Stereochemistry of Copper(I) Complexes. Part II.[1] The Molecular Structure of the 3 : 2 Reaction Product between Copper Iodide and Bis(diphenylphosphino)methane: Di-μ-[bis(diphenylphosphino)methane]-μ-iodo-di-μ_3-iodo-*triangulo*-tricopper(I)–0.5 Dichloromethane

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by the heavy-atom method and refined by anisotropic block-diagonal least-squares to *R* 0.056 for 3 504 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with cell parameters a = 13.266(8), b = 22.667(9), c = 20.887(8)Å, β = 121.94(7)°, Z = 4. The structure consists of a triangle of distorted tetrahedral copper atoms connected by a bridge of iodine atoms and the dpm ligand. Values of Cu–P and Cu–I bond lengths and the geometry of the halogen bridges are discussed on the basis of the structural results of similar compounds.

THE structures of the addition compounds formed between copper(I) halides (CuX) and bis(diphenylphosphino)methane (dpm) of formula $[(CuX)_2(dpm)]$ [1,2] and $[(CuCl)(dpm)]$ [3] have been described recently. Analogous compounds with triphenylphosphine of formula $[(CuX)(PR_3)]$ and $[(CuCl)_2(PPh_3)_3]$ have also been studied.[4,5]

All these compounds have strictly related polynuclear copper-atom structures with double- or triple-bridging X atoms, the degree of nucleation being essentially determined by the stoicheiometric ratio. Copper atoms do not exceed the co-ordination number four, with peculiar values for Cu–P bond lengths.[6]

Structural results allowed us to interpret some solution properties of the dpm derivatives, such as molecular weight and conductivity measurements. To obtain further insight into this class of compounds we report the results of a crystal structure analysis of the dpm derivative with stoicheiometric ratio 3 : 2, $[(CuI)_3(dpm)_2]$.

EXPERIMENTAL

Crystal Data.—$Cu_3I_3P_4C_{50}H_{44}$, M = 1 341.4, Monoclinic, a = 13.266(8), b = 22.667(9), c = 20.887(9)Å, β = 121.94(7)°, U = 5 329 Å^3, D_m = 1.78, Z = 4, D_c = 1.72 (with 0.5-CH_2Cl_2), μ(Mo-K_α) = 32 cm^{-1}, μr = 1.0. Space group $P2_1/c$. Cell parameters were determined from Weissenberg and precession photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer by use of Mo-K_α radiation (λ = 0.7107 Å). Preparation of the crystals is reported in ref. 7.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by means of the θ—2θ scan technique and Mo-K_α radiation for $2\theta_{max.}$ 50°. Reflections having $I < 3\sigma(I)$ were rejected, the remainder (3 504) being corrected for Lorentz and polarization factors and used in the subsequent refinement. No absorption correction was applied because of the small size of the crystal.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods, and refined to *R* 0.056. The I, Cu, and P atoms were treated anisotropically and no contribution for hydrogen atoms was included. A CH_2Cl_2 molecule with a half-occupancy factor was also detected from inspection of the Fourier. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where A = 30.0, B = 1.0, and C = 0.025, chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$.

Final atomic parameters are listed in Table 1, together with their estimated standard deviations calculated from the residual of the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme for the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21450 (11 pp., 1 microfiche †). Atomic scattering factors were calculated according to ref. 8.

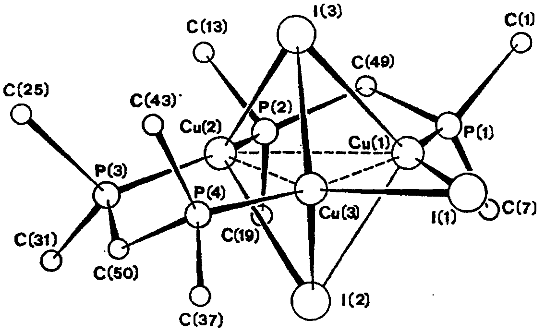

FIGURE 1 Numbering scheme for the $[(CuI)_3(dpm)_2]$ molecule. Only the first carbon atom of each phenyl group is shown

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 9. A local program was used to obtain best molecular planes whose equations were calculated according to ref. 10.

