Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 2.[1] Synthesis and Structure of $CuIL_2$ Complexes (L = nitrogen base) *

Peter C. Healy
School of Science, Griffith University, Nathan, Queensland 4111, Australia
Chaveng Pakawatchai and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009

The crystal structures of five complexes $CuIL_2$, L = 2-methylpyridine (1), 2-ethylpyridine (2), quinoline (as its solvate) (3), 3,5-dimethylpyridine (4), and 2,6-dimethylpyridine (5), have been determined by single-crystal *X*-ray diffraction methods at 295 K. Crystals of (1) are triclinic, space group $P\bar{1}$, with a = 10.662(5), b = 9.552(6), c = 7.936(6) Å, α = 112.35(4), β = 96.20(4), γ = 104.66(4)°, and Z = 2; R = 0.037 for 1 060 ' observed ' reflections. Crystals of (2) are tetragonal, space group $I4_1/acd$, with a = 14.826(5), c = 27.980(8) Å, and Z = 16; R = 0.035 for 1 000 ' observed ' reflections. Crystals of (3) are triclinic, space group $P\bar{1}$, with a = 15.85(1), b = 10.24(1), c = 7.696(7) Å, α = 105.72(7), β = 92.64(7), γ = 99.51(7)°, and Z = 2; R = 0.033 for 2 694 ' observed ' reflections. Crystals of (4) are monoclinic, space group $C2/m$, with a = 13.435(5), b = 16.127(5), c = 9.313(4) Å, β = 127.69(3)°, and Z = 2; R = 0.036 for 1 330 ' observed ' reflections. In each case, the complex is dimeric and of the form $L_2CuI_2CuL_2$; the asymmetric unit is the monomer in (1) and (3) and the half monomer in (2) and (4). The dimer in (1) and (3) includes a crystallographic inversion centre, while compounds (2) and (4) have *222* and *2/m* symmetry respectively. In all four complexes, each copper atom is pseudo-tetrahedrally co-ordinated by two nitrogen atoms, one from each base, and two bridging iodine atoms. Complex (5) crystallizes in two distinct monoclinic phases, both with space group $C2/c$ and Z = 4. For the α phase, a = 8.431(4), b = 14.018(8), c = 13.019(7) Å, and β = 96.19(5)°; R = 0.036 for 1 127 ' observed ' reflections. For the β phase, a = 16.060(22), b = 7.394(4), c = 14.715(10) Å, and β = 119.70(4)°; R = 0.026 for 1 679 reflections. The two phases differ in their mode of packing of discrete monomeric $[CuI(2,6Me_2\text{-py})_2]$ molecules; the copper atom is three-co-ordinate in each case with a planar environment. In the α phase, Cu–N,I are 1.984(5) and 2.682(2) Å respectively with N–Cu–I,N 105.2(1) and 149.6(2)°; in the β phase Cu–N,I are 1.984(4) and 2.642(2) Å and N–Cu–I,N 108.26(8) and 143.5(1)°. The adoption of the unusual three-cordination about the copper is ascribed to the steric crowding caused by the substituents in both the 2 positions of the base.

Adducts of copper(I) halides with nitrogen bases, where the ratio of base to halide is 2 : 1, have not been structurally characterized, despite earlier literature on the synthesis of such complexes,[2] and the structural characterization of a considerable number of complexes with phosphorus and arsenic ligands of general formula $(MXL_2)_2$ [3-7] and MXL_2.[8]

In this paper we report the synthesis and molecular structures of a series of dimeric adducts of general formula $(MXL_2)_2$, where the ligand L is a substituted pyridine base. The substituents are diverse: L = 2-methylpyridine, 2-ethylpyridine, quinoline (the complex of the latter incorporating a quinoline molecule of solvation), and 3,5-dimethylpyridine; the complexes are denoted (1), (2), (3), and (4) respectively. These results, added to the earlier work on phosphorus and arsenic complexes, suggest the dimer is a common structural form in this system, the co-ordination number of the copper being four. However, examples of the monomeric, unassociated $CuXL_2$ complex are rare, with structural results reported only for $[CuBr(PPh_3)_2]$,[8] the related gold(I) chloride, $[AuCl(PPh_3)_2]$,[9] and for chlorobis(2-thiouracil)copper.[10] If the definition of X is expanded to include all univalent anions, a number of ' pseudo-three-co-ordinate ' compounds can be added to the list. For L = PPh_3, complexes with X = BH_4^-,[11] NO_3^-,[12] $B_3H_8^-$,[13] trifluoroacetylacetonate,[14] ethyl trithiocarbonate,[15] α-nitro-α-*aci*-nitrotoluenate,[16] and acetate [17] have been structurally characterized. For L = $P(C_6H_{11})_3$, structural data are available for the nitrate [18] and perchlorate [19] complexes. Related complexes are also known where the two L groups form part of a bidentate ligand system.[20,21]

Construction of molecular models of pyridine bases substituted in both the 2 and 6 positions suggests that, for the models at least, steric crowding would be sufficient to prevent dimerization of the monomers should they form in solution. In the event, the reaction of excess of 2,6-dimethylpyridine with copper(I) iodide resulted in the formation of two distinct crystalline phases, (5α) and (5β), both containing monomeric $CuIL_2$. This complex represents the first nitrogen-base adduct of this type to be prepared and we now report the synthesis and structural characterization of both phases.

Experimental

Preparation of Complexes.—The copper(I) iodide–base adducts with 1 : 2 stoicheiometry were obtained as follows.

$[\{CuI(2Me\text{-py})_2\}_2]$, (1) Addition of copper(I) iodide (0.5 g) to a solution of 2-methylpyridine (2Me-py) (5 cm^3) in acetone (10 cm^3) resulted in rapid dissolution at room temperature. On cooling to −30 °C, or on slow addition of light petroleum (b.p. 40—60 °C), crystals of the complex were obtained as rectangular blocks.

$[\{CuI(2Et\text{-py})_2\}_2]$, (2) Addition of copper(I) iodide (0.5 g) to a solution of 2-ethylpyridine (2Et-py) (5 cm^3) in acetone (20 cm^3) resulted in rapid dissolution at room temperature. On cooling to −30 °C, crystals of the complex were obtained as well formed colourless octahedra.

$[CuI(C_9H_7N)_2]\cdot C_9H_7N$, (3). The adduct with quinoline (C_9H_7N) contains an additional molecule of solvent. Dissolution of copper(I) iodide in a solution of 2-methylpyridine

---

* *Supplementary data available* (No. SUP 23614, 54 pp.): thermal parameters, H-atom geometries, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

