Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 1. Synthesis and structure of CuILn complexes (L = nitrogen base, n < 1.5)

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Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 1. Synthesis and Structure of CuIL$_n$ Complexes (L = nitrogen base, $n \leqslant$ 1.5) *

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Crystallization of copper(I) iodide from triethylamine–acetone yields a white crystalline solid of novel stoicheiometry [Cu$_4$I$_4$(NEt$_3$)$_3$]; its structure determination by single-crystal X-ray diffraction shows trigonal symmetry [space group P3, a = 19.46(2), c = 7.119(7) Å, and Z = 3] and polymeric strings of Cu$_4$I$_4$ 'cubane' units, oriented with one body diagonal of each unit along c and linked to the next unit generated by the unit c translation by a copper–iodine interunit bond [2.93$_0$ Å (mean)]. There are three independent such polymeric strings in the unit cell. R was 0.074 for 2 942 'observed' reflections. The structures of the 1 : 1 complexes of copper(I) iodide with 2-methylpyridine, (2Me-py) (2), 2,2,6,6-tetramethylpiperidine, (tmpip) (3), and acridine, (4), have also been determined. Each crystallizes in a structural form determined by the steric properties of the ligand. Crystals of (2) are tetragonal, space group I4cm, with a = 20.10(2) and c = 15.94(1) Å; R = 0.055 for 782 independent observed reflections. The structure is a 'cubane'-type tetramer, [Cu$_4$I$_4$(2Me-py)$_4$], with Z = 8. Crystals of (3) are orthorhombic, space group Cmca, with a = 12.43(2), b = 9.964(7), and c = 19.30(3) Å; R = 0.071 for 278 independent observed reflections. The structure is a di-μ-iodo-bridged dimer [Cu$_2$I$_2$(tmpip)$_2$], with four molecules in the unit cell. Crystals of (4) are triclinic, space group P$\bar{1}$, with a = 14.381(4), b = 9.888(3), c = 4.117(1) Å, α = 83.96(2), β = 81.57(2), and γ = 86.03(2)°; R = 0.078 for 2 649 observed reflections. The structure is a 'split stair' polymer, ($^-$CuL$^-$I$^-$)$_\infty$. The structures of (3) and (4) are unsymmetrical as a consequence of ligand steric effects. The synthesis and structure determination at 295 K of [Cu$_4$I$_4$(2Me-py)$_6$] are also reported. Crystals are triclinic, space group P$\bar{1}$, with a = 12.856(8), b = 9.736(7), c = 9.472(7), Å, α = 105.38(5), β = 98.68(5), γ = 104.90(5)°, and Z = 1; 4 010 observed reflections were refined to a residual of 0.034. The molecule is centrosymmetric and based on the 'step' structure well known for Cu$_4$I$_4$L$_4$ species; however, the copper atoms at the periphery of the chair are co-ordinated by a pair of ligands, giving rise to the first known examples of 1 : 1 : 1.5 Cu : halide : base stoicheiometry observed in nitrogen-base systems, and the first example of this stoicheiometry based on the 'step' array.

Adducts of copper(I) and silver(I) halides with unidentate, substituted phosphine and arsine bases have recently been widely studied structurally. Among the 1 : 1 : 1 complexes, with appropriate relative sizes for metal, halide, and ligand or by other means such as the use of bidentate ligands, the tetrameric M$_4$X$_4$L$_4$ cluster with pseudo-'cubane' stereochemistry [1–10] may be topologically transformed into the 'chair' or 'step' structure by suitably unfolding the 'cube'.[1a,6,11–14] By separating the opposite faces of the 'cube,' or severing the 'step,' independent dimeric species are possible [15] (Table 1). By varying the stoicheiometry, and including pseudo-halides amongst the X moieties, monomeric species such as CuXL$_3$ [16] and CuXL$_2$ [17] have been isolated and characterized, while dimers of stoicheiometry Cu$_2$X$_2$L$_4$ [16,18,19] and Cu$_2$X$_2$L$_3$ [16,20] have also been reported (Table 2). A unique trinuclear species has been found with stoicheiometry Cu$_3$X$_3$-L$_2$ where L = the bidentate ligand CH$_2$(PPh$_2$)$_2$.[21]