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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RESULTS AND DISCUSSION

The structure of the discrete [(CuI)$_3$(dpm)$_2$] unit may be described as a triangle of copper atoms, connected by triple-bridging iodine atoms above and below the plane of copper atoms. One side of the triangle is bridged by the third iodine atom, whereas each of the other two sides are bridged by one dpm molecule. All the copper atoms have distorted tetrahedral geometry. The trinuclear species is shown in Figure 1. The overall structure may be related to that of the [(Cu$_3$Cl$_2$)(dpm)$_3$]$^+$ cation,[3] which is shown in Figure 2, assuming a formal substitution of the I(1) atom with a dpm bridge. This provokes a different orientation of the Cu, Cu, P, P planes with respect to those of the copper atoms. In the 3 : 2 derivative the two angles between the Cu, Cu, P, P planes and that of the copper atoms are 4.9 and 2.6°, whereas in the 1 : 1 derivatives they range from 17.1 to 22.8°.

TABLE 1

Fractional co-ordinates (× 10^4) and temperature factors (Å^2) with estimated standard deviations in parentheses

	x	y	z	B/Å^2
I(1)	5 399(1)	−3 852(1)	3 023(1)	*
I(2)	2 578(1)	−2 711(1)	2 079(1)	*
I(3)	4 640(1)	−3 124(1)	4 556(1)	*
Cu(1)	5 044(2)	−2 821(1)	3 407(1)	*
Cu(2)	2 772(2)	−2 521(1)	3 454(1)	*
Cu(3)	3 510(2)	−3 623(1)	3 102(1)	*
P(1)	5 731(3)	−1 911(2)	3 636(2)	*
P(2)	3 403(3)	−1 572(2)	3 662(2)	*
P(3)	1 016(3)	−2 909(2)	3 188(2)	*
P(4)	1 948(3)	−4 114(2)	2 944(2)	*
Cl(1)	3 549(13)	1 937(8)	3 597(9)	9.0(4)
Cl(2)	2 569(9)	835(6)	3 456(6)	5.6(3)
C(1)	7 292(12)	−1 762(7)	4 339(8)	2.4(3)
C(2)	8 101(16)	−2 099(10)	4 259(11)	4.7(5)
C(3)	9 333(18)	−1 988(11)	4 774(12)	5.7(5)
C(4)	9 740(15)	−1 564(9)	5 344(10)	4.0(4)
C(5)	8 941(15)	−1 241(9)	5 406(10)	4.1(4)
C(6)	7 682(15)	−1 342(9)	4 895(9)	3.8(4)
C(7)	5 551(13)	−1 487(8)	2 831(8)	2.9(4)
C(8)	5 953(16)	−918(9)	2 916(10)	4.3(4)
C(9)	5 744(19)	−626(11)	2 235(13)	6.4(6)
C(10)	5 110(21)	−881(12)	1 501(14)	7.2(6)
C(11)	4 838(22)	−1 448(13)	1 465(14)	7.5(7)
C(12)	5 034(16)	−1 790(9)	2 151(10)	4.6(5)
C(13)	3 301(13)	−1 206(7)	4 406(8)	2.6(3)
C(14)	3 549(17)	−602(10)	4 521(11)	4.9(5)
