Systematic Synthesis of Triply Bridged Binuclear Copper(I) Complexes containing Bis(diphenylphosphino)methane (dppm) Bridging Ligands: *X*-Ray Crystal Structures of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-mpyO})]BF_4$ and $[Cu_2(\mu\text{-dppm})(\mu\text{-mpyO})_2]$(mpyO = 6-methylpyridin-2-olate)†

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Triply bridged binuclear copper(I) complexes containing the moieties $Cu_2(\mu\text{-dppm})(\mu\text{-L-L})_2$ [dppm = bis(diphenylphosphino)methane] and $Cu_2(\mu\text{-dppm})_2(\mu\text{-L-L})$ have been prepared. The reaction in tetrahydrofuran (thf) at room temperature of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ with the sodium salts of the bidentate ligands L–L in 1 : 1 or 1 : 2 molar ratio gives, respectively, $[Cu_2(\mu\text{-dppm})_2(\mu\text{-L-L})]BF_4$ and $[Cu_2(\mu\text{-dppm})(\mu\text{-L-L})_2]$ [L–L = 6-methylpyridin-2-olate (mpyO) (**1a**), (**2a**); 3,5-dimethylpyrazolate (dmpz) (**1b**), (**2b**); 1,3-di-*p*-tolyltriazenide ($p\text{-}MeC_6H_4N_3C_6H_4Me\text{-}p$) (**1c**), (**2c**); or acetate (**1d**), (**2d**)]. The complex $[Cu_2(\mu\text{-mdppm})_2(\mu\text{-dmpz})]BF_4$ (**1e**) [mdppm = 1,1-bis(diphenylphosphino)ethane] has also been isolated. Complexes (**2a**) and (**2d**) have also been directly obtained by treatment of $[Cu(MeCN)_4]BF_4$ with dppm and Na(mpyO) or NaO_2CMe in 1 : 1 : 2 molar ratio, respectively, in thf. Crystal structures of the complexes (**1a**) and (**2a**) have been determined by *X*-ray diffraction methods. Crystals of (**1a**), containing dichloromethane molecules of crystallization, are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 14.569(4)$, $b = 15.299(5)$, $c = 14.324(4)$ Å, $\alpha = 104.37(2)$, $\beta = 115.84(2)$, and $\gamma = 67.91(2)°$. Crystals of (**2a**), containing dichloromethane molecules of crystallization, are triclinic, space group $P1$, with $Z = 1$ in a unit cell of dimensions $a = 9.595(4)$, $b = 11.274(5)$, $c = 9.414(4)$ Å, $\alpha = 66.44(2)$, $\beta = 82.67(2)$, and $\gamma = 81.70(2)°$. The structures have been solved from diffractometer data by Patterson and Fourier methods and refined by block-matrix [(**1a**)] and full-matrix [(**2a**)] least squares to $R = 0.0792$ and 0.0386 for 1 670 [(**1a**)] and 3 006 [(**2a**)] observed reflections. In the cationic complex (**1a**) the two copper atoms, in a slightly distorted trigonal arrangement, are held in close proximity [2.679(6) Å] by three bridging ligands, two dppm through P atoms and one mpyO through one O and one N atom. The latter ligand is disordered and distributed in two positions (of equal occupancy) whereby the copper atoms are bridged either by the O and N or by the N and O atoms. In the neutral complex (**2a**) the separation of the two three-co-ordinate copper atoms, bridged by one dppm and two mpyO ligands, is 2.566(2) Å. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. data are discussed.

The increasing interest in polynuclear copper(I) chemistry is mainly due to the studies related to the reactivity of molecular oxygen, not only in biological systems but also in catalytic oxidation and dioxygen-mediated processes.[1,2] Binuclear derivatives form a significant group of complexes involving different types of bridging ligands. (*a*) [2 + 2] Macrocyclic ligands containing furan and thiophene[3a] or aminotropone-imine groups[3b] and tripodal type N and N–O polydentate ligands[4a,e] which form special complexes some of them invoked to be appropriate models of haemocyanin.[4b–e] Catalytic hydroxylation of an arene moiety by molecular oxygen has also been recently reported.[5] The largest group involve ligands in which the donor atoms are connected by carbon chains usually long enough to consider the compounds as formed by two mononuclear copper complexes.[1a] (*b*) Anionic ligands X^- such as halide, sulphide, pseudo-halides,[1a] phenoxide,[6] hydride,[7] phosphide,[8] *etc.* which form binuclear complexes with one or two single X-atom bridges. (*c*) Bidentate anionic systems: (*i*) carboxylate bridging ligands[9a–c] which show special ability to stabilize carbonyl-bridged binuclear copper(I) complexes; (*ii*) phosphorus ylides[9d] and organo groups containing bridging C–N systems[9e,f] which are rare examples showing two-centre two-electron copper–carbon bonds; and (*iii*) *N,N′*-*p*-tolylformamidinate[9g] and *N,N′*-1,3-diphenyltriazenide groups.[9h] (*d*) Bridging bidentate phosphines $Ph_2PCH_2PPh_2$ (dppm)[10a,b] or $Pr^i{}_2PCH_2PPr^iH$[10c] and 2-(diphenylphosphino)pyridine (dppy) which form binuclear complexes containing the eight-membered ring moieties $Cu_2(\mu\text{-P-P})_2$[10] and $Cu_2(\mu\text{-dppy})_2$.[11] We have also reported[11] the first examples of triply bridged binuclear copper(I) complexes which contain the moiety $Cu_2(\mu\text{-dppy})_3$. One further example, $[Cu_2(\mu\text{-2Me-quin})_2(\mu\text{-dppm})]$ (2Me-quin = 2-methylquinolinate), has been recently characterized.[12]

The present paper reports the preparation of cationic, [Cu$_2$-

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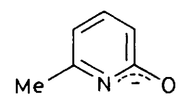
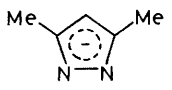
† Bis[μ-bis(diphenylphosphino)methane]-μ-6-methylpyridin-2-olato-dicopper(I) tetrafluoroborate and μ-bis(diphenylphosphino)methane-bis(μ-6-methylpyridin-2-olato)-dicopper(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

