Phosphite Complexes of Copper(II) Carboxylates and their Derivatives. Crystal Structure of Penta-μ-acetato-bis(triethyl phosphite)tricopper-(I,II)

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Copper(II) alkanecarboxylates, $[Cu_2(O_2CR^1)_4]$ (R^1 = Me, Et, or Pr^n), react with trialkyl phosphites, $P(OR^2)_3$ (R^2 = Me, Et, or Pr^i), in equimolar proportions in alcohol (R^2OH) solution to form pale blue-green $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ complexes, which have been characterised by microanalysis, spectroscopic (i.r., ^1H and ^{31}P n.m.r., e.s.r., u.v.–visible), and magnetic susceptibility measurements. The crystal structure of $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$ has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group C_c, with $Z = 4$ in a unit cell of dimensions $a = 13.77(4)$, $b = 19.10(3)$, $c = 17.08(4)$ Å, and $\beta = 125.6(2)°$. The structure was refined by least-squares methods to R 0.10 for 651 reflections. The structure shows that a $Cu_2(O_2CMe)_4$ unit provides a monoatomic *syn-anti* bridge through oxygen to a $Cu(O_2CMe)\{P(OEt)_3\}_2$ unit, the acetate group of which provides an *anti-anti* bridge between $Cu_2(O_2CMe)_4$ units to form a polymeric chain. In alcohol solution the chain is broken and the solvated fluxional monomeric $[Cu_3(O_2CMe)_5\{P(OR^2)_3\}_2]$ (R^2 = Me or Et) units rearrange so that the copper(I) atom is connected to one of the copper(II) atoms through two unidentate bridging acetates. In alcohol solution $[Cu_3(O_2CMe)_5\{P(OR^2)_3\}_2]$ (R = Me or Et) reacts with unidentate oxygen- or nitrogen-donor ligands, L, to form $[Cu_2(O_2CMe)_4L_2]$ and $[\{Cu(O_2CMe)[P(OR^2)_3]_2\}_2]$. The dimeric copper(I) complexes react with bidentate nitrogen- and phosphorus-donor ligands, L′, to form $[Cu(O_2CMe)\{P(OR^2)_3\}L']$ [L′ = 2,2′-bipyridine, 1,10-phenanthroline, 1,2-diaminoethane, or 1,2-bis(diphenylphosphino)ethane] which exist as fluxional monomers in solution.

THE observations by Ullmann that copper can both catalyse nucleophilic substitution of aryl halides[1] and assist coupling of aryl halides to form biaryls[2] have been developed so that these are now important widely used procedures in organic synthesis.[3,†] However, the nature of the copper-containing species which participate in these reactions is poorly defined, despite many investigations.[4] Recently it was shown that copper(II) salts promote the reaction between 2-bromodiarylazo-compounds and trialkyl phosphites to form the corresponding 2-(dialkylphosphonato)diarylazo-compounds.[5] In order to achieve a better understanding of the course of this interesting reaction which appears to have a superficial similarity to the Michaelis–Arbuzov[6] reaction, we have studied the reaction between some copper(II) carboxylates, $[Cu_2(O_2CR)_4]$, and trialkyl phosphites. This has led to the preparation of a new class of mixed-valence copper(I,II) complex, the reactions of which have been reported in a preliminary communication.[7]

RESULTS AND DISCUSSION

Anhydrous copper(II) acetate reacts with triethyl phosphite (1 : 1) under anaerobic conditions in dry ethanol at reflux to form a pale blue-green complex which was shown to have the composition $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$ (1) by microanalysis. Similar complexes $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ (R^1 = Et or Pr^i; R^2 = Me or Pr^i) can also be prepared. The phosphite is serving both as a ligand and as a reducing agent in the reaction, as was shown by the isolation of the corresponding trialkyl phosphate, $P(O)(OR^2)_3$, from the reaction. The complexes are air-sensitive solids, which dissolve in the corresponding alcohol, R^2OH, from which they can be recrystallised. Transesterification of the co-ordinated phosphite occurs when, for example, $[Cu_3(O_2CMe)_5\{P(OMe)_3\}_2]$ (2) is dissolved in ethanol, giving (1). The trinuclear complexes (1) and (2) can be recovered from acetonitrile solution, but in a range of other solvents, dioxan, acetone, chloroform, tetrahydrofuran, or pyridine, the trinuclear complexes decompose to form either copper(II) acetate or, with a donor solvent, L, the corresponding complex, $[Cu_2(O_2CMe)_4L_2]$. We shall return to this after establishing the nature and properties of the trinuclear complexes.

Structure of $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$.—The structure determination of (1) (see Experimental section and Figure) shows that the complex is a mixed-valence system in which a dimeric $Cu^{II}_2(O_2CMe)_4$ unit is associated with a $Cu^I(O_2CMe)\{P(OEt)_3\}_2$ unit *via* axial copper–oxygen bonding to form a polymeric chain. There are three distinct types of acetate ligand in the complex: three bridging the copper(II) ions in the *syn-syn* configuration; one *syn-syn* bridging acetate [O(2)–C(17)–O(8)] with one oxygen atom [O(8)] also forming a monoatomic *syn-anti* bridge to the copper(I) atom, Cu(3); and one *anti-anti* acetate [O(9)–C(18)–O(1)] connecting the two copper(II) atoms Cu(1) and Cu(2), and forming a monoatomic bridge to the copper(I) atom, Cu(3).

Within the copper(II) acetate fragment, the dimensions of the three acetate groups which are *not* involved in bonding to Cu(3) are all similar to those[8] in $[Cu_2(O_2CMe)_4(OH_2)_2]$, having interbond angles close to 120°. The fourth acetate ligand, which provides the bridging

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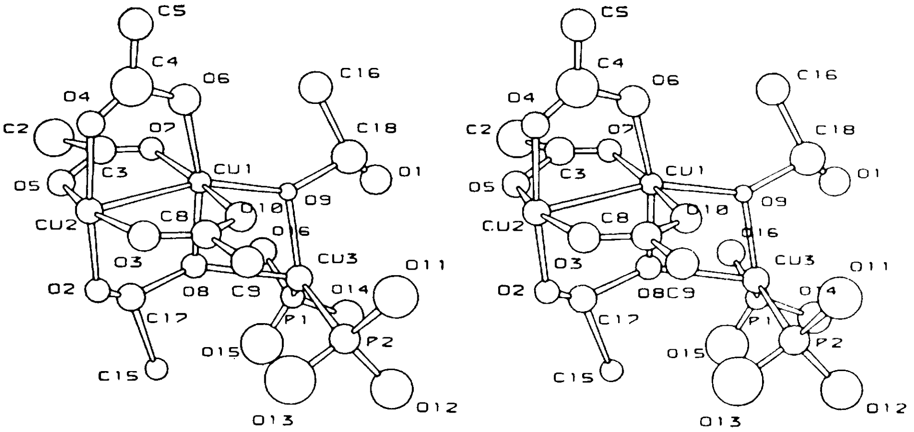
† For a survey of metal-catalysed biaryl coupling, see A. McKillop, A. G. Turrell, D. W. Young, and E. C. Taylor, *J. Am. Chem. Soc.*, 1980, **102**, 6504; M. Sainsbury, *Tetrahedron*, 1980, **36**, 3327.