C(15)	3 550(19)	−320(11)	5 214(12)	6.1(6)
C(16)	3 371(17)	−660(10)	5 677(11)	5.4(5)
C(17)	3 081(18)	−1 241(11)	5 518(12)	5.7(5)
C(18)	3 061(16)	−1 522(10)	4 865(11)	4.7(5)
C(19)	2 666(13)	−1 060(8)	2 855(8)	2.7(4)
C(20)	3 250(16)	−633(9)	2 751(10)	4.3(4)
C(21)	2 601(19)	−267(11)	2 081(12)	6.1(6)
C(22)	1 347(16)	−318(10)	1 613(10)	4.6(5)
C(23)	801(15)	−743(9)	1 791(10)	3.8(4)
C(24)	1 434(15)	−1 125(9)	2 403(10)	3.8(4)
C(25)	653(13)	−3 102(8)	3 918(8)	2.7(4)
C(26)	−445(15)	−3 279(9)	3 703(10)	3.8(4)
C(27)	−688(17)	−3 494(10)	4 240(11)	5.4(5)
C(28)	205(19)	−3 541(11)	5 012(12)	6.0(6)
C(29)	1 358(18)	−3 341(10)	5 231(12)	5.6(5)
C(30)	1 575(15)	−3 127(9)	4 663(9)	3.8(4)
C(31)	−227(13)	−2 443(8)	2 521(9)	2.9(4)
C(32)	−702(14)	−2 444(9)	1 733(9)	3.6(4)
C(33)	−1 606(17)	−2 035(10)	1 256(11)	5.1(5)
C(34)	−2 019(18)	−1 641(11)	1 543(12)	5.7(5)
C(35)	−1 613(20)	−1 629(12)	2 375(13)	6.5(6)
C(36)	−670(15)	−2 041(9)	2 876(10)	4.1(4)
C(37)	1 248(13)	−4 652(8)	2 172(8)	3.0(4)
C(38)	1 640(14)	−4 676(9)	1 659(9)	3.8(4)
C(39)	1 113(17)	−5 075(10)	1 038(11)	4.9(5)
C(40)	191(17)	−5 464(10)	969(11)	5.0(5)
C(41)	−217(16)	−5 415(10)	1 478(11)	4.8(5)
C(42)	319(15)	−5 014(9)	2 093(10)	3.8(4)
C(43)	2 169(13)	−4 533(8)	3 779(8)	2.7(4)
C(44)	3 191(16)	−4 889(10)	4 120(10)	4.8(5)
C(45)	3 448(19)	−5 260(11)	4 727(12)	6.3(6)
C(46)	2 694(18)	−5 243(11)	5 052(12)	5.7(5)
C(47)	1 689(18)	−4 883(10)	4 719(11)	5.5(5)
C(48)	1 426(16)	−4 530(9)	4 040(10)	4.3(4)
C(49)	5 035(13)	−1 477(7)	4 038(8)	2.6(3)
C(50)	682(12)	−3 619(7)	2 648(8)	2.4(3)
C(51)	3 473(33)	1 163(19)	3 448(21)	4.9(9)

* Anisotropic thermal parameters (× 10^4) in the form: $\exp[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$.

TABLE 1 (*Continued*)

	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
I(1)	72(1)	15(1)	60(1)	17(0)	−2(1)	40(0)
I(2)	59(1)	0(1)	29(1)	18(0)	2(1)	21(0)
I(3)	60(1)	10(1)	24(1)	19(0)	6(1)	20(0)
Cu(1)	95(2)	−24(2)	93(1)	13(0)	−15(1)	51(1)
Cu(2)	42(1)	−5(1)	25(1)	12(0)	−3(1)	23(1)
Cu(3)	52(1)	−14(2)	55(1)	16(1)	−7(1)	43(1)
P(1)	42(3)	−8(3)	27(3)	11(1)	−6(2)	22(1)
P(2)	40(3)	0(3)	29(3)	12(1)	0(2)	24(1)
P(3)	35(3)	−2(3)	22(2)	12(1)	−4(2)	20(1)
P(4)	43(3)	−5(3)	28(2)	10(1)	−4(2)	20(1)