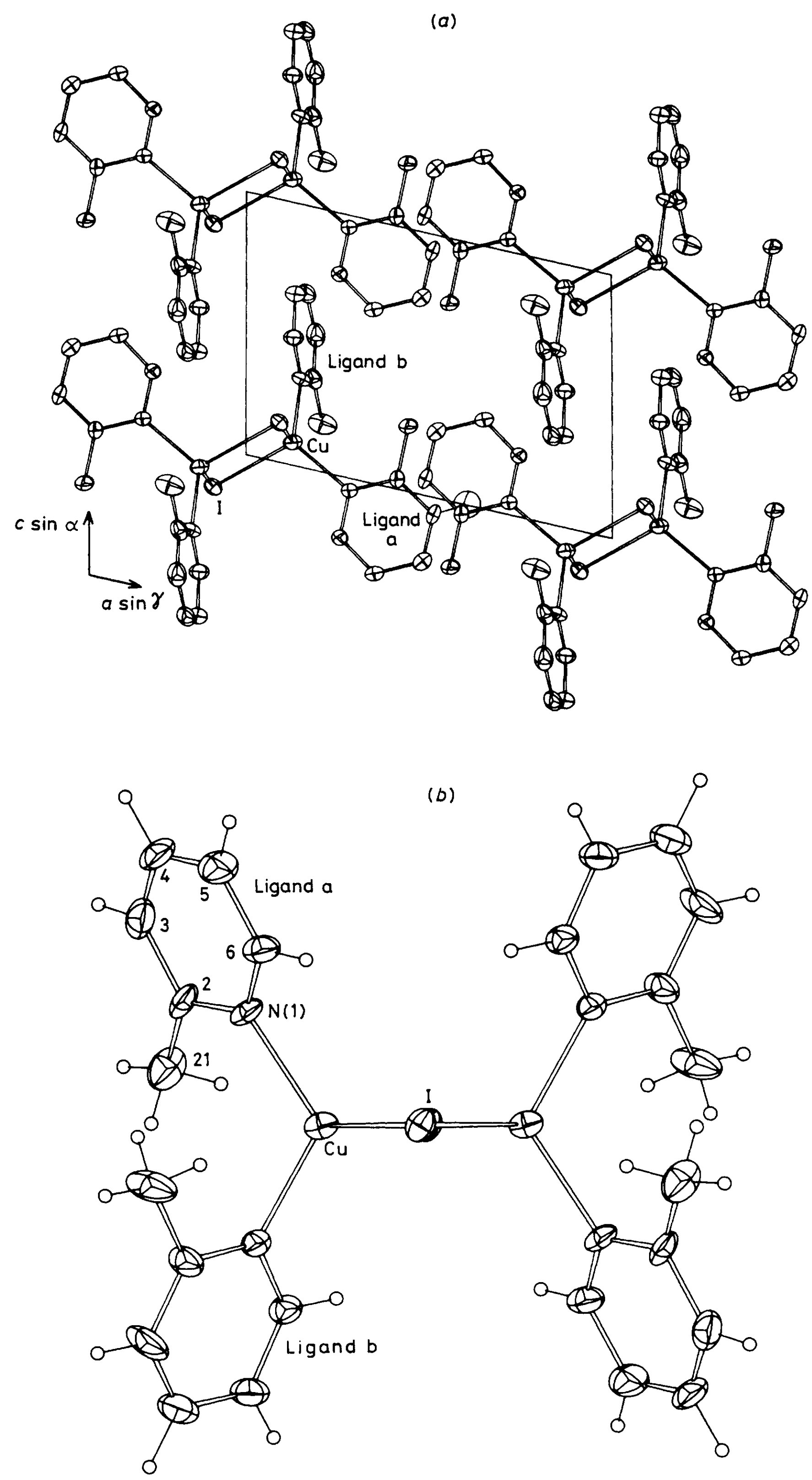


Figure 1. (*a*) Unit-cell contents of complex (1) projected down *b*, showing 20% thermal ellipsoids for the non-hydrogen atoms. (*b*) A projection of the dimer in the plane of the centrosymmetric Cu_2I_2 ring and normal to the Cu · · · Cu vector

(5 cm^3) in acetone (10 cm^3), followed by the addition of quinoline (5 cm^3), resulted in a colour change to orange-yellow and the deposition of a precipitate of fine needles. On standing after filtration, the mother-liquor yielded well formed rectangular blocks of the complex.

[{CuI(3,5Me$_2$-py)$_2$}$_2$], (4). The preparation of complex (4) was adventitious: in an attempt to prepare bis(2,4,6-trimethylpyridine)copper(I) iodide, copper(I) iodide (0.5 g) was dissolved in 2,4,6-trimethylpyridine (5 cm^3), with warming. On cooling the solution to −30 °C a small quantity of well formed crystals deposited; a fragment of one of these was sealed in a capillary and used for the crystallographic work. Solution of the structure showed the complex to be the title compound, rather than the expected 2,4,6-trimethylpyridine adduct.

[CuI(2,6Me$_2$-py)$_2$], (5). Copper(I) iodide (0.4 g) was dissolved in a solution of 2,6-dimethylpyridine (10 g) in acetone (20 cm^3). The pale yellow solution was filtered and cooled to −30 °C, depositing colourless crystals of the α form of the complex. Crystals of the β phase were fortuitously obtained during a series of experiments involving the use of 2,6-dimethylpyridine as a solvent, colourless crystals of different habit to the α form being deposited.

All five complexes decomposed only very slowly in the presence of oxygen and could be prepared under normal laboratory conditions. In the absence of excess of ligand, however, they rapidly dissociated to the parent halide and free ligand. Crystallographic data were collected on crystals sealed in glass capillaries under argon together with a small quantity of mother-liquor.

Crystallography.—For general details see ref. 1.

Crystal data. (1), $C_{12}H_{14}CuIN_2$, $M = 376.6$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 10.662(5)$, $b = 9.552(6)$, $c = 7.936(6)$ Å, $\alpha = 112.35(4)$, $\beta = 96.20(4)$, $\gamma = 104.66(4)$°, $U = 704.1(7)$ Å^3, D_c ($Z = 2$) = 1.78 g cm^{-3}, $F(000) = 364$, $\mu_{Mo} = 37$ cm^{-1}. Specimen: 0.37 × 0.27 × 0.12 mm. $2\theta_{max.} = 40°$; N,N_o = 1 325, 1 060; R,R' = 0.037, 0.046.

(2), $C_{14}H_{18}CuIN_2$, $M = 404.6$, Tetragonal, space group $I4_1/acd$ (D_{4h}^{20}, no. 142), $a = 14.826(5)$, $c = 27.980(8)$ Å, U = 6 162(6) Å^3, D_c ($Z = 16$) = 1.75 g cm^{-3}, $F(000)$ = 3 166, $\mu_{Mo} = 34$ cm^{-1}. Specimen size: 0.32 × 0.32 × 0.32 mm. $2\theta_{max.} = 40°$; N,N_o = 2 267, 1 000; R,R' = 0.035, 0.041.

(3), $C_{27}H_{21}CuIN_3$, $M = 586.6$, Triclinic, space group $P\bar{1}$, $a = 15.85(1)$, $b = 10.24(1)$, $c = 7.696(7)$ Å, $\alpha = 105.72(7)$, $\beta = 92.64(7)$, $\gamma = 99.51(7)$°, U = 1 180(2) Å^3, D_c ($Z = 2$) = 1.65 g cm^{-3}, $F(000) = 572$, $\mu_{Mo} = 22.3$ cm^{-1}. Specimen size: 0.08 × 0.14 × 0.21 mm. $2\theta_{max.} = 50°$; N,N_o = 4 163, 2 694; R,R' = 0.033, 0.037.

(4), $C_{14}H_{18}CuIN_2$, $M = 404.6$, Monoclinic, space group $C2/m$ (C_{2h}^3, no. 12), $a = 13.435(5)$, $b = 16.127(5)$, $c = 9.313(4)$ Å, $\beta = 127.69(3)$°, U = 1 596.9(8) Å^3, D_c ($Z = 2$) = 1.84 g cm^{-3}, $F(000) = 792$, $\mu_{Mo} = 34$ cm^{-1}. Specimen: irregular fragment *ca.* 0.2 mm in diameter (no absorption correction applied). $2\theta_{max.} = 50°$; N,N_o = 1 525, 1 330; R,R' = 0.036, 0.044.

(5), α phase, $C_{14}H_{18}CuIN_2$, $M = 404.6$, Monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 8.431(4)$, $b = 14.018(8)$, $c = 13.019(7)$ Å, $\beta = 96.19(5)$°, U = 1 530(1) Å^3, D_c ($Z = 4$) = 1.76 g cm^{-3}, $F(000) = 792$, $\mu_{Mo} = 34$ cm^{-1}. Specimen size: 0.18 × 0.09 × 0.25 mm. $2\theta_{max.} = 55°$; N,N_o = 1 768, 1 127; R,R' = 0.036, 0.040.

(5), β Phase, $C_{14}H_{18}CuIN_2$, $M = 404.6$, Monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 16.060(22)$, $b = 7.394(4)$, $c = 14.715(10)$ Å, $\beta = 119.70(4)$°, U = 1 518(2) Å^3, D_c ($Z = 4$) = 1.77 g cm^{-3}, $F(000) = 792$, $\mu_{Mo} = 34$ cm^{-1}. Specimen size: 0.30 × 0.30 × 0.30 mm. $2\theta_{max.} = 60°$; N,N_o = 2 142, 1 679; R,R' = 0.026, 0.036.

