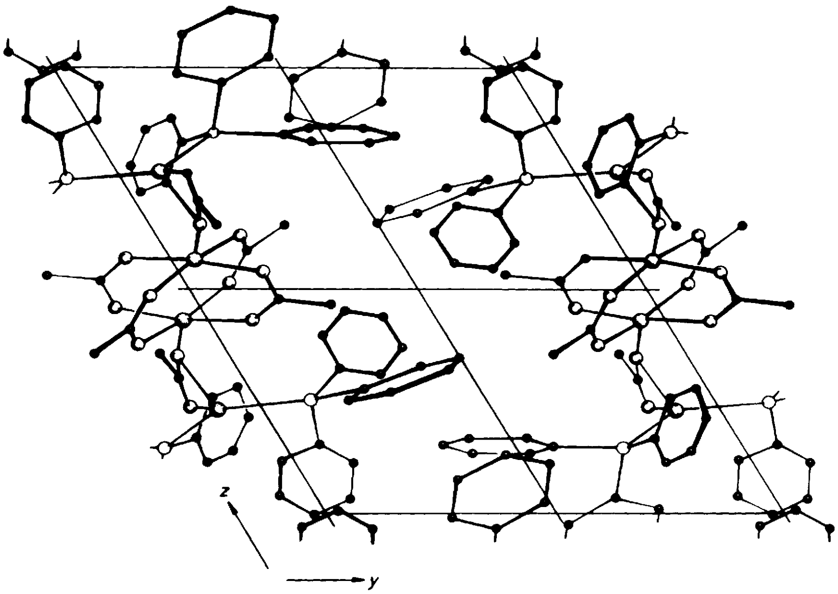


Figure 1. A perspective view of the molecular packing in the crystal of $[Cu_4(O_2CMe)_6(PPh_3)_4]$

bond lengths, 2.225(2), 2.249(2), and 2.124(4), 2.385(5) Å, respectively, in the $Cu(O_2CMe)(PPh_3)_2$ fragments of (**1**) are comparable with the values of 2.233(2), 2.240(3), and 2.162(5), 2.257(7) Å observed[17] in the structure of $[Cu(O_2CMe)(PPh_3)_2]$. Though for (**1**) the Cu(2)–O(2) distance is longer and the O(1)–Cu(2)–O(2) angle is smaller than the values found for $[Cu(O_2CMe)(PPh_3)_2]$,[17] the copper(I) co-ordination polyhedron can be regarded rather as distorted tetrahedral than as trigonal planar[17] (see also data for planes in SUP 56616).

A relationship between the Cu^{II}–O(apical) distances (average values) and the Cu^{II}–Cu^{II} separation in the dimeric $Cu_2(O_2CMe)_4$ unit is evident. The linear relationship (least-squares straight line, $r_{xy} = 0.998$ in Figure 3) has been found for those apical ligands which do not have an additional intramolecular interaction (points 1, 3, and 6) with the oxygen atoms of the acetate groups in the dimeric unit. As can be seen in Figure 3, points 2, 4, and 5 are below the straight line. They belong to the apical ligands which have the above mentioned additional interaction. The apical ligands MeOH (point 2)[18] and urea (point 4)[19] form hydrogen bonds with oxygen atoms of the dimeric unit. In $[\{Cu_3(O_2CMe)_5[P(OEt)_3]_2\}_n]$ (point 5), one of the four bridging acetate groups of the dimeric unit is bonded to