Systems involving nitrogen bases are less fully characterized structurally, although there is rather more wide-ranging earlier literature on synthetic aspects. For 1 : 1 : 1 metal : halide : base systems, the 'cubane' system is again familiar, being exemplified by [(CuIL)$_4$] (L = morpholine,[22] pyridine,[23] or piperidine [24]) and [(CuBrL)$_4$] (L = 2-methylpyridine).[25] The silver analogue of the iodo(piperidine) derivative also has a 'cubane' structure.[26] With regards to other possible structural configurations, no nitrogen-base analogue of the 'step' form

has been reported, instead a series of polymeric structures are found for which the 'step' might be considered to form the repeating unit. This commonly observed polymeric structure, labelled the 'ribbon' or 'stair' polymer, is exemplified by a second polymorph of CuI and pyridine (py), [{CuI(py)}$_\infty$],[27] the chloro-analogue [{CuCl(py)}$_\infty$],[28] and other adducts of CuCl, CuBr, and CuI with methyl cyanide,[29,30] benzonitrile,[31] and azomethane.[32] Interaction of AgSCN with tri-n-propylphosphine gives rise to a related structure.[33] When the ligand is methyl isocyanide rather than methyl cyanide, this 'polymer' form is transformed to a 'displaced stair polymer' as in [(CuI·MeNC)$_x$].[34] A third polymer form, the 'split stair polymer,' is observed for the adduct of the sterically bulky ligand 2,4,6-trimethylpyridine with CuI.[28] Only one nitrogen-base dimeric species has been reported, [{CuI(2,6Me$_2$-py)}$_2$],[28] having an analogous structure to the 1 : 1 tricyclohexylphosphine complex with CuI.[15] No other structural data are presently available for monomers, dimers, or tetramers where the metal : halide : base ratio differs from 1 : 1 : 1 (Scheme 1).

In the present series we report results of a programme of synthesis and structural characterization of the (MXL$_n$)$_m$ system, with M = Cu^I, X = halide, and L = aliphatic and aromatic nitrogen bases. The first paper describes the results of our attempt to prepare an adduct of copper(I) iodide with triethylamine that is structurally analogous with the triethylphosphine and -arsine (MXL)$_4$ 'cubane' systems, obtaining instead a complex with the novel stoicheiometry (Cu$_4$I$_4$L$_3$)$_\infty$, (1), comprising a 'linked cube' polymeric structural type.

To define further the constraints of the 1 : 1 CuX : nitrogen-base system, we have prepared and structurally characterized 1 : 1 adducts of copper(I) iodide with 2-methylpyridine (2),

(1) $[(MX)_1L_1]_\infty$

(*i*) 'stair polymer'   (*ii*) 'split-stair polymer'   (*iii*) 'displaced stair polymer'

(2) $[(MX)_1L_1]_4$

(*i*) 'cubane'   (*ii*) 'step'

