Macrocyclic Copper(II) Chelate Derivatives of 2,9-Bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic and 2,2,9,9-Tetramethyl-4,7-dithiadecanedioic Acids. The Crystal and Molecular Structures of Aqua, Pyridine, and Triphenylphosphine Adducts of [2,9-Bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioato]copper(II)

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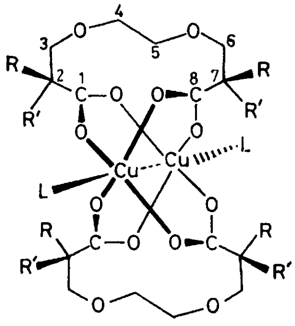
The preparation of 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid (1; H_2Y) as a mixture of diastereomers is reported, as is its conversion into the macrocyclic, carboxylate-bridged, dimeric copper(II) derivatives [{CuYL}$_2$] [L = water (2), no ligand (3), pyridine (4), or triphenylphosphine (5)]. Each of these has been obtained in two forms, namely (2a)—(5a) in which the carboxylate ligand is present in both DL and *meso* forms and (2b)—(5b) which contain only the *meso* form. Spectral data (i.r. and u.v.–visible) are discussed. Structures have been determined from diffractometer data for compounds (2a), (4b), and (5b) which crystallise in the triclinic space group $P\bar{1}$ with $Z = 1$. Unit cell dimensions are: $a = 11.506(4)$, $b = 7.149(2)$, $c = 13.085(3)$ Å, $\alpha = 101.01(1)$, $\beta = 114.06(2)$, $\gamma = 90.85(2)°$ for (2a); $a = 11.230(4)$, $b = 9.940(4)$, $c = 10.954(4)$ Å, $\alpha = 112.16(3)$, $\beta = 107.26(3)$, $\gamma = 81.22(3)°$ for (4b); and $a = 14.593(1)$, $b = 10.747(1)$, $c = 11.894(2)$ Å, $\alpha = 75.025(6)$, $\beta = 115.011(6)$, $\gamma = 99.567(6)°$ for (5b). The structures were solved by Fourier and Patterson methods and refined by full-matrix least-squares calculations to final *R* values of 0.078, 0.084, and 0.061 respectively. In all cases, the molecule is located around a crystallographic centre of symmetry and contains two copper atoms bridged by four carboxylate groups. The Cu–Cu distances are 2.626(2), 2.655(1), and 2.676(1) Å for the aqua, pyridine, and triphenylphosphine complexes respectively. For the pyridine and triphenylphosphine complexes, the dicarboxylate ligand is exclusively *meso* whereas the considerable disorder observed in the aqua complex indicates the presence of a mixture of D, L, and *meso* forms. The conversion of 2,2,9,9-tetramethyl-4,7-dithiadecanedioic acid (6) into $Cu(O_2CCMe_2CH_2SCH_2-)_2\cdot L$ [L = 0—1 H_2O (7) or pyridine (8)] is also described. It is suggested, on the basis of spectral and solubility properties, that these complexes have similar macrocyclic structures to those derived from (1).

In the course of an investigation of the complexing properties of a series of potentially multidentate, polyether polycarboxylate ligands,[1] we have found [2] that displacement of acetic acid from copper(II) acetate with 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid (1; H_2Y) leads to products in which only the carboxylate groups are co-ordinated.

The crude diacid (1) was prepared as a mixture of diastereomers as outlined in ref. 2 and in the Experimental section. This diacid was heated with an equimolar amount of copper(II) acetate monohydrate in refluxing benzene, water and acetic acid being removed azeotropically. The resulting intensely coloured greenish blue solution was chromatographed over silica gel. Recrystallisation, from aqueous acetone, of fractions eluted with benzene and diethyl ether–benzene gave two types of crystals, which were separated mechanically. The major component (2a) crystallised as thin blue-green parallelograms, while the minor (2b) formed small irregularly shaped nodules of a similar colour. Elemental analyses of both are consistent with their formulation as [{CuY(OH$_2$)}$_2$]. Stirring and heating of either (2a) or (2b) in benzene, with azeotropic removal of water, gave dark blue solutions from which anhydrous products {[(CuY)$_2$]$_n$; (3a) and (3b)} could be precipitated as pale blue powders by adding cyclohexane. These products readily absorb water from the air to regenerate the hydrates (2a) and (2b) as evidenced by the finding that their i.r. spectra are identical to those of the hydrates when mulls are prepared from them in the open. Indeed, when benzene solutions of (3a) and (3b) are allowed to stand in air, the hydrates are slowly deposited. Treatment of freshly prepared benzene solutions with stoicheiometric amounts (or a slight excess) of pyridine (py) or triphenylphosphine resulted in an immediate colour change from dark blue to bright green and dark green respectively. Complexes which can be formulated as [{CuY(py)}$_2$] [(4a) and (4b)] and



(2) L = H_2O
(3) No additional ligand
(4) L = py
(5) L = PPh_3
a; DL + *meso*; R, R' = Me or CH_2OMe but R $\neq$ R'
b; *meso*; R = Me, R' = CH_2OMe

TABLE 1

Bond lengths and angles of complexes (2a), (4b), and (5b)