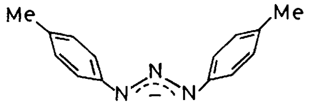
	P-P	L-L		L-L
(**1a**)	dppm	mpyO	(**2a**)	mpyO
(**1b**)	dppm	dmpz	(**2b**)	dmpz
(**1c**)	dppm	(p-MeC$_6$H$_4$)$_2$N$_3$	(**2c**)	(p-MeC$_6$H$_4$)$_2$N$_3$
(**1d**)	dppm	O$_2$CMe	(**2d**)	O$_2$CMe
(**1e**)	mdppm	dmpz		



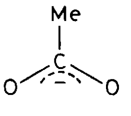
mpyO



dmpz



p-MeC$_6$H$_4$N$_3$C$_6$H$_4$Me-p



O$_2$CMe

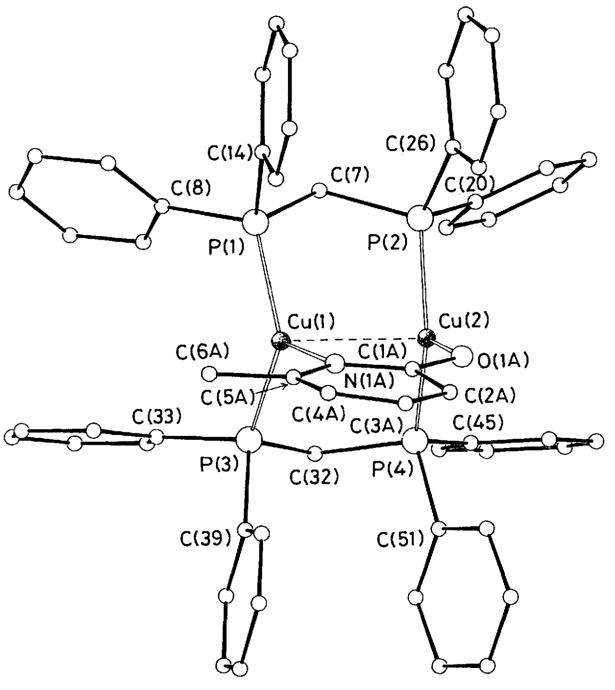
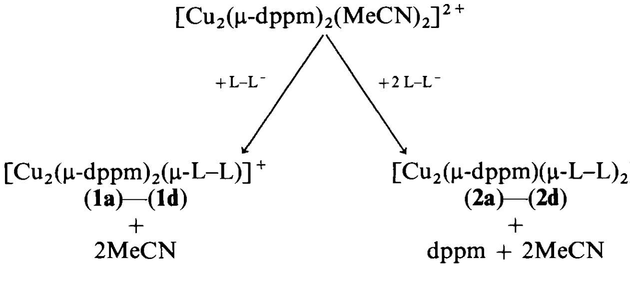


Figure 1. View of the cationic complex [Cu$_2$(μ-dppm)$_2$(μ-mpyO)]$^+$ (**1a**) with the atomic numbering scheme. Only one of the two disordered mpyO ligands (labelled A) is represented for clarity

(μ-P–P)$_2$(μ-L–L)]BF$_4$ (**1a**)—(**1e**), and neutral, [Cu$_2$(μ-dppm)(μ-L–L)$_2$] (**2a**)—(**2d**), binuclear copper(I) complexes with mixed bridges: P–P = bis(diphenylphosphino)methane (dppm) or 1,1-bis(diphenylphosphino)ethane (mdppm); L–L(bidentate anionic ligand) = 6-methylpyridin-2-olate (mpyO), 3,5-dimethylpyrazolate (dmpz), 1,3-di-p-tolyltriazenide (p-MeC$_6$H$_4$N$_3$C$_6$H$_4$Me-p), or acetate which are typical ligands of a class used by Cotton and Walton[13] for promoting 'exceedingly short' metal–metal bonds. The synthesis of this series of compounds provides a systematic method for the preparation of the scarcely known triply bridged binuclear copper(I) complexes.

Results and Discussion

Treatment of a solution of [Cu$_2$(μ-dppm)$_2$(MeCN)$_2$][BF$_4$]$_2$ in tetrahydrofuran (thf) at room temperature with an equimolar amount of the sodium salt of the anionic ligand L–L$^-$ (prepared *in situ* from the free ligand and sodium hydride in thf) gives a solution from which binuclear cationic complexes (**1a**)—(**1d**) can be isolated as tetrafluoroborate salts. The cationic complex [Cu$_2$(μ-mdppm)$_2$(μ-dmpz)]BF$_4$ (**1e**) is similarly obtained. By using a 1:2 molar ratio of complex to anionic ligand, one dppm is also displaced and the reactions lead to the formation of similar neutral complexes [Cu$_2$(μ-dppm)(μ-L–L)$_2$] (**2a**)—(**2d**).



Neutral complexes (**2a**) and (**2d**) can be alternatively obtained with better yields in a 'one-pot' synthesis according to the reaction (1) [L–L = mpyO (**2a**) or O$_2$CMe (**2d**)].

$$2[\mathrm{Cu(MeCN)_4}]^+ + \mathrm{dppm} + 2\,\mathrm{L{-}L}^- \longrightarrow [\mathrm{Cu_2}(\mu\text{-dppm})(\mu\text{-L{-}L})_2] + 8\mathrm{MeCN} \qquad (1)$$

All the complexes are air stable in the solid state and have been characterized by elemental analysis, conductance measurements in solution, and ^{1}H and ^{31}P-{^{1}H} n.m.r. spectroscopy. Table 1 collects selected data. In addition, the structures of the complexes (**1a**) and (**2a**) have been determined by *X*-ray diffraction methods.