Stereoscopic drawing of the molecular structure of (1)

oxygen, O(8), for the $Cu^{II}O_2Cu^{I}$ ring is distorted to the extent indicated by the bond angle Cu(1)–O(8)–C(17) and the angles at the carboxylate carbon atom C(17) (Table 1). The ability of a carboxylate ligand bridging two copper atoms to form a monoatomic bridge to a third copper atom has also been observed in anhydrous copper(II) butyrate,[9] which is formally similar to the structural feature found[10] in tetrakis[acetato(2-pyridylmethanolato)copper(II)] tetrahydrate and di-μ-malonato-bis[(1,3-diaminopropane)copper(II)], and related to that in bis(2,2′-bipyridine)bis(pyridine-2,6-dicarboxylato)dicopper(II) tetrahydrate.[11]

TABLE 1

Selected bond lengths and bond angles in $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$ with estimated standard deviations in parentheses

(*a*) Bond lengths/Å

Cu(1)–Cu(2)	2.56(2)	Cu(3)–O(8)	2.31(6)
Cu(1)–Cu(3)	3.28(2)	Cu(3)–P(1)	2.21(2)
Cu(1)–O(8)	2.02(5)	Cu(3)–P(2)	2.22(3)
Cu(1)–O(9)	2.15(5)	O(1)–O(9)	2.13(9)
Cu(2)–O(1)	2.21(6)	O(2)–O(8)	2.42(8)
Cu(3)–O(9)	1.95(5)	O(8)–O(9)	2.58(9)

(*b*) Bond angles/°

Cu(2)–Cu(1)–O(9)	160(1)	Cu(1)–O(8)–Cu(3)	98(2)
Cu(1)–Cu(2)–O(1)	171(1)	Cu(1)–O(9)–Cu(3)	106(2)
Cu(2)–Cu(1)–Cu(3)	125(2)	O(8)–Cu(3)–O(9)	74(2)
Cu(2)–O(2)–C(17)	116(2)	P(1)–Cu(3)–P(2)	127(1)
O(2)–C(17)–O(8)	145(11)	O(8)–Cu(3)–P(1)	102(1)
C(15)–C(17)–O(8)	83(5)	O(8)–Cu(3)–P(2)	107(1)
O(2)–C(17)–C(15)	131(10)	C(17)–O(8)–Cu(1)	102(4)

(*c*) Dihedral angles (°) between planes

Cu(1)–O(9)–O(8)/Cu(3)–O(9)–O(8)	23
Cu(2)–O(9)–Cu(3)/Cu(3)–O(8)–Cu(1)	29

The copper(II)–copper(II) separation, 2.56(2) Å, in (1) is slightly less than that [2.614(2), 2.616(1) Å] found[8,12] in $[Cu_2(O_2CMe)_4(OH_2)_2]$. The inverse correlation between M–M–OC(O)R angles and M–M separation observed[13] for various tetracarboxylate-bridged metal dimers $[M_2(O_2CR)_4]$ and $[M_2(O_2CR)_4L_2]$ is maintained in the present instance, where Cu(1)–Cu(2)–O is 86° and Cu(1)–Cu(2) is 2.56 Å. The copper(I)–copper(II) atom separation, Cu(1)–Cu(3), is 3.28 Å which is consistent with the absence of direct metal–metal interaction. Consequently, the $Cu(O_2CMe)\{P(OEt)_3\}_2$ moiety can be treated as effectively independent. The Cu(3)–P bond lengths [2.21(2), 2.22(3) Å] are similar to those observed[14] in $[Cu(O_2CMe)(PPh_3)_2]$ (2.23, 2.24 Å) and comparable with those found in tetrameric copper(I) complexes, $[\{CuX(PR_3)\}_4]$, which range from 2.18 Å in[15] $[\{CuCl(PEt_3)\}_4]$ to 2.25 Å in[16] $[\{CuI(PEt_3)\}_4]$. The atoms P(1), P(2), O(8), and O(9) surround Cu(3) in a non-regular tetrahedral arrangement, similar to that found[14] in $[Cu(O_2CMe)(PPh_3)_2]$. It is possible to view the co-ordination geometry of Cu(3) as distorted trigonal planar because of the significant asymmetry indicated by Cu(3)–O(9) [1.95(5) Å] and Cu(3)–O(8) [2.31(6) Å]. *X*-Ray powder diagrams indicate that the complexes $[Cu_3(O_3CMe)_5\{P(OR)_3\}_2]$ (R = Me or Et) are not isomorphous.

Magnetic Susceptibility and E.S.R. Spectra of $[Cu_3(O_2CMe)_5\{P(OR)_3\}_2]$ *Complexes.*—The variation in bulk magnetic susceptibility of a polycrystalline sample of (1) was measured over the temperature range 110—298 K. The results (Table 2) were fitted to the expression for the molar susceptibility per copper atom,

TABLE 2

Variation of magnetic susceptibility (χ) and magnetic moment (μ) with temperature for $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$

T/K	$10^6\chi_{exp.}$*/ c.g.s. units	$10^6\chi_{calc.}$/ c.g.s. units	$\mu_{exp.}$/B.M.	$\mu_{calc.}$/B.M.
298	1 065	1 048	1.58	1.57
277	1 065	1 070	1.53	1.53
257	1 092	1 088	1.49	1.49
225	1 118	1 104	1.41	1.40
205	1 065	1 098	1.31	1.33
193	1 091	1 086	1.29	1.29
181	1 118	1 066	1.26	1.24
174	1 012	1 050	1.18	1.20
167	1 011	1 030	1.15	1.17
155	958	986	1.08	1.09
144	932	932	1.02	1.03
133	878	864	0.96	0.95
110	691	673	0.77	0.76

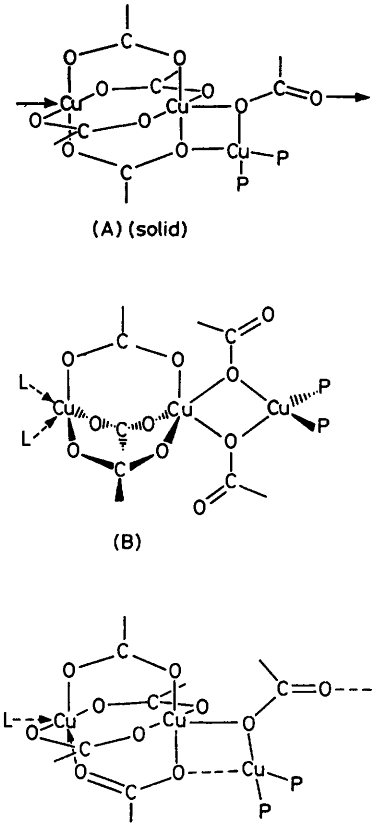
* $\chi_{exp.} = M\chi^{corr.}/2$; M = molecular weight. $\chi(S.I.) = 4\pi\chi(c.g.s.) \times 10^{-6}\ m^3\ mol^{-1}$.