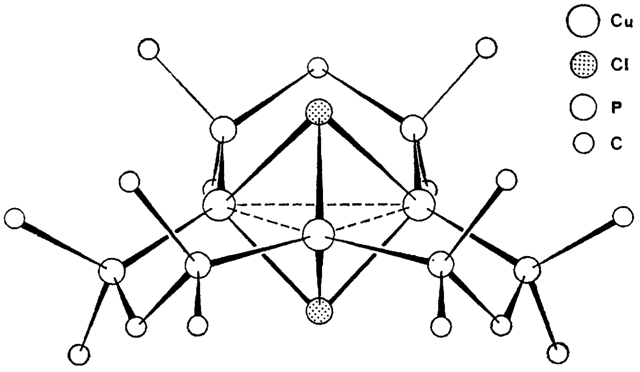

FIGURE 2 Perspective drawing of the [(Cu$_3$Cl$_2$)(dpm)$_3$]$^+$ cation (ref. 3)

The triple-bridging I(2) atom binds the copper atoms by means of two short [2.778(3) and 2.752(3) Å] and one long [2.976(2) Å] bond length, whereas I(3) binds the copper atoms with two long [2.807(3) and 2.816(3) Å] and one short [2.696(2) Å] bond lengths. A much more symmetrical triple-bridging I atom has been found[1] in the [(CuI)(dpm)] derivative, the Cu–I distances ranging from 2.718(4) to 2.787(4) Å.

The double-bridging I(1) atom binds Cu(I) and Cu(3) asymmetrically, the geometry of the bridge being characterized by two different bond lengths [2.648(3) and 2.594(3) Å] and angle Cu–I–Cu 58.09(9)°. The geometrical parameters of the Cu–X–Cu double bridge for a series of similar compounds are given in Table 2. The bridge asymmetry may be attributed only in part to the different hybridization of copper(I) atoms.

Table 2 shows that the Cu · · · Cu distances in Br and Cl derivatives are nearly equal, ranging from 2.909(2) to 2.992(2) Å, as well as the Cu–X–Cu angles which range from 74.5(2) to 78.8(2)°. However, the Cu · · · Cu distances and Cu–I–Cu angles are significantly lower for the iodo-derivatives. The former are in the range 2.546(3)—2.73 Å, the latter in the range 58.09(9)—63.9(2)°.

We can attribute the shortening of Cu · · · Cu distances to the ability of iodine to act as a bridging ligand making the Cu–I–Cu angles appreciably narrower than those for bromo- or chloro-ligands. Similarly, the iodine atoms involved in triple bridges make Cu–I–Cu angles ranging from 52.60(8) to 69.58(7)° whereas for chlorine the values are 78.3(1)—84.6(1)°.

TABLE 2

Geometrical parameters of Cu–X–Cu bridges in some $[(CuX)_nL_m]$ complexes

X	Cu · · · Cu	Cu–X–Cu(°)	C.N.*	Cu–X(Å)	Δ/Å	Compound
Cl	2.909(2)	76.1(2)	4	2.454(4)	0.036	
		76.3(2)	4	2.418(4)		$[(Ph_3P)CuCl_2Cu(PPh_3)_2]$ [a]
			3	2.298(4)	0.051	
			3	2.247(4)		
Cl	2.915(3)	78.8(2)	4	2.324(6)	0.054	$[(dpm)_2(CuCl)_4]$ [b]
			3	2.270(4)		
Cl	2.992(2)	75.2(1)	4	2.358(3)	0.106	$[(dpm)_2(CuCl)_4(CH_3)_2(CO)]$ [c]
			3	2.252(2)		
Br	2.990(2)	76.04(6)	4	2.477(2)	0.101	$[(Ph_3P)_4(CuBr)_4]$ [d]
			3	2.376(2)		
Br	2.939(6)	74.5(2)	4	2.524(6)	0.189	$[(dpm)_2(CuBr)_4]$ [e]
			3	2.335(5)		
I	2.685(5)	62.9(4)	4	2.633(4)	0.123	$[(dpm)_2(CuI)_4]$ [e,f]
			3	2.510(4)		
I	2.546(3)	58.09(9)	4	2.648(3)	0.054	$[(dpm)_2(CuI)_3]$ [g]
			4	2.594(3)		
I	2.73	63.9(2)	4	2.623(6)	0.096	$[(Me_2AsN)_2(CuI)_2]$ [h]
			4	2.527(6)		

