Crystal and Molecular Structure of Dichlorotris-[1,2-bis(diphenylphosphino)ethane]dicopper(I)–Bisacetone

By **Vincenzo G. Albano, Pier L. Bellon,** and **Gianfranco Ciani,** Istituto di Chimica Generale ed Inorganica, Università degli Studi, via Venezian 21, Milano 20133, Italy

The crystal structure of the title compound, $Cu_2Cl_2(dppe)_3,2(C_3H_6O)$, has been determined from counter data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions: $a = 12{\cdot}57(1)$, $b = 22{\cdot}09(2)$, $c = 16{\cdot}42(1)$ Å, $\beta = 121{\cdot}28(12)°$. The structure was solved from 1429 independent reflections and refined to R 0·062. It consists of dinuclear centrosymmetric $Cu_2Cl_2(dppe)_3$ molecules and of disordered acetone molecules in a ratio 1 : 2. The copper atoms are tetrahedrally co-ordinated to a chlorine and three phosphorus atoms. Two of the three diphosphine ligands are chelating, one for each copper atom, whereas the third one bridges the two metal atoms. Cu–Cl is 2·312(4) Å, and Cu–P are 2·291(5), 2·311(4), and 2·284(6) Å. The Cl–Cu–P and P–Cu–P angles exhibit large deviations from the ideal value. The conformation of the chelating diphosphine and the distortions in the tetrahedral co-ordination of the copper atoms are discussed.

COPPER(I) halides react with unidentate phosphine ligands to give a series of compounds of general formula $Cu_nX_nL_m$ (X = halide, L = phosphine). The species of known structure, $CuXL_3$, $Cu_2X_2L_3$, and $[CuXL]_4$ are obtained, depending on the relative amounts of reagents employed.[1,2] The first, $CuXL_3$, is a tetrahedral molecule of C_3 symmetry when $L = PPh_3$.[3] The structures of two different crystal species containing the molecule $Cu_2Cl_2(PPh_3)_3$ have recently been reported;[4,5] in this compound one copper atom is three- and the other four-co-ordinated and the two chloride ions are bridging. Finally, the tetrameric species, on the basis of the crystal structure of $[CuI(AsEt_3)]_4$,[6] is expected to have four metal atoms, at the apices of a tetrahedron, connected by face-bridging halide ions.

The corresponding reactions of CuX with 1,2-bis(diphenylphosphino)ethane (dppe) have also been carried out;[2,7] the variety of compounds obtained with the unidentate ligands has prompted us to investigate the molecular complexity and the stereochemistry of these products. A species of composition CuX(dppe) is obtained when 1 : 1 molar quantities of the reagents are employed and molecular-weight determinations indicate

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[1] G. Costa, E. Reisenhofer, and L. Stefani, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2581.

[2] F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 3.

[3] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.

[4] D. F. Lewis, S. J. Lippard, and P. S. Welker, *J. Amer. Chem. Soc.*, 1970, **92**, 3805.

[5] V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J.C.S. Dalton*, 1972, 171.

[6] A. F. Wells, *Z. Krist.*, 1936, **94**, 447.

[7] L. Naldini, personal communication.

for it a trimeric formulation [CuX(dppe)]$_3$ (I).[2] We now report the crystal structure of a colourless diamagnetic compound obtained by reaction of (I) with an excess of diphosphine in benzene, recrystallized from benzene after addition of acetone.[7] We wished to ascertain the molecular complexity of this compound, the conformations of the bidentate ligands, and the behaviour of the chloride ions. Moreover, it was considered interesting to get more data on the co-ordination around the copper atoms which, in the aforementioned structures, display large distortions in their tetrahedral environment.