	(2a) $C_{28}H_{52}Cu_2O_{18}$	(4b) $C_{38}H_{58}Cu_2N_2O_{16}$	(5b) $C_{64}H_{78}Cu_2O_{16}P_2$
(*a*) Bond lengths (Å). Unless otherwise indicated, standard deviations are 0.01 Å			
Cu–Cu′ [a]	2.626(2)	2.655(1)	2.676(1)
Cu–O(1)	1.948(4)	1.965(5)	1.955(3)
Cu–O(2)	1.963(4)	1.963(5)	1.975(3)
Cu–O(3)	1.965(4)	1.971(5)	1.972(3)
Cu–O(4)	1.937(4)	1.976(5)	1.967(4)
Cu–L [b]	2.144(3)	2.179(6)	2.570(2)
C(1)–O(1)	1.25	1.26	1.26
C(1)–O(2′)	1.27	1.26	1.25
C(1)–C(2)	1.60	1.52	1.53
C(2)–C(3)	1.53	1.53	1.52
C(2)–C(43)	1.59	1.53	1.53
C(2)–C(44)	1.49	1.52	1.52
C(3)–O(5)	1.41	1.41	1.42
O(5)–C(4)	1.35(2), 1.73(2)	1.45	1.44
C(4)–C(5)	1.45(4), 1.60(3)	1.45	1.49
C(5)–O(6)	1.39(2), 1.59(2)	1.44	1.42
O(6)–C(6)	1.47	1.41	1.43
C(6)–C(7)	1.55	1.51	1.52
C(7)–C(8)	1.55	1.53	1.55
C(7)–C(40)	1.55	1.54	1.53
C(7)–C(41)	1.59	1.50	1.53
C(8)–O(3′)	1.25	1.26	1.25
C(8)–O(4)	1.25	1.26	1.25
C(41)–O(7)	1.46, 1.45(2)	1.42	1.43
O(7)–C(42)	1.47, 1.52(3)	1.43	1.42
C(44)–O(8)	1.28, 1.37	1.43	1.42
O(8)–C(45)	1.54(2), 1.53(3)	1.41	1.41
(*b*) Valence angles (°). Unless otherwise indicated standard deviations in angles at Cu are 0.2° and in those at other atoms range from 0.5 to 0.9°			
Cu′–Cu–O(1)	85.1	81.4	86.2
Cu′–Cu–O(2)	83.8	86.0	80.6
Cu′–Cu–O(3)	83.8	85.7	81.6
Cu′–Cu–O(4)	84.8	82.1	85.2
L–Cu–O(1)	98.1	95.0	105.7
L–Cu–O(2)	93.1	97.6	87.5
L–Cu–O(3)	94.0	97.3	92.6
L–Cu–O(4)	97.5	95.0	100.7
O(1)–Cu–O(3)	89.7	89.0	88.3
O(1)–Cu–O(4)	88.7	90.0	89.0
O(2)–Cu–O(3)	90.5	88.8	91.2
O(2)–Cu–O(4)	89.0	89.5	88.5
O(1)–C(1)–O(2′)	127.2	124.1	125.0
O(1)–C(1)–C(2)	115.5	117.0	116.6
O(2′)–C(1)–C(2)	117.3	118.8	118.4
C(1)–C(2)–C(3)	105.9	107.8	109.1
C(1)–C(2)–C(43)	104.8	108.4	107.4
C(1)–C(2)–C(44)	109.8	109.6	109.8
C(3)–C(2)–C(43)	111.2	108.5	108.4
C(3)–C(2)–C(44)	115.9	111.0	112.7
C(43)–C(2)–C(44)	108.6	111.5	109.2
C(2)–C(3)–O(5)	105.2	109.3	106.6
C(3)–O(5)–C(4)	94.7, 124.7	113.8	113.7
O(5)–C(4)–C(5)	104(1), 98(2)	108.9	113.2
C(4)–C(5)–O(6)	100(1), 106(2)	113.5	108.6
C(5)–O(6)–C(6)	102.0, 120.9	115.7	114.6
O(6)–C(6)–C(7)	101.2	108.5	107.8
C(6)–C(7)–C(8)	110.2	109.2	107.5
C(6)–C(7)–C(40)	114.1	108.4	109.2
C(6)–C(7)–C(41)	106.4	110.4	111.3
C(8)–C(7)–C(40)	110.1	107.8	108.9
C(8)–C(7)–C(41)	108.3	110.6	108.8
C(40)–C(7)–C(41)	107.5	110.3	111.1

TABLE 1 (*continued*)

	(2a) $C_{28}H_{52}Cu_2O_{18}$	(4b) $C_{38}H_{58}Cu_2N_2O_{16}$	(5b) $C_{64}H_{78}Cu_2O_{16}P_2$
C(7)–C(8)–O(3′)	117.9	117.7	117.6
C(7)–C(8)–O(4)	114.8	117.2	116.8
O(3′)–C(8)–O(4)	127.3	125.1	125.6
(*c*) Torsion angles (°)			
C(1)–C(2)–C(3)–O(5)	−62.7	−66.5	−61.1
C(2)–C(3)–O(5)–C(4)	−171.2, 149.8	−163.1	140.4
C(3)–O(5)–C(4)–C(5)	−87.5, 180.0	−88.8	176.6
O(5)–C(4)–C(5)–O(6)	−75.2, 76.2	−63.6	59.2
C(4)–C(5)–O(6)–C(6)	173.3, 86.5	−177.5	98.1
C(5)–O(6)–C(6)–C(7)	−153.1, −177.31	−149.2	−157.4
O(6)–C(6)–C(7)–C(8)	62.4	59.9	69.6

[a] In text and tables the positions of primed atoms are related to those of the unprimed ones by the operation of the appropriate crystallographic centre of symmetry. [b] L represents the co-ordinated atom of the water, pyridine, and triphenylphosphine ligands in the respective complexes.

[$\{CuY(PPh_3)\}_2$] [(5a) and (5b)] were recovered from these solutions.

The solubilities of these complexes indicate that they do not have polymeric structures analogous to those adopted[3] by copper(II) decanedioate and its monopyridine adduct. However, i.r. and electronic spectral data (see Experimental section) suggest[4] the presence of dimeric copper carboxylate units similar to those found in copper(II) acetate monohydrate. For example, the i.r. spectra of the complexes * show bands at *ca.* 1 420 and above 1 600 cm^{-1} attributable[4–7] to bridging carboxylate groups in binuclear units. In addition, solution electronic spectra are similar to those reported[3–5] for complexes containing dimeric units of this type. Thus, all of these complexes show a broad asymmetric band at *ca.* 700 nm and strong charge-transfer absorption in the u.v. region. The pyridine adducts, in addition, show a pronounced maximum on the tail of the latter absorption at *ca.* 370 nm. This band is not discernible in solid-state spectra of the aqua-complexes, (2a) and (2b), in solution spectra of the anhydrous complexes, (3a) and (3b), nor in those of the triphenylphosphine adducts, (5a) and (5b). However, in the last pair the charge-transfer absorption has a more pronounced tail into the visible region. Relative molecular mass determinations (by osmometry) on the pyridine adducts give values in excellent agreement with the dimeric, [$\{CuY(py)\}_2$], formulation. The anhydrous complexes, (3a) and (3b), on the other hand, gave concentration-dependent values corresponding to [$\{CuY\}_n$] with n increasing from *ca.* 2 to *ca.* 4 for concentrations of copper in the range 1.0×10^{-3}—20×10^{-3} mol dm^{-3} respectively. Although these results may be somewhat suspect due to the possibility of absorption of water in the course of measurement, they do suggest that dimeric units are becoming increasingly associated as the concentration is increased. Association could be envisaged as involving the carboxylate [*cf.* solid-state structures of anhydrous copper(II) propionate[8,9] and butyrate[8,10]] and/or ether groups. Involvement of the former is suggested by the solution i.r. spectra of (3a) and (3b) (*ca.* 60×10^{-3} mol dm^{-3} copper in $CDCl_3$) which show a split band centred at *ca.* 1 575 cm^{-1} in addition to the band at *ca.* 1 610 cm^{-1} which is also split in this case. Lack of significant involvement of the ether groups in this association is suggested by the close similarity in the positions and shapes of the ether bands at *ca.* 1 100 cm^{-1} in the solution spectra of (3a) or (3b) and their pyridine adducts.