χ_M, to give the average gyromagnetic ratio, $\bar{g} = 2.16$, the singlet–triplet separation, $2J = -248$ cm^{-1}, and the temperature-independent paramagnetism, $N\alpha = 2.33 \times 10^{-6}$ c.g.s. units.* Comparison of the copper–copper separation, d/pm, and the singlet–triplet separation, $-2J$/cm^{-1}, in various copper(II) acetate complexes with the data for (1) provides further evidence in favour of the superexchange mechanism[17] for spin–spin interaction in these compounds. In (1), magnetic interaction is weakest, notwithstanding the smallest copper–copper separation. This is seen as a consequence of the O(8)–Cu(3) donor–acceptor interaction which disturbs the superexchange through the acetate bridges. The magnetic susceptibility of some other complexes of the type $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ was measured at room temperature. They all show values of μ in the range 1.56—1.62 B.M.

The e.s.r. spectrum of a polycrystalline sample of (1) was recorded at 9.53 GHz at room temperature. The spectrum resembles that of polycrystalline $[Cu_2(O_2CMe)_4(OH_2)_2]$, showing three rather broad absorptions at magnetic field values $H_1 = 170$, $H_2 = 5\,800$, and $H_3 = 4\,700$ G, from which the values of $g_{\parallel} = 2.41$, $g_{\perp} = 2.08$ and the energy separation between the $M_S = \pm 1$ and $M_S = 0$ levels, $D = 0.34$ cm^{-1}, can be calculated.

Infrared Spectra.—The solid-state mull i.r. spectra of the $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ complexes show two strong absorptions at *ca.* 1 640 and *ca.* 1 560 cm^{-1} which are assigned to the antisymmetric stretching vibrations of the *anti-anti* (and/or *anti-syn*) and the *syn-syn* carboxylate groups respectively. In $[Cu_2(O_2CMe)_4]$, which contains only *syn-syn* bound acetate, there is a single $\nu_{asym.}(CO_2)$ absorption at 1 595 cm^{-1}. The symmetric stretching vibration in the $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ complexes is observed as a single strong absorption in the 1 400—1 420 cm^{-1} region. Other absorptions in the i.r. spectra (600—4 000 cm^{-1}) of these complexes are unremarkable and may be readily assigned to the phosphite and carboxylate ligands.

Electronic Spectra.—The spectra of the compounds $[Cu_3(O_2CMe)_5\{P(OR)_3\}_2]$ (R = Me or Et) recorded in ROH solution over the range 10 000—50 000 cm^{-1} show five absorptions, which are insensitive to the nature of R, at $\lambda_{max.}$/cm^{-1} ($\log_{10} \varepsilon$) 14 300 (2.41), 28 600 (2.43), 33 600 (3.54), 42 700 (4.27), and 48 300 (4.34). The lowest-energy band is assigned to *d–d* transitions of the $Cu_2(O_2CMe)_4$ fragment. The band at 28 600 cm^{-1} corresponds to the absorption at 26 700 cm^{-1} in the spectrum of $[Cu_2(O_2CMe)_4(OH_2)_2]$ which has been shifted to higher energy as a consequence of the reduced exchange in the phosphite complexes. The band at 42 700 cm^{-1} is similar to the ligand-to-metal charge-transfer absorption observed[18] in $[Cu_2(O_2CMe)_4\{O(HO)CMe\}_2]$ at 40 100 cm^{-1}; the bands at 33 600 and 48 300 cm^{-1} are similar to those observed in $[Cu(O_2CMe)\{P(OEt)_3\}_2]$ at 33 400 and 47 600 cm^{-1} and are assigned to copper-to-phosphite charge transfer. A search for an intervalence charge-transfer absorption[19] in the low-energy (<12 000 cm^{-1}) region was unsuccessful. This is consistent with strictly localised valence (Class I behaviour) at the copper(I) and copper(II) centres in these compounds.



(A) (solid)

(B)

(C)

SCHEME 1 Solution behaviour of $[Cu_3(O_2CMe)_5\{P(OR)_3\}_2]$. L = solvent

Nuclear Magnetic Resonance Spectra.—Although the complexes (1) and (2) are paramagnetic, the linewidths of the proton resonances in alcohol solution at room temperature are sufficiently narrow and occur in the conventional range so that the spectra are easily interpretable (see Experimental section). The spectra of both (1) and (2) show the presence of two types of acetate methyl proton resonance which are in the ratio of 3 : 2 (9 H : 6 H). This can be explained (Scheme 1) in terms of structure (B), which contains three *syn-syn* acetate ligands bridging two copper(II) atoms and two unidentate acetate ligands linking copper(II) with four-co-ordinate copper(I). This arrangement is preferred to the alternative which would have three unidentate acetate ligands linking copper(II) with five-co-ordinate copper(I). It is thought likely that the terminal copper(II) atom [Cu(2) in the Figure] in structure (B) (Scheme 1) is also co-ordinated by one or more alcohol solvent molecules. We have not been able to demonstrate this experimentally (*e.g.* by the use of ^{17}O n.m.r.)

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 G = 10^{-4} T. 1 c.g.s. unit = $4\pi \times 10^{-6}$ m^3 mol^{-1}.

because the use of other possible solvents resulted in degradation of the complex. For example, (2) decomposes slowly even in methanol to form $[Cu(O_2CMe)\{P(OMe)_3\}_2]$ and $[Cu_2(O_2CMe)_4(HOMe)_2]$, a process which is accelerated in concentrated solution. It would appear that the ethanol solvent molecules successfully disrupt the one-dimensional polymer chain structure (A) (Scheme 1), relieving the strain in the carboxylate group [O(2)–C(17)–O(8)] which is bonded to all three copper atoms in the solid state, to form (B) without causing further disruption.

