Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 18.† Stereochemistries and Structures of the 1 : 1 Neutral Complexes of $\mathrm{Cu^{I}X}$ with 1,10-Phenanthroline (X = I) or 2,9-Dimethyl-1,10-phenanthroline (X = I, Br, or Cl)‡

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Single-crystal *X*-ray structure determinations have been carried out at 295 K on the compounds [CuI(phen)]·0.5MeOH (**1**) (phen = 1,10-phenanthroline), [CuI(dmphen)] (**2**), [CuBr(dmphen)] (**3**), and [CuCl(dmphen)] (**4**) (dmphen = 2,9-dimethyl-1,10-phenanthroline). Crystals of (**1**) are monoclinic, $P2_1/n$, a = 10.659(3), b = 23.585(9), c = 10.487(3) Å, β = 91.34(2)°, Z = 8; for N_o = 2 457 independent 'observed' diffractometer reflections, R = 0.034. Crystals of (**2**) are monoclinic, $C2/c$, a = 19.025(6), b = 8.489(3), c = 17.376(5) Å, β = 108.27(2)°, Z = 8; N_o = 1 582, R = 0.035. Crystals of (**3**) are isomorphous with (**2**), a = 18.497(6), b = 8.398(2), c = 17.419(5) Å, β = 110.14(2)°; N_o = 1 786, R = 0.040. Crystals of (**4**) are monoclinic, $P2_1/n$, a = 10.133(4), b = 18.388(5), c = 6.729(1) Å, β = 94.31(2)°, Z = 4; N_o = 889, R = 0.044. In (**1**)—(**3**), the species is a di-μ-halogeno-bridged dimer with four-co-ordinate copper atoms. For (**1**), Cu–I are 2.589(1)—2.632(1) Å with Cu–N 2.078(6)—2.103(6); Cu ··· Cu is 2.609(2) and I ··· I, 4.454(2) Å. In (**2**), Cu–I are 2.673(1), 2.563(1), Cu–N, 2.094(6), 2.092(5); Cu ··· Cu is 3.024(2) and I ··· I, 4.276(1) Å. In (**3**), Cu–Br are 2.400(1), 2.559(1), Cu–N, 2.083(5), 2.085(4) Å; Cu ··· Cu is 3.097(1) and Br ··· Br, 3.876(1) Å. Complex (**4**) is mononuclear with the copper atom pseudo-trigonally planar co-ordinated by the bidentate aromatic ligand [Cu–N 2.060(6) and 2.057(5) Å] and the halide [Cu–Cl, 2.126(2) Å]. The role of the ligand and halide substituents on the complexity of the complex is examined.

Elsewhere, it has been shown that dimeric,[1] and monomeric[1,2] adducts of the type $\mathrm{CuXL_2}$ may be prepared by reacting copper(I) halides with L = nitrogen base. For pyridine bases, the steric profile may be varied by the substitution of one or two methyl groups in the 2 and 6 positions; with pyridine, 3,5-dimethylpyridine, 2-methylpyridine, or quinoline, binuclear di-μ-halogeno-bridged adducts $\mathrm{L_2CuX_2CuL_2}$ may be formed in which the copper atom is four-co-ordinate. With 2,6-dimethylpyridine and quinaldine (2-methylquinoline) (but not 2,4,6-trimethylpyridine or acridine) mononuclear species may be obtained with pseudo-trigonal and trigonal planar copper atoms. With bidentate ligands, L′, adducts of the type $\mathrm{CuXL'_2}$ have been described for sterically hindered α-di-imine bases such as 2,9-dimethyl-1,10-phenanthroline (dmphen) and 4,4′,6,6′-tetramethyl-2,2′-bipyridine. Such adducts are ionic with $[\mathrm{CuL'_2}]^+$ cations and associated counter ions, the metal being pseudo-tetrahedrally co-ordinated by a pair of bidentate ligands.[3] By contrast, no structural work appears to have been carried out for the system of CuXL′ stoicheiometry, apart from a species containing X = $\mathrm{BH_4}^-$, in which the $\mathrm{BH_4}^-$ anion behaves as a bidentate ligand of small bite, and which is mononuclear.[4] This is surprising, given the continuing interest shown in the spectroscopic properties and redox chemistry of these systems in general.[5] Previous work on the CuX(dmphen) (X = halide) derivatives has suggested that they are 'probably dimeric with a tetrahedral arrangement of the ligand donor atoms.'[6,7] The steric requirements of 1,10-phenanthroline (phen) based ligands are likely to be quite different to those of substituted pyridines, since any variation in subsequent profile will take place within the plane of the metal and co-ordinated nitrogen atoms. Accordingly, structure determinations have been carried out on the air-stable adducts of $\mathrm{Cu^{I}I}$, with phen, (**1**), and $\mathrm{Cu^{I}X}$ with dmphen [X = I (**2**), Br (**3**), or Cl (**4**)].

The reaction of CuCl or CuBr with phen in a range of solvents has led, in general, to only microcrystalline products unsuitable for single-crystal *X*-ray diffraction studies. One reaction, however, of CuBr and phen in dichloromethane gives irregular crystals of adequate dimensions for *X*-ray analysis. Surprisingly, this has proved to be the ionic species, $[\mathrm{Cu(phen)_2}][\mathrm{CuBr_2}]$. Its structure is reported in the following paper.[8]

Experimental

Preparation of Complexes.§—[CuI(phen)] (**1**). 1,10-Phenanthroline (0.38g) was dissolved in $\mathrm{CH_3CN}$ (10 cm^3) and added to a suspension of copper(I) iodide (0.38 g) in $\mathrm{CH_3CN}$ (10 cm^3). An immediate brick-red microcrystalline product formed. Refluxing this precipitate for 3 d in $\mathrm{CH_3CN}$ (50 cm^3) resulted in large crystals suitable for *X*-ray analysis, m.p. 280—286 °C (with decomposition) (Found: C, 39.4; H, 2.6; N, 7.4. Calc. for $\mathrm{C_{12}H_8CuIN_2}$: C, 38.9; H, 2.2; N, 7.6. Calc. for $\mathrm{C_{12}H_8CuIN_2}$·0.5-MeOH : C, 38.8; H, 2.6; N, 7.2%).

[CuI(dmphen)] (**2**). 2,9-Dimethyl-1,10-phenanthroline (0.50 g) was dissolved in $\mathrm{CH_3CN}$ (20 cm^3) and added to a suspension of CuI (0.4 g) in $\mathrm{CH_3CN}$ (20 cm^3). The resultant solution turned a deep red which faded with time and from which pale orange crystals of the complex precipitated. Crystals suitable for *X*-ray analysis were prepared by slowly cooling a hot saturated

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† Part 17 is ref. 28.

‡ *Supplementary data available* (No. SUP 56323, 13 pp.): thermal parameters, least-squares planes data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

§ See also refs. 6 and 7.