EXPERIMENTAL

Crystal Data.—$C_{78}H_{72}Cl_2Cu_2P_6,2C_3H_6O$,* $M = 1507{\cdot}8$, Monoclinic, $a = 12{\cdot}57(1)$, $b = 22{\cdot}09(2)$, $c = 16{\cdot}42(1)$ Å, $\beta = 121{\cdot}28(12)°$, $U = 3896{\cdot}5$ Å^3, $D_m = 1{\cdot}28(2)$ (by flotation), $Z = 2$, $D_c = 1{\cdot}29$, $F(000) = 1572$. Space group $P2_1/c$ (No. 14) from systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 8{\cdot}1$ cm^{-1}. Unit cell parameters were determined by precession photographs taken with Mo-K_α radiation.

Intensity Measurements.—The crystal sample used for data collection was an irregular polyhedron with main dimensions $0{\cdot}44 \times 0{\cdot}41 \times 0{\cdot}30$ mm, mounted along the c axis, the direction of maximum elongation.

TABLE 1

Positional and thermal parameters of non-group atoms [a, b]

Atom	x	y	z	β_{11} [c]	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Cu	986(1)	4319(1)	2220(1)	86(2)	−7(2)	50(3)	24(1)	1(1)	49(1)
Cl	2044(4)	5228(2)	2740(3)	128(5)	−49(4)	37(6)	30(1)	−1(3)	60(3)
P(1)	−957(3)	4294(2)	2023(3)	82(4)	4(4)	47(6)	21(1)	3(3)	52(3)
P(2)	1632(3)	3582(2)	3383(3)	83(4)	7(4)	47(6)	21(1)	1(3)	52(3)
P(3)	975(3)	4157(2)	842(3)	85(4)	2(4)	49(5)	22(1)	7(3)	48(3)
C(1)	−912(12)	3560(7)	2562(10)	73(17)	−9(14)	73(24)	33(5)	−1(11)	59(11)
C(2)	290(13)	3507(6)	3534(12)	109(19)	6(13)	71(27)	18(4)	13(11)	79(12)
C(3)	599(13)	4836(6)	83(10)	111(18)	13(13)	63(25)	26(5)	4(11)	56(10)

[a] All values $\times 10^4$. [b] The numbers in parentheses here and in the succeeding tables are the estimated standard deviations on last significant digits. [c] The β_{ij} values are the coefficients of: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

The intensity measurements were performed on a Pailred linear equi-inclination diffractometer with Mo-K_α radiation monochromatized with a silicon crystal. 2750 reflections, corresponding to the reciprocal lattice levels, $hk0$—12, was collected with the ω-scan method within the sphere $2\theta < 43°$. No decay occurred during the intensity measurements so that the same scale factor was given to all the reflections belonging to the various levels. The integrated intensities were corrected for Lorentz and polarization factors. The latter were evaluated taking account of the partial polarization of the incident beam.[8] Transmission factors were computed with a programme based on the Busing and Levy method [9] for a representative set of sample reflections covering the entire range of θ and μ and were found to be in the range $0{\cdot}81$—$0{\cdot}84$, so the correction was not applied.

A final set of 1429 independent non-zero reflections, all having $\sigma(I)/I < 0{\cdot}25$, were used in the solution and refinement of the structure.

Determination and Refinement of the Structure.—The number of general positions in the space group $P2_1/c$ is four and therefore only a half $Cu_2Cl_2(dppe)_3$ molecule is independent. This implies that the molecule possesses a centre of symmetry. The atomic co-ordinates of the $CuClP_3$ moiety were found from a Fourier map calculated with a set of strong reflections phased by direct methods as described elsewhere.[10] After a preliminary refinement of the heavy-atom parameters, the positions of all carbon atoms were determined from a difference-Fourier synthesis. The refinement was done by full-matrix least squares; the Cu, P, Cl, and the aliphatic carbon atoms were assigned anisotropic temperature factors and the phenyl rings (assumed to possess D_{6h} symmetry, with C–C bonds $1{\cdot}392$ Å) were constrained to rigid-body motion. The contributions of all the hydrogen atoms, in their appropriate positions, were included in the structure-factor calculations. After a few cycles of least squares, a new difference-Fourier synthesis revealed four peaks of electron density in a region well separated from the molecule. These were attributed, on the basis of their mutual positions, to a solvating acetone molecule whose presence in the solid has been previously established by the i.r. spectra in Nujol.[7] Various attempts were made to refine the acetone molecule. The refinement of the individual atomic positions resulted in non-realistic bond lengths. Very high thermal factors and lack of convergence were obtained by adopting a rigid-body refinement of three independent acetone molecules, each one weighting one third, and possessing the three possible orientations. Finally a best fit was achieved for a model of disorder possessing a D_{3h} symmetry and consisting of a central carbon atom, of three oxygen atoms with occupancy of $\frac{1}{3}$ (C–O $1{\cdot}24$ Å) and of three carbon atoms with occupancy of $\frac{2}{3}$ (C–C $1{\cdot}52$ Å; C–C–O 120°).