In order to determine the structures of these products we turned to *X*-ray crystallography. The crystals of (2a) and (2b) isolated from aqueous acetone proved unsuitable for study. However, when acetonitrile and then cyclohexane were added to a solution of (3a) in benzene and crystallisation allowed to proceed in the open, (2a) was obtained as stout prisms. These proved suitable for *X*-ray work, as did (4b) and (5b) which in contrast to (4a) and (5a) crystallised as well formed prisms.

Geometric parameters determined from the *X*-ray analyses are presented in Table 1. In contrast to copper(II) succinate dihydrate which was found[11] to be polymeric with each carboxylate group of the succinate ligand bonding to two different pairs of copper atoms, the crystal structures of the present compounds (Figure 1) consist of discrete dimeric molecules separated by normal van der Waals contacts. Individual molecules (*e.g.* Figure 2) are centrosymmetric dimers in which each copper atom has a distorted octahedral environment similar to that found[4] for copper(II) acetate dihydrate. In the equatorial plane, the oxygen atoms of four separate carboxylate groups are situated at Cu–O distances ranging from 1.937 to 1.976 [mean 1.963(3) Å]. The axial positions are occupied by the centrosymmetrically related Cu atom [Cu–Cu = 2.626(2), 2.655(1), and 2.676(1) Å] and by the co-ordinating atom of the water, pyridine, or triphenylphosphine ligands [Cu–O = 2.144(3), Cu–N = 2.179(6), and Cu–P = 2.570(2) Å].

The ligand conformations are defined by the torsion

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* Differences in the i.r. spectra of the major and minor isomers of [$\{CuY(PPh_3)\}_2$] [(5a) and (5b)] are discussed later.

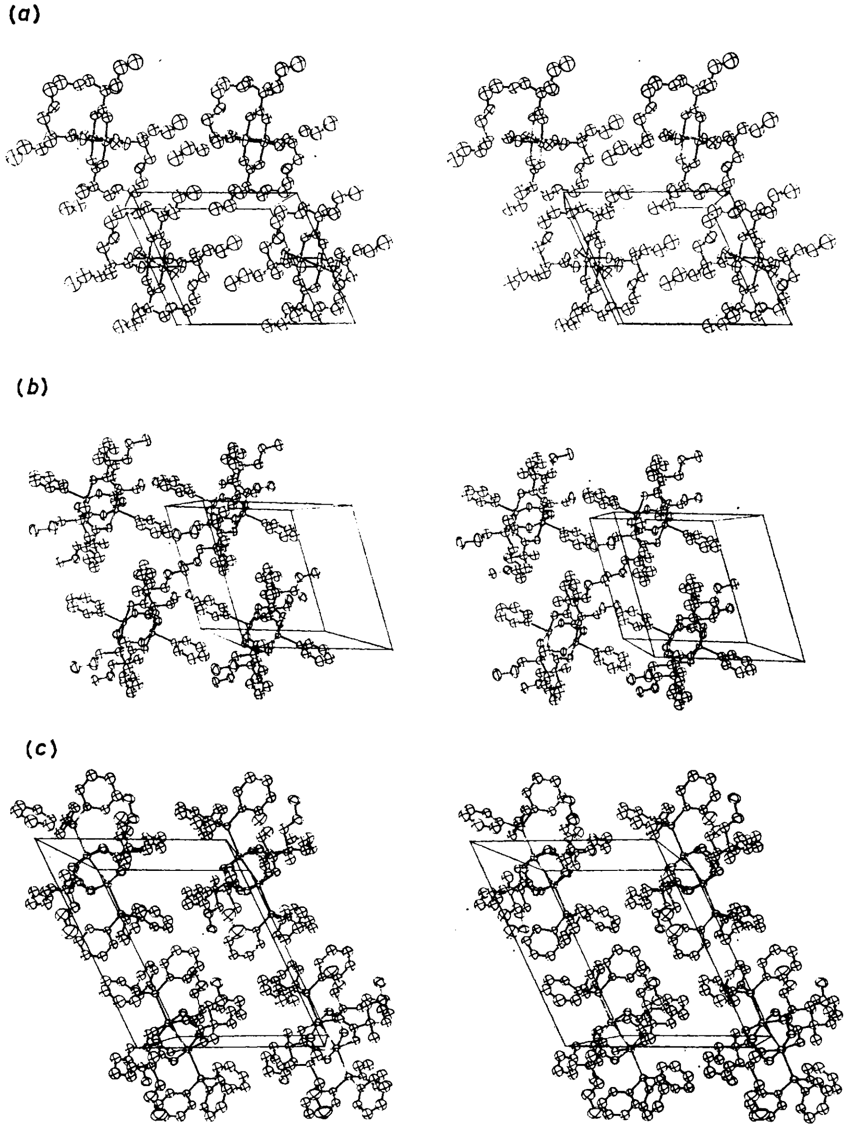

FIGURE 1 Stereoviews of (*a*) the aqua-complex (2a), (*b*) the pyridine complex (4b), and (*c*) the PPh_3 complex (5b)

angles given in Table 1(*c*). Two different disordered situations have been found in the aqua-complex. First, the C(4)–C(5) linkage adopts two distinct conformations [Table 1(*c*)] of occupancies 0.65(4) and 0.35(4), supporting evidence for considering those atoms to be disordered rather than suffering high thermal motion being provided by the observation that one of these conformations is closely paralleled in the pyridine complex whereas the other is found in the phosphine complex. Second, the methyl and methoxymethyl groups are present in occupancies which represent a mixture of D, L, and *meso* configurations for the ligand.

The finding, from these *X*-ray studies, that the major isomer (2a) contains both DL and *meso* forms of the ligand in a *ca.* 2 : 1 ratio, while the minor isomers (4b) and (5b) contain only the *meso* form, could account for the fact that (4a) and (5a) gave more poorly formed crystals than (4b) and (5b). Indeed, recrystallisation of (5a) gave a progressive improvement in crystal shape and increase in melting point while concomitant changes in the i.r. spectrum suggest that purer DL complex was being obtained. In the i.r. spectrum of (5b) the two out-of-plane aromatic C–H deformation bands are split into symmetrical pairs at 693, 699, and 748, 752 cm^{-1} while (5a) on initial isolation shows two relatively broad bands at 698 and 749 cm^{-1}. Recrystallisation of the latter gives material in which these bands are significantly sharper. Changes also occur in the 1 080—1 160 cm^{-1} region associated with C–O vibrations (see Experimental section) and elsewhere in the fingerprint region. For example, (5b) shows bands at 1 273m and 1 291w cm^{-1} while in recrystallised (5a) a similar pair of bands appears at 1 270w and 1 287m cm^{-1} with reversed relative intensities.