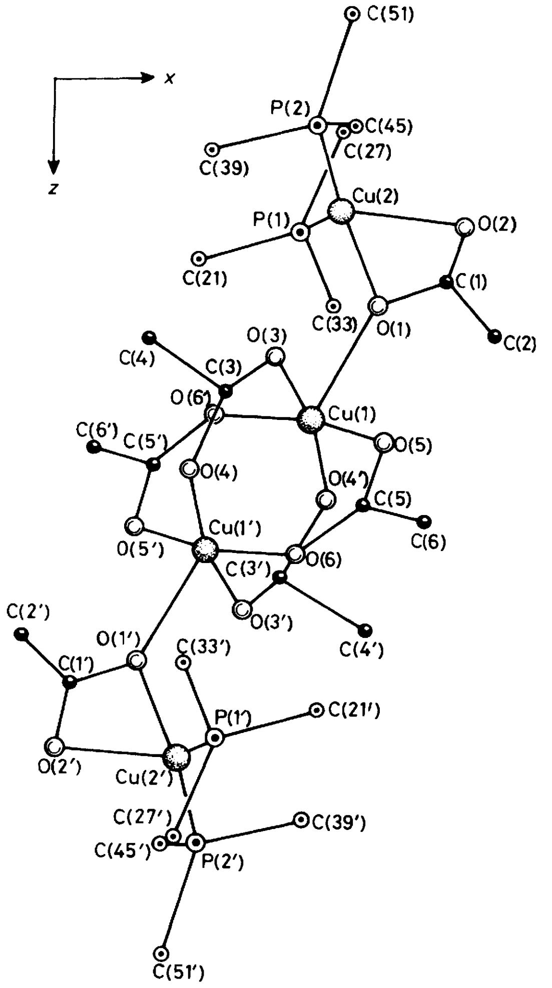


Figure 2. The molecular structure and the atomic numbering in $[Cu_4(O_2CMe)_6(PPh_3)_4]$; C(21), C(27), C(33), C(39), C(45), C(51), and the corresponding primed atoms are the phenyl α-carbons

all three copper atoms.[20] The additional interactions of the apical ligands (points 2, 4, and 5) slightly decrease both the Cu^{II}–O(apical) distance and Cu^{II}–Cu^{II} separation in the dimeric $Cu_2(O_2CMe)_4$ unit.

Besides complex (**1**) two other complexes,[20,21] $[\{Cu_3(O_2CMe)_5[P(OEt)_3]_2\}_n]$ and $\{[Cu_2(NH_3{}^+CH_2CO_2{}^-)_4][Cu_2Cl_6]\}_n$, have apical positions of the dimeric Cu_2(carboxylate)$_4$ unit occupied by the copper(I) complex. However, the structure of (**1**) shows that the copper(I) unit $Cu(O_2CMe)(PPh_3)_2$ is a terminal non-bridging ligand for copper(II), in contrast with the bridging copper(I) units in the polymeric structures of $[\{Cu_3(O_2CMe)_5[P(OEt)_3]_2\}_n]$ and $\{[Cu_2(NH_3{}^+CH_2CO_2{}^-)_4][Cu_2Cl_6]\}_n$.[20,21] From this point of view complex (**1**) represents a new structure type among the mixed-valence copper(I,II) carboxylate complexes.

Magnetic Susceptibility and E.S.R. Spectrum of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—The magnetic susceptibility of a polycrystalline sample of (**1**) was measured in the range 80—300 K (Table 3). An experimental temperature dependence of the magnetic susceptibility data (open circles in Figure 4) is characteristic of antiferromagnetic interactions between two magnetic centres. The least-squares fitting of experimental data with the modified Bleaney-Bowers equation,[22-24] using the spectroscopic splitting parameter $g = 2.21$ obtained from the e.s.r. spectrum, gives the energy of the singlet–triplet separation $2J = -270$ cm^{-1} and the percentage of monomeric impurities $x = 0$. The residual sum of squares (ERR), given by $\sum_i(\chi_i^{calc} - \chi_i^{exp})^2$ is 2.826×10^{-8} cm^6 mol^{-2}. The $2J$ value obtained for (**1**) is comparable with $2J = -284$ cm^{-1} obtained[25] for $[Cu_2(O_2CMe)_4(H_2O)_2]$, $2J = -270$ cm^{-1} observed[26] for $[Cu_2(O_2CMe)_4L_2]\cdot 2H_2O$ (L = urea), and $2J = -248$ cm^{-1} obtained[20] for $[\{Cu_3(O_2CMe)_5[P(OEt)_3]_2\}_n]$. The slightly lower $2J$ value for the last complex is in good agreement with the structure differences discussed above [*e.g.* the Cu^{II}–Cu^{II} distance, deformation of the $Cu_2(O_2CMe)_4$ moiety, and the involvement of one of its acetate groups in a donor–acceptor bond with copper(I)].