The final value of R was $0{\cdot}062$ and of the weighted factor, R' $0{\cdot}084$ $\{R' = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. Weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ where, in the final stages of refinement, A was $4{\cdot}0$, B $0{\cdot}4$, and C $5{\cdot}0 \times 10^{-4}$, in order to obtain a constant distribution of the weighted mean quadratic errors as a function of $\sin\theta/\lambda$ and F_o. The atomic scattering factors were taken from ref. 11 for neutral copper, chlorine, phosphorus, and carbon and from ref. 12 for hydrogen atoms. The real part of the anomalous scattering of the copper, chlorine, and phosphorus atoms was taken into account.[13] The final difference-Fourier synthesis had some peaks,

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* Analytical data: calc., C, 66·9; H, 5·5; Cu, 8·3%; found, C, 66·8; H, 5·6; Cu, 8·1%; m.p. 277 °C.

[8] W. L. Bond, *Acta Cryst.*, 1959, **12**, 375.

[9] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[10] V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1969, **16**, 461.

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[12] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

[13] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

0·2—0·4 eÅ^{-3}, mainly distributed in the region of the acetone molecule. Tables 1 and 2 report the final parameters of the atoms with their estimated standard deviations. The final list of computed and observed structure factor moduli is given in Supplementary Publication No. SUP 20434 (2 pp., 1 microfiche).*

TABLE 2

Positional and thermal parameters of the group atoms [a]

(*a*) Phenyl carbon atoms

Atom	*x*	*y*	*z*	*B*/Å^2
C(4)	−1332(11)	4791(6)	2732(8)	5·1(4)
C(5)	−2467(9)	4742(4)	2685(7)	6·2(4)
C(6)	−2678(9)	5074(6)	3308(9)	8·0(5)
C(7)	−1756(11)	5457(6)	3977(8)	7·6(5)
C(8)	−623(9)	5505(4)	4023(7)	7·4(5)
C(9)	−411(9)	5172(6)	3400(9)	5·9(4)
C(10)	−2383(9)	4275(5)	844(6)	4·6(3)
C(11)	−3056(11)	4804(4)	435(8)	6·0(4)
C(12)	−4092(10)	4792(4)	−485(8)	6·2(4)
C(13)	−4455(9)	4252(5)	−998(6)	7·2(4)
C(14)	−3782(11)	3723(4)	−589(8)	8·1(5)
C(15)	−2746(10)	3736(4)	333(8)	6·7(4)
C(16)	1873(13)	2816(5)	3136(9)	5·4(4)
C(17)	2902(11)	2719(5)	3047(10)	6·8(4)
C(18)	3123(10)	2145(6)	2814(10)	10·3(6)
C(19)	2317(13)	1670(5)	2674(9)	9·7(6)
C(20)	1289(11)	1768(5)	2762(10)	9·2(6)
C(21)	1066(10)	2342(6)	2993(10)	6·9(4)
C(22)	2975(9)	3700(5)	4602(6)	4·6(3)
C(23)	3614(10)	4249(4)	4819(7)	5·4(4)
C(24)	4621(10)	4352(4)	5733(8)	6·4(4)
C(25)	4993(9)	3907(5)	6430(6)	7·4(5)
C(26)	4354(10)	3360(4)	6212(7)	7·3(4)
C(27)	3345(10)	3257(4)	5298(8)	6·3(4)
C(28)	−49(16)	3560(5)	42(8)	4·4(3)
C(29)	−918(15)	3643(4)	−922(8)	5·4(4)
C(30)	−1694(8)	3168(5)	−1460(6)	7·2(5)
C(31)	−1560(16)	2609(5)	−1033(8)	7·4(5)
C(32)	−731(15)	2527(4)	−70(8)	7·4(5)
C(33)	45(8)	3002(5)	468(6)	5·8(4)
C(34)	2479(12)	3931(19)	1015(9)	5·0(3)
C(35)	2540(8)	3660(10)	274(7)	6·8(4)
C(36)	3681(13)	3466(11)	421(8)	7·9(5)
C(37)	4760(11)	3544(19)	1307(9)	8·0(5)
C(38)	4699(8)	3814(10)	2048(7)	8·2(5)
C(39)	3559(13)	4007(11)	1901(8)	7·1(5)