As a preliminary step in an investigation of the factors favouring formation of the macrocyclic chelate structure described above as opposed to polymers given [3] by simple α,ω-dicarboxylates or structures involving ether co-ordination, we have prepared copper(II) derivatives of 2,2,9,9-tetramethyl-4,7-dithiadecanedioic acid, (6).[12] Since copper(II) shows [13] a significantly greater affinity for thioethers than ethers, it was of interest to determine if (6) would (*i*) act as a quadridentate ligand, (*ii*) behave in an analogous fashion to (1), or (*iii*) form polymeric chains.

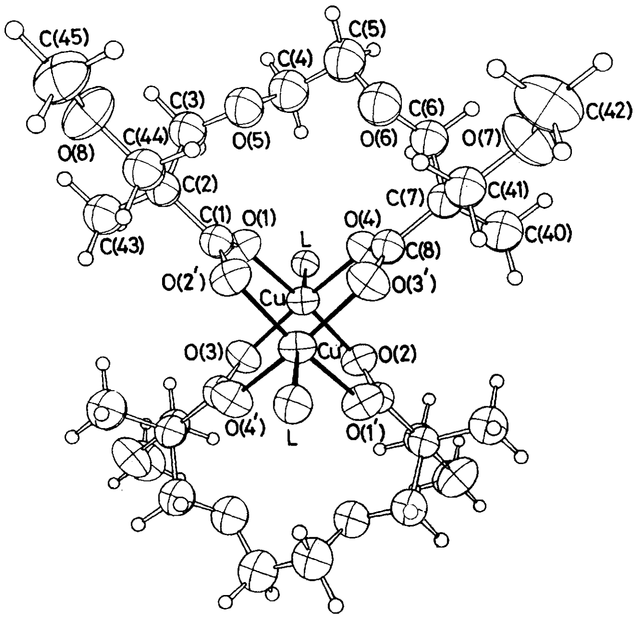

FIGURE 2 A detailed view of the [{CuY(PPh$_3$)}$_2$] structure, (5b). L represents the PPh$_3$ ligand

Mixing ethanolic, or aqueous ethanolic, solutions of (6) and of copper(II) acetate led to the precipitation of pale green powders, the analyses of which were consistent with the formulations $C_{12}H_{20}CuO_4S_2 \cdot xH_2O$ (x = 0—1), (7). These materials were insoluble in all common solvents, but could be induced to dissolve in hot benzene in the presence of pyridine. The resulting green solution, on cooling, deposited a bright green powder of composition $C_{12}H_{20}CuO_4S_2 \cdot py$, (8). This power proved to be insoluble in hot benzene and indeed resisted redissolution in benzene containing relatively large amounts of pyridine. However, it did dissolve in hot pyridine to give a blue-green solution which became deep blue on cooling. Tight clumps of bright blue crystals grew slowly, leaving a virtually colurless supernatant. These crystals turned green upon standing in air due to a partial loss [14] of pyridine. Dilution of the deep blue pyridine solution with benzene afforded a bright green solution from which (8) gradually separated.

Infrared and u.v.–visible spectra of (7) and (8) are again consistent (see Experimental section) with the presence of dimeric copper carboxylate units. Indeed, the i.r. spectra of (7) and (8) in Nujol are very similar, the only major differences being ascribable to pyridine-derived bands in the latter. This suggests that the formation of (8) from (7) does not involve displacement of co-ordinated sulphur. It has been reported [15] that for thioethers containing $-CH_2SCH_2-$ moieties a band at *ca.* 1 240 cm^{-1} moves to higher energies by *ca.* 20 cm^{-1} and decreases in relative intensity upon complexation to copper(II). The ligand (6) shows a band of weak–medium intensity at 1 252 cm^{-1} and an associated weak band at 1 263 cm^{-1}, while (7) and (8) show a broadened band of medium intensity at 1 256 cm^{-1} suggesting that sulphur is not co-ordinated in either (7) or (8). For comparison, the adduct CuCl$_2$ with (6), in which sulphur co-ordination is expected, was prepared (see Experimental section) and showed retention of the sharp band (at 1 253 cm^{-1}) but loss of the weak one at 1 263 cm^{-1}. The u.v.–visible spectra of (7) and (8) are comparable with those of (3) and (4) in that (7) shows no discernible band in the tail of the charge-transfer absorption while (8) shows a shoulder at *ca.* 375 nm.

In conclusion, the spectroscopic evidence indicates the presence of dimeric copper carboxylate units and the absence of sulphur co-ordination in (7) and (8). The solubility properties of these complexes suggest that they adopt a macrocyclic structure analogous to that described above, rather than a polymeric one. Unfortunately, we have been unable to obtain (7) or (8) in a form suitable for *X*-ray crystallographic examination.

EXPERIMENTAL

Melting points were determined in glass capillary tubes since those determined on a Kofler hot stage were not reproducible. Elemental analyses were obtained from Guelph Chemical Laboratories Ltd., Guelph, Ontario or were determined by Mr. H. S. McKinnon in this department. Hydrogen-1 n.m.r. (CDCl$_3$ solution), i.r., and u.v.–visible spectra were run on Varian A-60A, Beckman IR-12, and Unicam SP.800 or Cary 118 instruments respectively. Relative molecular masses were determined on a Hitachi–Perkin-Elmer 115 osmometer.

2,9-*Bis*(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioic Acid*, (1).—*N*-Bromosuccinimide (134 g) was added in portions with stirring to an ice-cooled solution of 3-hydroxymethyl-3-methyloxetane [16] (75.5 g) and triphenyl phosphite (230 g) in dichloromethane (500 cm^3). The resulting mixture was stirred at ambient temperature overnight. After removal of the solvent at atmospheric pressure, the residue was distilled at the water pump until triphenyl phosphate began to collect. The distillate was shaken with aqueous sodium hydroxide, then water and dried. Redistillation at the water pump gave 3-bromomethyl-3-methyloxetane (90.8 g, 74%, b.p. 55—58 °C); δ 1.41 (s, 3 H, C–*Me*), 3.64 (s, 2 H, C*H*$_2$Br), 4.41 (d, 2 H, *J* = *ca.* 6 Hz, oxetane C*H*$_2$), and 4.42 (d, 2 H, *J* = *ca.* 6 Hz, oxetane C*H*$_2$). Ethylene glycol (6.2 g) and then 3-bromomethyl-3-methyloxetane (33.0 g) were added to a solution of sodium (4.8 g) in t-pentyl alcohol (200 cm^3) and this mixture was heated at reflux for 24 h. Most of the solvent was then distilled out and the residue was partitioned between diethyl ether and water. The ether layer was separated, dried, evaporated, and the residue distilled at the water pump to give 1,6-*bis*(3-*methyloxetan*-3-*yl*)-2,4-*dioxahexane* (18.4 g, 79.9%, b.p. 155—158 °C); δ 1.30 (s, 6 H, C–*Me*), 3.56 (s, 4 H, neopentyl C*H*$_2$), 3.67 (s, 4 H, OC*H*$_2$C*H*$_2$O), 4.35 and 4.53 (both d, 4 H,