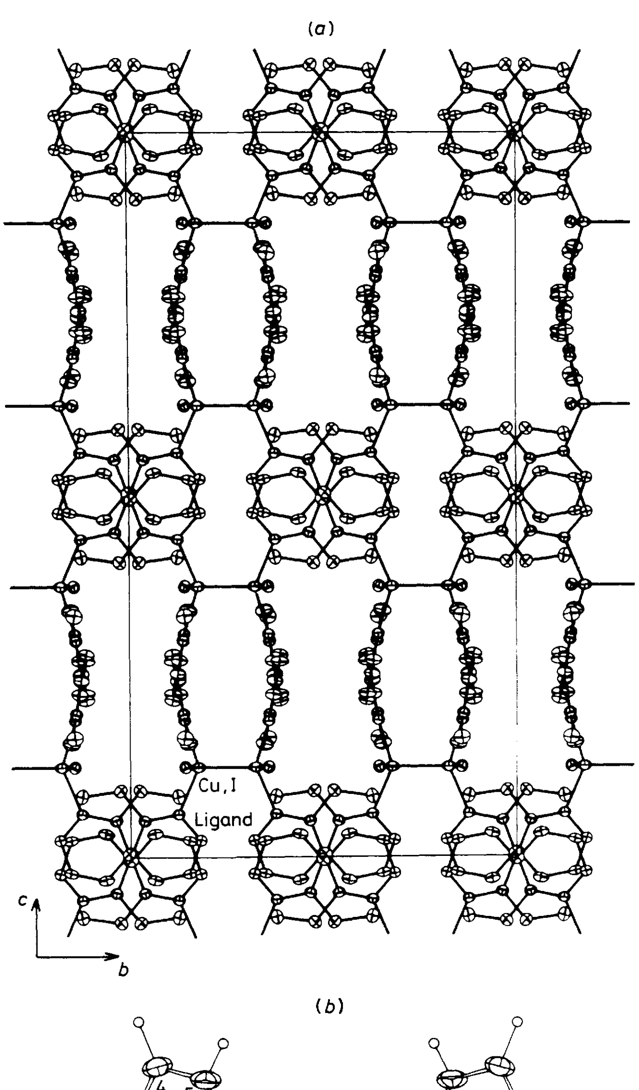


Figure 2. (*a*) Unit-cell contents of complex (2) projected down *a*, showing the layering of the structure along *c*. (*b*) A projection of the dimer similar to that in Figure 1(*b*)

Abnormal features. Assignment of the nitrogen atom of the quinoline solvent molecule in complex (3) was made on the basis of molecular geometry and thermal parameters. However, thermal motion is high and hydrogen atoms could not be located, and the result must be considered uncertain.

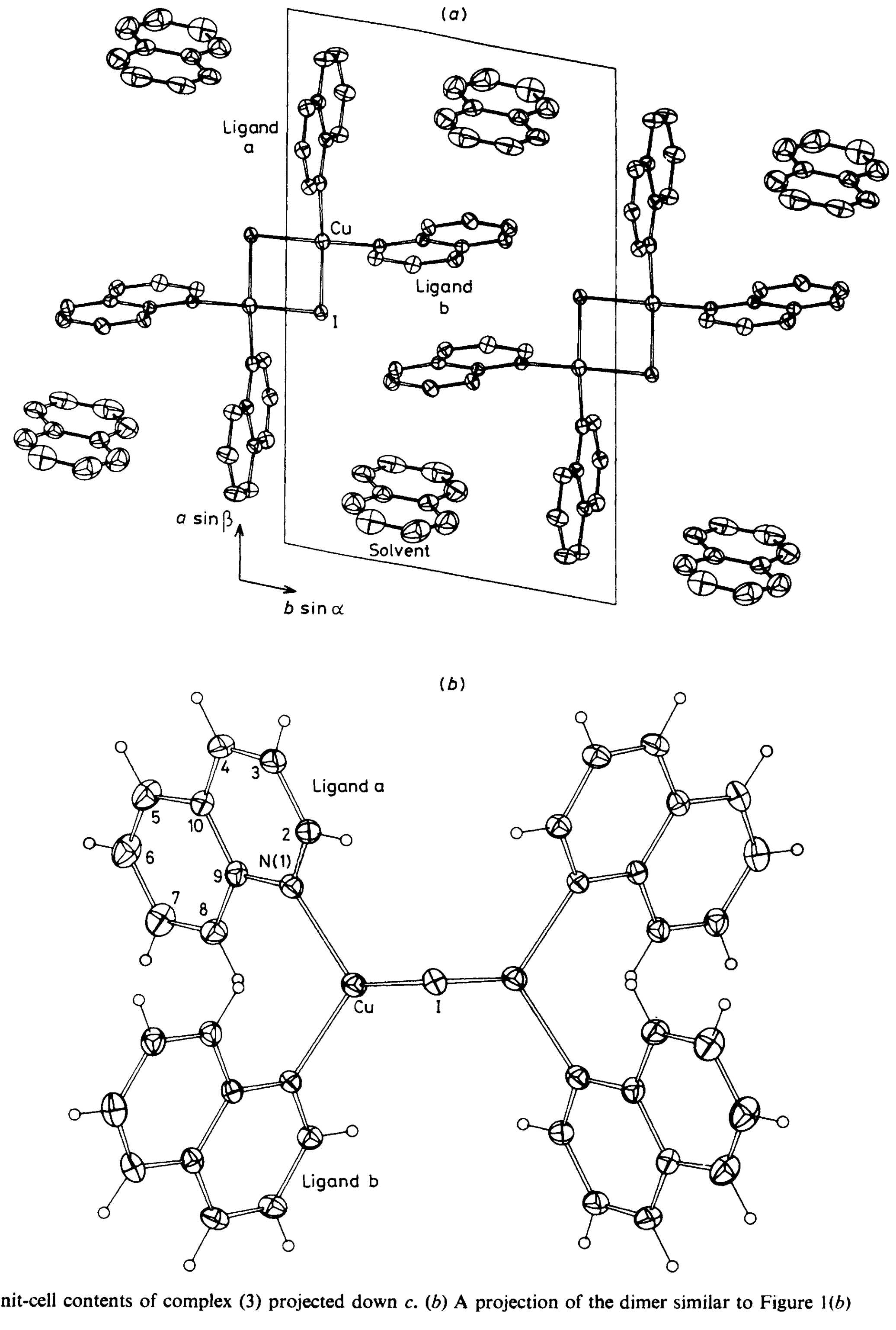
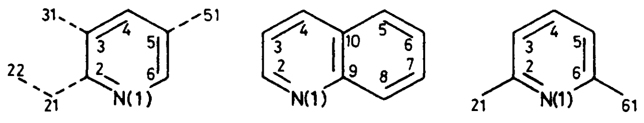


Figure 3. (*a*) Unit-cell contents of complex (3) projected down *c*. (*b*) A projection of the dimer similar to Figure 1(*b*)

Solution of the structure of (4) showed it to be the 1 : 2 adduct of copper(I) iodide, not with 2,4,6-trimethylpyridine the base used in the preparation, but with 3,5-dimethylpyridine which must have been present in the solution as an impurity. In order to check that the 3,5 positions were fully substituted, the methyl carbon atoms were refined with unconstrained population parameters; these were not found to differ significantly from 1.0, and were restored and fixed at that value.

Ligand atom numbering is as follows:



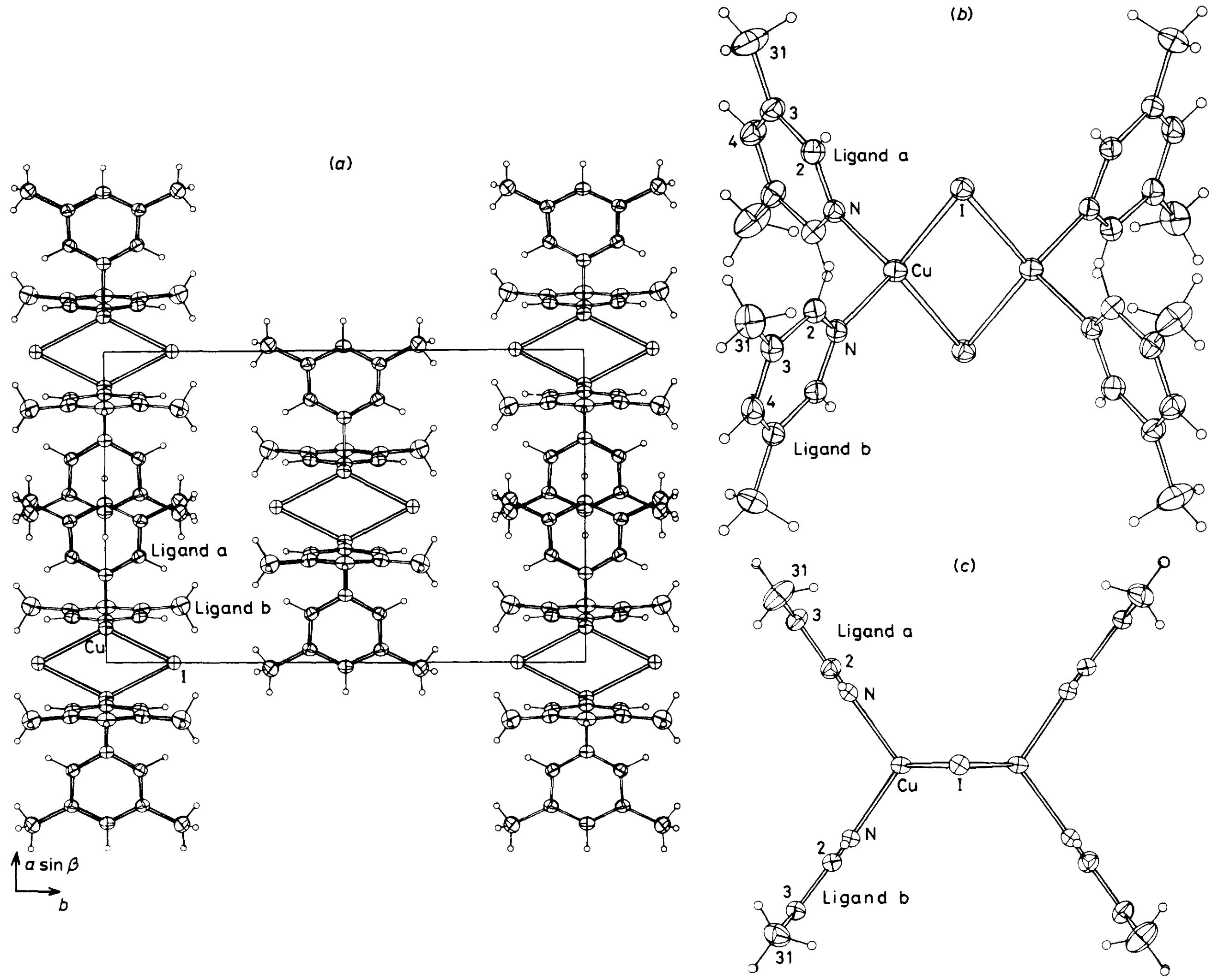


Figure 4. (*a*) Unit-cell contents of complex (4) projected down *c*. (*b*) Molecular projection oblique to the Cu_2I_2 plane. (*c*) Molecular projection down the I · · · I vector

Table 1. Non-hydrogen atom co-ordinates of $[\{CuI(2Me\text{-}py)_2\}_2]$, (1)

Atom	*x*	*y*	*z*
I	−0.090 87(8)	0.114 41(9)	−0.151 2(1)
Cu	0.127 8(1)	0.145 7(1)	0.087 3(2)
Ligand a			
N(1)	0.281 8(9)	0.149 3(11)	−0.046 4(13)
C(2)	0.412 0(13)	0.192 1(17)	0.038 0(18)
C(21)	0.443 2(14)	0.253 3(25)	0.249 1(19)
C(3)	0.510 9(14)	0.188 4(26)	−0.063 8(24)
C(4)	0.480 1(16)	0.136 9(23)	−0.252 7(24)
C(5)	0.349 1(15)	0.090 2(19)	−0.339 9(18)
C(6)	0.255 0(12)	0.098 7(15)	−0.233 3(18)
Ligand b			
N(1)	0.150 5(10)	0.341 1(12)	0.333 0(13)
C(2)	0.184 5(12)	0.490 9(17)	0.343 7(20)
C(21)	0.208 5(18)	0.517 3(17)	0.181 6(22)
C(3)	0.189 6(14)	0.617 0(18)	0.513 2(29)
C(4)	0.165 0(16)	0.591 2(24)	0.663 7(25)
C(5)	0.133 4(15)	0.441 7(27)	0.652 2(21)
C(6)	0.129 2(13)	0.317 3(16)	0.483 7(20)

Discussion

Complexes (1)—(4).—The crystal structures are shown in Figures 1—4, with corresponding parameters in Tables 1—8. In each case the molecular stoicheiometry is that of 1 : 2 CuI : base complex, associated to form a dimeric system in which the two copper atoms are each four-co-ordinated by a pair of nitrogen atoms and a pair of bridging iodide atoms. In complex (3) the molecule is solvated by an extra molecule of the free ligand per $CuI(C_9H_7N)_2$ unit so that the overall stoicheiometry is $CuI(C_9H_7N)_3$; the potential usefulness of this structure in providing a geometry of unco-ordinated quinoline is not fully realized because of the relative imprecision of the light-atom geometry. (The last aspect is true of the ligand geometries in all the complexes, which, moreover, appear to be somewhat affected by libration, so that we do not discuss their general features further.) In complex (1) the asymmetric unit of the structure is the CuI(base)$_2$ unit; the dimer is centrosymmetric about a crystallographic inversion centre. The same is true of (3), where, however, the asymmetric unit also includes the solvent molecule. In complex (2) only a quarter of the dimer is crystallographically independent. Both copper and iodine atoms lie on Wyckoff sites *f* with point symmetry *2*; the overall symmetry of the dimer is *222*, the two-fold axes lying through the Cu$_2$ and I$_2$ lines which intersect at $(0, \frac{1}{4}, \frac{1}{8})$. The symmetry of the dimers (1) and (3) are also good approximations to *2*/*m*. In each case, the planes defined by the non-hydrogen ligand atoms of the aromatic skeleton lie almost normal to the Cu$_2$I$_2$ plane [(dihedral) interplanar angles: 73.5 and 68.7° in (1); 80.3° in (2); and 76.7 and 68.9° in (3)]; the determinant of this angle in each case appears to be the van der Waals contact between the hydrogen atoms of the substituent carbon atoms α to the aromatic ring. In no case, however, does this cause deviation of the α-carbon atom to any appreciable extent from the ring plane, and σ (defining atoms) values for the ring planes themselves are generally good [0.011 and 0.010 Å in (1); 0.012 Å in (2); and 0.022, 0.005, and 0.007 Å (solvent) in (3)]. Copper-atom deviations from the ligand planes are, however, appreciable [−0.065 and −0.123 Å in (1); 0.230 Å in (2); and 0.274 and 0.135 Å in (3)] and there are minor asymmetries in the angular geometry about the nitrogen and the attachment of the α-substituent, seemingly non-systematic in complexes (1) and (2). The structural determination of complex (4) shows that the structural unit is also a dimer. The crystallographically imposed symmetry in this structure is high, being *2*/*m*; the ligand planes necessarily lie normal to the Cu$_2$I$_2$ plane. Deviations of the copper atoms from the two ligand planes are 0.012 and 0.091 Å.

The comparative geometries for the present systems are assembled in Table 9, together with the geometry of the three-co-ordinate dimeric 1 : 1 : 1 species [{CuI(2,6Me$_2$-py)}$_2$] and [{CuI(tmpip)}$_2$] (tmpip = 2,2,6,6-tetramethylpiperidine). As discussed previously,[1] it is to be expected that highly polarizable molecules, as in the present examples, will display large variations in geometric parameters, variations that may be reasonably attributed to interspecies contacts of no immediate significance. In complex (1), for example, we find that the Cu–I distances, crystallographically equivalent in (2) and (4), are 2.714(3) and 2.663(3) Å, a significant and non-trivial difference. The same may be said of the variations in the N–Cu–I angles in any given compound. A certain amount of caution is therefore always necessary in discussions of observed variations, since significant differences within a compound in some cases overlap those between compounds.