(*b*) Phenyl hydrogen atoms [b]

Atom	*x*	*y*	*z*
H(5)	−3185	4446	2163
H(6)	−3561	5034	3272
H(7)	−1920	5716	4462
H(8)	94	5803	4544
H(9)	472	5208	3435
H(11)	−2775	5225	833
H(12)	−4618	5203	−804
H(13)	−5261	4244	−1715
H(14)	−4065	3303	−987
H(15)	−2220	3325	653
H(17)	3528	3090	3158
H(18)	3922	2067	2742
H(19)	2491	1223	2495
H(20)	661	1398	2649
H(21)	266	2420	3063
H(23)	3327	4596	4278
H(24)	5116	4779	5901
H(25)	5779	3986	7143
H(26)	4642	3014	6755
H(27)	2847	2831	5127
H(29)	−992	4077	−1254
H(30)	−2370	3232	−2211
H(31)	−2202	2239	−1451
H(32)	−658	2093	263
H(33)	721	2936	1219
H(35)	1700	3600	−416
H(36)	3728	3255	−155
H(37)	5648	3394	1421
H(38)	5539	3873	2738
H(39)	3511	4218	2478

TABLE 2 (*Continued*)

(*c*) Aliphatic hydrogen atoms of the dppe ligands [c]

Atom	*x*	*y*	*z*
HE(11)	−1702	3524	2651
HE(12)	−946	3201	2102
HE(21)	323	3072	3844
HE(22)	321	3862	3998
HE(31)	1363	5153	419
HE(32)	447	4706	−604

(*d*) Atoms of the disordered acetone model [d]

Atom	*x*	*y*	*z*
CA(1)	−3211(17)	1705(12)	74(18)
CA(2)	−2659(37)	1979(18)	1064(20)
CA(3)	−2837(41)	1070(16)	−44(29)
CA(4)	−4136(26)	2066(16)	−798(23)
OA(1)	−2761(31)	1926(16)	879(19)
OA(2)	−2905(35)	1190(14)	−19(25)
OA(3)	−3966(23)	2000(15)	−637(21)

[a] *x*, *y*, and *z* × 10^4. [b] The phenyl hydrogen atoms have the same labels and the same thermal parameters as the corresponding carbon atoms. [c] Atoms HE(11) and HE(12) are bonded to C(1); all these atoms were assigned with an isotropic thermal parameter of 4·0 Å^2. [d] The value of the mean group thermal parameter is 23·3(9) Å^2.

Computations.—All computations were carried out on an IBM 7040 computer. The transmission factors were calculated by use of a local programme, in which the directions of primary and diffracted beams are evaluated as recently described.[14] Counter data reduction, phase determination, and statistical analysis for weighting schemes were also based upon Fortran programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532, and 7535 in the 1966 'International World List of Crystallographic Programs' were used for Fourier analysis, structure-factors, and least-squares calculations.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Crystal Packing and the Overall Molecular Structure.—The crystal structure consists of dinuclear centrosymmetric molecules $Cu_2Cl_2(dppe)_3$ and of disordered acetone molecules in a molecular ratio 1 : 2. A projection of the structure down the *a* axis is shown in Figure 1; the positions of the centres of gravity of the acetone molecules are indicated by black balls. An examination of all possible intermolecular distances has shown the usual van der Waals contacts only.