J = 5.7 Hz, oxetane CH_2) (Found: C, 62.45; H, 9.6. $C_{12}H_{22}O_4$ requires C, 62.6; H, 9.65%). Concentrated sulphuric acid (3 cm^3) was added to a solution of the bis(oxetane) (46.2 g) in methanol (500 cm^3). The resulting solution was heated at reflux for 6 h, cooled, treated with solid sodium hydroxide (5 g), and the methanol was then distilled out. Benzene (500 cm^3) was added and residual methanol and water were removed azeotropically. The solution was then filtered and distilled to give 2,9-bis-(methoxymethyl)-2,9-dimethyl-4,7-dioxadecane-1,10-diol (44.3 g, b.p. 150—160 °C, 0.1 mmHg *) which was characterised by ^{1}H n.m.r. only; δ 1.03 (s, 6 H, C–*Me*), 3.10 (br s, 2 H, O*H*), 3.33 (s, 10 H, O*Me* + neopentyl CH_2), 3.45 (m, 4 H, neopentyl CH_2), 3.55 (m, 4 H, neopentyl CH_2), and 3.59 (s, 4 H, OCH_2CH_2O). This diol (44.3 g) was added dropwise with stirring and cooling in ice to nitric acid (100 cm^3, specific gravity 1.42) containing sodium nitrite (0.5 g) at such a rate that the temperature did not rise above 20 °C. When addition was complete and the reaction had subsided, the temperature was allowed to rise to ambient and stirring was continued overnight. The resulting dark green mixture was heated on the steam bath for 90 min and then evaporated to small bulk on the rotary evaporator at 90 °C. The residual yellow oil was partitioned between benzene and aqueous ammonium sulphate (*ca.* 3 mol dm^{-3}). Separation of the benzene layer and evaporation gave crude 2,9-bis-(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid, (1) (22.0 g); δ 1.22 (s, 6 H, C–*Me*), 3.38 (s, 6 H, O*Me*), 3.54 (s, 4 H, OCH_2CH_2O), 3.62 (br s, 8 H, neopentyl CH_2), and 11.24 (br s, 2 H, O*H*). The crude diacid (22.0 g) was dissolved in methanol (50 cm^3) containing toluene-*p*-sulphonic acid (0.5 g) and the resulting solution heated at reflux overnight. Toluene (20 cm^3) was added and the solvent was distilled until 60 cm^3 of distillate had been collected. Fresh methanol (40 cm^3) was then added and heating, addition of toluene, and distillation repeated as above. The acid catalyst was neutralised with solid potassium carbonate (0.2 g), the solvent evaporated, the residue dissolved in diethyl ether, and filtered. Distillation of the filtrate, finally at 0.005 mmHg, gave *dimethyl* 2,9-*bis*-(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioate* (7.65 g, b.p. 120—125 °C); δ 1.17 (s, 6 H, C–*Me*), 3.32 (s, 6 H, CH_2OMe), 3.50 (s, 4 H, OCH_2CH_2O), 3.57 (br s, 8 H, neopentyl CH_2), and 3.68 (s, 6 H, CO_2Me) (Found: C, 54.8; H, 8.45. $C_{16}H_{30}O_8$ requires C, 54.85; H, 8.65%). This ester was the major component in the forerun (11.8 g, b.p. 80—120 °C) of the above distillation.

Copper Complexes of (1).—The diester (5.00 g, 0.014 3 mol) was hydrolysed by heating to reflux for 3 h with excess of aqueous sodium hydroxide (50 cm^3, *ca.* 1 mol dm^{-3}) which had been standardised against a hydrochloric acid solution. The resulting hydrolysate was treated with one equivalent of the acid solution and the solvent then removed *in vacuo*. The residue was extracted with benzene, the last traces of water being removed azeotropically. The solution was filtered and copper(II) acetate monohydrate (2.74 g, 0.013 7 mol) was added. The mixture was heated at reflux, with stirring, for 90 min to give a dark blue-green solution from which benzene was distilled to azeotrope water and acetic acid. The resulting solution was cooled and transferred to a chromatography column containing silica gel (60 g, Merck SG60). Successive elution with benzene, diethyl ether–benzene (1 : 3), and methanol–benzene (1 : 9) gave fractions (2.14, 1.39, and 2.22 g respectively) the first two of which, on repeated crystallisation from aqueous acetone, afforded two types of crystals, a major, (2a) (2.52 g), and a minor, (2b) (0.446 g), component. The second chromatographic fraction appeared to give a higher proportion of (2b) while the third fraction consisted of a gum which could not be induced to crystallise. The major component (2a) formed clumps of long slender, green, parallelograms, m.p. 183 °C (with loss of water *ca.* 130 °C) (Found: C, 41.7; H, 6.5. $C_{28}H_{48}Cu_2O_{16}\cdot H_2O$ requires C, 41.8; H, 6.55%); $\lambda_{max.}$ (Nujol mull) at 707 nm; $\nu_{max.}$ (Nujol mull) at 3 482m br ν(O–H), 1 612vs $\nu_{asym.}$ (CO_2), 1 424s $\nu_{sym.}$ (CO_2), 1 143m, 1 114s, and 1 093ms cm^{-1}. The minor component, *aqua*[meso-2,9-*bis*(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioato*]*copper*(II), (2b), crystallised as irregular nodules which initially appeared blue but ultimately grew together into green sheets which tended to adhere to the walls of the crystallisation flask. These crystals had m.p. 170 °C (with loss of water *ca.* 130 °C) (Found: C, 42.2; H, 6.75%); $\nu_{max.}$ (Nujol mull) at 3 450m br ν(O–H), 1 622vs $\nu_{asym.}$ (CO_2), 1 424s $\nu_{sym.}$ (CO_2), 1 148m, 1 117s, and 1 083ms cm^{-1}. A suspension of (2a) in benzene was heated at reflux until dissolution to give a dark blue solution took place. Some benzene was distilled out to remove water, then cyclohexane was added to the refluxing solution until precipitation of a blue powder commenced. The mixture was then allowed to cool to ambient temperature and the blue solid collected, leaving a colourless supernatant. This powder, (3a), had m.p. 174—177 °C (Found: C, 43.5; H, 6.45. $C_{28}H_{48}Cu_2O_{16}$ requires C, 43.8; H, 6.3%); $\lambda_{max.}$ (4.00 × 10^{-3} mol dm^{-3} for Cu in benzene) at 666 nm (ε 111), ε_{350} 122 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (22 mg cm^{-3} in $CDCl_3$) at 1 622s, 1 616 (sh), 1 580m, and 1 574m $\nu_{asym.}$ (CO_2), 1 425s $\nu_{sym.}$ (CO_2), 1 137 (sh), 1 111s cm^{-1}. [The spectrum of a Nujol mull of (3a) prepared in air was very similar to that of its hydrate (2a).] Relative molecular mass (mol dm^{-3} copper in benzene) 810 (2.00 × 10^{-3}) (Calc. for $C_{14}H_{24}CuO_8$ 384), 1 160 (5.00 × 10^{-3}), 1 290 (1.00 × 10^{-2}), 1 320 (1.50 × 10^{-2}), and 1 420 (2.00 × 10^{-2}). The anhydrous form (3b) of the minor isomer was prepared similarly. [meso-2,9-*Bis*(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioato*]*copper*(II) was obtained as a blue powder, m.p. 167—168 °C (Found: C, 43.95; H, 6.5%); $\nu_{max.}$ (24 mg cm^{-3} in $CDCl_3$) at 1 620s, 1 615s, 1 579m, and 1 573m $\nu_{asym.}$ (CO_2), 1 426s $\nu_{sym.}$ (CO_2), 1 135 (sh), 1 112 (sh), and 1 101s cm^{-1}. Relative molecular mass (mol dm^{-3} copper in benzene) 840 (1.75 × 10^{-3}), 1 230 (4.00 × 10^{-3}), 1 560 (1.50 × 10^{-2}), and 1 630 (2.00 × 10^{-2}).