Table 1. Crystallographic data for complexes (**1**)—(**4**)

Compound	[CuI(phen)]·0.5MeOH (**1**)	[CuI(dmphen)] (**2**)	[CuBr(dmphen)] (**3**)	[CuCl(dmphen)] (**4**)
Formula	$C_{12.5}H_{10}CuIN_2O_{0.5}$	$C_{14}H_{12}CuIN_2$	$C_{14}H_{12}BrCuN_2$	$C_{14}H_{12}ClCuN_2$
M	386.7	398.8	351.7	307.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a/Å	10.659(3)	19.025(6)	18.497(6)	10.133(4)
b/Å	23.585(9)	8.489(3)	8.398(2)	18.388(5)
c/Å	10.487(3)	17.376(5)	17.419(5)	6.729(1)
β/°	91.34(2)	108.27(2)	110.14(2)	94.31(2)
U/Å^3	2 636(1)	2 665(1)	2 540(1)	1 250.3(6)
D_m/g cm^{-3}	1.95(1)	1.99(1)	1.84(1)	1.63(1)
D_c/g cm^{-3}	1.95	1.99	1.84	1.63
Z	8 (monomer)	8 (monomer)	8 (monomer)	4 (monomer)
F(000)	1 480	1 536	1 392	624
μ_{Mo}/cm^{-1}	39.5	39	47	18.6
Dimensions/mm	0.22 × 0.20 × 0.15	0.25 × 0.10 × 0.10	0.46 × 0.16 × 0.06	0.25 × 0.10 × 0.08
$2\theta_{max.}$/°	45	50	65	45
N	3 325	2 340	3 732	1 537
N_o	2 457	1 582	1 786	889
R	0.034	0.035	0.040	0.044
R'	0.043	0.040	0.047	0.047

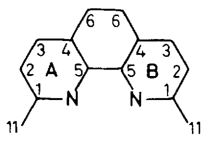
CH_3CN solution of the complex, m.p. 358—360 °C (with decomposition) (Found: C, 42.4; H, 3.3; N, 5.2. Calc. for $C_{14}H_{12}CuIN_2$: C, 42.2; H, 3.0; N, 7.0%).

[CuBr(dmphen)] (**3**). CuBr (0.31 g) and dmphen (0.21 g) were left to stand overnight in CH_3CN (20 cm^3). Crystals of the complex formed which were suitable for *X*-ray analysis, together with considerable amounts of pale green powdered oxidation products; m.p. 315—330 °C (with decomposition) (Found: C, 47.9; H, 3.6; N, 8.0. Calc. for $C_{14}H_{12}BrCuN_2$: C, 47.8; H, 3.4; N, 8.0%).

[CuCl(dmphen)] (**4**). CuCl (0.20 g) was added to a solution of dmphen (0.44 g) in CH_3CN (20 cm^3). A deep red solution formed immediately, followed by precipitation of microcrystals of the complex. Slow cooling of a hot saturated CH_3CN solution of the complex afforded crystals suitable for *X*-ray analysis, together with a range of pale green oxidation products; m.p. 310—320 °C (with decomposition) (Found: C, 58.6; H, 4.0; N, 9.5. Calc. for $C_{14}H_{12}ClCuN_2$: C, 54.7; H, 3.9; N, 9.1%).

Crystallography.—Following an initial photographic examination to establish approximate cell dimensions, probable space group (ultimately justified by solution), and the extent of available data, unique data sets were measured within a predetermined $2\theta_{max.}$ limit using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with graphite-monochromated radiation sources (λ = 0.710 69 Å) in conventional $2\theta/\theta$ scan mode at 295 K. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the least-squares refinement after solution of the structure by vector methods. Where the size of the asymmetric unit permitted, full-matrix least-squares refinement was used; for the larger species, block-diagonal refinement was used with metal-atom environment, ligand group parameters, *etc.* blocked together unless the structure was very large. Unless stated otherwise, analytical absorption corrections were applied. Non-hydrogen atom thermal parameters were refined anisotropically, with $(x, y, z, U_{iso})_H$ estimated and constrained in idealized positions. Residuals at convergence, R, R', are quoted on $|F|$, reflection weights being $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral complex scattering factors were used.[9] Computation used the *X*-RAY 76 program system[10] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Specific details for compounds (**1**)—(**4**) are given in Table 1. Atomic co-ordinates for (**1**)—(**4**) are given in Tables 2 and 3.

Atom numbering for the parent ligand system is given below.



Discussion

Complex (**1**).—Structure determination confirmed the Cu^{I}I:phen stoicheiometry to be 1:1 as expected; unexpectedly, the complex is found to be a hemisolvate, peaks in the difference-map being most satisfactorily modelled as methanol. The thermal motion of the latter is high [Figure 1(*a*)] and there does not appear to be any significant interaction with any other moiety. The complex molecule is binuclear with one binuclear species and one solvent molecule making up the asymmetric unit of the structure; the binuclear species is a di-μ-iodo-bridged dimer. The CuI_2Cu core of the molecule deviates grossly from planarity, all four atom deviations being ±0.16—0.17 Å; the phen ligand skeletons form quite reasonable planes [σ(defining atoms) 0.018, 0.028 Å], the deviations of the associated copper atoms being 0.034, 0.062 Å. Copper–iodine distances range from 2.589(1) to 2.632(1) Å (Table 4). Copper–nitrogen distances range from 2.078(6) to 2.103(6) Å; the mean (2.088 Å) is 0.033 Å longer than the mean (2.055 Å) observed for bis(1,10-phenanthroline)copper(I) perchlorate.[8] The copper–copper distance is short [2.609(2) Å]; the shortest non-bonded copper–copper contact in an oligonuclear complex appears to be the distance of 2.45 Å observed in [{Cu^I(PhN=NNPh)}$_2$].[11] The iodine–iodine distance [4.454(2) Å] is close to the usual van der Waals contact distance.[12] The molecular core geometry thus appears to be a comfortable compromise between normal van der Waals interactions and copper(I)–iodide bonds. Intramolecular constraints appear to be loose in the light of the Cu_2I_2 non-coplanarity, and responsive to packing forces; of interest in this context is the observation that although the phen planes lie pseudo-normal to the Cu_2I_2 'plane' (dihedral angles 88.5, 87.7°