The proton-decoupled ^{31}P n.m.r. spectra of compounds (1) and (2) in alcohol solution both show two signals. In the case of (2) these are a singlet centred at δ 123 p.p.m. and a quartet centred at δ 126 p.p.m. $[^1J(^{63}Cu-^{31}P) = 1\,210 \pm 35$ Hz] both of which are at higher field than free trimethyl phosphite, δ 141 p.p.m. There was no signal due to free phosphite in solutions of (2). The same pattern of a broad ($\omega_{\frac{1}{2}}$ 283 Hz) singlet (δ 174 p.p.m.) and a quartet [δ 179 p.p.m.; $^1J(^{63}Cu-^{31}P) = 1\,221 \pm 33$ Hz] is observed in the ^{31}P n.m.r. spectrum of (1), but these signals are at lower field than free triethyl phosphite in ethanol, δ 138 p.p.m. Once again no signal due to free phosphite was observed in solutions of (1). The difference in behaviour between the two homologous phosphite complexes may be explained by a difference in the magnetic anisotropy of the central copper ion [Cu(1) in the Figure] between the labile trimethyl phosphite complex (2) and its less dissociated triethyl phosphite analogue (1). The observation of two ^{31}P resonances, only one of which shows $^{63}Cu-^{31}P$ coupling, suggests that there may be two isomers [20] present in solution, the one with a high degree of symmetry at the copper(I) nucleus, the other having lower, possibly trigonal,[21] symmetry represented by (C) (Scheme 1). The absence of a signal due to free phosphite and the magnitude of the observed shift from that of the free ligand both argue against a rapid exchange of phosphite being responsible for a decrease in symmetry at copper(I). Tetrahedral copper(I) in $[Cu\{P(OEt)_3\}_4][ClO_4]$ has [21] a value of $^1J(^{63}Cu-^{31}P) = 1\,209 \pm 8$ Hz which is very close to that measured in (1). The other, broad singlet ^{31}P signal could arise from a structure (C) wherein the two acetate ligands bound to copper(I) are no longer equivalent. This would be the result if interchange of acetate groups occurs between the $Cu_2(O_2CMe)_4$ fragment and the $Cu(O_2CMe)\{P(OR)_3\}_2$ fragment *via* the central copper(II) atom [Cu(1) in the Figure] acting as a pivot. Intramolecular unidentate–bidentate carboxylate ligand exchange has been observed [22] in $[M(O_2CMe)(CO)(PPh_3)_2]$ (M = Ru or Os). The observation of time-averaged acetate proton resonances in (1) and (2) further supports the ' mobile acetate ' hypothesis in the present instance, as does the apparent competition between methanol and acetate for co-ordination to the central copper(II) atom [Cu(1) in the Figure] in the trimethyl phosphite complex, (2).

Reactions of $[Cu_3(O_2CMe)_5\{P(OR)_3\}_2]$ *with Unidentate Donor Ligands.*—Mention has already been made of the fact that complexes (1) and (2) cannot be recovered from their solutions in various polar and non-polar solvents. Taking compound (1) as an example we have studied these reactions in greater detail.

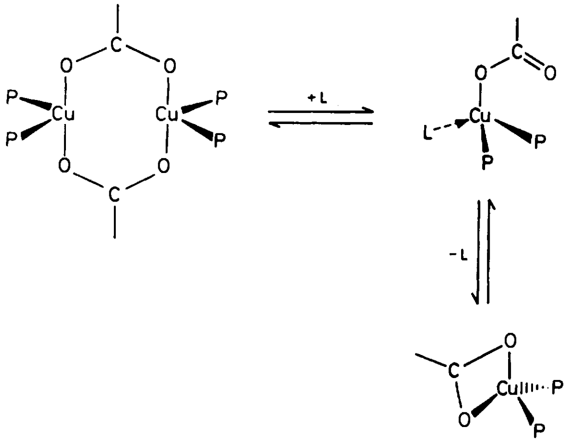
Compound (1), which is indefinitely stable in ethanol in an anaerobic closed system, reacts with unidentate nitrogen-donor (pyridine, 2-, 3-, and 4-methylpyridine, and quinoline) and with oxygen-donor (urea and triphenylphosphine oxide) ligands, L, in ethanol at ambient temperature under nitrogen to give the known complexes, $[Cu_2(O_2CMe)_4L_2]$, which precipitated from the solution. No precipitation occurred with triethylamine or acetonitrile. With certain other solvents (chloroform, dichloromethane, diethyl ether, dioxan, tetrahydrofuran, and acetone) precipitation of $[Cu_2(O_2CMe)_4]$ occurred. The disruption of (1) and (2) by certain donor ligands and solvents with precipitation of the copper(II) acetate fragment left the corresponding copper(I) acetate complex $[Cu(O_2CMe)\{P(OR)_3\}_2]$ (3, R = Me; 4, R = Et) in solution. Similar splitting of a mixed-valence copper complex into its component copper(I) and copper(II) moieties has been observed [23] for the complex $[Cu_3L_6]X_4$ (L = 2,5-dithiahexane; X = ClO_4 or BF_4) in dichloromethane solution.

The reaction of (1) and (2) with the corresponding phosphite in excess in boiling ROH also produced (4) and (3) respectively together with the phosphate, $P(O)(OR)_3$. Complete reduction to copper(I) occurred. The relatively involatile phosphate proved difficult to remove so this route to (3) and (4) was abandoned.

The preferred route to (3) and (4) involves reaction between (1) or (2) and excess of pyridine (py) in alcohol (ROH) solution. Precipitation of $[Cu_2(O_2CMe)_4(py)_2]$ is rapid and the supernatant can be isolated easily by filtration. Complexes (3) and (4) are isolated as very air- and moisture-sensitive liquids. Microanalysis of (4) (m.p. 286 K) confirms the composition $[Cu(O_2CMe)\{P(OEt)_3\}_2]$.

Characterisation of $[Cu(O_2CMe)\{P(OR)_3\}_2]$ *Complexes.*—The wavenumber difference between the symmetric and antisymmetric carboxylate stretching vibrations, Δν [165 cm^{-1} (R = Me), 170 cm^{-1} (R = Et)], in these complexes is consistent with a bidentate *syn-syn* acetate ligand bridging two copper(I) atoms in a dimeric structure $[\{Cu(\mu-O_2CMe)[P(OR)_3]_2\}_2]$. Similar values of Δν are observed [24] in $[Cu_2(O_2CMe)_4(OH_2)_2]$ (Δν 180 cm^{-1}) and $[Cu_2(O_2CMe)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] (Δν 187 cm^{-1}). The absorption spectrum of (4; R = Et) in ethanol solution in the range 10 000—50 000 cm^{-1} contains three bands at $\nu_{max.}$/cm^{-1} ($\log_{10} \varepsilon$) 27 800 (2.20), 33 400 (2.81), and 47 600 (4.20). The intensities of these absorptions are all less than in (1), in which they are also observed at similar energies.