Deep blue solutions of (3a) and (3b) (1.0 mmol) in benzene (15 cm^3) were treated with pyridine (0.5 cm^3) to give bright green solutions which were evaporated to dryness. Crystallisation (cyclohexane) of the green product from the former gave (4a), m.p. 132—133 °C (Found: C, 49.05; H, 6.5; N, 3.15. $C_{38}H_{58}Cu_2N_2O_{16}$ requires C, 49.3; H, 6.35; N, 3.05%); $\lambda_{max.}$ (4.00 × 10^{-3} mol dm^{-3} for Cu in benzene) at 705 (ε 216) and 365 nm (ε 124), ε_{350} 122 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (Nujol mull) at 1 630vs $\nu_{asym.}$ (CO_2), 1 424s $\nu_{sym.}$ (CO_2), 1 135m 1 114s, and 1 100m cm^{-1}; $\nu_{max.}$ (26 mg cm^{-3} in $CDCl_3$) 1 631vs $\nu_{asym.}$ (CO_2), 1 422s $\nu_{sym.}$ (CO_2), 1 110 (sh), and 1 102s cm^{-1}. Relative molecular mass 928 (2.00 × 10^{-2} mol dm^{-3} copper in 1,2-dichloroethane; calc. for $C_{19}H_{29}CuNO_8$ 463). Crystallisation of the adduct, *bis*{[meso-2,9-*bis*(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioato*]*pyridinecopper*(II)}, (4b), from benzene–cyclohexane (or better, ethanol), gave green prisms m.p. 156—158 °C (Found: C, 49.15; H, 6.5; N, 3.1%); $\lambda_{max.}$ (Nujol mull) at 710 and 370 nm; $\lambda_{max.}$ (7.00 × 10^{-3} mol dm^{-3} for Cu in benzene) at 705 (ε 240) and 379 nm (ε

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

111), ε_{350} 98 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (Nujol mull) at 1 627vs $\nu_{asym.}$ (CO_2), 1 424s $\nu_{sym.}$ (CO_2), 1 145m, 1 136m, 1 111s, 1 103s, and 1 095s cm^{-1}; $\nu_{max.}$ (27 mg cm^{-3} in $CDCl_3$) 1 630vs $\nu_{asym.}$ (CO_2), 1 422s $\nu_{sym.}$ (CO_2), 1 130 (sh), 1 110 (sh), 1 100s, and 1 093s cm^{-1}. Relative molecular mass 925 (2.00 × 10^{-2} mol dm^{-3} copper in 1,2-dichloroethane).

Triphenylphosphine (145 mg, 0.55 mmol) was added to a solution of (3a) (190 mg, 0.5 mmol) in benzene (15 cm^3). The resulting dark green solution was evaporated *in vacuo* and the residue was crystallised from cyclohexane and gave dull green, irregularly shaped crystals of (5a), m.p. 131—132 °C. Recrystallisation twice, from ethanol, afforded clumps of dark green blades, m.p. 169—172 °C (Found: C, 59.75; H, 6.3. $C_{64}H_{78}Cu_2O_{16}P_2$ requires C, 59.45; H, 6.1%); $\lambda_{max.}$ (6.00 × 10^{-3} mol dm^{-3} for Cu in benzene) at 686 nm (ε 225), ε_{350} 328 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (Nujol mull) at 1 625vs $\nu_{asym.}$ (CO_2), 1 420s $\nu_{sym.}$ (CO_2), 1 159m, 1 125m, 1 109s, 748s, 705m, 698s, and 680 (sh) cm^{-1}. The adduct (5b), *bis*{[meso-2,9-*bis*(*methoxymethyl*)-2,9-*dimethyl*-4,7-*dioxadecanedioato*]-(*triphenylphosphine*)*copper*(II)}, was prepared as described above for (5a). After crystallisation from cyclohexane it had m.p. 147.5—148 °C and on recrystallisation from ethanol it gave well formed, dark green prisms, m.p. 153—154 °C (Found: C, 59.7; H, 5.95%); $\nu_{max.}$ (6.00 × 10^{-3} mol dm^{-3} for Cu in benzene) at 682 nm (ε 252), ε_{350} 335 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (Nujol mull) at 1 621vs $\nu_{asym.}$ (CO_2), 1 418s $\nu_{sym.}$ (CO_2), 1 140 (sh), 1 134m, 1 117ms, 1 094s, 752ms, 748ms, 705m, 699ms, 693ms, and 684 (sh) cm^{-1}.

TABLE 2

Crystal data and experimental parameters [a]

	(2a) $C_{28}H_{52}Cu_2O_{18}$	(4b) $C_{38}H_{58}Cu_2N_2O_{16}$	(5b) $C_{64}H_{78}Cu_2O_{16}P_2$
M	803.8	926.0	1 292.3
a (Å)	11.506(4)	11.230(4)	14.593(1)
b (Å)	7.149(2)	9.940(4)	10.747(1)
c (Å)	13.085(3)	10.954(4)	11.894(2)
α (°)	101.01(1)	112.16(3)	75.025(6)
β (°)	114.06(2)	107.26(3)	115.011(6)
γ (°)	90.85(2)	81.22(3)	99.567(6)
U (Å^3)	959.5	1 080.3	1 629.6
D_x (g cm^{-3})	1.39	1.42	1.32
$F(000)$	418	482	674
μ (cm^{-1})	11.2	10.0	7.2
θ(Mo-K_α)$_{max.}$ (°)	25	22	20
Number of observed [$>3\sigma(I)$] reflections	2 694	2 368	3 038
Final value of overall U (Å^2) for hydrogens	0.063(10)	0.098(5)	0.099(4)
Final R	0.078	0.084	0.061
Final R' [b]	0.051	0.102	0.065