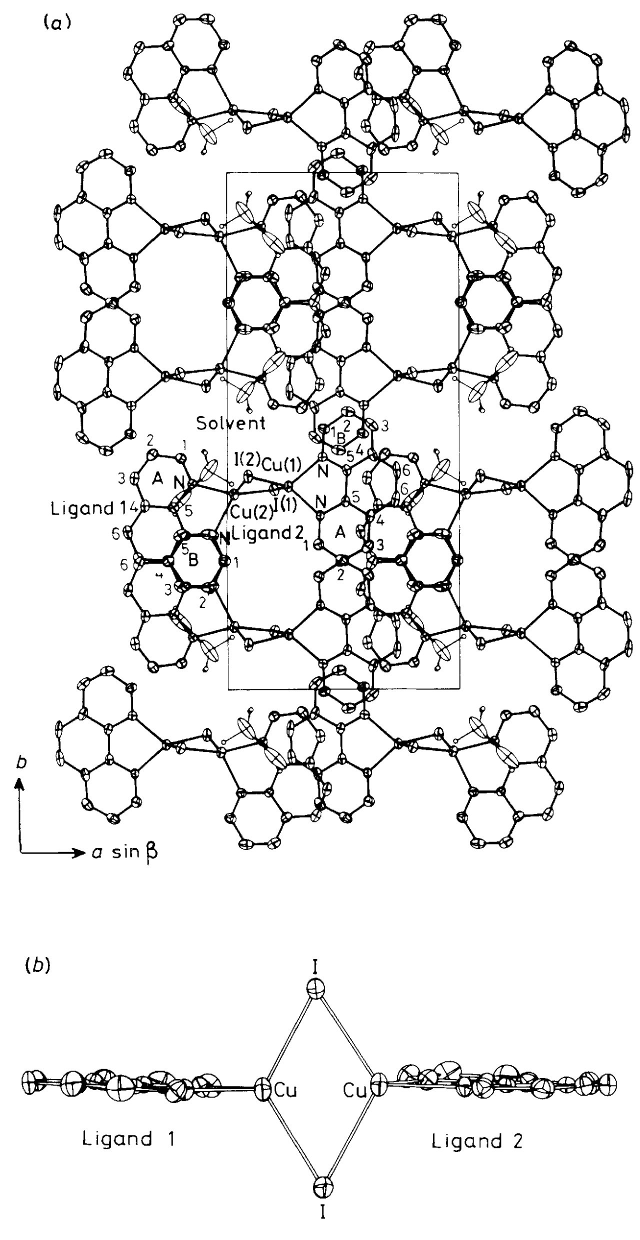


Figure 1. (*a*) Unit-cell contents of (**1**) projected down *c*; 20% thermal ellipsoids are shown for the non-hydrogen atoms. (*b*) A dimer of (**1**) projected normal to the Cu_2I_2 plane. (*c*) A dimer of (**1**) projected normal to the Cu ··· Cu vector and in the plane of the Cu_2I_2 core

respectively), they display the same deviations from the potential *mm* symmetry of the system that the Cu_2I_2 core plane does. The two CuI_2 planes meet with a dihedral angle of 28.6°; deviations of the associated pair of nitrogen atoms from each such plane are substantially symmetrical (−1.75, 1.53; 1.23, −1.44 Å respectively); distances between the pairs of confronting C(1) atoms of each ligand are grossly different (Figure 1) [4.28(1), *cf.* 4.78(1) Å], and in spite of their confrontation, the phenanthroline ligands have a dihedral angle of only 1.6° between planes while the deviations of the nitrogen atoms from the plane of the opposite ligand range from 0.21 to 0.36 Å. Copper atom deviations from the plane of the opposite ligand are 0.251, 0.216 Å. The overall phenanthroline disposition thus indicates that ligand–ligand intramolecular interactions impose no constraint on the molecular geometry; indeed, since the nearer of the above two carbon–carbon contacts has an associated hydrogen–hydrogen estimate of 2.55 Å, idealization of the geometry to *mm* symmetry could be accompanied by a shortening of the copper–copper distance by up to 0.25 Å before significant interligand interaction occurred.

Complex (**2**).—Again the complex is confirmed to have a 1 : 1 $Cu^{I}I$: bidentate ligand stoicheiometry as expected; the molecular species is binuclear (Figure 2) with the broad general features observed for complex (**1**) described above. In space group *C*2/*c*, however, the metal–halogen moiety lies close to a crystallographic inversion centre, so that only one metal–halide–base unit is crystallographically independent, the dimer being centrosymmetric. In consequence, the Cu_2I_2 group is required to be rigorously planar, while the two ligand planes must lie parallel to each other.

In contrast to the relaxed disposition of the dimer (**1**), the molecular parameters and aspect of the molecule of (**2**) indicate that introduction of methyl substituents in the ligand has appreciably increased the steric constraints on the system. Relative to the Cu_2I_2 plane, nitrogen atom deviations are quite symmetrical (1.31, 1.39 Å). Although the iodine–iodine distance [4.276(1) Å, Table 5] is slightly shorter than in (**1**) (by 0.178 Å), the copper–copper distance is increased from 2.609(2) Å to 3.024(2) Å and the mean copper–nitrogen distance may have also marginally increased from 2.088 to 2.093 Å. In bis(2,9-dimethyl-1,10-phenanthroline)copper(I) cation geometries, a wide range of Cu–N values is observed. If the mean is taken to be 2.046 Å, then the change on passing to the present complex is 0.047 Å, slightly greater than the change of 0.033 Å found for the unsubstituted phenanthroline analogues. A more pronounced asymmetry is observed in the copper–iodine distances [2.563(1), 2.673(1) Å] and this is seen to be coupled with a ligand disposition such that the ligand plane is now not nearly coincident with the copper–copper axis but deviates from it substantially, so much so that the associated copper deviation is 0.267 Å, while the opposed copper deviation has increased to 1.48 Å. Methyl substituent carbon atoms deviate from the ligand plane on the opposite side to the copper atom by 0.06, 0.04 Å. The obvious source of these constraints and deviations from ideal symmetry is intramolecular, arising from contacts between the methyl substituents of opposite ligands, the carbon–carbon distance being 3.72(1) Å. Distances from each of the methyl carbon atoms to the two iodine atoms are also unsymmetrical [4.26(1), 4.60(1); 4.234(8), 4.462(9) Å].

It is of interest to compare the CuI_2Cu molecular core geometries for complexes (**1**) and (**2**) with those found for the $L'CuX_2CuL'$ systems where L′ are the highly substituted aliphatic bidentate ligands *NNN′N′*-tetramethylethylenediamine (tmen) or di-isopropylethylenediamine (dieda). For dieda,[13] the M ··· M and I ··· I distances are similar [2.733(1), 4.467(1) Å], despite the change in electronic character of the nitrogen and, perhaps because of, a marked increase in the Cu–N distances