(3) $[(MX)_1L_1]_2$, dimer   (4) $[(MX)_2L_3]_1$, dimer   (5) $[(MX)_1L_2]_2$, dimer
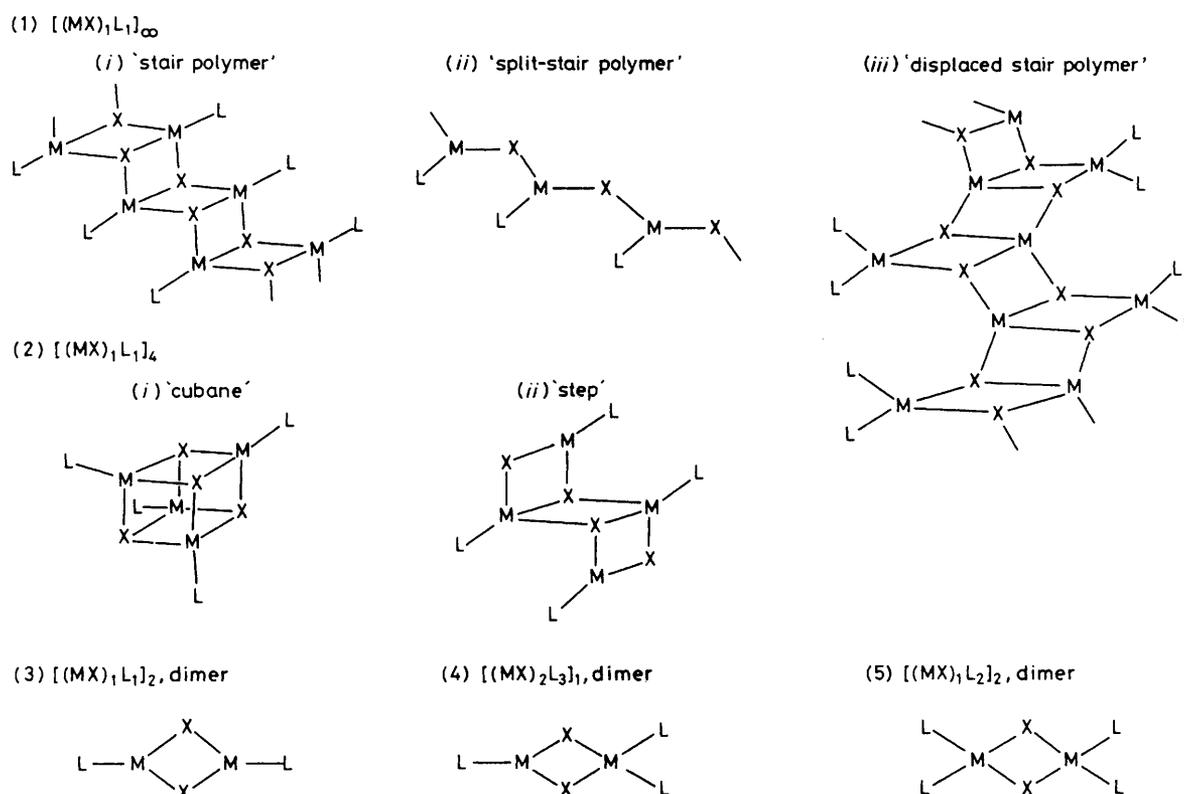
Scheme 1. Representation of the molecular configurations of structurally characterized compounds of general formula $(MX)_nL_m$

Table 1. Compilation of the structures of 1 : 1 : 1 copper(I) or silver(I)–halide–unidentate phosphine or arsine base complexes $[(Cu,Ag)XL]_n$

Complex	Ref.	Stereochemistry	Complex	Ref.	Stereochemistry
[{CuCl(PPh₃)}₄]	1	Cube	[{Cu₂I₂[CH₂(PPh₂)₂]}₂]	11	Step
[{CuBr(PPh₃)}₄]	1a, 13	Step	[{Cu₂Cl₂[CH₂(PPh₂)₂]}₂]	12	Step
[{CuI(PPh₃)}₄]	14	Step	[{CuCl[P(C₆H₁₁)₃]}₄]	15	Dimer
[{CuI(AsPh₃)}₄]	10	Cube	[{AgCl(PPh₃)}₄]	5	Cube
[{CuCl(PEt₃)}₄]	3	Cube	[{AgBr(PPh₃)}₄]	7	Cube
[{CuBr(PEt₃)}₄]	3	Cube	[{AgI(PPh₃)}₄]	5, 6	Cube, step
[{CuI(PEt₃)}₄]	2	Cube	[{AgCl(PEt₃)}₄]	8	Cube
[{CuI(AsEt₃)}₄]	2	Cube	[{AgBr(PEt₃)}₄]	8	Cube
[{CuI(PMePh₂)}₄]	9	Cube	[{AgI(PEt₃)}₄]	4	Cube

Table 2. Compilation of the structures of $x : y : z$ (1 : 1 : 1) copper or silver: halide or pseudo halide: unidentate phosphine or arsine base complexes

$x : y : z$	Complex	Ref.	Stereochemistry
1 : 1 : 3	[CuCl(PPh₃)₃]	16	Monomer
	[CuCl(PMePh₂)₃]	16	Monomer
1 : 1 : 2	[CuBr(PPh₃)₂]	17	Monomer
	[{CuCl(AsMe₂Ph)₂}₂]	16	Dimer
	[{CuN₃(PPh₃)₂}₂]	18	Dimer
	[{Cu(SCN)(PMePh₂)₂}₂]	19	Dimer
	[{AgBr(PPh₃)₂}₂]	7	Dimer
1 : 1 : 1.5	[{CuCl(PPh₃)₁.₅}₂]	16, 20	Dimer