[a] Properties common to all three complexes: triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $Z = 1$, Mo-K_α radiation, λ = 0.710 69 Å. [b] $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Copper Complexes of (6).—A solution of copper(II) acetate monohydrate (580.6 mg, 2.91 mmol) in absolute ethanol (25 cm^3) was filtered into a solution of 2,2,9,9-tetramethyl-4,7-dithiadecanedioic acid, (6) [12] (949.3 mg, 3.23 mmol), in the same solvent (10 cm^3) and gave a pale green, powdery precipitate. This solid was filtered off, washed several times with absolute ethanol, then dried first in air and finally *in vacuo*. This complex, (2,2,9,9-*tetramethyl*-4,7-*dithiadecanedioato*)*copper*(II), (7) (751 mg), had m.p. 208—210 °C (decomp.) (Found: C, 40.15; H, 6.0. $C_{12}H_{20}CuO_4S_2$ requires C, 40.5; H, 5.65%). When the synthesis was repeated using aqueous ethanol the product had m.p. 190 °C (Found: C, 38.75; H, 5.7. $C_{12}H_{20}CuO_4S_2 \cdot H_2O$ requires C, 38.55; H, 5.95%). The anhydrous material showed $\lambda_{max.}$ (Nujol mull) at 673 nm; $\nu_{max.}$ (Nujol mull) at 3 440vw br ν(O–H), 1 617vs $\nu_{asym.}$ (CO_2), 1 407s $\nu_{sym.}$ (CO_2), and 1 256m cm^{-1}. The i.r. spectrum of the hydrate is very similar to the above apart from an apparent increase in the relative intensity of the 3 440 cm^{-1} band.

A suspension of (7) (356 mg, 1 mmol) in benzene (30 cm^3) was heated at reflux and a portion of the solvent was distilled to remove traces of water. Pyridine was then added in aliquots (50 mm^3) to the hot suspension with stirring. After the addition of three aliquots the suspended material dissolved to give a bright green solution from which a powder of similar colour deposited on cooling. This material was redissolved in hot benzene (5 cm^3)–pyridine (3 cm^3) to give a green solution which turned blue on cooling. The latter gradually deposited the green powdery *monopyridine adduct* (8), which tends to lose pyridine on washing or pumping, m.p. 228—230 °C (decomp.) (loss of pyridine commences at 136 °C) (Found: C, 46.05; H, 5.65; N, 3.05; S, 14.35. $C_{17}H_{25}CuNO_4S_2$ requires C, 46.9; H, 5.8; N, 3.2; S, 14.75%; $\lambda_{max.}$ (Nujol mull) at 713 and 375 nm; $\lambda_{max.}$ [6.00 × 10^{-3} mol dm^{-3} for Cu in benzene–pyridine, prepared by dissolving (7) (21.4 mg) and pyridine (50 mm^3) in benzene] 723 (ε 236) and 380 (sh) nm, ε_{350} 259 dm^3 mol^{-1} cm^{-1}; $\nu_{max.}$ (Nujol mull) at 1 618vs $\nu_{asym.}$ (CO_2), 1 406s $\nu_{sym.}$ (CO_2), and 1 255m cm^{-1}.

Copper(II) chloride hexahydrate (485 mg, 2 mmol) in absolute ethanol (20 cm^3) was treated with a solution of (6) (588 mg, 2 mmol) in the same solvent (15 cm^3). The solvent was removed *in vacuo* and the residue crystallised from acetone to give olive-green *dichloro*(2,2,9,9-*tetramethyl*-4,7-*dithiadecanedioic acid*)*copper*(II), m.p. 155—157 °C (Found: C, 33.3; H, 5.05. $C_{12}H_{22}Cl_2CuO_4S_2$ requires C, 33.6; H, 5.2%); $\nu_{max.}$ (Nujol mull) at 3 300—2 500 ν(O–H), 1 718vs ν(C=O), 1 253wm, and 1 214s cm^{-1}.

Crystal Structure Analyses.—For each compound, (2a), (4b), and (5b), preliminary Weissenberg and precession photographs were used to determine unit-cell dimensions which were refined by least-squares treatment of the diffractometer co-ordinates of 12 reflections for which θ(Mo-K_α) was greater than 10°.

Table 2 summarises the crystal data as well as parameters of the collection and analysis of the structure amplitudes.

Three-dimensional intensity data were collected by our standard method [17] using a four-circle Hilger and Watts Y290 diffractometer equipped with a graphite monochromator. Lorentz and polarization corrections were applied but, because of the low values of μ and the regular habits of the particular crystals used, absorption corrections were not. The non-hydrogen atoms were located by Patterson and Fourier techniques and their positions were refined by full-matrix least-squares methods.* The hydrogen atoms were located from difference maps calculated in the latter stages of the refinements but rather than allowing them to refine freely, they were given a single overall isotropic temperature factor (Table 2) and constrained to ride at ideal positions (C–H = 1.08 Å, H–C–H = 109.5°) relative to the atoms to which they are bonded. To simplify the refinement of the triphenylphosphine complex, the phenyl rings were treated as rigid, regular hexagons with a C–C distance of 1.395 Å. In the refinements of all three structures, the function minimised was $\Sigma w\Delta^2$ where $w = [\sigma(F)]^{-2}$ and $\sigma(F)$ is derived from counting statistics. The scattering factors of ref. 18 were used for the hydrogen atoms, while the remaining atom types were given the scattering factors of ref. 19 which included a correction for anomalous dispersion.[20] The copper atoms, carboxylate oxygens, and methoxy-groups were all given anisotropic thermal parameters whereas the remaining atoms were treated isotropically.