The proton n.m.r. spectra of these diamagnetic copper(I) complexes confirm the stoicheiometry $[Cu(O_2CMe)\{P(OR)_3\}_2]$ (R = Me or Et). The shift of the acetate proton resonance in (3) (δ 1.82 p.p.m.) and (4) (δ 1.75 p.p.m.) is similar to that observed [24] in $[\{Cu(O_2CMe)(dppe)\}_2]$ (δ 1.85 p.p.m.) which is known to contain a bridging acetate ligand. The ^{31}P n.m.r. spectra of the complexes (3) and (4) consist of a single broad resonance ($R = Me$, δ 127 p.p.m., $\omega_{\frac{1}{2}}$ 363 Hz; $R = Et$, δ 118 p.p.m., $\omega_{\frac{1}{2}}$ 320 Hz) which indicates that the phosphite ligands are equivalent and in an environment of low symmetry (Scheme 2). This would be consistent with asymmetric bridging in the dimeric complexes. There is no evidence for solvation as represented by $[Cu(O_2CMe)\{P(OR)_3\}_2(HOR)]$, but this cannot be excluded rigorously.



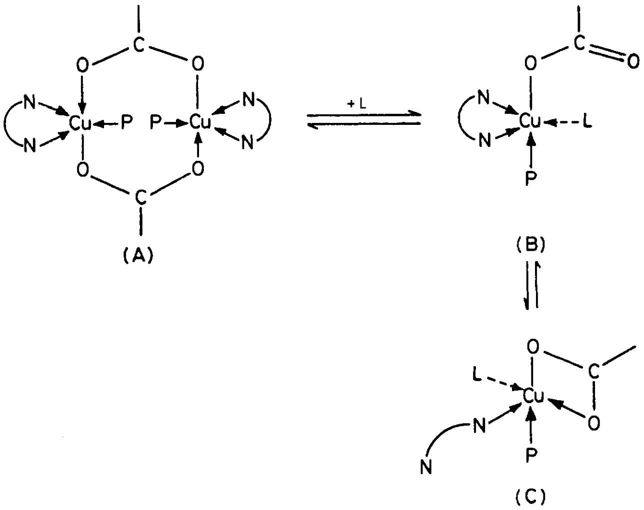
SCHEME 2 Solution behaviour of $[Cu(O_2CMe)\{P(OR)_3\}_2]$. L = solvent

Reaction of $[Cu(O_2CMe)\{P(OR)_3\}_2]$ *with Bidentate Donor Ligands.*—The liquid copper(I) complexes (3) and (4) react in ROH solution with bidentate ligands, L′, such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 1,2-diaminoethane (en), and 1,2-bis(diphenylphosphino)ethane (dppe) to form air-sensitive copper(I) compounds which are variously orange (L′ = phen), yellow (L′ = bipy or dppe), and colourless (L′ = en) and for which a stoicheiometry $[Cu(O_2CMe)\{P(OR)_3\}L']$ is indicated by microanalysis. It is pertinent to recall that when unidentate ligands, L, such as pyridine were used, the analogous complex $[Cu(O_2CMe)\{P(OR)_3\}L_2]$ was *not* formed (see above). Complexes of the general formula $[Cu(O_2CR)(PPh_3)L']$ have been prepared [25] and described as containing unidentate carboxylate ligands on the basis of i.r. evidence ($\Delta\nu > 200$ cm^{-1}). It is also reported [25] that $[Cu(O_2CMe)(PPh_3)_2]$ reacts with L′ to form $[Cu(O_2CMe)L']$ which have been described as dimeric complexes with bridging *syn-syn* acetate ligands. The same $[Cu(O_2CMe)L']$ complexes can be prepared [24] from the reaction between copper(I) acetate and L′ in benzene or diethyl ether solution.

The wavenumber difference between the symmetric and antisymmetric carboxylate stretching vibration $\Delta\nu$ in these $[Cu(O_2CMe)\{P(OR)_3\}L']$ complexes suggests that, in the solid state, these complexes are probably dimeric with acetate ligands bridging two copper(I) atoms. However, some values of $\Delta\nu$ (*e.g.* for L′ = dppe) lie within the range usually associated [24] with unidentate acetate so this criterion is ambiguous.

The electronic absorption spectra of the 2,2′-bipyridine complexes in the range 11 000—50 000 cm^{-1} are solvent dependent. The yellow solids form red solutions in alcohols, in acetonitrile the solutions are orange; the complexes dissolve in pentane to give solutions which are pale yellow.

The n.m.r. spectra of $[Cu(O_2CMe)\{P(OR)_3\}(bipy)]$ (5, R = Me; 6, R = Et) are particularly interesting. The ^{31}P n.m.r. spectra in $CDCl_3$ solution show a single resonance [(5), δ 122 p.p.m.; (6), δ 120 p.p.m.] which are both to high field of the free ligand resonance. There is no evidence of dissociation of the phosphite ligand from these complexes. The appearance of the ^1H n.m.r. spectra of these complexes is markedly temperature dependent. Integration of the proton n.m.r. spectra confirms the stoicheiometry $[Cu(O_2CMe)\{P(OR)_3\}(bipy)]$ of (5) and (6). In $CDCl_3$ the O_2CCH_3 signal appears as two triplets. In CS_2 solution this signal is a singlet (δ 2.10 p.p.m.), and in C_2D_5OD the O_2CCH_3 signal is also a singlet (δ 3.46 p.p.m.). The position of the O_2CCH_3 signal is apparently solvent dependent. The signals from the protons of the bipy ligand in (5) and in (6) show none of the expected fine structure (two triplets, two doublets) but appear as broad resonances, shifted to low field of the free ligand values. Taken together the spectroscopic evidence suggests that (5) and (6) are fluxional in solution. We believe that the solvated monomer $[Cu(O_2CMe)\{P(OR)_3\}(bipy)]$ achieves fluxionality as a result of interconversion of bidentate and unidentate acetate and 2,2′-bipyridine as shown in the idealised structures (B) and (C) in Scheme 3.



SCHEME 3 Solution behaviour of $[Cu(O_2CMe)\{P(OR)_3\}(bipy)]$. L = solvent

Conclusions.—Copper(II) carboxylates, and copper(II) acetate in particular, react with trialkyl phosphites in alcohol solution to form trinuclear mixed-valence complexes $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$. In the case of (1), it is established that the complex has a one-dimensional chain structure with acetate bridging between copper(II) acetate units in the solid state. This breaks down in ROH (alcohol) solution to form trinuclear monomers of a different structure, and there is evidence from ^{31}P n.m.r. spectroscopy that this is fluxional [Scheme 1, (B) and (C)]. In most other solvents the chain structure [Scheme 1, (A)] is broken down completely to its constituent copper(II) and copper(I) components. The copper(I) mononuclear complexes have been isolated and shown to be dimeric. These copper(I) complexes $[\{Cu(O_2CMe)[P(OR)_3]_2\}_2]$ react with bidentate (but *not* unidentate) ligands to form $[Cu(O_2CMe)\{P(OR)_3\}L']$ which are probably dimers in the solid state, but in solution exist as solvated fluxional monomers.