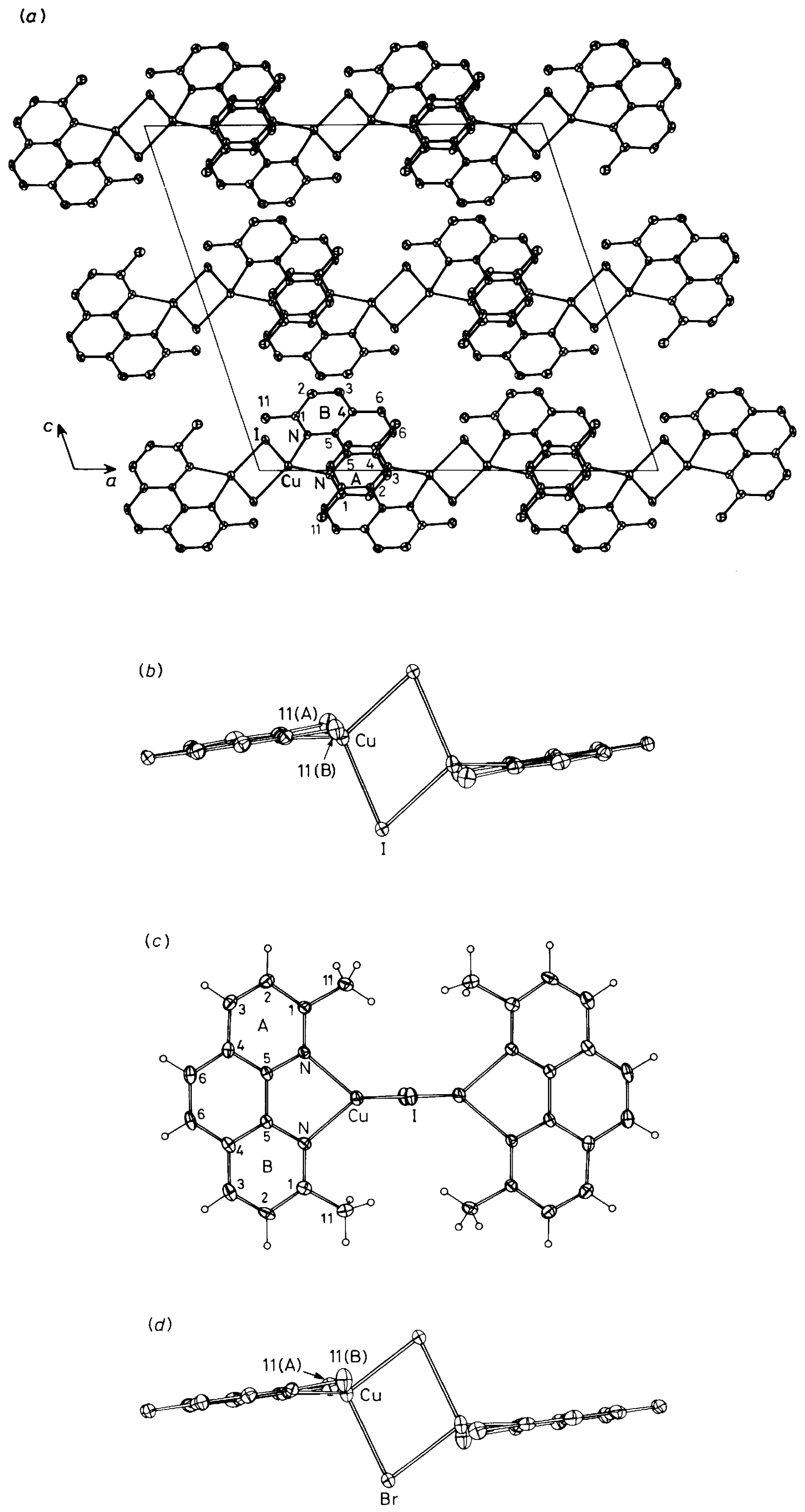


Figure 2. (*a*) Unit-cell contents of (**2**) projected down *b*. (*b*) A dimer of (**2**), projected normal to the Cu_2I_2 plane. (*c*) A dimer of (**2**) projected normal to the Cu $\cdots$ Cu vector and in the plane of the Cu_2I_2 core. (*d*) A dimer of (**3**) projected normal to the Cu_2Br_2 plane

Table 2. Atomic co-ordinates for complex [CuI(phen)]·0.5MeOH (**1**) *

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.264 45(9)	0.392 68(5)	0.269 53(10)	0.029 07(9)	0.377 74(5)	0.204 22(10)
I	0.201 74(5)	0.386 19(3)	0.029 96(5)	0.090 43(5)	0.412 08(3)	0.432 49(5)
Phenanthroline ligand 1						
N	0.400 1(5)	0.336 8(3)	0.339 9(6)	0.411 1(6)	0.449 8(3)	0.301 3(6)
C(1)	0.393 5(8)	0.281 1(4)	0.358 1(8)	0.416 4(8)	0.504 6(4)	0.283 4(7)
H(1)	0.311(–)	0.263(–)	0.336(–)	0.346(–)	0.523(–)	0.243(–)
C(2)	0.494 0(9)	0.249 5(4)	0.410 2(8)	0.520 2(10)	0.537 3(4)	0.314 9(9)
H(2)	0.484(–)	0.208(–)	0.414(–)	0.513(–)	0.576(–)	0.299(–)
C(3)	0.605 1(8)	0.276 7(4)	0.445 2(8)	0.622 2(9)	0.512 3(4)	0.367 7(9)
H(3)	0.679(–)	0.256(–)	0.480(–)	0.690(–)	0.536(–)	0.386(–)
C(4)	0.614 1(7)	0.335 2(4)	0.426 9(7)	0.625 7(7)	0.453 5(4)	0.385 8(7)
C(5)	0.509 4(7)	0.363 9(3)	0.374 1(6)	0.515 2(7)	0.423 8(3)	0.353 3(6)
C(6)	0.724 5(8)	0.367 1(5)	0.455 9(8)	0.730 5(7)	0.423 4(5)	0.435 7(8)
H(6)	0.800(–)	0.350(–)	0.489(–)	0.806(–)	0.443(–)	0.453(–)
Phenanthroline ligand 2						
N	–0.150 6(5)	0.398 3(2)	0.131 2(5)	–0.057 3(6)	0.298 4(3)	0.210 9(6)
C(1)	–0.198 2(8)	0.447 8(4)	0.096 8(7)	–0.009 3(8)	0.249 3(4)	0.250 6(8)
H(1)	–0.145(–)	0.481(–)	0.103(–)	0.077(–)	0.250(–)	0.288(–)
C(2)	–0.321 7(8)	0.454 9(4)	0.051 0(8)	–0.077 7(10)	0.198 7(4)	0.248 0(9)
H(2)	–0.353(–)	0.493(–)	0.028(–)	–0.044(–)	0.164(–)	0.280(–)
C(3)	–0.398 5(7)	0.409 2(4)	0.044 7(7)	–0.198 5(10)	0.200 2(4)	0.199 1(9)
H(3)	–0.486(–)	0.413(–)	0.013(–)	–0.254(–)	0.166(–)	0.200(–)
C(4)	–0.352 4(7)	0.356 2(4)	0.079 8(7)	–0.250 2(8)	0.250 7(3)	0.154 8(7)
C(5)	–0.226 8(7)	0.352 4(3)	0.124 3(6)	–0.176 6(6)	0.299 3(3)	0.165 2(6)
C(6)	–0.426 0(8)	0.305 5(4)	0.070 8(8)	–0.378 1(8)	0.254 4(4)	0.107 3(8)
H(6)	–0.510(–)	0.308(–)	0.045(–)	–0.430(–)	0.221(–)	0.105(–)
Methanol						
C	0.079 3(13)	0.576 0(7)	0.226 0(10)			
H(A)	0.094(–)	0.542(–)	0.161(–)			
H(B)	0.100(–)	0.539(–)	0.260(–)			
H(C)	–0.019(–)	0.602(–)	0.268(–)			
O	0.203 9(11)	0.634 1(5)	0.220 3(6)			
H	0.223(–)	0.659(–)	0.185(–)			

* Estimated standard deviations are given in parentheses here and in the other Tables.

[2.124(3)—2.230(4) Å]. For tmeda,[14] however, while the Cu–N distances are comparable to dieda [2.13(2)—2.19(2) Å] there exists a marked change in the core geometry, with Cu ··· Cu decreasing to 2.566(4) Å, the shortest distance yet observed for these dimeric species containing four-co-ordinate copper, and I ··· I elongating to 4.491(3) Å.