Table 2. Interatomic distances (Å), angles (°), and torsion angles (°), with estimated standard deviations in parentheses

(*a*) Distances		(*b*) Angles	
Cu(1)–O(1)	2.126(4)	O(1)–Cu(1)–O(3)	96.0(2)
Cu(1)–O(3)	1.973(5)	O(1)–Cu(1)–O(4′)	96.3(2)
Cu(1)–O(4′)	1.982(4)	O(1)–Cu(1)–O(5)	102.7(2)
Cu(1)–O(5)	1.989(5)	O(1)–Cu(1)–O(6′)	89.5(2)
Cu(1)–O(6′)	1.980(5)	O(1)–Cu(1)–Cu(1′)	171.6(1)
Cu(2)–O(1)	2.124(4)	O(3)–Cu(1)–O(4′)	167.6(2)
Cu(2)–O(2)	2.385(5)	O(3)–Cu(1)–O(5)	89.0(2)
Cu(2)–P(1)	2.249(2)	O(3)–Cu(1)–O(6′)	89.6(2)
Cu(2)–P(2)	2.225(2)	O(4)–Cu(1)–O(5)	89.3(2)
C(1)–O(1)	1.267(8)	O(4)–Cu(1)–O(6)	89.5(2)
C(1)–O(2)	1.254(7)	O(5)–Cu(1)–O(6)	167.8(2)
C(1)–C(2)	1.494(10)	O(1)–Cu(2)–O(2)	57.3(2)
C(3)–O(3)	1.216(9)	O(1)–Cu(2)–P(1)	115.4(1)
C(3)–O(4)	1.263(6)	O(1)–Cu(2)–P(2)	115.1(1)
C(3)–C(4)	1.552(11)	O(2)–Cu(2)–P(1)	96.3(1)
C(5)–O(5)	1.264(7)	O(2)–Cu(2)–P(2)	121.5(1)
C(5)–O(6)	1.246(8)	P(1)–Cu(2)–P(2)	127.9(1)
C(5)–C(6)	1.519(11)	Cu(1)–O(1)–Cu(2)	125.1(2)
P(1)–C(21)	1.818(8)	Cu(1′)–Cu(1)–O(3)	84.1(1)
P(1)–C(27)	1.834(6)	Cu(1′)–Cu(1)–O(4)	83.6(1)
P(1)–C(33)	1.828(7)	Cu(1′)–Cu(1)–O(5)	85.7(1)
P(2)–C(39)	1.804(7)	Cu(1′)–Cu(1)–O(6)	82.1(1)
P(2)–C(45)	1.826(7)	Cu(2)–O(1)–C(1)	135.6(4)
P(2)–C(51)	1.836(6)	Cu(2)–O(2)–C(1)	85.8(4)
Cu(1)–Cu(1′)	2.642(1)		
Cu(1)–Cu(2)	3.772(1)		

(*c*) Torsion angles	
O(3)–Cu(1)–O(1)–Cu(2)	61.1(7)
O(5)–Cu(1)–O(1)–Cu(2)	151.5(3)

The e.s.r. spectrum of a polycrystalline sample of (**1**) shows three absorptions and its similarity to e.s.r. spectra of other complexes containing symmetric binuclear units allows the following assignment: $H_{\parallel 1} = 427$, $H_{\perp} = 4\,653$, and $H_{\parallel 2} = 5\,869$ G (G = 10^{-4}T). The calculated magnetic and e.s.r. spectra parameters are listed in Table 4.