Conductance values of the cationic complexes in acetone show that they are 1:1 electrolytes and i.r. spectra (Nujol mulls) exhibit the expected ν(B–F) absorptions as well as those characteristic for the bridging ligands (see Experimental section). Significantly, i.r. spectra of acetate complexes (**1d**) and (**2d**) show, respectively, absorptions at 1 540, 1 430 and 1 570, 1 410 cm^{-1} assigned to ν_{asym} and ν_{sym}(COO) ($\nu_{asym} - \nu_{sym}$ = 110 and 160 cm^{-1}), which are typical values for bridging acetate complexes.[14]

Description of the Crystal Structures of [Cu$_2$(μ-dppm)$_2$(μ-mpyO)]BF$_4$·0.5CH$_2$Cl$_2$ (**1a**) *and* [Cu$_2$(μ-dppm)(μ-mpyO)$_2$]·CH$_2$Cl$_2$ (**2a**).—The crystal structure of complex (**1a**) consists of binuclear [Cu$_2$(μ-dppm)$_2$(μ-mpyO)]$^+$ cations, BF$_4^-$ anions, and dichloromethane molecules of crystallization. The structure of the cation is depicted in Figure 1 together with the atomic numbering scheme. In the binuclear cation the two copper atoms are held in close proximity, 2.679(6) Å, by three bridging ligands, two dppm ligands acting through the P atoms and one mpyO anion acting as a bridge through the O and N atoms. This latter ligand is disordered and distributed in two positions (labelled A and B respectively) of equal occupancy factors in such a way that the Cu(1) and Cu(2) atoms are bridged by half of the mpyO ligands through the N(1A) and O(1A) atoms and by half through the O(1B) and N(1B) atoms. The two positions of the mpyO ligand have the two bridging atoms in common. In Figure 1 only the position A of this ligand is shown for clarity. Because of this disorder the two N and O are exchangeable at the two copper atoms whose co-ordination spheres are thus similar; the Cu–N and Cu–O bond distances quoted are average

Table 1. Microanalytical,[a] molar conductance,[b] and n.m.r.[c] data

	Complex	Analysis (%) C	N	H	^{1}H(δ)	^{31}P-{^{1}H}(δ)	Λ_M
(1a)	[$Cu_2(\mu$-dppm$)_2(\mu$-mpyO)]BF_4	61.20 (61.70)	1.20 (1.30)	4.70 (4.60)	2.27 (s, 3 H, Me), 3.19 and 3.78 (m, 4 H, CH_2P_2), 7.38 (m, 40 H, C_6H_5)	−9.22(s)	144
(1b)	[$Cu_2(\mu$-dppm$)_2(\mu$-dmpz)]BF_4	60.65 (61.35)	2.80 (2.60)	5.20 (4.75)	2.25 (s, 6 H, Me), 3.49 (m, 4 H, CH_2P_2), 6.12 (s, 1 H, pz), 7.10 (m, 40 H, C_6H_5)	−10.65(s)	150
(1c)	[$Cu_2(\mu$-dppm$)_2${μ-(p-$MeC_6H_4)_2N_3$}]BF_4	64.20 (63.65)	3.70 (3.50)	5.00 (5.00)	2.34 (s, 6 H, p-Me), 3.24 and 3.87 (m, 4 H, CH_2P_2), 6.67—7.65 (m, 48 H, C_6H_5)	−9.37(s)	127
(1d)	[$Cu_2(\mu$-dppm$)_2(\mu$-O_2CMe)]BF_4	60.30 (60.00)	— —	4.65 (4.50)	2.46 (s, 3 H, Me), 3.44 and 3.51 (m, 4 H, CH_2P_2), 7.12 (m, 40 H, C_6H_5)	−8.63(s)	160
(1e)	[$Cu_2(\mu$-mdppm$)_2(\mu$-dmpz)]BF_4	61.65 (61.95)	2.55 (2.55)	5.45 (5.00)	[d] 0.86 (m, 6 H, $MeCHP_2$), 2.24 (s, 6 H, dmpz), 3.94 (m, 2 H, CHP_2), 7.22 (m, 40 H, C_6H_5)	−10.08(s)	107
(2a)	[$Cu_2(\mu$-dppm)(μ-mpyO$)_2$]·CH_2Cl_2	56.50 (56.20)	3.45 (3.45)	4.40 (4.40)	2.34 (s, 6 H, Me), 3.08 [t, ^2J(PH) 9.5, CH_2P_2], 6.13 and 6.44 (dd, 6 H, C_5H_3NO), 7.25 (m, 20 H, C_6H_5)	−10.08(s)	—
(2b)	[$Cu_2(\mu$-dppm)(μ-dmpz$)_2$]	59.50 (59.95)	7.80 (8.00)	5.40 (5.15)	2.11 (s, 12 H, Me), 3.08 [t, ^2J(PH) 5.9, CH_2P_2], 5.76 (s, 2 H, pz), 7.25 (m, 20 H, C_6H_5)	−15.90(s)	—
(2c)	[$Cu_2(\mu$-dppm)(μ-(p-$MeC_6H_4)_2N_3)_2$]	66.85 (66.40)	9.15 (8.75)	5.30 (5.00)	2.25 (s, 12 H, p-Me), 2.98 [t, ^2J(PH) 9.2, CH_2P_2], 7.20 (m, 36 H, C_6H_5)	−13.15(s)	—
(2d)	[$Cu_2(\mu$-dppm)(μ-$O_2CMe)_2$]	54.75 (55.35)	— —	4.60 (4.45)	2.10 (s, 6 H, Me), 3.07 [t, ^2J(PH) 9.55, CH_2P_2], 7.18 (m, 20 H, C_6H_5)	−6.89(s)	—

[a] Calculated values are given in parentheses. [b] In acetone solution at 20 °C (ohm^{-1} cm^2 mol^{-1}). [c] Proton (300 MHz) and ^{31}P-{^{1}H} n.m.r. (79.54 MHz) chemical shifts (δ) in p.p.m. measured in $CDCl_3$ at ambient temperature. Coupling constants in Hz. [d] At 32.20 MHz.

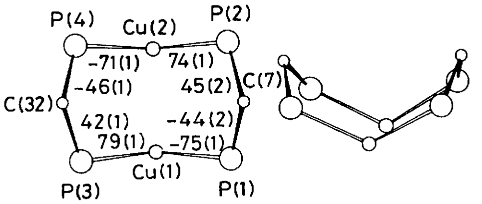


Figure 2. Two views of the eight-membered Cu(μ-dppm)$_2$Cu ring showing the conformation and the torsion angles (°)

values. The copper atoms are in a trigonal environment determined by two P and one N (or O) atoms. The two planes through the co-ordinating atoms are tilted by 14.7(6)° (because of the narrower 'bite' angle of the mpyO ligand) with each copper atom displaced by about 0.05 Å from the plane towards the other copper (so a soft attractive Cu^I–Cu^I interaction cannot be excluded).