Complex (**3**).—The structure of this complex (Figure 2) is isomorphous with that of (**2**); the distortions observed in (**2**) are, if anything, increased. The copper–copper distance in the Cu_2Br_2 core is now increased to 3.097(1) Å, while the interhalogen distance lies at the van der Waals limit, being 3.876(1) Å. Copper–nitrogen distances, however, are shorter than in (**2**) and comparable with those of (**1**). The asymmetry in the copper–halide distances is increased in both absolute and relative terms [2.400(1), 2.559(1) Å]. The copper atom deviates from the ligand plane by 0.234 Å, the methyl substituents deviating to the opposite side by 0.02, 0.08 Å; the opposed copper deviation is 1.52 Å. Interligand methyl carbon–carbon substituent distances are 3.73(1) Å, a value identical with that of (**2**); methyl–bromide distances are 4.263(8), 4.417(8); 4.024(7), 4.406(7) Å. Seemingly, the increased proximity of the bromides to the molecular core is causing an increased copper–copper distance by interaction with the methyl substituents, arguably to the point [see complex (**4**) below] where a further increment of strain created by the substitution of chloride results in the dimer being energetically untenable. This evidence of steric strain on the Cu_2Br_2 core is highlighted by comparison of the core geometries with those of the adducts of tmen[15] and tris(pyrrolidine-1-dithiocarbonato)cobalt(III)[16] with CuBr. For the dithiocarbonate complex, in which the interactions of the Cu_2Br_2 unit with the sulphur atoms are very weak and thus may be considered more akin to a matrix isolated dimer, Cu ··· Cu is 2.697(2), Br ··· Br 4.012(1) Å, and Cu–Br range from 2.421(1) to 2.463(1) Å. In the tmen adduct, as is found for the iodide analogue, Cu ··· Cu decreases to 2.600(1), 2.612(1) Å while the Br ··· Br distances increase to 4.179(1), 4.177(1) Å.

Although these arguments are very plausible in the present context, it should be noted that oligomer equilibria of this type are strongly dependent on other factors such as recrystallization solvents, other lattice species, *etc.*, as is shown by the existence of the 1:1 CuBr:phen adduct as an ionic compound formed by ligand disproportionation,[8] while the $[CuBr_2]^-$ species may exist as monomer,[8] polymer,[17] or dimer, $[BrCuBr_2CuBr]^{2-}$.[18] In the dimer, Cu–Br are 2.472(3), 2.490(2) Å, Br–Cu–Br is 115.4(1)°, and Cu ··· Cu, 2.660(3) Å.

Complex (**4**).—The structure determination confirms the assigned stoicheiometry. One formula unit comprises the asymmetric unit of the structure, being now a mononuclear

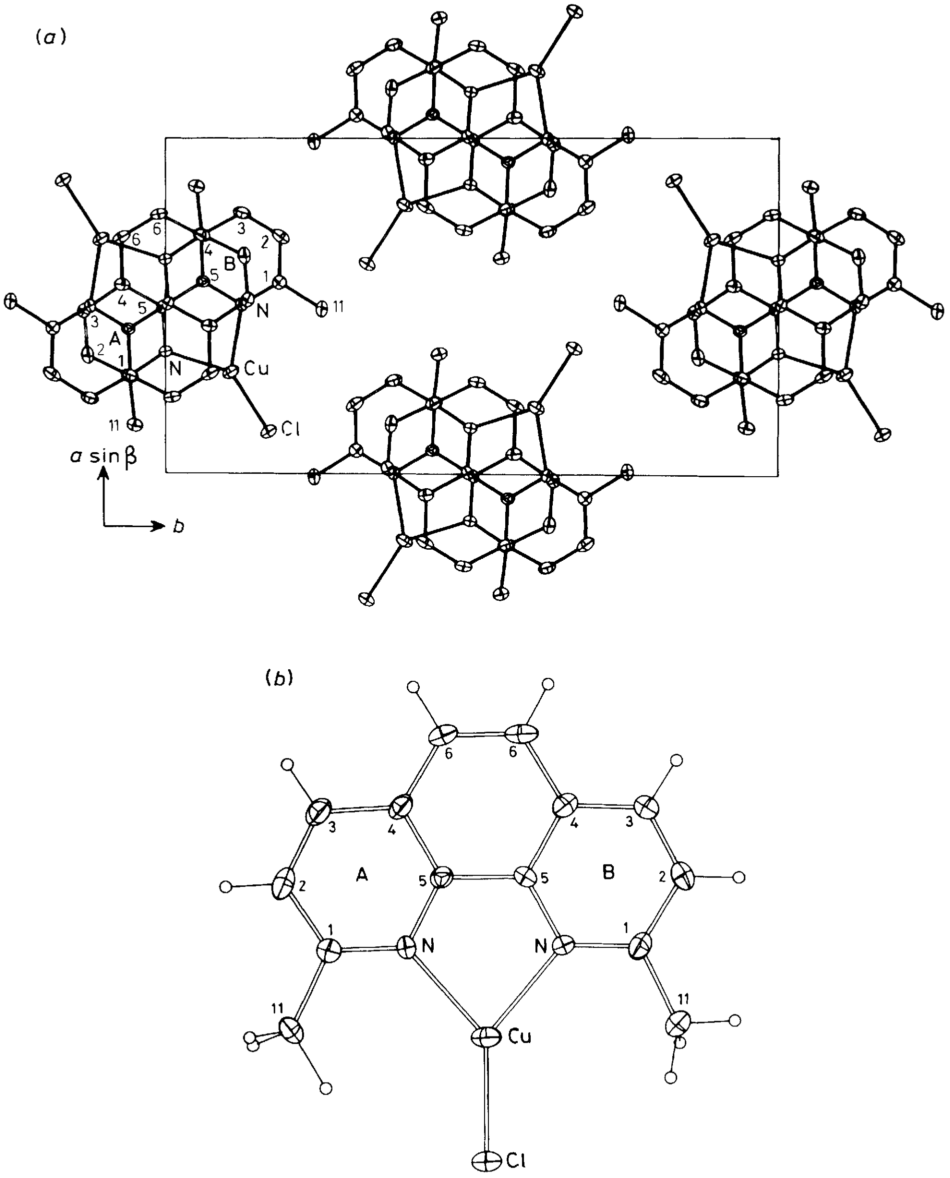


Figure 3. (*a*) Unit-cell contents of (4) projected down *c*. (*b*) A single molecule of (4) projected normal to the ligand plane

species containing three-co-ordinate copper(I), the local environment of which is now the bidentate dmphen ligand and the chlorine (Figure 3). Inspection of the unit-cell contents shows the molecules to be disposed in a columnar stack up *c*, the molecular planes lying almost normal to that axis, with successive members generated by the crystallographic inversion centres at $(\frac{1}{2}, 0, 0$ or $\frac{1}{2})$; the relationship and spacing of the molecular units at $c/2$ suggests the presence of strong charge-transfer interactions and this impression is further enhanced by the characteristic overlap disposition of the inversion related pair. A tabulation of close contacts is given in Table 6. The copper atom lies out of the ligand plane (σ ring atoms 0.011 Å) by 0.056 Å, with the chloride further out of the plane by 0.209 Å, so that the molecule is 'dished'; methyl substituent deviations are 0.01, 0.02 Å. Copper–nitrogen distances [2.060(6), 2.057(5) Å] are appreciably shorter than in the other complexes, as expected both on the grounds of lower co-ordination number and diminished steric constraint. Inspection of the ligand geometries shows no non-trivial differences between the three compounds; in particular in (2), (3), and (4) there are no substantial differences in the angular geometry at the ring junction with the methyl substituents.