Infrared Spectra of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—The Nujol (mull) and KBr (pellet) i.r. spectra of (**1**) in the region 400—1 700 cm^{-1} are rather complicated, due to the presence of triphenylphosphine, with many absorptions, but most of them are assignable to vibrations of phenyl rings and they are not sensitive[27] to the co-ordination of PPh_3. Two strong absorptions at 1 629 and 1 574 cm^{-1} may be assigned to ν_{asym}(COO) vibrations, while two shoulders at 1 426 and 1 400 cm^{-1} may be assigned to ν_{sym}(COO) vibrations. A comparison with i.r. spectra of other copper acetate complexes and an analysis[28] of $\Delta\tilde{\nu}$ values ($\Delta\tilde{\nu} = \tilde{\nu}_{asym} - \tilde{\nu}_{sym}$) allow assignment of the absorptions at 1 629 and 1 426 cm^{-1} ($\Delta\tilde{\nu} = 203$ cm^{-1}) to the vibrations of the acetate groups in the $Cu_2(O_2CMe)_4$ unit, and

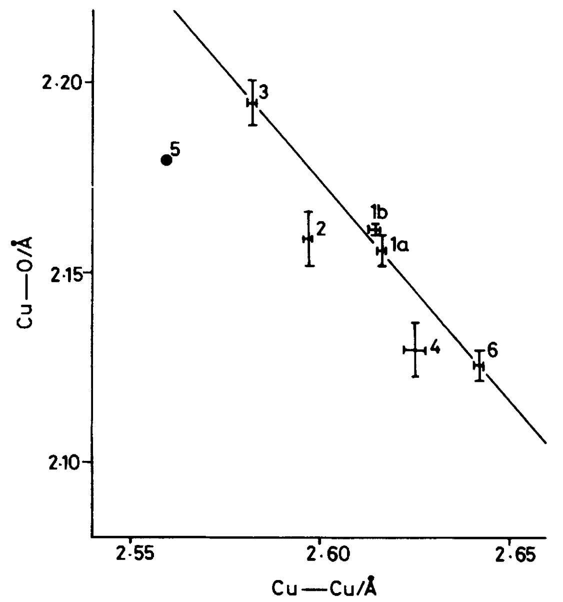


Figure 3. Plot of Cu^{II}–O(apical) distance *vs.* Cu^{II}–Cu^{II} separation for $[Cu_2(O_2CMe)_4L_2]$ complexes with oxygen-donor ligands L in apical positions: 1a, L = H_2O (ref. 15); 1b, L = H_2O (ref. 16); 2, L = MeOH (ref. 18); 3, L = HO_2CMe (ref. 18); 4, L = urea (ref. 19); 5, L = $\frac{1}{2}Cu(O_2CMe)\{P(OEt)_3\}_2$ (ref. 20); 6, L = $Cu(O_2CMe)(PPh_3)_2$ (this work)

Table 3. Variation of magnetic susceptibility $(\chi)^a$ and magnetic moment^b with temperature, for $[Cu_4(O_2CMe)_6(PPh_3)_4]$

T/K	$10^6\chi_{Cu}^{corr}$/cm³ mol⁻¹	$\mu_{eff.}$
82	295	0.44
101	445	0.60
111	494	0.66
125	569	0.75
135	610	0.81
146	670	0.88
161	776	1.00
172	826	1.07
182	867	1.12
193	900	1.18
207	925	1.24
227	950	1.31
239	958	1.35
252	967	1.40
279	967	1.47
292	967	1.50

^{a} $\chi_{Cu}^{corr} = M\chi^{corr}/2$, M = molecular weight; χ(S.I.) = $(4\pi \times 10^6)$-χ_{Cu}^{corr}(c.g.s.). ^{b} $\mu_{eff.} = 2.83(\chi_{Cu}^{corr}.T)^{\frac{1}{2}}$.