The conformations of the two Cu(μ-dppm)Cu and the CuO(N)N(O)Cu bridges are approximately 'eclipsed' as indicated by the P(1)Cu(1)Cu(2)P(2), P(3)Cu(1)Cu(2)P(4), and N(1A)Cu(1)Cu(2)O(1A) torsion angles [−0.8(4), −3.0(4), and −3.2(9)° respectively] so that the two PCuCuP and the NCuCuO bridges are only slightly 'twisted' around the Cu–Cu vector. In the precursor [$Cu_2(\mu$-dppm$)_2(MeCN)_2]^{2+}$ the twist angle of the two dppm bridges is larger [15.4(1)°].[10b] The eight-membered Cu(μ-dppm)$_2$Cu ring adopts a boat–boat conformation requiring an approximate C_{2v} symmetry.[15] Two views of this ring together with the torsion angles are represented in Figure 2.

The crystal structure of complex (**2a**) consists of binuclear neutral [$Cu_2(\mu$-dppm)(μ-mpyO$)_2$] molecules and dichloromethane of crystallization (Figure 3). The two copper atoms are held in close proximity, 2.566(2) Å, by three bridging ligands, two mpyO anions 'head to tail' co-ordinating through the O and N atoms and one dppm ligand acting through the P atoms. Both copper atoms are in a trigonal arrangement determined by one P, one N, and one O atom with the two planes through the donor atoms tilted by 13.0(2)°. The Cu–N bond lengths, 1.987(6) and 1.999(8) Å, and those of Cu–O, 1.983(8) and 1.994(6) Å, are practically identical, whereas in the tetranuclear complex [$Cu_4(\mu$-mpyO$)_4$] the Cu–O bond lengths in the range 1.823(4)—1.843(4) Å have been found to be shorter than those of the Cu–N bonds in the range 1.878(4)—1.892(4) Å.[16] The Cu–N and Cu–O bonds in the tetranuclear complex, in which the copper atoms are two-co-ordinate, are shorter than those found for the three-co-ordinate copper atoms of (**2a**), a trend in agreement with the shorter distances found for three- with respect to four-co-ordinate copper atoms.[11]

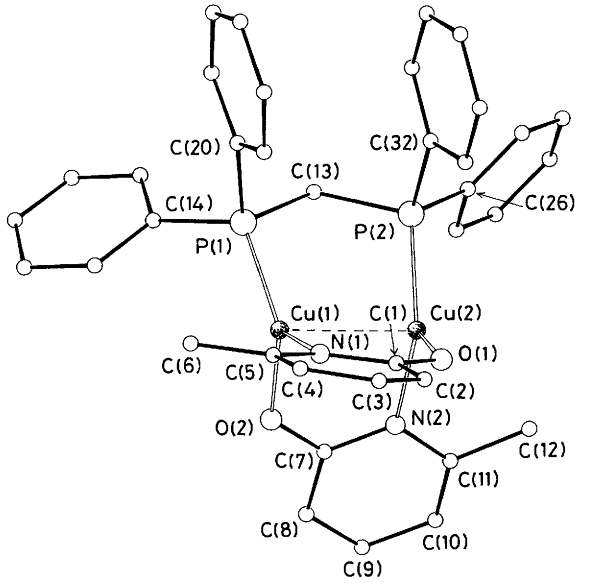
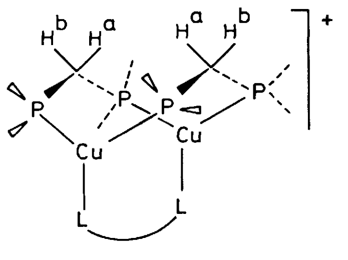


Figure 3. View of the neutral complex [$Cu_2(\mu$-dppm)(μ-mpyO$)_2$] (**2a**) with the atomic numbering scheme

The conformations of the two CuNOCu bridges are 'eclipsed' [the N(1)Cu(1)Cu(2)O(1) and N(2)Cu(1)Cu(2)O(2) torsion angles are 3.1(3) and −4.2(3)°, the opposite signs being probably due to the different steric hindrance towards the phenyl rings], whereas that of the Cu(μ-dppm)Cu bridge is a little more 'twisted' [the P(1)Cu(1)Cu(2)P(2) torsion angle is 10.8°] than those of (**1a**).

N.M.R. Studies.—Proton n.m.r. spectra in $CDCl_3$ at room temperature exhibit aromatic, methylene (CH_2P_2), and methyl signals of the ligands (Table 1) in accord with the proposed binuclear nature of the complexes. Thus, the spectra of all complexes show a single resonance for the methyl groups of the bidentate ligands L–L, *i.e.* those which contain two groups are chemically equivalent. This is consistent with the proposed symmetrical μ-(L–L) bridging system and in agreement with the *X*-ray structure determinations of **(1a)** and **(2a)**.

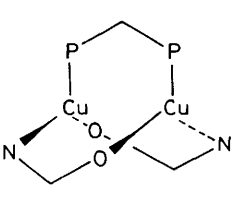
The proton n.m.r. spectra of all the neutral complexes **(2a)**—**(2d)** exhibit methylene resonances (CH_2P_2) at δ *ca.* 3.0 as a typical triplet characteristic of an A_2X_2 spin system. The corresponding resonances in the spectra of the cationic complexes **(1a)**—**(1d)** appear as one or two unresolved multiplets showing the $(ABX_2)_2$ or $(ABXX')_2$ spin system expected for the two sets of chemically inequivalent protons $CH_aH_bP_2$ which are typical of the boat–boat (or saddle) conformations in some platinum(II) complexes containing two mutually *cis* $(RO)_2PCH_2P(OR)_2$ or dppm ligands.[15,17]



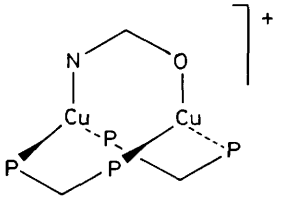
(1a)-**(1d)**

$^{31}P-\{^1H\}$ N.m.r. spectra at room temperature show a single resonance (Table 1) showing that all phosphorus atoms in each molecule are chemically equivalent. For the neutral complex **(2a)** it seems to indicate a 'head-to-tail' configuration of the unsymmetrical mpyO ligands as has been shown by the *X*-ray structure in the solid state.