We have recently also examined[1,2] a series of planar three-co-ordinate copper(I) compounds of the type $CuXL''_2$, where L″ = sterically hindered, monodentate, nitrogen base, *e.g.* 2,6-dimethylpyridine ($2,6Me_2$-py). For $[CuCl(2,6\text{-}Me_2py)_2]$, the copper–chlorine and –nitrogen distances are 2.276(3); 1.995(8) and 2.004(9) Å respectively; N–Cu–N is 139.7(3)°. For the more regularly trigonal planar species iodobis(2-methylquinoline)-copper(I), the mean copper–nitrogen distances are 2.034 and 2.015 Å.[2] In complex (4), therefore, we find the copper–chlorine distance to be much shorter [2.126(2) Å], presumably in consequence of the greatly decreased N–Cu–N′ angle [81.8(2)°], while the copper–nitrogen distances [2.060(6), 2.057(5) Å] are rather longer, being more typical of four-co-ordinate rather than three-co-ordinate copper; the copper–nitrogen distances

Table 3. Atomic co-ordinates

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) [CuI(dmphen)] (**2**)						
Cu	0.076 38(5)	−0.068 38(12)	0.013 95(6)			
I	0.040 82(3)	0.179 06(6)	0.089 43(3)			
Phenanthroline ligand						
N	0.174 4(3)	−0.016 0(7)	−0.011 3(3)	0.150 8(3)	−0.204 0(6)	0.103 7(3)
C(1)	0.186 1(4)	0.071 4(8)	−0.069 2(4)	0.137 6(4)	−0.299 1(8)	0.158 8(4)
C(11)	0.118 7(5)	0.129 3(10)	−0.134 1(5)	0.059 3(4)	−0.332 3(10)	0.152 0(5)
H(11A)	0.089(−)	0.040(−)	−0.160(−)	0.052(−)	−0.443(−)	0.147(−)
H(11B)	0.089(−)	0.191(−)	−0.110(−)	0.052(−)	−0.299(−)	0.202(−)
H(11C)	0.125(−)	0.192(−)	−0.178(−)	0.019(−)	−0.286(−)	0.110(−)
C(2)	0.257 5(4)	0.107 8(9)	−0.072 1(5)	0.196 7(4)	−0.368 3(9)	0.222 0(5)
H(2)	0.265(−)	0.170(−)	−0.116(−)	0.186(−)	−0.437(−)	0.261(−)
C(3)	0.318 0(4)	0.052 1(9)	−0.012 6(5)	0.267 0(4)	−0.337 4(9)	0.226 7(4)
H(3)	0.367(−)	0.078(−)	−0.013(−)	0.308(−)	−0.382(−)	0.270(−)
C(4)	0.308 0(4)	−0.043 2(8)	0.049 7(4)	0.283 4(4)	−0.240 1(8)	0.169 8(4)
C(5)	0.235 3(4)	−0.075 8(8)	0.047 4(4)	0.222 3(3)	−0.175 3(8)	0.109 0(4)
C(6)	0.368 6(4)	−0.109 4(9)	0.111 9(5)	0.356 8(4)	−0.204 4(9)	0.169 7(5)
H(6)	0.419(−)	−0.086(−)	0.114(−)	0.399(−)	−0.251(−)	0.211(−)
(*b*) [CuBr(dmphen)] (**3**)						
Cu	0.080 50(4)	−0.073 90(10)	0.015 53(4)			
Br	0.039 77(3)	0.172 59(8)	0.076 83(4)			
Phenanthroline ligand						
N	0.182 6(3)	−0.025 9(5)	−0.005 5(2)	0.157 1(2)	−0.206 4(5)	0.110 0(2)
C(1)	0.194 2(3)	0.062 1(7)	−0.064 2(3)	0.143 6(3)	−0.299 3(6)	0.165 5(3)
C(11)	0.124 1(4)	0.123 1(8)	−0.130 4(4)	0.060 6(4)	−0.330 2(8)	0.153 7(4)
H(11A)	0.134(−)	0.070(−)	−0.180(−)	0.061(−)	−0.354(−)	0.201(−)
H(11B)	0.083(−)	0.052(−)	−0.141(−)	0.057(−)	−0.449(−)	0.157(−)
H(11C)	0.120(−)	0.257(−)	−0.120(−)	0.026(−)	−0.257(−)	0.120(−)
C(2)	0.268 6(4)	0.096 3(7)	−0.063 9(4)	0.203 4(3)	−0.365 4(7)	0.231 5(3)
H(2)	0.276(−)	0.159(−)	−0.107(−)	0.192(−)	−0.427(−)	0.272(−)
C(3)	0.331 4(4)	0.036 8(8)	−0.002 8(4)	0.278 0(3)	−0.339 1(7)	0.238 8(3)
H(3)	0.382(−)	0.063(−)	−0.003(−)	0.319(−)	−0.386(−)	0.284(−)
C(4)	0.321 5(3)	−0.055 8(6)	0.059 3(3)	0.294 5(3)	−0.245 0(7)	0.180 5(3)
C(5)	0.245 0(3)	−0.083 5(6)	0.055 0(3)	0.231 5(3)	−0.180 4(6)	0.116 8(3)
C(6)	0.383 5(3)	−0.121 5(7)	0.125 0(4)	0.371 1(3)	−0.210 5(7)	0.183 1(3)
H(6)	0.436(−)	−0.098(−)	0.129(−)	0.414(−)	−0.257(−)	0.226(−)
(*c*) [CuLl(dmphen)] (**4**)						
Cu	0.301 46(9)	0.107 21(7)	0.234 05(17)			
Cl	0.124 7(2)	0.169 4(1)	0.237 0(4)			
Phenanthroline ligand						
N	0.361 9(5)	0.000 2(3)	0.236 6(9)	0.502 4(5)	0.124 8(3)	0.245 4(9)
C(1)	0.289 4(7)	−0.059 9(5)	0.232 6(14)	0.568 9(9)	0.187 1(4)	0.245 4(12)
C(11)	0.143 4(7)	−0.050 7(5)	0.218 5(14)	0.489 7(8)	0.256 3(5)	0.234 5(16)
H(11A)	0.103(−)	−0.044(−)	0.040(−)	0.372(−)	0.258(−)	0.178(−)
H(11B)	0.079(−)	−0.017(−)	0.299(−)	0.497(−)	0.293(−)	0.141(−)
H(11C)	0.097(−)	−0.097(−)	0.248(−)	0.524(−)	0.293(−)	0.341(−)
C(2)	0.350 5(7)	−0.129 3(4)	0.237 8(12)	0.706 5(7)	0.189 0(5)	0.261 6(14)
H(2)	0.296(−)	−0.173(−)	0.225(−)	0.755(−)	0.236(−)	0.267(−)
C(3)	0.483 3(7)	−0.135 1(4)	0.255 4(12)	0.777 4(6)	0.125 7(5)	0.271 2(13)
H(3)	0.524(−)	−0.183(−)	0.267(−)	0.874(−)	0.126(−)	0.282(−)
C(4)	0.561 3(6)	−0.071 7(5)	0.259 4(12)	0.709 5(6)	0.058 4(4)	0.268 7(13)
C(5)	0.495 3(6)	−0.004 6(4)	0.252 3(11)	0.571 0(6)	0.061 6(4)	0.253 6(11)
C(6)	0.703 3(7)	−0.073 4(5)	0.270 9(15)	0.773 6(6)	−0.010 9(5)	0.276 4(13)
H(6)	0.750(−)	−0.119(−)	0.276(−)	0.870(−)	−0.012(−)	0.287(−)

are even further increased on passing to the binuclear species (**1**)—(**3**), now being well above the $[Cu(dmphen)_2]^+$ value.