In the molecule $Cu_2Cl_2(dppe)_3$ each metal atom is tetrahedrally co-ordinated to one chlorine and three phosphorus atoms. The diphosphine ligands exhibit two different conformations: two of them are chelating, one on each copper atom, whereas the third acts as a bridge between two CuCl(dppe) units. The bond connecting the two (PPh_2CH_2) moieties of the bridging ligand passes through a crystallographic centre of symmetry.

The Copper Co-ordination Sphere.—The co-ordination around the copper atom is shown in Figure 2; a selection

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[14] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

of interatomic distances and angles within the molecule is reported in Table 3. The values of the Cu–Cl and Cu–P distances are in the range found for a number of copper(I) complexes (see ref. 5 and refs. therein). The Cu–Cl bond length [2·312(4) Å] is nearly equal to the sum of the Pauling covalent radii (1·35 and 0·99 Å for Cu and Cl respectively) [15] and slightly lower than the value found in $CuCl(PPh_2Me)_3$ (2·36 Å).* The Cu–P bonds are essentially equivalent and their mean length (2·30 Å) is very similar to the corresponding distances in $CuCl(PPh_2Me)_3$ (2·29 Å). Assuming for the phosphorus atom a single-bond covalent radius is of 1·10 Å there is, for the Cu–P mean distance, a shortening of 0·15 Å compared with the expected value which indicates a certain amount of π character for these interactions.

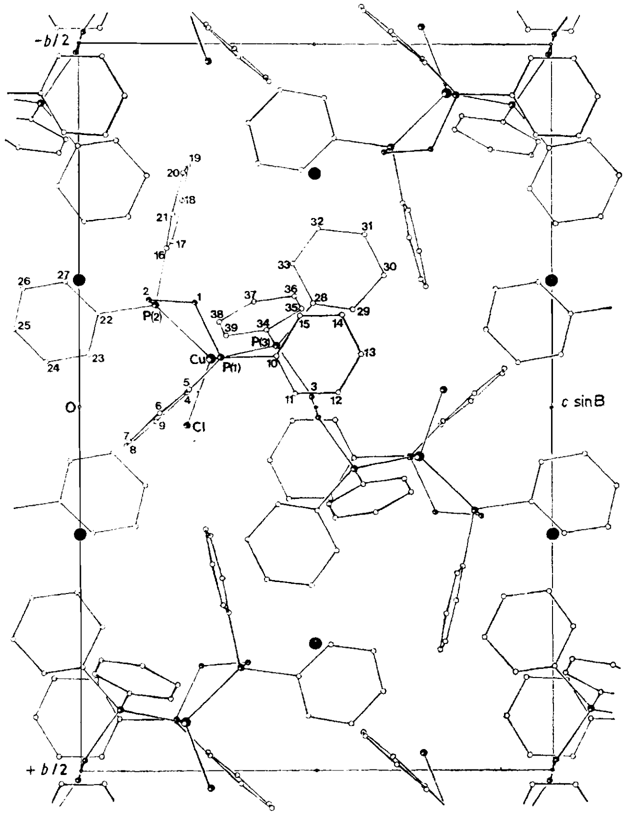

FIGURE 1 Projection of the structure along the *a* axis

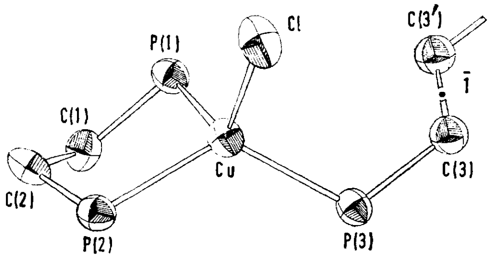

FIGURE 2 Perspective view of a half $Cu_2Cl_2(dppe)_3$ molecule without phenyl rings. The centre of symmetry lies between atoms C(3) and C(3′)