These observations emphasise two characteristics of the complexes (1)—(6) in solution, that they are fluxional, and that the solvent is critical in determining their behaviour.

EXPERIMENTAL

All preparations and manipulations were carried out in an atmosphere of dry deoxygenated dinitrogen using conventional Schlenk-tube techniques. Solvents were dried, deaerated, and distilled before use. Infrared spectra were recorded as mulls (Nujol, hexachlorobutadiene) on a Perkin-Elmer 257 i.r. spectrometer in the range 600—4 000 cm^{-1} and calibrated with polystyrene. Electronic spectra were recorded with a Perkin-Elmer u.v.–visible spectrometer. Proton and ^{31}P n.m.r. spectra were recorded on a WP80 spectrometer. Magnetic measurements were performed by the Gouy method using a tube calibrated with $Hg[Co(NCS)_4]$. Microanalyses and molecular-weight determinations were carried out by Mr. M. Hart, Manchester University.

Commercial grade trialkyl phosphites were treated with sodium and then distilled in a nitrogen atmosphere. Copper(II) acetate was reagent grade (B.D.H. Ltd.). Copper(II) propionate and copper(II) butyrate were prepared by adding a large excess of 2 mol dm^{-3} aqueous RCO_2H (R = Et or Pr^n) to basic copper carbonate. The suspension was stirred at room temperature until the effervescence had ceased; after settling, filtration, and concentration, the crude carboxylate precipitated from the aqueous solution. The pure $Cu[O_2CR]_2$ compound was obtained by recrystallisation from RCO_2H–H_2O (1 : 1 w/v) and dehydration over P_2O_5 *in vacuo*.

Preparation of Penta(alkanecarboxylato)bis(trialkyl phosphite)tricopper(I,II) *Complexes*.—Anhydrous copper(II) alkanecarboxylate (10 mmol) was added to dry alcohol (50 cm^3) and stirred under nitrogen. Trialkyl phosphite (10 mmol) was added to the solution and the mixture was boiled under reflux for 4 h. The mixture was allowed to cool to room temperature and then the alcohol was removed by distillation under reduced pressure leaving an emerald green gum. Light petroleum (b.p. 40—60 °C) (20 cm^3) was added with stirring, allowing the air-sensitive pale blue-green complex to precipitate. The powder was isolated by filtration, washed with light petroleum (3 × 10 cm^3) to remove any trialkyl phosphate, and then dried. Yields were generally in the range 30—40%, based on copper(II) carboxylate. Crystalline material was obtained by setting aside the green gum–light petroleum mixture for several weeks. The following compounds $[Cu_3(O_2CR^1)_5\{P(OR^2)_3\}_2]$ were prepared, analysed, and characterised: R^1 = Me, R^2 = Me (2) {Found: C, 26.0; H, 4.6; Cu, 25.2; P, 8.5. Calc. for $C_{16}H_{33}Cu_3O_{16}P_2$: C, 26.2; H, 4.5; Cu, 26.0; P, 8.5%. $\nu_{asym.}(CO_2)$ 1 640, 1 560; $\nu_{sym.}(CO_2)$ 1 400 cm^{-1}; $\delta(^1H)$ (in CD_3OD) 3.71 [18 H, $P(OCH_3)_3$], 3.35 (9 H, O_2CCH_3), 4.84 (6 H, O_2CCH_3) p.p.m.}; R^1 = Me, R^2 = Et (1) {Found: C, 32.0; H, 5.5; Cu, 23.1; P, 7.6. Calc. for $C_{22}H_{45}Cu_3O_{16}P_2$: C, 32.3; H, 5.5; Cu, 23.3; P, 7.6%. $\nu_{asym.}(CO_2)$ 1 630, 1 560; $\nu_{sym.}(CO_2)$ 1 400 cm^{-1}; $\delta(^1H)$ (in C_2D_5OD) 1.43 (9 H, O_2CCH_3), 1.56 [18 H, $P(OCH_2CH_3)_3$], 3.80 (6 H, O_2CCH_3), 4.35 [12 H, $P(OCH_2CH_3)_3$] p.p.m.}; R^1 = Me, R^2 = Pr^i (Found: C, 37.0; H, 6.4; Cu, 20.6; P, 7.1. Calc. for $C_{28}H_{57}Cu_3O_{16}P_2$: C, 37.2; H, 6.3; Cu, 21.1; P, 6.9%); R^1 = Et, R^2 = Me (Found: C, 31.9; H, 5.4; Cu, 23.9; P, 9.1. Calc. for $C_{21}H_{43}Cu_3O_{16}P_2$: C, 31.4; H, 5.4; Cu, 23.7; P, 7.7%); R^1 = Et, R^2 = Et (Found: C, 35.8; H, 6.0; Cu, 24.5; P, 6.2. Calc. for $C_{27}H_{55}Cu_3O_{16}P_2$: C, 36.6; H, 6.2; Cu, 21.3; P, 7.0%); R^1 = Pr^n, R^2 = Me (Found: C, 35.4; H, 6.0; Cu, 20.5; P, 7.2. Calc. for $C_{26}H_{53}Cu_3O_{16}P_2$: C, 35.7; H, 6.1; Cu, 21.8; P, 7.1%); and R^1 = Pr^n, R^2 = Et (Found: C, 40.5; H, 7.0; Cu, 19.6; P, 6.9. Calc. for $C_{32}H_{65}Cu_3O_{16}P_2$: C, 40.1; H, 6.8; Cu, 19.6; P, 6.5%).