Two phosphorus resonances are expected for complex **(1a)** because of the presence of only one mpyO bidentate group. We have shown[10b,11] that analogous dicopper(I) complexes undergo dissociation of bridging phosphines and rapid exchange processes, the phosphorus atoms becoming effectively equivalent in solution. However ^{31}P n.m.r. spectra of solutions in $CDCl_3$ of complex **(1a)**, when stoicheiometric amounts of dppm have been added, show the corresponding signal of the free ligand along with that of the complex, indicating that dppm exchange processes are not taking place.



(2a)



(1a)

The observed phosphorus atom equivalence in complex **(1a)** is probably a result of the very small difference in their electronic shielding produced by atoms such as nitrogen and oxygen with very similar electronic environments. On the other hand, variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectra of the complex **(1a)** in CH_2Cl_2 also exhibit a single phosphorus resonance at δ −9.05, −10.20, −10.36, and −10.45 p.p.m. at +20, −30, −60, and −80 °C respectively. Similar results are obtained with the precursor complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (δ −8.02, −11.62, and −12.02 p.p.m. at +20, −60, and −80 °C, respectively).

Table 2. Selected bond distances (Å) and angles (°) in complex **(1a)***

Cu(1)–Cu(2)	2.679(6)	Cu(2)–P(2)	2.230(9)
Cu(1)–P(1)	2.231(8)	Cu(2)–P(4)	2.249(9)
Cu(1)–P(3)	2.236(9)	Cu(2)–O(1)	2.02(3)
Cu(1)–N(1)	2.04(2)	P(3)–C(32)	1.87(3)
P(1)–C(7)	1.84(4)	P(3)–C(33)	1.84(3)
P(1)–C(8)	1.84(2)	P(3)–C(39)	1.80(3)
P(1)–C(14)	1.80(3)	P(4)–C(32)	1.85(2)
P(2)–C(7)	1.87(2)	P(4)–C(45)	1.76(5)
P(2)–C(20)	1.81(4)	P(4)–C(51)	1.80(3)
P(2)–C(26)	1.84(3)		
P(1)–Cu(1)–P(3)	122.8(4)	P(2)–Cu(2)–P(4)	125.3(4)
P(1)–Cu(1)–N(1)	120.2(7)	P(2)–Cu(2)–O(1)	117.8(7)
P(3)–Cu(1)–N(1)	116.8(7)	P(4)–Cu(2)–O(1)	116.8(7)
P(1)–Cu(1)–Cu(2)	95.0(3)	P(2)–Cu(2)–Cu(1)	94.3(3)
P(3)–Cu(1)–Cu(2)	95.7(3)	P(4)–Cu(2)–Cu(1)	93.6(3)
N(1)–Cu(1)–Cu(2)	83.2(7)	O(1)–Cu(2)–Cu(1)	84.8(7)
Cu(1)–P(1)–C(7)	111(1)	Cu(2)–P(2)–C(7)	111(1)
Cu(1)–P(1)–C(8)	114(1)	Cu(2)–P(2)–C(20)	113(1)
Cu(1)–P(1)–C(14)	116(1)	Cu(2)–P(2)–C(26)	116(1)
Cu(1)–P(3)–C(32)	112(1)	Cu(2)–P(4)–C(32)	112(1)
Cu(1)–P(3)–C(33)	118(1)	Cu(2)–P(4)–C(45)	117(1)
Cu(1)–P(3)–C(39)	116(1)	Cu(2)–P(4)–C(51)	115(1)
Cu(1)–N(1)–C(1A)	114(2)	Cu(2)–O(1)–C(1A)	120(2)
Cu(1)–N(1)–C(1B)	122(2)	Cu(2)–O(1)–C(1B)	114(2)

* Because of the disorder in the mpyO ligand, N(1) refers to the atoms N(1A) and O(1B), occupying the same position, and O(1) refers to the atoms O(1A) and N(1B), occupying the same position.

Table 3. Selected bond distances (Å) and angles (°) in complex **(2a)**

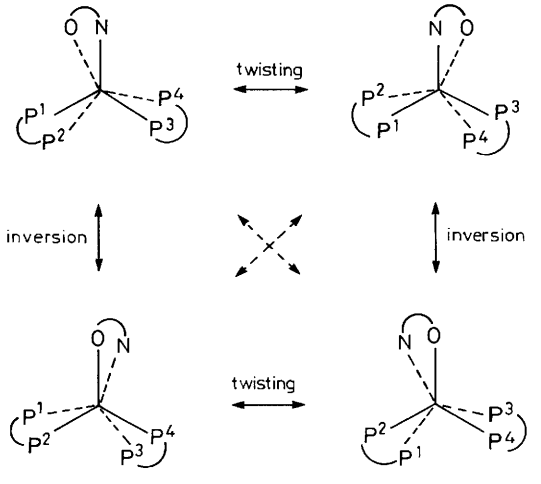
Cu(1)–Cu(2)	2.566(2)	Cu(2)–P(2)	2.165(2)
Cu(1)–P(1)	2.181(2)	Cu(2)–N(2)	1.987(6)
Cu(1)–N(1)	1.999(8)	Cu(2)–O(1)	1.983(8)
Cu(1)–O(2)	1.994(6)	P(2)–C(13)	1.846(9)
P(1)–C(13)	1.847(6)	P(2)–C(26)	1.829(7)
P(1)–C(14)	1.830(9)	P(2)–C(32)	1.824(8)
P(1)–C(20)	1.814(7)	O(2)–C(7)	1.30(1)
O(1)–C(1)	1.28(1)	N(2)–C(7)	1.34(1)
N(1)–C(1)	1.36(1)	C(7)–C(8)	1.43(1)
C(1)–C(2)	1.41(2)	C(8)–C(9)	1.36(1)
C(2)–C(3)	1.34(1)	C(9)–C(10)	1.39(1)
C(3)–C(4)	1.42(3)	C(10)–C(11)	1.33(1)
C(4)–C(5)	1.39(2)	C(11)–N(2)	1.37(1)
C(5)–N(1)	1.36(1)	C(11)–C(12)	1.51(1)
C(5)–C(6)	1.49(2)		
P(1)–Cu(1)–N(1)	130.4(2)	P(2)–Cu(2)–N(2)	129.5(2)
P(1)–Cu(1)–O(2)	115.3(2)	P(2)–Cu(2)–O(1)	123.1(2)
N(1)–Cu(1)–O(2)	114.4(3)	N(2)–Cu(2)–O(1)	107.3(3)
P(1)–Cu(1)–Cu(2)	97.8(1)	P(2)–Cu(2)–Cu(1)	93.9(1)
N(1)–Cu(1)–Cu(2)	89.0(3)	N(2)–Cu(2)–Cu(1)	89.7(2)
O(2)–Cu(1)–Cu(2)	82.3(2)	O(1)–Cu(2)–Cu(1)	83.2(2)
Cu(1)–P(1)–C(13)	109.5(3)	Cu(2)–P(2)–C(13)	109.5(3)
Cu(1)–P(1)–C(14)	117.8(3)	Cu(2)–P(2)–C(26)	117.2(3)
Cu(1)–P(1)–C(20)	116.3(3)	Cu(2)–P(2)–C(32)	117.3(3)
Cu(1)–N(1)–C(1)	119.0(5)	Cu(2)–N(2)–C(7)	119.0(5)
Cu(1)–N(1)–C(5)	120.8(7)	Cu(2)–N(2)–C(11)	121.9(6)
Cu(2)–O(1)–C(1)	128.1(7)	Cu(2)–O(2)–C(7)	128.2(6)
N(1)–C(1)–O(1)	120.4(8)	N(2)–C(7)–O(2)	120.5(7)
P(1)–C(13)–P(2)	110.5(4)		