All the P–Cu–P and Cl–Cu–P angles exhibit deviations from the ideal value of 109·5°. The P(1)–Cu–P(2) angle, 89·5(2)°, is predominantly imposed by the geometry of the five-membered ring. The two Cl–Cu–P angles involving the phosphorus atoms of the chelate diphosphine, are much larger [114·7(1) and 116·1(2)°] than the third [102·0(2)°], which is comparable with the mean (104°) of the Cl–Cu–P angles in $CuCl(PPh_2Me)_3$. The distortion can be described as a movement, around the co-ordination centre, of the whole chelate ligand away from the chlorine atom; this can also be seen from the values of the non-bonding P · · · Cl distances: 3·905(6) and 3·893(6) Å for P(1) · · · Cl and P(2) · · · Cl as compared with 3·572(6) Å for P(3) · · · Cl. Further distortions are found in the P(1)–Cu–P(3) and P(2)–Cu–P(3) angles, the latter being 8·3° larger than the former.

TABLE 3

Selected interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses, within the molecule

(*a*) Bond lengths

Cu–Cl	2·312(4)	P(2)–C(16)	1·80(1)
Cu–P(1)	2·291(5)	P(2)–C(22)	1·85(1)
Cu–P(2)	2·311(4)	P(3)–C(3)	1·85(1)
Cu–P(3)	2·284(6)	P(3)–C(28)	1·84(1)
P(1)–C(1)	1·83(2)	P(3)–C(34)	1·83(2)
P(1)–C(4)	1·83(2)	C(1)–C(2)	1·53(2)
P(1)–C(10)	1·83(1)	C(3)–C(3′)	1·56(2)
P(2)–C(2)	1·84(2)		

(*b*) Bond angles

P(1)–Cu–P(2)	89·5(2)	Cu–P(3)–C(34)	114·5(5)
P(1)–Cu–P(3)	113·5(2)	P(1)–C(1)–C(2)	109·7(10)
P(2)–Cu–P(3)	121·8(2)	P(2)–C(2)–C(1)	109·3(14)
Cl–Cu–P(1)	116·1(2)	P(3)–C(3)–C(3′)	112·3(13)
Cl–Cu–P(2)	114·7(1)	C(1)–P(1)–C(4)	100·1(8)
Cl–Cu–P(3)	102·0(2)	C(1)–P(1)–C(10)	104·9(6)
Cu–P(1)–C(1)	100·9(5)	C(4)–P(1)–C(10)	104·6(5)
Cu–P(1)–C(4)	120·2(4)	C(2)–P(2)–C(16)	102·7(7)
Cu–P(1)–C(10)	122·5(5)	C(2)–P(2)–C(22)	104·6(7)
Cu–P(2)–C(2)	102·8(5)	C(16)–P(2)–C(22)	102·2(5)
Cu–P(2)–C(16)	120·8(5)	C(3)–P(3)–C(28)	105·2(5)
Cu–P(2)–C(22)	121·8(4)	C(3)–P(3)–C(34)	102·1(12)
Cu–P(3)–C(3)	114·1(4)	C(28)–P(3)–C(34)	101·5(12)
Cu–P(3)–C(28)	117·5(6)		

(*c*) Torsion angles in the dppe ring

τ[Cu–P(1)]	−18·9	τ[C(2)–P(2)]	38·3
τ[P(1)–C(1)]	48·5	τ[P(2)–Cu]	−6·9
τ[C(1)–C(2)]	−59·1		

Deviations from the ideal angular value are very common in tetrahedral complexes. The reasons seem to lie both in steric and electronic effects, the latter being more effective in complexes containing strong π ligands such as carbonyl and nitrosyl groups.[16] On the other hand, the influence of various steric factors on the co-ordination geometry has been discussed [17] for a series of tetrahedral phosphine complexes of copper(I). In the

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* Some values of the bonding parameters in the complex $CuCl(PPh_2Me)_3$ are quoted in ref. 17.