It is of interest to note the similarity between the present structure of (**4**) and that of $[Cu(BH_4)(dmphen)]$. The latter is orthorhombic, space group *Pnma*, with $a = 18.76(1)$, $b = 6.799(3)$, and $c = 10.489(5)$ Å. Although (**4**) is monoclinic, β in the $P2_1/n$ setting differs only slightly from 90° being 94.31(2)°. The *Pnma* structure has $Z = 4$; the molecule has *m* symmetry, *m*

Table 4. Ligand non-hydrogen geometry * for [CuI(phen)]·0.5MeOH(**1**); primed atoms belong to the alternate ligand/section

Ligand	1		2	
Ligand section	A	B	A	B
Cu–I	2.589(1)	2.592(1)	2.632(1)	2.596(1)
Cu · · · Cu	2.609(2)			
I · · · I	4.454(2)			
Cu–N	2.078(6)	2.084(6)	2.103(6)	2.088(6)
N–C(1)	1.33(1)	1.31(1)	1.32(1)	1.33(1)
N–C(5)	1.37(1)	1.37(1)	1.35(1)	1.35(1)
C(1)–C(2)	1.41(1)	1.38(1)	1.40(1)	1.40(1)
C(2)–C(3)	1.39(1)	1.34(1)	1.35(1)	1.38(1)
C(3)–C(4)	1.40(1)	1.40(1)	1.39(1)	1.39(1)
C(4)–C(5)	1.41(1)	1.41(1)	1.41(1)	1.39(1)
C(4)–C(6)	1.42(1)	1.41(1)	1.43(1)	1.44(1)
C(5)–C(5′)	1.43(1)		1.43(1)	
C(6)–C(6′)	1.35(2)		1.36(1)	

Ligand	1		2	
Ligand section	A	B	A	B
I–Cu–I	118.53(4)		116.85(4)	
I–Cu–N	117.9(2)	111.7(2)	112.0(2)	114.0(2)
I′–Cu–N	112.4(2)	109.0(2)	118.1(2)	110.5(2)
N–Cu–N	80.8(2)		79.7(2)	
Cu–I–Cu	59.96(4)		60.38(4)	
Cu–N–C(1)	129.7(5)	130.6(5)	130.2(5)	128.7(5)
Cu–N–C(5)	112.2(5)	111.9(5)	112.0(5)	112.7(5)
C(1)–N–C(5)	118.0(7)	117.5(7)	117.7(6)	118.6(7)
N–C(1)–C(2)	122.6(8)	123.7(8)	123.6(8)	122.7(8)
C(1)–C(2)–C(3)	119.6(8)	119.2(8)	119.0(8)	117.9(9)
C(2)–C(3)–C(4)	118.8(8)	120.6(9)	119.5(7)	120.5(9)
C(3)–C(4)–C(5)	118.2(7)	116.1(7)	118.1(7)	117.5(7)
C(3)–C(4)–C(6)	123.4(8)	124.5(8)	123.0(7)	122.2(8)
C(5)–C(4)–C(6)	118.3(8)	119.4(8)	118.9(7)	120.2(7)
N–C(5)–C(4)	122.8(7)	122.8(7)	122.1(7)	122.7(7)
N–C(5)–C(5′)	117.4(6)	117.7(6)	117.8(6)	117.7(6)
C(4)–C(5)–C(5′)	120.0(7)	119.5(7)	120.1(7)	119.6(6)
C(4)–C(6)–C(6′)	122.0(8)	120.9(8)	121.3(7)	120.0(8)

* C–O (methanol) = 1.91(2) Å.

Table 5. Molecular non-hydrogen geometry for complexes [CuX(dmphen)] [X = I (**2**), Br (**3**), or Cl (**4**)]; primed atoms belong to the alternate ligand/section

Compound	(**4**)		(**2**)		(**3**)	
Ligand section	A	B	A	B	A	B
X · · · X			4.276(1)		3.876(1)	
Cu–X,X′	2.126(2)		2.673(1)	2.563(1)	2.559(1)	2.400(1)
Cu · · · Cu			3.024(2)		3.097(1)	
Cu–N	2.060(6)	2.057(5)	2.094(6)	2.092(5)	2.083(5)	2.085(4)
N–C(1)	1.327(10)	1.329(10)	1.323(10)	1.335(10)	1.337(8)	1.331(7)
N–C(5)	1.350(8)	1.354(9)	1.377(8)	1.356(9)	1.357(6)	1.359(7)
C(1)–C(2)	1.418(11)	1.391(10)	1.409(12)	1.428(9)	1.405(10)	1.407(7)
C(1)–C(11)	1.485(10)	1.503(11)	1.501(10)	1.486(11)	1.496(8)	1.499(9)
C(2)–C(3)	1.346(10)	1.368(12)	1.368(10)	1.342(12)	1.372(8)	1.360(9)
C(3)–C(4)	1.407(11)	1.416(11)	1.411(12)	1.396(11)	1.394(9)	1.401(9)
C(4)–C(5)	1.404(11)	1.401(9)	1.399(10)	1.416(8)	1.411(5)	1.411(6)
C(4)–C(6)	1.436(10)	1.429(11)	1.426(9)	1.428(11)	1.423(7)	1.430(8)
C(5)–C(5′)	1.438(10)		1.444(10)		1.439(8)	
C(6)–C(6′)	1.351(12)		1.360(12)		1.339(9)	
X–Cu–X′			109.48(4)		102.77(3)	
X–Cu–N	139.8(2)	138.3(2)	108.4(2)	106.4(2)	109.4(1)	108.7(1)
X′–Cu–N			124.6(1)	123.9(1)	129.5(1)	124.4(1)
N–Cu–N′	81.8(2)		80.4(2)		80.3(2)	
Cu–X–Cu′			70.52(4)		77.23(4)	
Cu–N–C(1)	129.2(5)	129.5(5)	130.7(4)	129.2(5)	129.4(4)	129.8(4)
Cu–N–C(5)	111.0(5)	111.7(4)	111.3(5)	112.4(4)	112.0(4)	112.1(3)
C(1)–N–C(5)	119.8(6)	118.8(6)	117.8(6)	118.0(5)	118.3(5)	117.9(4)
N–C(1)–C(2)	120.6(6)	121.8(7)	123.0(6)	121.4(7)	121.7(5)	122.3(5)
N–C(1)–C(11)	117.0(7)	117.4(6)	116.5(6)	117.9(6)	117.0(6)	116.2(4)
C(2)–C(1)–C(11)	122.3(7)	120.7(7)	120.5(7)	120.7(7)	121.4(6)	121.6(5)
C(1)–C(2)–C(3)	120.3(7)	120.2(8)	119.3(8)	119.7(7)	119.7(6)	120.0(6)
C(2)–C(3)–C(4)	119.5(7)	119.3(6)	119.6(7)	120.9(6)	120.2(6)	119.5(5)
C(3)–C(4)–C(5)	117.6(6)	116.6(7)	117.5(6)	116.4(7)	116.6(5)	117.3(5)
C(3)–C(4)–C(6)	122.9(7)	124.0(6)	122.4(7)	124.2(6)	123.8(6)	123.5(5)
C(5)–C(4)–C(6)	119.6(7)	119.4(7)	120.1(7)	119.4(7)	119.6(5)	119.2(5)
N–C(5)–C(4)	122.1(6)	123.2(7)	122.8(6)	123.6(7)	123.5(5)	123.0(5)
N–C(5)–C(5′)	118.4(6)	117.0(5)	117.7(6)	117.1(5)	117.6(5)	117.2(4)
C(4)–C(5)–C(5′)	119.5(6)	119.7(7)	119.4(5)	119.3(6)	118.9(4)	119.8(5)
C(4)–C(6)–C(6′)	120.5(8)	121.3(6)	120.8(7)	121.0(6)	121.6(6)	120.9(5)

lying in the ligand plane; the molecules lie stacked up the short axis parallel to each other, as in (**4**), with an interplanar separation of 3.40 Å. Although tetrahydroborate behaves as a bidentate ligand of small bite, the analogy invited by the above is that of a pseudo-halide; we note that this can be extended to related complexes which we have recently studied: *e.g.* [CuI(PPh_3)$_2$][19] and [Cu(BH_4)(PPh_3)$_2$];[20] [CuCl(PPh_3)$_2$]·0.5C_6H_5[19,21] and [Cu(BH_4)(PPh_3)$_2$]·0.5C_5H_5N;[22] and [CuCl-