TABLE 3

Final co-ordinates (fractional, × 10^4) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(*a*) $C_{28}H_{52}Cu_2O_{18}$ (2a)			
Cu	4 538(1)	3 491(2)	203(1)
O(1)	4 717(7)	5 198(8)	1 622(5)
O(2)	4 451(6)	2 227(8)	−1 299(5)
O(3)	6 347(6)	3 048(8)	938(5)
O(4)	2 890(6)	4 394(8)	−565(5)
C(1)	5 193(10)	6 893(14)	1 891(8)
C(2)	5 370(10)	8 058(14)	3 127(8)
C(3)	4 018(12)	8 169(16)	3 072(10)
O(5)	3 400(8)	9 220(12)	2 225(7)
C(4A)	2 242(25)	9 862(41)	2 003(21)
C(4B)	1 894(33)	8 085(50)	1 810(27)
C(5A)	1 256(27)	8 110(43)	1 095(24)
C(5B)	1 192(32)	9 095(43)	918(29)
O(6)	1 452(7)	8 310(10)	−15(7)
C(6)	685(11)	6 583(16)	−852(10)
C(7)	1 377(10)	6 239(14)	−1 659(8)
C(8)	2 777(10)	5 838(14)	−989(8)
C(40)	1 350(12)	7 891(16)	−2 282(10)
C(41)	639(12)	4 375(16)	−2 614(10)
O(7A)	−666(29)	4 714(37)	−3 289(25)
O(7B)	14(13)	7 987(17)	−3 027(10)
C(42A)	−1 373(54)	3 764(69)	−4 554(45)
C(42B)	−109(20)	9 090(27)	−3 899(16)
C(43)	6 164(12)	6 775(16)	3 991(10)
C(44)	6 145(12)	9 925(15)	3 422(10)
O8A)	6 165(14)	7 691(20)	5 014(13)
O(8B)	6 545(24)	10 699(33)	4 489(19)
C(45A)	6 745(22)	6 416(30)	5 881(18)
C(45B)	7 442(44)	12 539(61)	4 876(33)
O(9)	3 852(6)	911(7)	478(5)
(*b*) $C_{38}H_{58}Cu_2N_2O_{16}$ (4b)			
Cu	379(1)	105(1)	4 002(1)
O(1)	959(5)	1 963(5)	5 426(5)
O(2)	−365(4)	−1 781(5)	2 878(5)
O(3)	−1 273(4)	1 063(6)	3 518(5)
O(4)	1 893(4)	−912(6)	4 780(5)
C(1)	882(6)	2 434(7)	6 645(7)
C(2)	1 417(6)	3 907(8)	7 566(8)
C(3)	2 674(7)	3 951(9)	7 301(9)
O(5)	3 492(5)	2 839(6)	7 630(6)
C(4)	4 255(8)	2 113(10)	6 688(10)
C(5)	5 106(8)	1 057(10)	7 171(11)
O(6)	4 485(5)	−28(6)	7 296(7)
C(6)	4 345(7)	−1 367(9)	6 193(9)
C(7)	3 276(6)	−2 121(7)	6 193(8)
C(8)	2 052(6)	−1 293(7)	5 790(8)
C(40)	3 228(8)	−3 659(9)	5 101(10)
C(41)	3 449(7)	−2 208(8)	7 568(8)
O(7)	4 574(5)	−3 024(7)	7 904(6)
C(42)	4 928(9)	−2 843(14)	9 317(9)
C(43)	529(8)	5 091(9)	7 159(10)
C(44)	1 579(7)	4 104(8)	9 048(8)
O(8)	2 096(6)	5 482(6)	9 878(6)
C(45)	2 353(9)	5 717(10)	11 285(8)
N	1 136(5)	355(6)	2 488(6)
C(11)	1 134(7)	−743(9)	1 297(8)
C(12)	1 623(8)	−615(11)	312(11)
C(13)	2 141(9)	634(11)	573(12)
C(14)	2 196(9)	1 757(12)	1 793(11)
C(15)	1 651(7)	1 585(9)	2 720(9)

TABLE 3 (*continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(*c*) $C_{64}H_{78}Cu_2O_{16}P_2$ (5b)			
Cu	−805(1)	172(1)	193(1)
O(1)	67(3)	1 456(4)	1 149(4)
O(2)	−1 394(3)	−1 177(4)	−786(3)
O(3)	−1 033(3)	1 499(4)	−1 377(3)
O(4)	−277(3)	−1 203(3)	1 738(3)
C(1)	960(5)	1 748(5)	1 214(5)
C(2)	1 535(4)	2 867(5)	1 858(5)
C(3)	1 588(5)	2 558(6)	3 202(5)
O(5)	2 204(3)	1 497(4)	3 873(4)
C(4)	2 102(6)	841(7)	5 040(7)
C(5)	1 282(6)	−209(6)	4 870(7)
O(6)	1 531(3)	−1 172(4)	4 446(4)
C(6)	822(5)	−2 273(6)	4 293(6)
C(7)	825(4)	−2 803(5)	3 231(5)
C(8)	508(5)	−1 723(5)	2 017(5)
C(40)	43(5)	−3 957(6)	3 010(6)
C(41)	1 881(5)	−3 187(6)	3 530(5)
O(7)	2 181(3)	−4 202(4)	4 635(4)
C(42)	3 181(5)	−4 520(7)	4 969(6)
C(43)	925(6)	4 060(6)	1 116(6)
C(44)	2 578(5)	3 125(6)	1 811(6)
O(8)	3 072(4)	4 191(5)	2 384(5)
C(45)	4 015(7)	4 567(9)	2 294(10)
P	−2 584(1)	318(1)	77(1)
C(11)	−3 546(3)	856(4)	−1 510(3)
C(12)	−3 470(3)	503(4)	−2 515(3)
C(13)	−4 203(3)	843(4)	−3 743(3)
C(14)	−5 013(4)	1 535(4)	−3 967(3)
C(15)	−5 090(3)	1 888(4)	−2 962(3)
C(16)	−4 356(3)	1 549(4)	−1 734(3)
C(21)	−3 102(3)	−1 282(3)	621(3)
C(22)	−4 043(3)	−1 806(3)	−111(3)
C(23)	−4 373(3)	−3 062(3)	314(3)
C(24)	−3 762(3)	−3 794(3)	1 472(3)
C(25)	−2 821(3)	−3 270(3)	2 204(3)
C(26)	−2 491(3)	−2 015(3)	1 779(3)
C(31)	−2 706(3)	1 339(3)	1 011(4)
C(32)	−3 305(3)	981(3)	1 711(4)
C(33)	−3 330(3)	1 799(3)	2 436(4)
C(34)	−2 756(3)	2 974(3)	2 460(4)
C(35)	−2 157(3)	3 332(3)	1 760(4)
C(36)	−2 132(3)	2 515(3)	1 035(4)

In (2a) considerable difficulties were experienced with disorder. The ethylene linkage [C(4), C(5)] occupies two sites of population 0.65 and 0.35, and the ether oxygens were allowed anisotropic motion. The methyl and methoxymethyl groups are also disordered, their relative populations refining to final values of 0.60 and 0.40. In Table 3 are

* All Fourier and least-squares calculations were performed using the program system SHELX written by G. M. Sheldrick, University Chemical Laboratory, Cambridge.

given the final co-ordinates for all three structures, together with the standard deviations in these quantities calculated from the final refinement cycles. Lists of calculated and observed structure factors have been deposited with the final co-ordinates of the hydrogen atoms, and tables of temperature factors as Supplementary Publication No. SUP 23044 (58 pp.).*

We are grateful to the Natural Sciences and Engineering Research Council of Canada for a Grant in Aid of Research (to R. McC. and G. F.).

[1/025 *Received*, 6*th January*, 1981]

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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