the absorptions at 1 574 and 1 400 cm⁻¹ ($\Delta\tilde{\nu}$ = 174 cm⁻¹) to those of the acetate groups bonded to copper(I) in the $Cu(O_2CMe)(PPh_3)_2$ moieties. Absorptions at 680 and 628 cm⁻¹ may be assigned to the δ_{sym}(COO) and ρ(COO) vibrations of the acetate groups of the $Cu_2(O_2CMe)_4$ unit. They are close to the values of 690 and 625 cm⁻¹ found[29] for $[Cu_2(O_2CMe)_4(OH_2)_2]$. Absorptions at 707 and 614 cm⁻¹ may be assigned to δ_{sym}(COO) and ρ(COO) vibrations of the acetate groups bonded to copper(I) in the $Cu(O_2CMe)(PPh_3)_2$ moieties; for $[Cu(O_2CMe)(PPh_3)_2]$ we found these absorption bands at 707 and 618 cm⁻¹. A vibration band sensitive to the group X in Ph_3P–X in complex (**1**) was found at 1 097 cm⁻¹ (for unco-ordinated PPh_3 it was observed[27] at 1 090 cm⁻¹).

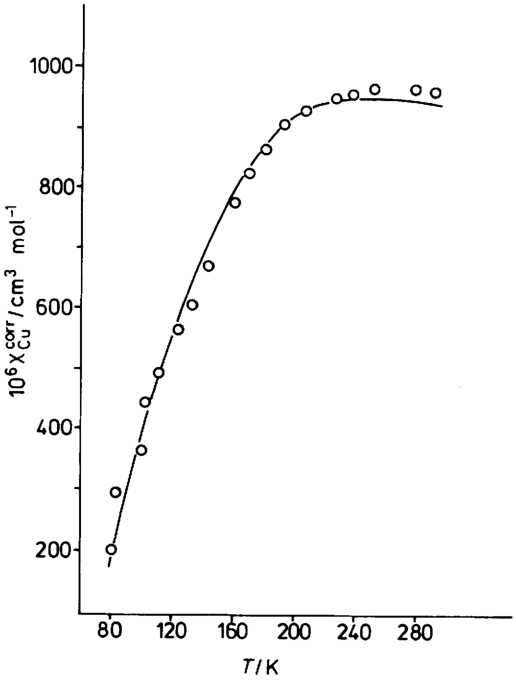


Figure 4. Variation of magnetic susceptibility with temperature. Circles denote the experimental data for which the line plot was optimized (see text)

Table 4. Magnetic and e.s.r. parameters^a of $[Cu_4(O_2CMe)_6(PPh_3)_4]$

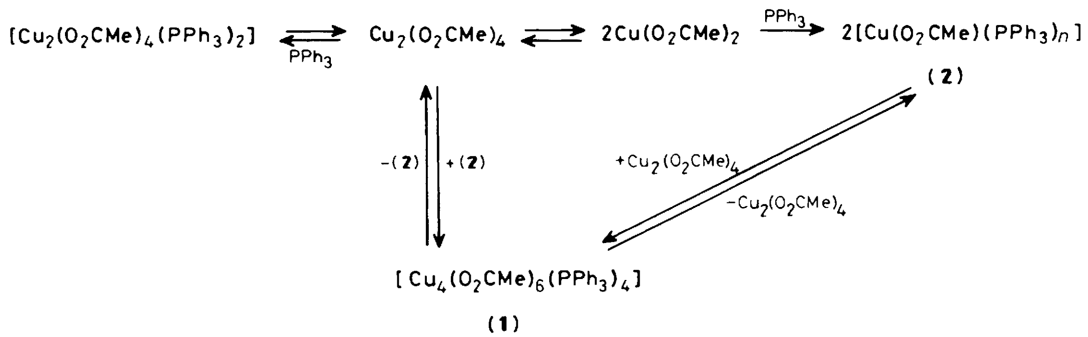
Exchange parameter J/cm⁻¹	Spectroscopic splitting factors			Zero-field splitting parameters	
	$g_{\parallel}$	$g_{\perp}$	$g_{av.}{}^b$	$\lvert D\rvert$/cm⁻¹	E/cm⁻¹
−135	2.43	2.09	2.21	0.356	0.0021

^{a} No monomeric form of the complex was observed. ^{b} $g_{av.}{}^2 = \frac{1}{3}(g_{\parallel}{}^2 + 2g_{\perp}{}^2)$.