Clear trends are evident, however. In passing from the three-co-ordinate copper 1 : 1 : 1 dimeric species [(6) and (7), Table 9] to the four-co-ordinate copper 1 : 1 : 2 dimeric species [(1)—(4), Table 9], the Cu–I bond length increases by *ca.* 0.15 Å from an average value of *ca.* 2.55 to 2.65—2.70 Å, a variation consistent with expectations on the effect of increasing co-ordination number on molecular geometry. No equivalent effect is observed for Cu–N bond lengths. Within

Table 2. Molecular non-hydrogen geometry of [{CuI(2Me-py)$_2$}$_2$], (1); distances in Å, angles in degrees. Where two entries are given, these are for ligands a, b respectively. Primed atoms are generated by the intradimer inversion centre

Cu–I	2.714(3)	C(2)–C(3)	1.39(2), 1.41(2)
Cu–I′	2.663(3)	C(3)–C(4)	1.36(3), 1.35(3)
Cu–N	2.05(1), 2.06(1)	C(4)–C(5)	1.37(2), 1.35(3)
N–C(2)	1.36(2), 1.35(2)	C(5)–C(6)	1.38(2), 1.40(2)
N–C(6)	1.34(2), 1.33(2)		
C(2)–C(21)	1.51(2), 1.44(3)		
I–Cu–N	107.9(3), 106.5(3)	N–C(2)–C(21)	116(1), 120(1)
I′–Cu–N	104.6(3), 109.7(4)	N–C(2)–C(3)	122(1), 118(1)
N(a)–Cu–N(b)	117.9(2)	C(21)–C(2)–C(3)	123(1), 122(2)
I–Cu–I′	110.05(6)		
Cu–I–Cu′	69.95(6)	C(2)–C(3)–C(4)	121(2), 121(2)
Cu–N–C(2)	125.0(9), 121.8(9)	C(3)–C(4)–C(5)	120(2), 118(2)
Cu–N–C(6)	119.2(8), 118.5(9)	C(4)–C(5)–C(6)	119(1), 119(2)
C(2)–N–C(6)	115.7(11), 119.7(11)	C(5)–C(6)–N(1)	125(1), 122(2)

Table 3. Non-hydrogen atom co-ordinates of [{CuI(2Et-py)$_2$}$_2$], (2)

Atom	*x*	*y*	*z*
I	0.107 12(3)	0.142 88(−)	0.125 00(−)
Cu	−0.073 14(6)	0.176 86(−)	0.125 00(−)
Ligand a			
N(1)	−0.109 0(3)	0.124 6(3)	0.059 9(2)
C(2)	−0.111 6(4)	0.036 7(5)	0.050 5(2)
C(21)	−0.098 0(6)	−0.025 4(5)	0.092 1(3)
C(22)	−0.107 3(6)	−0.124 6(5)	0.084 4(3)
C(3)	−0.124 7(5)	0.003 7(5)	0.004 5(3)
C(4)	−0.138 8(5)	0.063 3(6)	−0.032 2(2)
C(5)	−0.137 6(6)	0.153 7(6)	−0.022 8(2)
C(6)	−0.121 1(5)	0.182 1(5)	0.023 6(2)

Table 4. Molecular non-hydrogen geometry of [{CuI(2Et-py)$_2$}$_2$], (2); distances in Å, angles in degrees. Primed atoms are generated by the symmetry operation $\bar{x}, \frac{1}{2} - y, z$ and doubly primed atoms by $y - \frac{1}{4}, \frac{1}{4} + x, \frac{1}{4} - z$

Cu–I	2.720(1)	C(2)–C(21)	1.499(10)	C(3)–C(4)	1.370(11)
Cu–N	2.050(5)	C(21)–C(22)	1.493(11)	C(4)–C(5)	1.366(12)
N–C(2)	1.330(9)	C(2)–C(3)	1.391(9)	C(5)–C(6)	1.385(10)
N–C(6)	1.339(9)				
I–Cu–N	100.7(1)	Cu–N–C(6)	118.0(4)	C(2)–C(21)–C(22)	118.6(7)
I–Cu–N″	108.9(1)	C(2)–N–C(6)	117.9(5)	C(2)–C(3)–C(4)	119.2(7)
N–Cu–N″	126.4(2)	N–C(2)–C(21)	116.3(6)	C(3)–C(4)–C(5)	119.1(7)
I–Cu–I′	111.35(3)	N–C(2)–C(3)	122.2(6)	C(4)–C(5)–C(6)	118.7(7)
Cu–I–Cu′	68.65(2)	C(21)–C(2)–C(3)	121.5(6)	C(5)–C(6)–N(1)	122.8(7)
Cu–N–C(2)	123.7(4)				

Table 5. Non-hydrogen atom co-ordinates of $[CuI(C_9H_7N)_2]\cdot C_9H_7N$, (3)

Atom	*x*	*y*	*z*
I	0.439 87(3)	0.108 27(4)	0.243 35(5)
Cu	0.572 80(5)	0.110 64(7)	0.043 06(9)
Ligand a			
N(1)	0.680 7(3)	0.100 9(4)	0.205 5(6)
C(2)	0.669 8(4)	0.068 1(6)	0.358 6(7)
C(3)	0.736 6(4)	0.047 6(6)	0.467 7(8)
C(4)	0.816 9(5)	0.059 0(6)	0.417 7(8)
C(5)	0.915 3(4)	0.112 5(8)	0.190 8(10)
C(6)	0.927 7(5)	0.151 8(8)	0.041 2(10)
C(7)	0.858 4(5)	0.175 4(8)	−0.057 8(9)
C(8)	0.778 1(4)	0.159 7(7)	−0.004 5(8)
C(9)	0.763 1(4)	0.118 1(6)	0.152 8(7)
C(10)	0.832 3(4)	0.094 0(6)	0.256 0(8)
Ligand b			
N(1)	0.584 3(3)	0.285 1(4)	−0.048 6(6)
C(2)	0.560 5(4)	0.272 2(6)	−0.219 9(7)
C(3)	0.561 6(4)	0.386 0(6)	−0.290 4(7)
C(4)	0.586 9(4)	0.515 5(6)	−0.180 3(8)
C(5)	0.640 5(4)	0.665 4(6)	0.129 2(9)
C(6)	0.664 1(4)	0.677 5(7)	0.306 5(9)
C(7)	0.663 1(4)	0.559 2(6)	0.366 5(8)
C(8)	0.636 2(4)	0.432 6(6)	0.249 5(7)
C(9)	0.610 9(3)	0.415 0(5)	0.067 2(7)
C(10)	0.612 8(3)	0.534 8(5)	0.004 9(7)
Solvent			
N(1)	0.098 7(5)	0.208 6(8)	0.506 1(12)
C(2)	0.070 4(8)	0.260 5(16)	0.664 4(16)
C(3)	0.066 8(9)	0.396 9(19)	0.735 4(17)
C(4)	0.093 5(8)	0.489 9(13)	0.639 5(20)
C(5)	0.155 3(7)	0.517 1(12)	0.357 7(21)
C(6)	0.183 4(8)	0.460 8(19)	0.199 1(22)
C(7)	0.183 8(6)	0.323 9(16)	0.141 0(15)
C(8)	0.156 6(5)	0.237 9(10)	0.243 0(14)
C(9)	0.125 6(5)	0.295 2(9)	0.413 8(11)
C(10)	0.124 3(5)	0.434 6(9)	0.468 4(13)

Table 6. Molecular non-hydrogen atom geometry of $[CuI(C_9H_7N)_2]\cdot C_9H_7N$, (3); distances in Å, angles in degrees

(*a*) Copper environment. The first column in the matrix is the copper–ligand distance; other entries are the angles subtended by the atoms at the head of the row and column. Primed atoms are generated by the intra-dimer inversion centre. Cu–I–Cu′ is 65.14(2)°

	r(Cu–X)	I′	N(a1)	N(b1)
I	2.668(2)	114.87(5)	107.1(1)	108.1(1)
I′	2.657(3)		104.1(1)	108.1(1)
N(a1)	2.104(5)			114.8(2)
N(b1)	2.076(5)			

(*b*) Quinoline geometries

	Ligand a	Ligand b	Solvent
N(1)–C(2)	1.321(8)	1.319(7)	1.32(1)
N(1)–C(9)	1.383(8)	1.371(6)	1.31(1)
C(2)–C(3)	1.398(10)	1.410(9)	1.37(2)
C(3)–C(4)	1.343(10)	1.349(8)	1.38(2)
C(4)–C(10)	1.406(10)	1.416(9)	1.43(2)
C(10)–C(9)	1.417(9)	1.429(9)	1.38(1)
C(10)–C(5)	1.431(10)	1.404(7)	1.40(2)
C(5)–C(6)	1.331(12)	1.365(10)	1.33(2)
C(6)–C(7)	1.339(11)	1.407(11)	1.35(2)
C(7)–C(8)	1.352(10)	1.351(7)	1.36(2)
C(8)–C(9)	1.406(9)	1.396(8)	1.43(1)
Cu–N(1)–C(2)	119.4(4)	119.6(3)	
Cu–N(1)–C(9)	122.6(4)	121.6(4)	
C(2)–N(1)–C(9)	117.8(5)	118.7(5)	117.0(10)
N(1)–C(2)–C(3)	123.6(6)	123.1(4)	124.3(14)
C(2)–C(3)–C(4)	120.2(6)	119.9(5)	119.8(12)
C(3)–C(4)–C(10)	118.6(7)	119.1(6)	116.2(12)
C(4)–C(10)–C(5)	123.8(6)	123.2(6)	122.6(10)
C(4)–C(10)–C(9)	119.2(6)	118.1(5)	118.0(10)
C(5)–C(10)–C(9)	117.0(6)	118.7(5)	119.3(9)
C(10)–C(5)–C(6)	121.9(7)	120.5(6)	120.4(13)
C(5)–C(6)–C(7)	120.0(7)	120.5(5)	121.3(17)
C(6)–C(7)–C(8)	121.4(7)	119.9(6)	121.5(12)
C(7)–C(8)–C(9)	119.8(6)	121.6(6)	118.4(10)
C(8)–C(9)–N(1)	119.6(6)	120.3(5)	116.5(8)
C(8)–C(9)–C(10)	119.9(6)	118.7(4)	118.9(9)
N(1)–C(9)–C(10)	120.5(6)	121.0(5)	124.6(8)