[15] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

[16] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1479; V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organometallic Chem.*, 1972, **38**, 155.

[17] S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 1971, **10**, 1322.

present case the distortions observed arise from a number of intramolecular interactions. The aforementioned enlargement of the Cl–Cu–P(1) and Cl–Cu–P(2) angles is very probably attained to minimize the non-bonded interactions of the chlorine atom with some of the phenylic hydrogen atoms of the chelate ligand; the widening of the angles proceeds until a compromise is reached between forces acting from different directions. The resulting environment of the chlorine atom exhibits three short contacts with phenylic hydrogens, two to the chelate ligand [Cl · · · H(9) 2·75 and Cl · · · H(23) 2·59 Å], and the third to the bridging diphosphine [Cl · · · H(29′) 2·59 Å]. The conformation of the bridging group also determines the enlargement of the angle P(2)–Cu–P(3) with respect to the angle P(1)–Cu–P(3) through a number of contacts between the phenyl rings bonded to atoms P(2) and P(3).

The P(1)–Cu–P(2) angle [89·5(2)°] is one of the largest P–M–P angles found in chelate diphosphine complexes. Table 4 lists the mean values of some bonding parameters for such rings in a series of compounds. A correlation is apparent, at first sight, between P–M–P angles and M–P distances, *i.e.* larger angles correspond to shorter distances and *vice versa*. The metal–phosphorus interactions in the present structure do not fit this trend. However, in all the species listed the metal atoms possess co-ordination numbers higher than in the $Cu_2Cl_2(dppe)_3$ molecule, except for the $[Rh(dppe)_2]^+$ cation which is square-planar. The ' ideal ' P–M–P angles required by the co-ordination geometries of these complexes are 90° or less. The high value of the P–Cu–P angle found here is a consequence of the tetrahedral geometry of this complex; the enlargement favours a better overlap between the orbitals of copper and phosphorus atoms and proceeds until it is impeded by the strain of the chelate group.

TABLE 4

Selected bonding parameters (mean values) in some metal–diphosphine rings

Compound	M–P/Å	P–M–P/°	M–P–C(Et)/°	M–P–C(Ph)/°
$NiBr(CH_2CMeCH_2)(dppe)$ [a]	2·18	88·8	105·0	118·2
$OsH(C_{10}H_7)(dmpe)_2$ [b]	2·30	83·7	110	123 [c]
$RuH(C_{10}H_7)(dmpe)_2$ [b]	2·30	83·9	110	123 [c]
$[Rh(dppe)_2]^+ClO_4^-$ [d]	2·31	82·7	109·0	118·4
$ReH_3(dppe)_2$ [e]	2·34	83·6	109	122
$ReH_3(PPh_3)_2(dppe)$ [f]	2·34	81·4	109·5	120·5
$[Rh(O_2)(dppe)_2]^+PF_6^-$ [g]	2·35	83·4	106·9	118·1
$[Ir(O_2)(dppe)_2]^+PF_6^-$ [g]	2·36	83·5	106·3	118·7
$[Ir(CO)(dppe)_2]^+Cl^-$ [h]	2·37	83·0	109	119
$MoCl(CO)(C_5H_5)(dppe)$ [i]	2·47	75·2	110·9	119·0

[a] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1970, 206. [b] U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc.* (*A*), 1971, 1118. [c] These are the mean values of the $M–P–(CH_3)$ angles. [d] Ref. 20. [e] V. G. Albano and P. L. Bellon, *J. Organometallic Chem.*, 1972, **37**, 151. [f] V. G. Albano, P. L. Bellon, and V. Scatturin, *Ist. Lomb. Rend. Sci.*, 1966, *A*, **100**, 989. [g] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301. [h] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Comm.*, 1966, 906. [i] J. H. Cross and R. H. Fenn, *J. Chem. Soc.* (*A*), 1970, 3019.