Electronic Spectra of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—The spectrum of (**1**) in methanol recorded over the range of 200—1 100 nm shows five absorptions at wavelengths $\lambda_{max.}(\log_{10}\varepsilon)$ 235 (4.58), 263 (4.57), 278 (4.52), 375 (2.38), and 716 nm (2.01). The lowest-energy band is broad and may be assigned to a *d–d* transition of the $Cu_2(O_2CMe)_4$ fragment. The presence of the dimeric $Cu_2(O_2CMe)_4$ fragment in solution is also indicated[30] by the characteristic shoulder at 375 nm. The absorptions in the u.v. region of the spectrum are charge-transfer bands. Their correct assignment is difficult because partial dissociation of complex (**1**) occurs in solution, and both copper(II) and the copper(I) moieties, and PPh_3 itself, have absorption bands in this region of the spectrum. The reflectance spectrum of the solid complex (**1**) shows five absorptions at wavelengths $\lambda_{max.}$ 220, 270, 286, 375, and 730 nm. These values, compared with those found for (**1**) in solution, indicate that dissociation of complex (**1**) occurs in methanol.

Synthesis of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—The equilibrium between dimeric and monomeric species of copper(II) acetate, together with the temperature of the reaction mixture are the most important factors affecting the reduction of copper(II) to copper(I) by triphenylphosphine (Scheme).

The formation of complex (**1**) is a consequence of the equilibrium between the $Cu_2(O_2CMe)_4$ and $Cu(O_2CMe)$-



Scheme. Behaviour of the reaction mixture of copper(II) acetate and triphenylphosphine in solution

$(PPh_3)_2$ fragments originated by reduction of copper(II). Suitable conditions for such an equilibrium consist, in dilute ethanolic solution, of copper(II) acetate and a molar ratio of PPh_3 to Cu^{II} of 1—2:1. If a highly concentrated ethanolic solution of copper(II) acetate were used it would be necessary, either to carry out the reaction at higher temperature, or to achieve the equilibrium by a longer reaction time. Complex (**1**) was a dominant product of the reaction in these cases and was prepared and isolated according to methods A and B in the Experimental section. Moreover, it can also be synthesized by reaction of copper(II) acetate with complexes $[Cu(O_2CMe)(PPh_3)_n]$ (**2**) using method C (Experimental section).

Experimental

Chemicals.—Triphenylphosphine was of reagent grade (Labora) and was recrystallized from ethanol. Copper(II) acetate of analytical grade (Labora) was used as received. All solvents were purified and dried by standard methods.

Preparations.—$[Cu(O_2CMe)(PPh_3)_n]$ (n = 2 *or* 3). The complexes were prepared according to a published method.[2]

$[Cu_4(O_2CMe)_6(PPh_3)_4]$. *Method A.* To copper(II) acetate monohydrate (5 mmol) and triphenylphosphine (10 mmol) was added dried ethanol (50 cm^3). The reaction mixture was refluxed for 10 min to obtain a clear solution. On cooling to room temperature a pale blue-green powder precipitated which was filtered off, washed with a small amount of ethanol, then diethyl ether, and dried *in vacuo*; yield 1 g. The crystalline product for *X*-ray structure determination was obtained from the cooled reaction mixture as above, to which an additional portion of dried ethanol was added to produce a clear solution for crystallization.

Method B. The reaction mixture from method A was kept at room temperature. The initially precipitated dark green complex $[Cu_2(O_2CMe)_4(PPh_3)_2]$ dissolved completely in the reaction mixture and after *ca.* 5 h $[Cu_4(O_2CMe)_6(PPh_3)_4]$ precipitated from the clear solution; yield 1 g.

Method C. Equivalent amounts of $Cu(O_2CMe)_2{\cdot}H_2O$ and $[Cu(O_2CMe)(PPh_3)_n]$ (n = 2 or 3) were dissolved in a small amount of dried ethanol. After cooling to room temperature a pale blue-green powder, $[Cu_4(O_2CMe)_6(PPh_3)_4]$, precipitated; yield *ca.* 85%.