Table 7. Non-hydrogen atom co-ordinates of $[\{CuI(3,5Me_2\text{-}py)_2\}_2]$, (4)

Atom	*x*	*y*	*z*
I	0	0.142 33(2)	0
Cu	0.122 5(7)	0	0.164 98(10)
Ligand a			
N(1)	0.284 4(5)	0	0.214 1(6)
C(2)	0.342 9(4)	0.070 3(3)	0.232 4(6)
C(3)	0.457 7(4)	0.074 2(3)	0.262 5(7)
C(31)	0.518 2(7)	0.156 2(4)	0.281 6(13)
C(4)	0.514 3(6)	0	0.278 8(10)
Ligand b			
N(1)	0.136 8(4)	0	0.404 9(6)
C(2)	0.148 6(4)	0.070 7(3)	0.490 4(6)
C(3)	0.171 4(4)	0.074 7(3)	0.656 7(6)
C(31)	0.183 0(7)	0.156 6(4)	0.741 4(9)
C(4)	0.180 9(7)	0	0.736 9(9)

the Cu_2I_2 cluster, I · · · I (although variable) does not appear to lengthen greatly [4.414(4) Å in (6) and 4.493(7) Å in (7) *versus* 4.407(3)—4.591(2), mean 4.46$_2$ Å, in (1)—(4)]. The Cu · · · Cu distance, however, increases quite dramatically, passing from 2.535(9) Å in (7) to 3.083(3) Å in complex (1). Within the 1 : 1 : 2 series, a further trend is apparent, with compound (4), unsubstituted in the 2 position, manifesting the lowest Cu · · · Cu distance [2.683(1) Å]. Further structural studies on unhindered 1 : 1 : 2 dimers are necessary to confirm this point. Unfortunately, our attempts to date to prepare and structurally characterize the complex $[\{CuI(py)_2\}_2]$ have been frustrated by severe crystal-twinning problems.

Finally, it is of interest to note the isolation of the three adducts of copper(I) iodide with 2-methylpyridine of stoicheiometries 1 : 1 : 1 (' cubane ' structure), 1 : 1 : 1.5 (' step ' structure), and 1 : 1 : 2 (' dimer '). First, the preparation of the three complexes, all of which may be induced to co-crystallize under the appropriate experimental conditions, clearly illustrates the small energy differences between the various aggregates of copper(I) halide, and base, and suggests the nature of species in solution to be variable and complex. Secondly, it is noteworthy that the Cu–N bond length is unchanged in passing from the ' dimer ' to ' step ' structure, despite changes in molecular configuration and copper coordination environment (CuI_3N *versus* CuI_2N_2).

Complex (5).—The crystal structures are shown in Figures

5 and 6, corresponding parameters in Tables 10 and 11. In both phases the unit cells are of the same symmetry and comparable volume, with one half of the stoicheiometric $CuIL_2$ unit, L = 2,6-dimethylpyridine, making up the asymmetric unit. Crystallographic necessity demands that in both structures the copper and iodine atoms lie on special positions; the solutions show the presence of Cu–I units disposed on crystallographic two-fold axes, with the copper atoms co-ordinated each by a pair of 2,6-dimethylpyridine ligands. The copper atoms are thus three-co-ordinate, and together with their co-ordination environments are constrained by symmetry considerations to be coplanar.

Projections of the unit-cell contents shown in Figures 5 and 6 show the two polymorphs to differ significantly in their modes of packing. Although in each case the axis of projection is not the unique axis (which in each case lies parallel to the Cu–I bond), the Figures show clearly for the α phase the interleaving of the ligand planes, and for the β phase the pairwise packing; also in each case, the ligand planes lie parallel to the projection axis. It is of interest that adjacent molecules in the β form are in appropriate orientations for the formation of a dimeric species. That such a species is not formed is a consequence of the steric hindrance provided by the presence of the methyl groups in each α position.

For the molecules of the two phases the ligand geometries differ only trivially. Of interest are the exocyclic angles at C(2,6) which are unsymmetrically disposed with the larger of the two angles in each case being that away from the nitrogen, suggesting the methyl-H(3,5) repulsions to be greater than the repulsions between the methyl groups and the centre of the molecule or the opposite ligand. Such a conclusion is reasonable, since the dihedral angles between the $ICuN_2$ planes and the ligand non-hydrogen skeletal planes are 87.6 (α) and 71.2° (β) respectively.

It would be expected that the decrease in co-ordination number from four to three in passing from the $(CuIL_2)_2$ dimer to the $CuIL_2$ monomer would result in a significant decrease in the Cu–N and Cu–I bond lengths. In the case of the Cu–N distances (1.98_4, *cf.* 2.05 Å for the 2-methyl- and 2-ethyl-pyridine dimers) this is clearly so; the value agrees well with that found in the three-co-ordinate dimeric species

Table 8. Molecular non-hydrogen geometry of $[\{CuI(3,5Me_2\text{-}py)_2\}_2]$, (4); distances in Å, angles in degrees. Where two entries are given these are for ligands a, b respectively

Cu–I	2.658 8(8)
Cu–N	2.067(7), 2.049(7)
N–C(2)	1.330(6), 1.343(6)
C(2)–C(3)	1.391(9), 1.384(9)
C(3)–C(4)	1.370(7), 1.382(7)
C(3)–C(31)	1.504(9), 1.497(9)
I–Cu–N	106.87(7), 106.67(7)
N–Cu–N	110.3(2)
I–Cu–I	119.38(5)
Cu–I–Cu	60.62(5)
Cu–N–C(2)	121.4(4), 121.9(3)
C(2)–N–C(2)	117.1(6), 116.2(6)
N–C(2)–C(3)	124.0(5), 124.6(5)
C(2)–C(3)–C(4)	116.5(5), 116.6(5)
C(2)–C(3)–C(31)	121.0(6), 120.8(5)
C(31)–C(3)–C(4)	122.4(7), 122.6(6)
C(3)–C(4)–C(3)	121.8(8), 121.3(8)

Table 9. Molecular core geometries *

	(1)	(2)	(3)	(4)	(6)	(7)
Cu–I/Å	2.714(3)	2.720(1)	2.668(2)	2.658 8(8)	2.539(5)—2.583(5)	2.505(9)
	2.663(3)		2.657(3)		(mean: 2.56)	2.652(8)
Cu–N/Å	2.05(1)	2.050(5)	2.104(5)	2.067(7)	1.99(2)	2.12(4)
	2.06(1)		2.076(5)	2.049(7)	2.00(2)	
Cu–I–Cu/°	69.95(6)	68.65(2)	65.14(2)	60.62(5)	60.1(1)	58.8(2)
					61.2(2)	
I–Cu–I/°	110.05(6)	111.35(3)	114.87(5)	119.38(5)	118.9(2)	121.2(3)
					119.3(2)	
N–Cu–I/°	104.6(3)—109.7(4)	100.7(1)	104.1(1)—108.1(1)	106.9(1)		131.9(1)
		108.9(1)		106.7(1)	116.8(7)	106.9(1)
(mean)	107.1	104.8	106.9	106.8	116.8(7)	
N–Cu–N	117.9(2)	126.4(2)	114.8(2)	110.3(2)		
Cu · · · Cu	3.083(3)	3.067(1)	2.866(3)	2.683(1)	2.586(5)	2.535(9)
I · · · I	4.407(3)	4.492(1)	4.487(4)	4.591(2)	4.414(4)	4.493(7)

* Complex (6) is $[\{CuI(2,6Me_2\text{-}py)\}_2]$, (7) is $[\{CuI(tmpip)\}_2]$ (J. A. Campbell, C. L. Raston, and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937; ref. 1).