The dppe Ligands.—As already mentioned, the $Cu_2Cl_2(dppe)_3$ molecule contains two types of dppe ligands: the chelating and the bridging ones. All the P–C distances and C–P–C angles in this structure are substantially equivalent and are comparable with the corresponding values found in a number of phosphine complexes. On the other hand, the Cu–P–C angles exhibit large differences in the two ligands: the mean values of the Cu–P–C(Ph) and Cu–P–C(Et) angles are 121·3 and 101·8° in the chelating *vs.* 116·0 and 114·1° in the bridging one. The values found in the latter are comparable with the corresponding ones in the unconstrained ' model ' group (PPh_2Et), *e.g.* in the complex $Pt(CO)_2(PPh_2Et)_2$ [Pt–P–C(Ph) 115·0 and Pt–P–C(Et) 117·7°].[18] The deviations found in the case of the chelate ring follow a pattern common to all structures containing this ligand, although the present values for Cu–P–C(Et) are exceptionally low (see Table 4). The pattern can be taken as an indication of the bent character of the M–P bonds; in other words, because of the strain in the ring, the phosphorus donor orbitals do not point exactly towards the metal atom.

In the bridging diphosphine, which possesses a crystallographic inversion centre, the P(3)–C(3)–C(3′)–P(3′) chain is constrained to an exact *trans*-planar conformation; in this way the two CuCl(dppe) moieties are kept as far away as possible.

The conformation of the chelate ring is best described by assigning the torsion angles about the bonds of the chain (see Table 3). Gollogly and Hawkins have performed theoretical calculations of the conformational energies of five-membered chelate diamine rings.[19] The results of these calculations have been recently discussed in connection with diphosphine rings by Kilbourn *et al.*;[20] these authors have also reported a tabulation of the experimental torsion angles in a number of complexes. The conformation energy of the rings depends mainly on the torsion angle τ(C–C), other important parameters being the P–M–P and the M–P–C(Et) angles. This energy is essentially unaffected by the displacement of the two carbon atoms with respect to the P–M–P plane. A variety of conformations of equivalent stability is therefore possible. In the present case the ring has an asymmetric conformation, as indicated by the different

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[18] V. G. Albano, P. L. Bellon, and M. Manassero, *J. Organometallic Chem.*, 1972, **35**, 423.

[19] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.

[20] M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc.* (*A*), 1970, 2539.

values of the two τ(Cu–P) torsion angles. The out-of-plane displacements of atoms C(1) and C(2), on opposite sides of the P(1)–Cu–P(2) plane, are +0·58 and −0·22 Å, respectively. The torsion angle about the C(1)–C(2) bond (59·1°) is almost exactly the value expected for an ideally staggered conformation (60°) and higher than the values reported in literature, which fall in the range 36—55°.[20] The present ring is rather exceptional: here, a conformation of minimum energy is attained through the contemporary presence of τ(C–C) and P–M–P angles larger and M–P–C(Et) angles smaller than are usually found. This occurs because of the tetrahedral co-ordination around the copper atom, which favours the enlargement of the P–Cu–P angle as already stated. It would be interesting to confirm the presence of such an enlargement in other tetrahedral complexes of dppe in order to investigate further the flexibility of this kind of ring-forming ligand. This will be the major interest in the structure determination of $[CuCl(dppe)]_3$ and of similar compounds.*

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* *Note added in proof.* The bonding parameters and overall conformations of the $Cu_2(dppe)_3$ moieties in the complexes $Cu_2(N_3)_2(dppe)_3$ (A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chem.*, 1971, **10**, 2776) and $Cu_2(CF_3CN_4)_2(dppe)_3$ (A. P. Gaughan, K. S. Bowman, and Z. Dori, *Inorg. Chem.*, 1972, **11**, 601) are strictly comparable with those determined above for $Cu_2Cl_2(dppe)_3,2(C_3H_6O)$.