[a] Ref. 5. [b] Ref. 2(*b*). [c] Ref. 2(*c*). [d] Ref. 4(*a*). [e] Ref. 1. [f] Ref. 2(*a*). [g] Present work. [h] R. Graziani, G. Bombieri, and E. Forsellini, *J.C.S. Dalton*, 1972, 1938.

* C.N. = Co-ordination no.

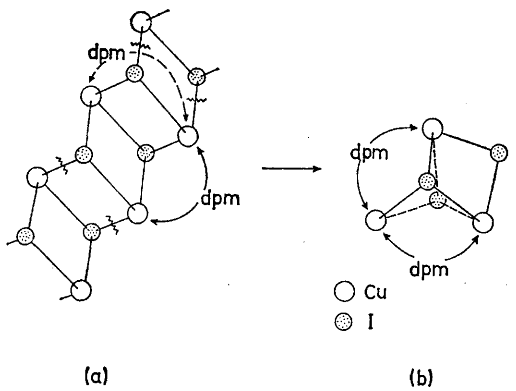

FIGURE 3 Scheme for the formation of $[(CuI)_3(dpm)_2]$

We are not able to find a simple electronic interpretation for this observation, because the total electronic scheme in all cases must be the same. It therefore seems more acceptable to ascribe it to the intrinsic ability of iodine to form narrow angles, which imposes short Cu · · · Cu distances. This would imply little, if any, electronic interaction between copper atoms.

It has been already observed [6] that Cu–P bond lengths in similar compounds are mainly influenced by the number of phosphorus atoms bonded to the same copper atom. Here we have further evidence for this observation. In the present compound Cu(2) is co-ordinated by two phosphorus atoms, whereas each of the other copper atoms is co-ordinated by only one. As expected Cu(2)–P(3) and Cu(2)–P(2) are 2.267(5) and 2.265(5) Å respectively whereas Cu(1)–P(1) and Cu(3)–P(4) are 2.203(5) and 2.218(5) Å. The latter values are in agreement with the mean [6] obtained for ' one-phosphorus ' Cu–P distances [2.194(2) Å], the former with the mean value obtained for ' two-phosphorus ' distances [2.261(3) Å].

TABLE 3

Relevant bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Cu(1) · · · Cu(2)	3.142(4)	I(1)–Cu(1)	2.594(3)
Cu(1) · · · Cu(3)	2.546(3)	I(1)–Cu(3)	2.648(3)
Cu(2) · · · Cu(3)	2.916(4)	I(2)–Cu(1)	2.978(2)
Cu(1)–P(1)	2.203(5)	I(2)–Cu(2)	2.778(3)
Cu(2)–P(2)	2.265(5)	I(2)–Cu(3)	2.752(3)
Cu(2)–P(3)	2.267(5)	I(3)–Cu(1)	2.807(3)
Cu(3)–P(4)	2.218(5)	I(3)–Cu(2)	2.816(3)
		I(3)–Cu(3)	2.696(2)
P(1)–C(1)	1.83(1)	P(3)–C(25)	1.88(2)
P(1)–C(7)	1.84(2)	P(3)–C(31)	1.83(2)
P(1)–C(49)	1.83(2)	P(3)–C(50)	1.88(2)
P(2)–C(13)	1.83(2)	P(4)–C(37)	1.83(2)
P(2)–C(19)	1.84(2)	P(4)–C(43)	1.87(2)
P(2)–C(49)	1.88(2)	P(4)–C(50)	1.83(2)
(*b*) Angles			
I(1)–Cu(1)–I(2)	94.4(1)	I(2)–Cu(2)–I(3)	110.2(1)
I(1)–Cu(1)–I(3)	101.1(1)	I(2)–Cu(2)–P(2)	99.7(2)
I(1)–Cu(1)–P(1)	142.1(2)	I(2)–Cu(2)–P(3)	99.5(1)
I(2)–Cu(1)–I(3)	101.8(1)	I(3)–Cu(2)–P(2)	103.8(1)
I(2)–Cu(1)–P(1)	104.4(1)	I(3)–Cu(2)–P(3)	111.9(1)
I(3)–Cu(1)–P(1)	106.7(2)	P(2)–Cu(2)–P(3)	130.0(2)
I(1)–Cu(3)–I(2)	98.6(1)	Cu(1)–I(1)–Cu(3)	58.09(9)
I(1)–Cu(3)–I(3)	99.5(1)	Cu(1)–I(2)–Cu(2)	66.08(8)
I(1)–Cu(3)–P(4)	137.1(2)	Cu(1)–I(2)–Cu(3)	52.60(7)
I(2)–Cu(3)–I(3)	107.4(1)	Cu(2)–I(2)–Cu(3)	63.64(8)
I(2)–Cu(3)–P(4)	105.1(1)	Cu(1)–I(3)–Cu(2)	69.58(9)
I(3)–Cu(3)–P(4)	106.5(2)	Cu(1)–I(3)–Cu(3)	53.83(8)
		Cu(2)–I(3)–Cu(3)	63.81(7)