Table 10. Non-hydrogen atom co-ordinates of $[CuI(2,6Me_2\text{-}py)_2]$, (5)

	α Phase			β Phase		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.500 0(–)	0.322 05(9)	0.250 0(–)	0.500 0(–)	–0.230 55(8)	0.250 0(–)
I	0.500 0(–)	0.130 73(4)	0.250 0(–)	0.500 0(–)	0.126 74(4)	0.250 0(–)
N(1)	0.462 4(5)	0.359 1(3)	0.392 4(3)	0.419 3(2)	–0.314 6(3)	0.309 0(2)
C(2)	0.312 9(6)	0.363 4(5)	0.419 4(4)	0.331 2(2)	–0.381 7(4)	0.243 2(3)
C(21)	0.177 8(7)	0.352 5(5)	0.335 9(5)	0.307 2(3)	–0.414 4(6)	0.132 6(3)
C(3)	0.283 5(7)	0.378 1(5)	0.520 7(5)	0.265 3(2)	–0.416 2(5)	0.276 1(3)
C(4)	0.408 2(8)	0.390 3(5)	0.595 4(5)	0.290 2(3)	–0.380 8(5)	0.378 5(3)
C(5)	0.561 0(7)	0.386 7(5)	0.569 4(5)	0.379 6(3)	–0.315 4(5)	0.445 4(3)
C(6)	0.586 7(7)	0.370 8(4)	0.466 8(4)	0.443 5(2)	–0.284 9(4)	0.409 4(2)
C(61)	0.750 9(7)	0.365 4(6)	0.434 7(5)	0.543 0(2)	–0.216 4(5)	0.482 3(2)

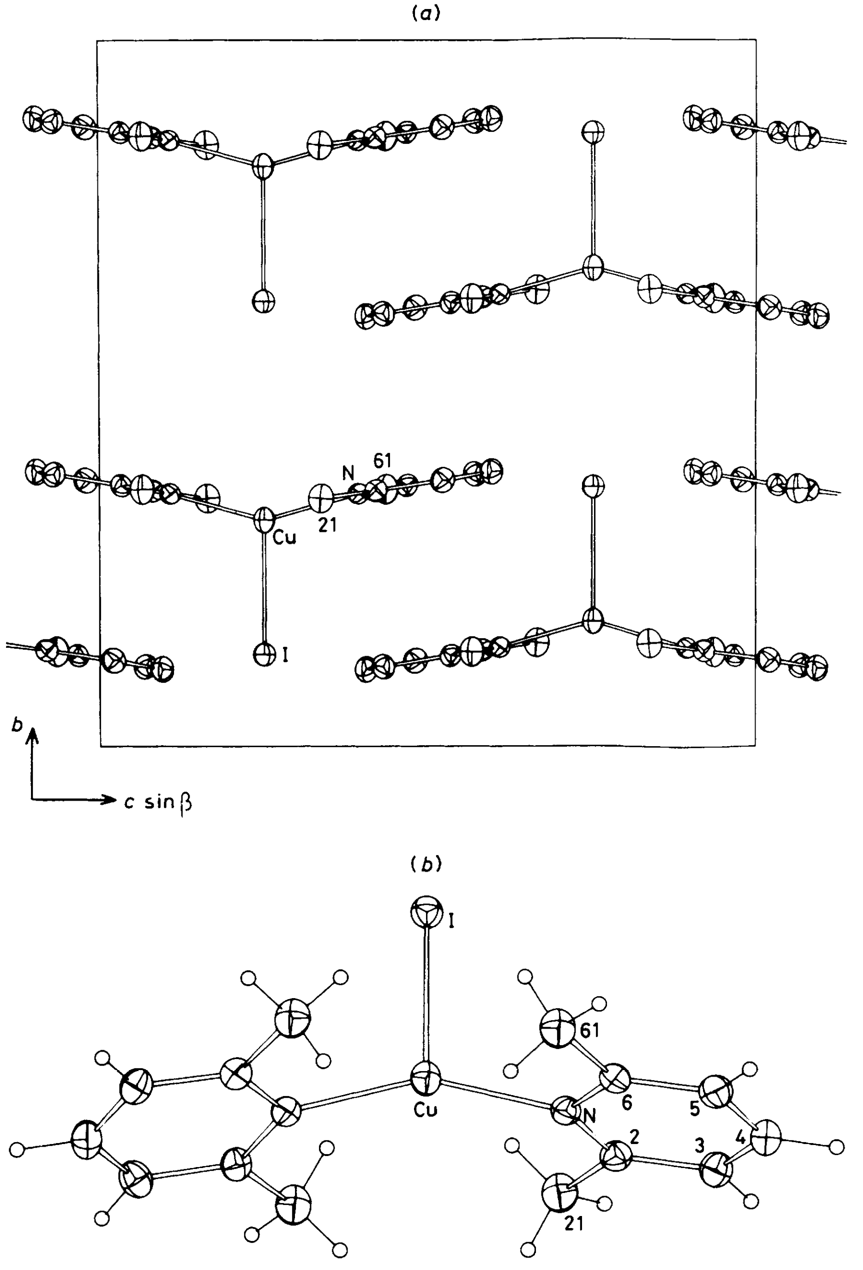


Figure 5. (*a*) Unit-cell contents of (5), α phase, projected down *a*. Non-hydrogen atoms in this and subsequent figures are shown with 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å, where given. (*b*) A single molecule of the α phase projected on the $ICuN_2$ plane

[{$CuI(2,6Me_2$-py)}$_2$] (1.99 Å) (Table 9); Cu–N (mean) in the trigonal [Cu(2Me-py)$_3$]$^+$ species is 1.99 Å.[22] However, the Cu–I distances [2.682(2) Å in α and 2.642(2) Å in β] are *ca.* 0.07 Å longer than the values observed for the above complex [2.583(5) and 2.576(5) Å], and approach the range of values observed for the tetrahedrally co-ordinated dimers [2.714(3) and 2.663(3) Å, 2-methylpyridine; 2.720(1) Å, 2-ethylpyridine; 2.668(2) and 2.657(3), quinoline; 2.658(2), 3,5-dimethylpyridine].

An important parameter in these complexes is the L–M–L angle. For trigonally co-ordinated systems this might be expected to be 120°, increasing or decreasing as a function of the stereochemical and electronic factors involved in arranging the ligands L, and X, around the central copper(I) atom.[20] In these complexes, the N–Cu–N angles of 149.6(2)° in α and 143.5(1)° in β are amongst the highest L–Cu–L angles yet observed, and are comparable to the values observed for the copper(I) perchlorate and nitrate complexes with tricyclohexylphosphine (144 and 140° respectively). Values for other complexes range from 120 to 133° as detailed in Table 12.

Previous attempts to explain the size and variation in these angles have been made in terms of increases from tetrahedral or trigonal geometry due to steric repulsion effects. While a considerably greater number of structural examples are required before all the factors involved can be isolated, the large angles observed in these structures suggest that it might be more appropriate to consider these complexes as being derived from interaction of the linear cation [ML_2]$^+$ and the anion X^-, the geometry finally assumed being a function of the X–L and L–L steric repulsions and the extent of covalent-