The behaviour of complex **(1a)**, both in solution and in the solid state, could be subtly explained if a dynamic intramolecular rearrangement (which may also be postulated for the

Table 4. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (**1a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	7 188(3)	2 723(3)	2 067(3)
Cu(2)	7 989(3)	1 519(2)	3 507(3)
P(1)	6 274(6)	1 834(5)	788(6)
P(2)	7 162(6)	479(5)	2 427(7)
P(3)	6 421(6)	3 974(5)	2 968(6)
P(4)	7 404(6)	2 637(5)	4 649(7)
C(7)	5 955(19)	1 058(17)	1 319(19)
C(32)	6 208(19)	3 602(15)	3 990(17)
N(1)	8 764(14)	2 479(15)	2 383(17)
C(1A)	9 476(14)	1 860(15)	3 142(17)
C(2A)	10 578(14)	1 657(15)	3 449(17)
C(3A)	10 968(14)	2 074(15)	2 998(17)
C(4A)	10 256(14)	2 694(15)	2 239(17)
C(5A)	9 154(14)	2 896(15)	1 931(17)
C(6A)	8 339(56)	3 560(50)	1 242(54)
O(1)	9 423(15)	1 407(16)	3 529(17)
C(1B)	9 371(15)	1 999(16)	2 895(17)
C(2B)	10 311(15)	2 027(16)	2 883(17)
C(3B)	11 304(15)	1 464(16)	3 503(17)
C(4B)	11 356(15)	872(16)	4 137(17)
C(5B)	10 415(15)	843(16)	4 150(17)
C(6B)	10 148(39)	167(35)	4 520(37)
C(8)	4 965(20)	2 524(18)	−85(22)
C(9)	4 803(28)	2 487(24)	−1 118(28)
C(10)	3 802(32)	3 081(26)	−1 756(29)
C(11)	3 062(27)	3 603(23)	−1 371(28)
C(12)	3 198(33)	3 592(27)	−341(33)
C(13)	4 197(28)	3 021(23)	297(26)
C(14)	6 940(23)	1 049(20)	−49(22)
C(15)	6 509(29)	366(25)	−816(28)
C(16)	7 192(28)	−269(23)	−1 374(25)
C(17)	8 050(34)	−193(28)	−1 159(31)
C(18)	8 489(36)	497(33)	−552(34)
C(19)	7 896(27)	1 129(24)	64(26)
C(20)	6 680(22)	−52(19)	3 046(20)
C(21)	5 774(30)	419(27)	3 185(27)
C(22)	5 431(32)	51(29)	3 807(30)
C(23)	5 967(25)	−848(23)	4 101(23)
C(24)	6 817(32)	−1 317(28)	3 877(29)
C(25)	7 253(25)	−959(23)	3 337(23)
C(26)	7 935(24)	−508(19)	1 764(22)
C(27)	8 940(31)	−585(26)	1 964(28)
C(28)	9 565(37)	−1 359(33)	1 472(35)
C(29)	9 053(36)	−1 895(30)	794(33)
C(30)	8 082(36)	−1 930(29)	553(32)
C(31)	7 463(26)	−1 145(23)	1 078(24)
C(33)	5 090(26)	4 765(23)	2 255(26)
C(34)	4 200(28)	4 942(22)	2 514(25)
C(35)	3 227(32)	5 540(27)	1 905(30)
C(36)	3 140(39)	5 973(31)	1 241(36)
C(37)	4 006(35)	5 843(28)	935(31)
C(38)	5 002(31)	5 144(27)	1 451(31)
C(39)	7 137(20)	4 831(17)	3 626(19)
C(40)	6 741(23)	5 613(20)	4 236(21)
C(41)	7 334(23)	6 243(20)	4 783(21)
C(42)	8 317(21)	6 054(18)	4 708(20)
C(43)	8 679(23)	5 312(21)	4 084(22)
C(44)	8 157(21)	4 658(19)	3 602(20)
C(45)	6 982(31)	2 273(25)	5 431(26)
C(46)	6 012(31)	2 605(26)	5 500(28)
C(47)	5 765(33)	2 271(29)	6 174(32)
C(48)	6 508(34)	1 619(27)	6 816(28)
C(49)	7 429(50)	1 221(42)	6 699(43)
C(50)	7 706(53)	1 610(47)	6 079(50)
C(51)	8 362(22)	3 226(18)	5 572(20)
C(52)	8 053(22)	4 097(19)	6 153(21)
C(53)	8 786(24)	4 523(21)	6 876(22)
C(54)	9 849(27)	4 064(23)	7 105(25)
C(55)	10 215(27)	3 201(23)	6 573(25)
C(56)	9 449(23)	2 805(20)	5 812(21)
C(57)	553(37)	4 638(40)	174(47)
Cl	−466(17)	4 462(14)	255(16)
F(1)	3 633(14)	3 617(12)	3 513(14)
F(2)	3 360(17)	2 226(14)	3 185(16)
F(3)	4 267(15)	2 526(13)	2 435(15)
F(4)	2 527(18)	3 204(17)	1 990(17)
B	3 423(30)	2 865(26)	2 747(29)

precursor), as shown below,[15] is taken into account, even if the mpyO is rather rigid and the twisting motion very limited. If we consider the two dppm ligands in (**1a**) to be distinguishable, the twisting motion transforms the two enantiomers, present in solution, into two different enantiomers so that the phosphorus atoms are, on the average, equivalent in solution, in agreement with the n.m.r. data. Moreover the presence of these four complexes can justify the fact that in the solid state two centrosymmetric complexes have been found with the ligand statistically exchanged.