Preparation of Acetatobis(trialkyl phosphite)copper(I) *Complexes*.—A solution of $[Cu_3(O_2CMe)_5\{P(OR)_3\}_2]$ (R′ = Me or Et, 2 mmol) in dry alcohol, ROH (25 cm^3), was prepared. Excess of freshly distilled pyridine (5 mmol) was added to this solution which was stirred magnetically throughout. After 10 min, during which a green solid precipitated from the solution, the alcohol solvent was evaporated under reduced pressure leaving a green oil. Light petroleum (20 cm^3) was added and the green solid removed by filtration. The solid was washed with light petroleum (3 × 10 cm^3) and dried. Microanalysis showed the solid to be $[Cu_2(O_2CMe)_4(py)_2]$ (Found: C, 41.2; H, 4.3; Cu, 23.9; N, 4.8. Calc. for $C_9H_{11}CuNO_4$: C, 41.5; H, 4.3; Cu, 24.4; N, 5.4%). The petrol was removed from the filtrate under reduced pressure, leaving a colourless air-sensitive oil, m.p. 285 K. Yield 90% [R = Et (4)] {Found: C, 37.0; H, 7.5; Cu, 13.1; P, 13.1. Calc. for $C_{14}H_{33}CuO_8P_2$: C, 37.0; H, 7.3; Cu, 14.0; P, 13.6%. $\nu_{asym.}(CO_2)$ 1 575, $\nu_{sym.}(CO_2)$ 1 410 cm^{-1}. $\delta(^1H)$ (in $CDCl_3$ solution) 1.20 [18 H, s, $P(OCH_2CH_3)_3$], 1.75 (3 H, s, O_2CCH_3), 3.92 [12 H, qnt (^3J 6.8 Hz), $P(OCH_2CH_3)_3$] p.p.m.}. For $[Cu(O_2CMe)\{P(OMe)_3\}_2]$ (3): $\nu_{asym.}(CO_2)$ 1 575, $\nu_{sym.}(CO_2)$ 1 405 cm^{-1}; $\delta(^1H)$ (in $CDCl_3$ solution) 1.82 (3 H, s, O_2CCH_3), 3.70 [18 H, d (^3J 11.9 Hz), $P(OCH_3)_3$] p.p.m.

Preparation of Acetato(2,2′-*bipyridine*)(*trialkyl phosphite*)*copper*(I) *and Related Complexes*.—A colourless solution of $[Cu(O_2CMe)\{P(OR)_3\}_2]$ (2 mmol) in dry alcohol, ROH (R = Me or Et, 25 cm^3), was prepared and to it was added 2,2′-bipyridine (2 mmol) with magnetic stirring throughout. The colour of the solution darkened immediately. The mixture was stirred at room temperature for 0.25 h, after which the solvent was evaporated under reduced pressure leaving a deep red oil. On standing, a yellow crystalline solid was deposited from the oil. The crystals were washed repeatedly with dry light petroleum and then dried *in vacuo*. The following compounds $[Cu(O_2CMe)\{P(OR)_3\}L']$ were prepared, analysed, and characterised: R = Me, L′ = bipy (5) {Found: C, 44.1; H, 5.1; Cu, 15.8; N, 6.6; P, 7.8. Calc. for $C_{15}H_{20}CuN_2O_5P$: C, 44.7; H, 5.0; Cu, 15.8; N, 7.0; P, 7.7%. $\nu_{asym.}(CO_2)$ 1 555, $\nu_{sym.}(CO_2)$ 1 380 cm^{-1}. $\delta(^1H)$ (in $CDCl_3$ solution) 0.81 (2 H, t), 1.16 (1 H, t), 3.54 [9 H, d (^3J 10.8 Hz), $P(OCH_3)_3$], 7.35 (2 H, m), 7.85 (2 H, m), 8.82 (2 H, m) p.p.m.}; R = Et, L′ = bipy (6) {Found: C, 48.6; H, 6.0; Cu, 14.2; N, 6.0; P, 7.0. Calc. for $C_{18}H_{26}CuN_2O_5P$: C, 48.6; H, 5.9; Cu, 14.2; N, 6.3;

P, 7.0%. $\nu_{asym.}(CO_2)$ 1 560, $\nu_{sym.}(CO_2)$ 1 375 cm^{-1}. $\delta(^1H)$ (in $CDCl_3$ solution) 0.87 (2 H, t), 1.17 (10 H, t), 3.98 [6 H, qnt (^3J 6.7 Hz), $P(OC\mathit{H}_2CH_3)_3$], 7.50 (2 H, m), 7.90 (2 H, m), 9.00 (2 H, m): (in C_2D_5OD solution) 1.15 [9 H, t, $P(OCH_2C\mathit{H}_3)_3$], 3.46 (3 H, s, $O_2CC\mathit{H}_3$), 3.79 [6 H, qnt (^3J 6.7 Hz), $P(OC\mathit{H}_2CH_3)_3$], 7.74, 8.17, 8.63, 8.89 (8 H, m, bipy) p.p.m.}; R = Et, L′ = phen [Found: C, 50.1; H, 5.6; Cu, 13.4; N, 5.7; P, 6.2. Calc. for $C_{20}H_{26}CuN_2O_5P$: C, 51.2; H, 5.6; Cu, 13.5; N, 6.0; P, 6.6%. $\nu_{asym.}(CO_2)$ 1 585, $\nu_{sym.}(CO_2)$ 1 375 cm^{-1}]; R = Et, L′ = 1,2-diaminoethane [Found: C, 34.5; H, 7.8; Cu, 17.3; N, 10.8; P, 8.1. Calc. for $C_{10}H_{26}CuN_2O_5P$: C, 34.4; H, 7.5; Cu, 18.2; N, 8.0; P, 8.9%. $\nu_{asym.}(CO_2)$ 1 570, $\nu_{sym.}(CO_2)$ 1 390 cm^{-1}]; and R = Et, L′ = dppe [Found: C, 58.8; H, 6.1; Cu, 8.7; P, 12.6. Calc. for $C_{34}H_{42}CuO_5P_3$: C, 59.4; H, 6.1; Cu, 9.2; P, 13.5%. $\nu_{asym.}(CO_2)$ 1 600, $\nu_{sym.}(CO_2)$ 1 380 cm^{-1}.

Yields of these complexes are usually in the range 35—45% based on $[Cu(O_2CMe)\{P(OR)_3\}_2]$.

Crystal and Molecular Structure of $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$.—*Data collection.* Air-sensitive emerald green needle-shaped crystals of (1), elongated along the *c* axis, were prepared. A crystal of cross-section 0.1 × 0.1 mm was sealed under dinitrogen in a thin-walled glass capillary and 0.3 mm of its length was exposed to *X*-ray radiation in a Weissenberg camera. Equi-inclination data were collected for $h,k,l = 0$—10 layers using a four-film pack. The films were processed by the S.E.R.C. Microdensitometer Service, Daresbury and the data were reduced to a unique set of 651 reflections. Intensity fell rapidly with increasing θ so that this work was restricted to a low resolution study.

Crystal data. $C_{22}H_{45}Cu_3O_{16}P_2$, $M = 817.81$, Monoclinic, $a = 13.77(4)$, $b = 19.10(3)$, $c = 17.08(4)$ Å, $\beta = 125.6(2)°$, $U = 3\,652.1$ Å^3, $Z = 4$ (calc.), $D_c = 1.49$ g cm^{-3}, $F(000) = 1\,688$, space group Cc (no. 9) from systematic absences $h\,k\,l$; $h + k = 2n + 1$, $h0l$; $l = 2n + 1$, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 38 cm^{-1}.