Table 6. Non-hydrogen intermolecular contacts <3.5 Å for [CuCl(dmphen)] (**4**); transformations refer to the *second* of the two atoms

Atoms	Distances (Å)	
	$1 - x, \bar{y}, 1 - z$	$1 - x, \bar{y}, \bar{z}$
Cu $\cdots$ C(6A)	3.39(1)	3.45(1)
C(1A) $\cdots$ C(4B)	3.36(1)	3.37(1)
C(3A) $\cdots$ N(B)	3.36(1)	3.39(1)
C(5A) $\cdots$ C(5A)	3.33(1)	3.41(1)

(bipy)(PPh$_3$)]·H$_2$O[23] (bipy = 2,2′-bipyridine) and [Cu(BH$_4$)(phen)(PPh$_3$)].[24] In these latter cases, the pairs of complexes are strictly isomorphous. While the mononuclear nature of [Cu(BH$_4$)(dmphen)] and the chloride (**4**) suggests that the steric profile of the BH$_4^-$ group is more akin to the chloride rather than the bromide (**3**) or iodide (**2**) which are bimetallic, the analogy cannot be drawn too far. For example, the reaction of [Cu(BH$_4$)(PPh$_3$)$_2$] with perchloric acid gives rise to the single bridged dimeric species [(PPh$_3$)$_2$Cu(BH$_4$)Cu(PPh$_3$)$_2$]$^+$,[25] a reaction as yet unreported for any halide system.

The i.r. spectrum of complex (**4**) exhibits a strong broad band at 330 cm^{-1}, which can be confidently assigned to a terminal Cu–Cl stretching vibrational mode. For (2,2′-biquinoline)chlorocopper(I), which might be expected to also adopt a monomeric structure, a similar strong i.r. band has been observed at 340 cm^{-1}.[26] It is of interest, also, to compare the energy of these modes with that of Cu–Cl in [CuCl(PPh$_3$)$_2$] (293 cm^{-1});[27] a decrease in energy consistent with the increased Cu–Cl bond length observed [2.208(2) Å][19] for [CuCl(PPh$_3$)$_2$] compared to 2.126(2) Å in complex (**4**).

The general stereochemistries of the structures reported here contrast with those found for the 1:1 adducts of phen with Cu(CN)[28] and dmphen with Cu(CN) or Cu(SCN).[29] The dominance of the single strand polymer in the chemistry of the copper(I) pseudohalides is again illustrated (see also ref. 30) with the formation of single strand polymers [(CuXL′)$_\infty$].

References

1 P. C. Healy, C. Pakawatchai, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1917; J. C. Dyason, L. M. Engelhardt, P. C. Healy, C. Pakawatchai, and A. H. White, *Inorg. Chem.*, 1985, **24**, 1950.
2 J. C. Dyason, P. C. Healy, C. Pakawatchai, V. A. Patrick, and A. H. White, *Inorg. Chem.*, 1985, **24**, 1957; J. C. Dyason, L. M. Engelhardt, P. C. Healy, and A. H. White, unpublished work.
3 J. F. Dobson, B. E. Green, P. C. Healy, C. H. L. Kennard, C. Pakawatchai, and A. H. White, *Aust. J. Chem.*, 1984, **37**, 649 and refs. therein.
4 B. E. Green, C. H. L. Kennard, C. J. Hawkins, G. Smith, B. D. James, and A. H. White, *Acta Crystallogr., Sect. B*, 1980, **36**, 2407.
5 For example, G. Speier, and Z. Tyeklár, *J. Chem. Soc., Dalton Trans.*, 1983, 1995; C-W. Lee and F. C. Anson, *Inorg. Chem.*, 1984, **23**, 837; P. A. Breddels, P. A. M. Berdowski, G. Blasse, and D. R. McMillin, *J. Chem. Soc., Faraday Trans. 2*, 1982, 595.
6 J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, 1962, **15**, 480.
7 J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, 1963, **16**, 34.
8 P. C. Healy, L. M. Engelhardt, V. A. Patrick, and A. H. White, following paper.
9 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.
10 'The *X*-RAY System—Version of March, 1976,' ed. J. M. Stewart, Technical Report TR-446, Computer Science Center, University of Maryland, U.S.A.
11 I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1961, **14**, 480.
12 L. I. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960, p. 260.
13 D. A. Haitko, *J. Coord. Chem.*, 1984, **13**, 119.
14 L. M. Engelhardt, R. I. Papasergio, and A. H. White, *Aust. J. Chem.*, 1984, **37**, 2207.
15 M. R. Churchill, G. Davies, M. A. El-Sayed, J. A. Fournier, J. P. Hutchinson, and J. A. Zubieta, *Inorg. Chem.*, 1984, **23**, 783.
16 L. M. Engelhardt, P. C. Healy, R. I. Papsergio, and A. H. White, *Inorg. Chem.*, 1984, **24**, 382.
17 J. A. Baglio and P. A. Vaughan, *J. Inorg. Nucl. Chem.*, 1970, **32**, 803.
18 R. P. Shibaeva and V. F. Kaminski, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, 1981, **26**, 188.
19 P. C. Healy, L. M. Engelhardt, H. Klich, C. Pakawatchai, V. A. Patrick, and A. H. White, unpublished work.
20 S. K. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.
21 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowers, and S. J. Lippard, *Inorg. Chem.*, 1976, **15**, 1155.
22 L. M. Engelhardt, C. Pakawatchai, A. H. White, and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
23 B. E. Green, C. H. L. Kennard, G. Smith, B. D. James, and A. H. White, *Acta Crystallogr., Sect. C*, 1984, **40**, 426.
24 B. E. Green, C. H. L. Kennard, G. Smith, B. D. James, and A. H. White, *Cryst. Struct. Commun.*, 1981, **10**, 1245.
25 B. E. Green, C. H. L. Kennard, G. Smith, B. D. James, P. C. Healy, and A. H. White, *Inorg. Chim. Acta*, 1984, **81**, 147.
26 S. Kitagawa and M. Munakata, *Inorg. Chem.*, 1981, **20**, 2261.
27 G. A. Bowmaker and D. A. Rogers, *J. Chem. Soc., Dalton Trans.*, 1984, 1249.
28 J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 839.
29 G. Dessy, V. Fares, and G. O. Morpurgo, *Cryst. Struct. Commun.*, 1982, **11**, 1805; G. M. Morpurgo, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1984, 785.
30 P. C. Healy, C. Pakawatchai, R. I. Papasergio, V. A. Patrick, and A. H. White, *Inorg. Chem.*, 1984, **23**, 3769.

Received 17*th July* 1984; *Paper* 4/1240