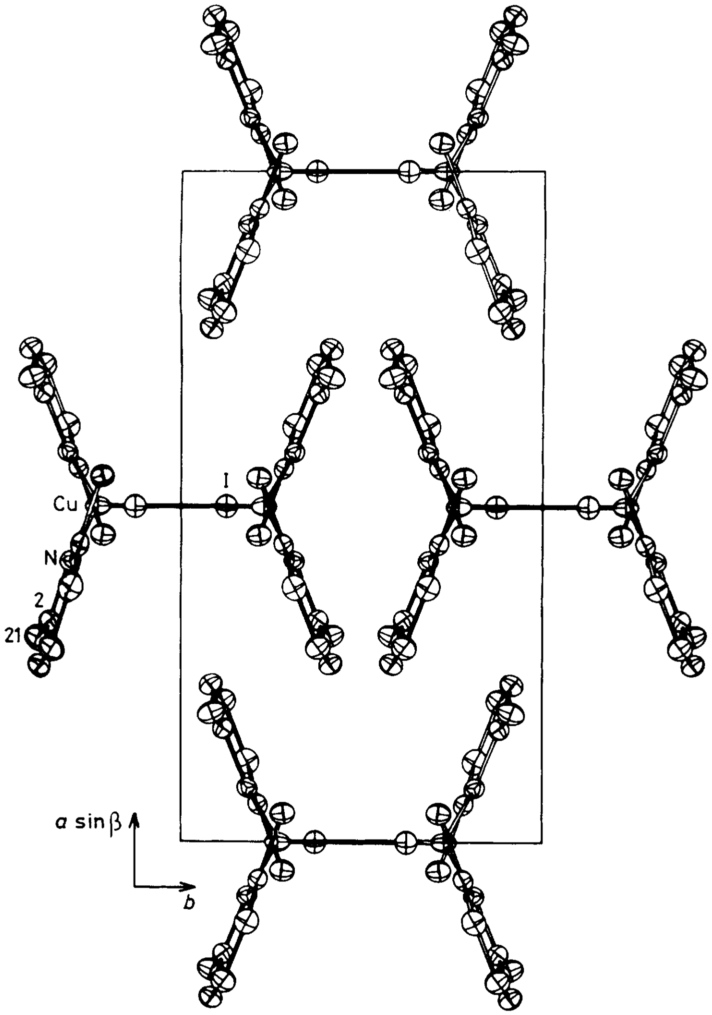


Figure 6. Unit-cell contents of (5), β phase, projected down *c*

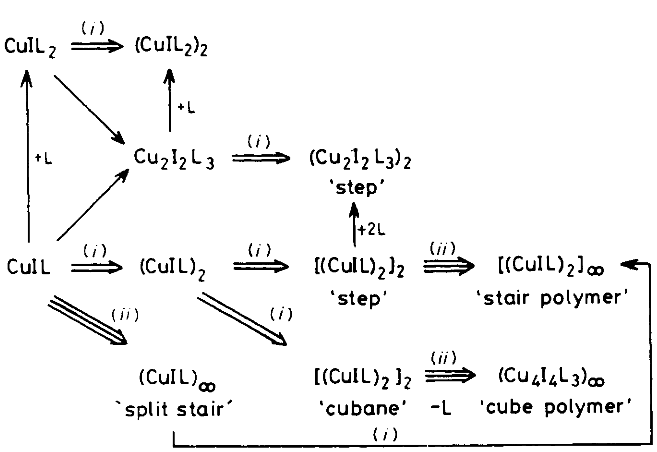
Table 11. Molecular non-hydrogen geometries of [CuI(2,6Me$_2$-py)$_2$], (5); distances in Å, angles in degrees

	α Phase	β Phase		α Phase	β Phase
Cu–I	2.682(2)	2.642(2)	C(2)–C(21)	1.495(8)	1.493(6)
Cu–N(1)	1.984(5)	1.984(4)	C(3)–C(4)	1.364(8)	1.378(7)
N(1)–C(2)	1.346(7)	1.352(4)	C(4)–C(5)	1.368(9)	1.364(5)
N(1)–C(6)	1.359(7)	1.346(4)	C(5)–C(6)	1.393(8)	1.387(7)
C(2)–C(3)	1.384(9)	1.389(7)	C(6)–C(61)	1.490(9)	1.504(4)
Cu–N(1)–C(2)	120.3(3)	118.6(3)	C(3)–C(4)–C(5)	119.5(6)	119.3(5)
Cu–N(1)–C(6)	120.6(4)	122.2(2)	C(4)–C(5)–C(6)	119.4(5)	119.6(4)
C(2)–N(1)–C(6)	118.7(5)	118.5(3)	N(1)–C(6)–C(5)	121.0(5)	121.8(3)
N(1)–C(2)–C(3)	121.6(5)	121.6(3)	N(1)–C(6)–C(61)	117.5(5)	117.7(3)
N(1)–C(2)–C(21)	117.9(5)	117.1(4)	C(5)–C(6)–C(61)	121.5(5)	120.5(3)
C(21)–C(2)–C(3)	120.5(5)	121.3(3)	N(1)–Cu–I	105.2(1)	108.26(8)
C(2)–C(3)–C(4)	119.7(6)	119.1(3)	N(1)–Cu–N(1)	149.6(2)	143.5(1)

Table 12. Comparison of the L–M–L angle for a range of three-co-ordinate and pseudo-three-co-ordinate complexes of the type MXL$_2$

Compound *	Ref.	L–M–L/°	Compound *	Ref.	L–M–L/°
[CuBr(PPh$_3$)$_2$]	8	126	[Cu(S$_2$CSEt)(PPh$_3$)$_2$]	15	126
[AuCl(PPh$_3$)$_2$]	9	132	[Cu{O$_2$NCPh(NO$_2$)}(PPh$_3$)$_2$]	16	133
[CuCl(tuc)]	10	120	[Cu(O$_2$CMe)(PPh$_3$)$_2$]	17	133
[Cu(BH$_4$)(PPh$_3$)$_2$]	11	123	[Cu(NO$_3$){P(C$_6$H$_{11}$)$_3$}$_2$]	18	140
[Cu(NO$_3$)(PPh$_3$)$_2$]	12	131	[Cu(ClO$_4$){P(C$_6$H$_{11}$)$_3$}$_2$]	19	144
[Cu(B$_3$H$_8$)(PPh$_3$)$_2$]	13	120	α-[CuI(2,6Me$_2$-py)$_2$]	This work	149
[Cu(tfacac)(PPh$_3$)$_2$]	14	127	β-[CuI(2,6Me$_2$-py)$_2$]	This work	144

* tuc = 2-Thiouracil, tfacac = trifluoroacetylacetonate.



Scheme. (*i*) Dimerization; (*ii*) polymerization

bond formation between M and X. Certainly, in these circumstances, the Cu–I distances would be expected to be longer than a ' normal ' three-co-ordinate value.

In conclusion we note that it is possible to represent schematically all structurally characterized neutral copper(I) halide–Group 5 unidentate base complexes as being built up of associated units of the $CuIL_2$ monomer characterized in this paper and/or the, as yet, uncharacterized two-co-ordinate molecule CuIL (see Scheme).

The results obtained to date, here and elsewhere, suggest that, in general, steric factors play the major role in determining which of the above configurations is adopted by any particular metal–halide–base combination. Although at present polymeric configurations are only found with nitrogen ligands, suggesting that electronic factors such as donor strength and/or lack of available *d* orbitals for bond stabilization may still be significant structural determinants for these complexes, we also note that the spatial disposition or ' shape ' of the ligand bulk about the co-ordinating atom is different in the substituted pyridine bases to that observed in the tertiary phosphines and arsines.

References

1 P. C. Healy, C. Pakawatchai, C. L. Raston, B. W. Skelton, and A. H. White, preceding paper.
2 A. U. Malik, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2106; *Z. Anorg. Allg. Chem.*, 1966, **334**, 107.
3 A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, 1970, **4**, 640.
4 R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, 1971, **10**, 1289.
5 B. K. Teo and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 1976, 185.
6 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, 1976, **15**, 1155.
7 M. R. Churchill and J. R. Missert, *Inorg. Chem.*, 1981, **20**, 619.
8 P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 1973, **12**, 213.
9 N. C. Baenzinger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805.
10 G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1973, 869.
11 S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.
12 G. G. Messmer and G. J. Palenik, *Can. J. Chem.*, 1969, **47**, 1440; *Inorg. Chem.*, 1969, **8**, 2750.
13 S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8**, 2755.
14 M. Bartlett and G. J. Palenik, *Acta Crystallogr., Sect. A*, 1969, **25**, S173.
15 A. Avdéef and J. P. Fackler, jun., *J. Coord. Chem.*, 1975, **4**, 211.
16 A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1975, 2560.
17 M. G. B. Drew, A. H. Bin Othman, D. A. Edwards, and R. Richards, *Acta Crystallogr., Sect. B*, 1975, **31**, 2695.
18 W. A. Anderson, A. J. Carty, G. J. Palenik, and G. Schreiber, *Can. J. Chem.*, 1971, **49**, 761.
19 R. J. Restivo, A. Costin, G. Ferguson, and A. J. Carty, *Can. J. Chem.*, 1975, **53**, 1949.
20 E. W. Ainscough, H. A. Bergen, A. M. Brodie, and K. A. Brown, *J. Chem. Soc., Dalton Trans.*, 1976, 1649; E. W. Ainscough, A. M. Brodie, and K. A. Brown, *ibid.*, 1980, 1042.
21 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.
22 A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 1972, 661.

Received 17*th September* 1982; *Paper* 2/1601