Experimental

The experimental techniques used and the instrumentation employed have been described in a previous paper.[11] The compound $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ was prepared as described earlier.[10] Ligands were from commercial sources and used without further purification; *p*-$MeC_6H_4N{=}N{-}N(H)C_6H_4$-Me-*p* was synthesized by literature methods.[18] Phosphorus-31 n.m.r. chemical shifts (hydrogen-1 decoupled) are given in p.p.m., positive values being to high frequency of 85% H_3PO_4 (external).

Synthesis of Cationic Complexes.—(*a*) $[Cu_2(\mu\text{-dppm})_2(\mu\text{-L–L})]BF_4$ [L–L = mpyO (**1a**), dmpz (**1b**), *p*-$MeC_6H_4N_3C_6H_4$-Me-*p* (**1c**), *or* O_2CMe (**1d**)]. To a solution of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (1.15 g, 1 mmol) in thf (40 cm^3) an equimolar amount of the sodium salt of L–L in thf (10 cm^3) was added at room temperature (prepared *in situ* by treatment of a solution of HL–L in thf with NaH and filtering the resulting suspension after 30 min of stirring). A solution of NaO_2CMe in thf–EtOH (5:1) was added. The mixture was stirred for 12 h and evaporated to dryness giving a solid residue which was

Table 5. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of complex (**2a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0	0	0
Cu(2)	−52(1)	2 461(1)	−1 571(1)
P(1)	−1 936(2)	−295(2)	−749(2)
P(2)	−2 186(2)	2 655(2)	−2 214(2)
O(1)	386(6)	2 474(6)	426(8)
O(2)	1 731(6)	−33(6)	−1 408(7)
N(1)	328(7)	289(7)	1 887(7)
N(2)	1 775(7)	2 171(6)	−2 701(7)
C(1)	438(8)	1 520(10)	1 755(10)
C(2)	660(10)	1 722(12)	3 092(13)
C(3)	672(11)	751(16)	4 501(13)
C(4)	505(11)	−520(16)	4 643(12)
C(5)	338(9)	−705(11)	3 304(10)
C(6)	191(12)	−2 015(11)	3 352(12)
C(7)	2 330(7)	947(7)	−2 449(8)
C(8)	3 558(9)	719(9)	−3 376(9)
C(9)	4 171(9)	1 749(10)	−4 476(9)
C(10)	3 601(10)	3 005(9)	−4 666(10)
C(11)	2 444(10)	3 185(8)	−3 801(9)
C(12)	1 777(13)	4 524(11)	−3 950(14)
C(13)	−2 502(7)	1 166(6)	−2 442(7)
C(14)	−1 864(8)	−1 614(7)	−1 429(8)
C(15)	−998(10)	−2 732(8)	−736(10)
C(16)	−883(13)	−3 788(9)	−1 183(14)
C(17)	−1 701(12)	−3 668(9)	−2 360(12)
C(18)	−2 513(12)	−2 571(9)	−3 082(12)
C(19)	−2 646(10)	−1 549(9)	−2 630(11)
C(20)	−3 471(7)	−510(6)	636(8)
C(21)	−4 743(9)	−773(9)	345(10)
C(22)	−5 911(9)	−843(9)	1 424(11)
C(23)	−5 820(10)	−646(10)	2 768(11)
C(24)	−4 541(10)	−422(9)	3 060(9)
C(25)	−3 386(9)	−331(8)	2 001(9)
C(26)	−2 630(8)	3 926(7)	−4 090(8)
C(27)	−1 794(12)	3 898(8)	−5 399(10)
C(28)	−2 060(16)	4 798(11)	−6 850(11)
C(29)	−3 142(15)	5 787(10)	−7 012(14)
C(30)	−3 960(11)	5 833(8)	−5 757(12)
C(31)	−3 712(10)	4 916(8)	−4 296(11)
C(32)	−3 626(8)	2 844(7)	−832(9)
C(33)	−3 313(9)	3 165(8)	359(9)
C(34)	−4 383(10)	3 289(9)	1 446(10)
C(35)	−5 734(9)	3 106(9)	1 328(10)
C(36)	−6 038(9)	2 800(9)	136(10)
C(37)	−4 969(9)	2 666(8)	−953(9)
Cl(1)	−7 464(7)	−3 837(6)	1 061(7)
Cl(2A)	−6 701(11)	−3 240(9)	−2 332(11)
Cl(2B)	−5 654(20)	−3 198(17)	−1 621(21)
C(38A)	−6 553(32)	−3 049(27)	−322(33)
C(38B)	−7 427(45)	−2 938(38)	−1 092(48)

extracted with dichloromethane. The addition of diethyl ether to the concentrated solution yielded the desired compound by precipitation in *ca.* 70–80% yield. I.r. (Nujol mulls): ν(B–F) 1 100—1 000; ν(dppm) 1 435s, 1 094m, 775m, 735s, and 689s cm^{-1}. Colours and other significant i.r. absorptions: (**1a**), white, ν(mpyO) 1 540s and 1 340s cm^{-1}; (**1b**), white, ν(dmpz) 1 580s cm^{-1}; (**1c**), yellow, ν[(*p*-$MeC_6H_4)_2N_3$] 1 355s and 1 215s cm^{-1}; (**1d**), white, ν(O_2CMe) 1 540s and 1 430s cm^{-1}.

(*b*) [Cu_2(μ-mdppm)$_2$(μ-dmpz)]BF_4(**1e**). This was prepared in a similar way to that described above and isolated as a white solid in 70% yield. I.r. (Nujol mull): ν(mdppm) 1 520s, 770s, 750s, and 700s; ν(dmpz) 1 580s cm^{-1}.