The alternative space group *C2/c*, which required the molecule to have centro- or two-fold symmetry, was rejected after examination of the Patterson synthesis which yielded a solution for the copper atoms.

Structure solution and refinement. A Fourier synthesis with phases based on the three copper atoms indicated the dispositions of the phosphorus atoms and the oxygen atoms of the bridging acetate groups. The full skeletal structure was revealed by cautious alternation of Fourier syntheses and least-squares refinements of the partial structure. There were insufficient data to provide a meaningful refinement of the carbon atoms in the $P(OC_2H_5)_3$ ligands, and the model structure with these ethyl groups removed refined to an *R* value of 0.128. A final agreement factor of 0.10 was achieved by allowing for anisotropic thermal motion of the copper and phosphorus atoms. Although the analysis has resolved the overall molecular geometry, it is clear that little reliance should be placed on individual values of bond lengths and angles. Evidence for systematic error in the observations is indicated by the shapes of the thermal ellipsoids for the copper atoms. These problems were not resolved due to the difficulties encountered in the collection of diffraction data and the severe limitation placed on the number and kind of reflections recorded as observed with data accessible only about one axis.

Fractional atomic co-ordinates for the refined structure are listed in Table 3 and the resultant bond lengths and bond angles are given in Table 1. The molecular structure is illustrated in the Figure. Observed and calculated structure factors are deposited in Supplementary Publication No. SUP 23111 (8 pp.).*

TABLE 3

Crystal co-ordinates for $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	0	0.002 4(6)	0
Cu(2)	0.016 0(14)	0.039 1(6)	0.151 7(13)
Cu(3)	0.222 5(14)	−0.050 4(5)	−0.005 5(13)
P(1)	0.268 8(23)	−0.162 5(12)	0.005 9(21)
P(2)	0.342 5(22)	0.040 2(13)	0.029 2(24)
O(1)	0.058 5(53)	−0.067 1(32)	−0.205 7(47)
O(2)	0.169 8(45)	0.006 4(30)	0.228 7(39)
C(3)	0.076 3(47)	0.131 1(28)	0.134 3(37)
O(4)	−0.144 2(50)	0.075 5(27)	0.059 2(45)
O(5)	−0.044 4(47)	−0.062 5(28)	0.138 9(45)
O(6)	−0.160 1(53)	0.040 8(30)	−0.069 2(46)
O(7)	−0.079 9(43)	−0.086 2(28)	−0.000 2(44)
O(8)	0.160 5(48)	−0.043 2(26)	0.094 2(42)
O(9)	0.050 1(39)	−0.036 9(24)	−0.089 8(37)
O(10)	0.075 1(48)	0.085 4(31)	0.009 1(43)
O(11)	0.271 5(61)	0.109 6(36)	−0.057 7(51)
O(12)	0.454 9(59)	0.028 1(37)	0.034 3(51)
O(13)	0.397 5(74)	0.053 9(43)	0.133 3(75)
O(14)	0.333 7(52)	−0.201 0(32)	−0.038 1(46)
O(15)	0.355 1(72)	−0.178 8(39)	0.094 5(64)
O(16)	0.170 4(47)	−0.217 7(28)	−0.023 7(40)
C(2)	−0.137 0(98)	−0.172 0(56)	0.081 4(82)
C(3)	−0.095 2(82)	−0.095 8(48)	0.053 8(81)
C(4)	−0.200 7(110)	0.072 5(56)	−0.024 1(104)
C(5)	−0.312 2(84)	0.103 4(47)	−0.089 2(69)
C(8)	0.093 0(74)	0.135 7(47)	0.071 2(69)
C(9)	0.150 3(75)	0.205 2(45)	0.069 3(62)
C(15)	0.348 4(64)	−0.060 7(37)	0.250 7(58)
C(16)	−0.142 7(76)	−0.040 1(48)	−0.240 2(72)
C(17)	0.195 6(76)	−0.013 4(46)	0.200 3(73)
C(18)	0.004 0(96)	−0.055 3(54)	−0.200 7(90)

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REFERENCES

[1] F. Ullmann, *Chem. Ber.*, 1903, **36**, 2382.

[2] F. Ullmann and J. Bielecki, *Chem. Ber.*, 1901, **34**, 2174.

[3] P. E. Fanta, *Synthesis*, 1974, 9.

[4] S. Arai, A. Tanaka, M. Hida, and T. Yamagishi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1731.

[5] N. Hall and R. Price, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2134.

[6] A. Michaelis and R. Kaehne, *Chem. Ber.*, 1898, **31**, 1048; A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687.

[7] J. A. Connor, A. C. Jones, and R. Price, *J. Chem. Soc., Chem. Commun.*, 1980, 137.

[8] P. de Meester, S. R. Fletcher, and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 2575.

[9] M. J. Bird and T. R. Lomer, *Acta Crystallogr., Sect. B*, 1972, **28**, 242.

[10] W. Choong and N. C. Stephenson, *Cryst. Struct. Commun.*, 1975, **4**, 275; A. Pajunen and E. Nasakkala, *Finn. Chem. Lett.*, 1977, 100.

[11] G. Nardini, L. Randaccio, R. P. Bonomo, and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1980, 369.

[12] G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, 1973, **29**, 2393.

[13] Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, 1979, **18**, 1122.

[14] M. G. B. Drew, A. H. bin Othman, D. A. Edwards, and R. Richards, *Acta Crystallogr., Sect. B*, 1975, **31**, 2695.

[15] M. R. Churchill, B. G. De Boer, and S. U. Mendak, *Inorg. Chem.*, 1975, **14**, 2041.

[16] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1899.

[17] M. Gerloch and J. H. Harding, *Proc. R. Soc. London, Ser. A*, 1978, **360**, 211.

[18] D. P. Graddon, *J. Inorg. Nucl. Chem.*, 1960, **14**, 161.

[19] R. R. Gagné, C. A. Koval, T. J. Smith, and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571.

[20] U. Ochsenbein and C. W. Schläpfer, *Helv. Chim. Acta*, 1980, **63**, 1926.

[21] P. Kroneck, O. Lutz, A. Nolle, and H. Oehler, *Z. Naturforsch., Teil A*, 1980, **35**, 221.

[22] C. J. Creswell, A. Dobson, D. S. Moore, and S. D. Robinson, *Inorg. Chem.*, 1979, **18**, 2055.

[23] W. K. Musker, M. M. Olmstead, R. M. Kessler, M. B. Murphey, C. H. Neagley, P. B. Rousch, N. L. Hill, T. L. Wolford, H. Hope, G. Delker, K. Swanson, and B. Gorewit, *J. Am. Chem. Soc.*, 1980, **102**, 1225.

[24] D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1975, 637.

[25] B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1017.