The products obtained using the above methods have the same composition, and electronic, i.r., and e.s.r. spectra (Found: C, 60.25; H, 4.70; Cu, 15.35. Calc. for $C_{84}H_{78}Cu_4O_{12}P_4$: C, 60.30; H, 4.70; Cu, 15.20%).

Physical Measurements.—Magnetic susceptibility was measured in the temperature range 80—300 K using a Gouy balance calibrated with $Hg[Co(SCN)_4]$. Magnetic susceptibility calculated per one mol of Cu^{II} ions was corrected using Pascal's constants for diamagnetism ($\chi_{Cu}^{dia} = -370 \times 10^{-6}$ cm^3 mol^{-1}) and for temperature independent paramagnetism ($N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}). Effective magnetic moments were calculated using the equation $\mu_{eff.} = 2.83\ (\chi_{Cu}^{corr}T)^{\frac{1}{2}}$. The least-squares fitting of experimental magnetic susceptibility data with the modified Bleaney-Bowers equation and calculation of the exchange integral value $2J$ was done using the ODRA 1305 computer at the Computer Centre, University of Wrocław.

The i.r. spectra in the region 400—4 000 cm^{-1} were measured on Nujol mulls with a Specord 75 IR instrument and on KBr pellets with a Perkin-Elmer 180 spectrophotometer. Spectra obtained from the two instruments did not show significant differences.

The electronic spectra of solutions or Nujol mulls in the region 330—800 nm were measured on a Specord UV VIS spectrophotometer. The electronic spectra of solutions and the diffusion reflectance spectra of the undiluted compound were measured in the region 300—2 000 nm with a Beckman UV 5240 spectrophotometer. Magnesium oxide was used as standard for light reflectance. Reflectance spectra of diluted compounds in Li_2CO_3 were measured in the range 200—800 nm on a Hitachi 356 spectrophotometer. No significant differences in reflectance spectra were observed when measured with different instruments.

The e.s.r. spectra of a polycrystalline sample at *X*-band frequency were measured at laboratory temperature on a JES-ME-3X instrument.

Crystal and Molecular Structure of $[Cu_4(O_2CMe)_6(PPh_3)_4]$.—*Data collection.* An irregularly shaped crystal of $[Cu_4(O_2CMe)_6(PPh_3)_4]$ (average dimension 0.3 mm) was used for data collection. The preliminary crystallographic data were obtained from oscillation and Weissenberg photographs and were refined by using the positions of 10 reflections centred on a Syntex P2$_1$ instrument. Intensity measurements were carried out on the Syntex P2$_1$ four-cycle computer-controlled diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) and a scintillation counter. 2 415 Independent reflections were collected in the range $0 \leqslant 2\theta \leqslant 55°$ and 2 227 with $I \geqslant 1.96\sigma(I)$ were used in the analysis. The θ—2θ scanning technique with a variable scan speed (4.88—29.3° min^{-1}) was used. Two check reflections in intervals of 100 were measured and no significant intensity deterioration was observed. Lorentz and polarization corrections were applied in the usual way. Since the μ value was 24.4 cm^{-1} (μR = 0.4, R is cylinder radius of crystal), no absorption correction was made.

Crystal data. $C_{84}H_{78}Cu_4O_{12}P_4$, M = 1 673.61, triclinic, space group $P\bar{1}$, a = 10.898(8), b = 12.850(4), c = 19.877(8) Å, α = 121.03(2), β = 90.14(5), γ = 117.98(4)°, U = 1 993.4(21) Å^3, D_m = 1.376, Z = 1, D_c = 1.38 g cm^{-3}, $F(000)$ = 842.

Structure solution and refinement. The structure of $[Cu_4(O_2CMe)_6(PPh_3)_4]$ was solved using the heavy-atom method and refined by full-matrix least-squares methods anisotropically to $R = \Sigma||F_o| - |F_c||/|F_o| = 0.0565$ ($w = 1$, $R' = R$), involving all non-hydrogen atoms. Positions of hydrogen atoms were obtained from differential Fourier syntheses. The final positional parameters of the non-hydrogen atoms are listed in Table 1.

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