Synthesis of Neutral Complexes [Cu_2(μ-dppm)(μ-L–L)$_2$] [L–L = mpyO (**2a**), dmpz (**2b**), *p*-$MeC_6H_4N_3C_6H_4Me$-*p* (**2c**), *or* O_2CMe (**2d**)].—(*a*) A mixture of [Cu_2(μ-dppm)$_2$(MeCN)$_2$]-[BF_4]$_2$ (1.15 g, 1 mmol) and the sodium salt of L–L (2 mmol) (prepared *in situ* as described above) in thf (50 cm^3) was stirred at room temperature for 12 h. After evaporation to dryness the solid residue was extracted with dichloromethane (30 cm^3). Concentration of the resulting solution and addition of hexane led to the precipitation of the desired compound (**2b**) or (**2c**). Colours, yields, and i.r. bands (Nujol mulls): (**2b**), white, 60%, ν(dmpz) 1 580s cm^{-1}; (**2c**), yellow, 65%, ν[(*p*-$MeC_6H_4)_2N_3$] 1 355s and 1 215s cm^{-1}.

(*b*) A mixture of [Cu(MeCN)$_4$]BF_4 (0.314 g, 1 mmol), dppm (0.768 g, 2 mmol), and NaO_2CMe (0.164 g, 2 mmol) in thf–MeOH (5:1, 50 cm^3) was stirred at room temperature for 12 h. Working up as above gave complex (**2d**) as a white solid (yield 60%). I.r. (Nujol mull): ν(O_2CMe) 1 570s and 1 410s cm^{-1}.

Complex (**2a**) can be similarly obtained (yield 60%) as a white solid. I.r. (Nujol mull): ν(mpyO) 1 578s and 1 343s cm^{-1}.

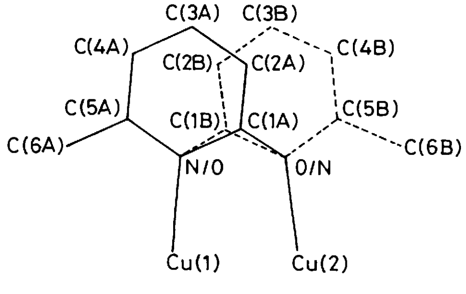
Crystal Structure Determinations of [Cu_2(μ-dppm)$_2$-(μ-mpyO)]BF_4·0.5CH_2Cl_2 (**1a**) *and of* [Cu_2(μ-dppm)(μ-mpyO)$_2$]·CH_2Cl_2 (**2a**).—White prismatic crystals of approximate dimensions 0.15 × 0.25 × 0.30 (**1a**) and 0.18 × 0.22 × 0.35 mm (**2a**) were used for the *X*-ray analyses.

Crystal data. $C_{56}H_{50}BCu_2F_4NOP_4$·0.5$CH_2Cl_2$, (**1a**), M = 1 133.27, triclinic, space group $P\bar{1}$, a = 14.569(4), b = 15.299(5), c = 14.324(4) Å, α = 104.37(2), β = 115.84(2), γ = 67.91(2)°, U = 2 649(1) Å^3 (by least-squares refinement from the θ values of 27 accurately measured reflections, λ = 0.710 73 Å), Z = 2, D_c = 1.421 g cm^{-3}, F(000) = 1 162, μ(Mo-K_α) = 10.27 cm^{-1}.

$C_{37}H_{34}Cu_2N_2O_2P_2$·$CH_2Cl_2$, (**2a**) M = 812.66, triclinic, space group $P1$, a = 9.595(4), b = 11.274(5), c = 9.414(4) Å, α = 66.44(2), β = 82.67(2), γ = 81.70(2)°, U = 920.9(7) Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections, λ = 0.710 73 Å), Z = 1, D_c = 1.465 g cm^{-3}, F(000) = 416, μ(Mo-K_α) = 14.24 cm^{-1}.

Data collection and processing. A Siemens AED single-crystal diffractometer (θ—2θ scan mode, niobium-filtered Mo-K_α radiation) was employed. All reflections with θ in the ranges 3—24 for (**1a**) and 3—27° for (**2a**) were measured; of 8 366 (**1a**) and 4 043 (**2a**) independent reflections, 1 670 for (**1a**), having $I > 3\sigma(I)$, and 3 006 for (**2a**), having $I > 2\sigma(I)$, were considered observed and used in the analyses.

Structure solutions and refinements. Patterson and Fourier methods, full-matrix [(**1a**)] and block-matrix [(**2a**)] least-squares refinements with anisotropic thermal parameters in the last cycles for the Cu, P, and methylenic carbon atoms of dppm [(**1a**)] and for all the non-hydrogen atoms except those of the dichloromethane molecule [(**2a**)]. In complex (**1a**) the mpyO ligand was disordered and distributed in two positions (of equal occupancy) bridging the two Cu atoms through the N,O or O,N atoms (see below). All the hydrogen atoms of the dppm ligands



were placed in calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. Also the solvent of crystallization was disordered in the proximity of an inversion centre and distributed in two positions with the chlorine atoms in common. The refinement was carried out on the basis of 2 057 observed reflections [having $I > 2\sigma(I)$]. Because of the very poor quality of the crystal and probably the disorder of the ligand, the final R value was rather high (0.1025). So the refinement was performed using 1 670 reflections, having $I > 3\sigma(I)$; not only R decreased remarkably, but also an improvement of the structural parameters was obtained.

In complex (**2a**) independent final cycles of refinement were carried out using the co-ordinates $-x,-y,-z$ for all the non-hydrogen atoms because of the acentric space group. A significant improvement in the R value was obtained [$R(x,y,z) = 0.0441$; $R(-x,-y,-z) = 0.0386$]. The second model was selected and the reported data refer to this model. The positions of all the hydrogen atoms, clearly localized in the final Fourier difference map, were not refined, but introduced in the final structure-factor calculations with fixed isotropic thermal parameters ($U = 0.1$ Å^2). The dichloromethane of solvation was disordered and distributed in two positions (occupancy factors 0.6 and 0.4 respectively) having a chlorine atom in common. For both structures a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.898$ for (**1a**) and 0.566 for (**2a**) and $g = 0.0058$ and 0.0051 respectively. Final R and R' values were 0.0792 and 0.0843 for (**1a**) and 0.0386 and 0.0415 for (**2a**) respectively.

Programs and sources of scattering factors are given in refs. 19 and 20. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 4 and 5. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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