It must be stressed that these values are for arylphosphine ligands, for it seems that change in the nature of the phosphine gives different results: the structure analysis of [(CuCl)(PEt_3)]^{4b} gives a 'one-phosphorus' Cu–P distance of 2.254(3) Å.

Relevant bond lengths and angles are reported in Table 3, and equations of least-squares planes in Table 4.

TABLE 4

Equations of least-squares planes and, in square brackets, distances (Å) of atoms from the plane. Equations are referred to the crystal axes and x, y, and z are fractional co-ordinates

Plane (1): Cu(1)—(3)

$$-0.412x - 5.852y + 17.458z = 7.391$$

[I(1) −0.082, I(2) −2.281, I(3) 2.200, P(1) −0.161, P(2) −0.218, P(3) −0.165, P(4) 0.076]

Plane (2): Cu(1), Cu(2), P(1), P(2)

$$-0.271x - 3.959y + 17.674z = 7.015$$

[Cu(1) −0.013, Cu(2) 0.013, P(1) 0.013, P(2) −0.013]

Plane (3): Cu(2), Cu(3), P(3), P(4)

$$-0.909x - 5.258y + 17.956z = 7.216$$

[Cu(2) 0.059, Cu(3) −0.060, P(3) −0.055, P(4) 0.056]

Angles (°) between planes (1)–(2) 4.94, (1)–(3) 2.64, (2)–(3) 4.37.

A simple rationalization of the structures of compounds of general formula $(CuX)_nL_m$, resulting from a common parent structure, the double-stranded chain of Figure 3(a), has already been reported.[1] Figure 3 suggests a method of formation of the present trinuclear species on the basis of this scheme.

The structure of [$(CuX)_2$(dpm)] derivatives[1] is in agreement with molecular-weight and conductivity measurements, suggesting that the same neutral tetranuclear species found in the solid state is present in solution in non-polar solvents. Similarly the structure of [(CuCl)(dpm)],[3] which consists of [$(Cu_3Cl_2)$$(dpm)_3$]$^+$ cations and Cl^- anion in the solid state, suggests that these ionic species predominate in solutions of $C_2H_4Cl_2$, the compound behaving as a uni-univalent electrolyte.

In the case of the present compound, molecular-weight measurements give values exceeding that expected for the trinuclear species and conductivity measurements suggest [$(CuI)_3$$(dpm)_2$] to behave as a uni-univalent electrolyte in dichloroethane solutions. This confirms the previous suggestion,[7] that for this derivative solution properties depend on equilibria between different species in solution.

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