2,2,6,6-tetramethylpiperidine (3), and acridine (4). The preparation of adduct (2) was undertaken on the surmise that the increased bulk of the ligand compared with pyridine might be sufficient to convert the structural type from the 'cubane' into either a 'step' or 'stair' structure. The second adduct (3) was prepared to explore the effect of the steric hindrance

introduced by substitution of *two* methyl groups in *both* the 2 and 6 positions of piperidine on the molecular structure, while the third (4) introduces similar steric effects with the added constraint of fixed hydrogen positions in the ligand plane. The results show that complex (2) crystallizes in the 'cubane' configuration, albeit highly distorted and with the ligand atoms exhibiting a high level of disorder, and that (3) crystallizes in the dimeric form previously observed only for the adduct of copper(I) chloride with tricyclohexylphosphine [15] and of copper(I) iodide with 2,6-dimethylpyridine.[28] Complex (4) is found to be an infinite one-strand $(-CuL-I-)_\infty$ polymer of the type previously observed for the 1 : 1 adduct of copper(I) iodide and 2,4,6-trimethylpyridine.[28]

With an appropriate ratio of ligand : copper iodide, a further derivative may be obtained with 2-methylpyridine, with stoicheiometry $Cu_4I_4L_6$, (5). This tetramer has the 'chair' or 'step' structure, familiar for the copper(I) halide–phosphorus and arsenic base systems (Table 1), but now reported for the first time with a nitrogen-base ligand and in a system of novel stoicheiometry.

Experimental

Copper(ı) *Iodide*.—Crude copper(ı) iodide was prepared according to the method outlined in ref. 35, but exhibited i.r. bands due to the presence of water, even after drying. It was purified as follows. The crude iodide was dissolved in a solution of 2-methylpyridine (2Me-py) in dry distilled acetone; the resultant pale yellow solution was filtered and cooled to −30 °C, depositing pure, anhydrous crystals of [CuI(2Me-py)₂]. These were filtered off, washed with dry diethyl ether, and dried overnight in an air oven at 100 °C. The i.r. spectrum of the resultant copper(ı) iodide showed no traces of water, ligand, or solvent. Subsequent reaction with nitrogen-base ligands showed a marked enhancement in dissolution rate relative to that of the original compound.

Nitrogen Bases.—Reagent-grade nitrogen bases were used without further purification.

Solvents.—Solvents were dried and redistilled according to standard procedures.

Apparatus.—Standard Schlenk vacuum/gas-line apparatus and techniques were used to prepare the complexes which were sensitive to oxidation to copper(ıı) salts. Special grade argon was used without further purification.

Analysis and Characterization.—Many of the complexes prepared exhibited substantial vapour pressures of ligand, and lost ligand on exposure to the atmosphere. Accordingly, in these cases, characterization depended solely on the structure determination. Densities could not be determined for similar reasons.

Preparation of Complexes.—[{(CuI)₄(NEt₃)₃}ₓ] (1). Re-purified copper(ı) iodide (0.5 g) was dissolved in a solution of excess of triethylamine (5 cm³) in acetone (30 cm³) under anhydrous, oxygen-free conditions. The colourless solution was filtered and cooled to −30 °C; colourless hexagonal blocks of the complex were obtained.

[{CuI(2Me-py)}₄] (2). Copper(ı) iodide (0.5 g) was suspended in a solution of 2-methylpyridine (0.25 g) in dry distilled acetone (10 cm³). Heating and stirring of the solution resulted in partial dissolution of the copper(ı) iodide. After filtration and cooling to −30 °C overnight, the complex was obtained as a mass of colourless needles. Selection of a crystal suitable for X-ray analysis was seriously hampered by the fact that most of the crystals examined were, despite appearances, either twinned or polycrystalline. The crystal for data collection was selected on the basis of a minimum of polycrystalline effects, and in spite of its small dimensions along the axes perpendicular to the needle axis.

[{CuI(tmpip)}₂] (3). Copper(ı) iodide (0.4 g) was dissolved in a solution of 2,2,6,6-tetramethylpiperidine (tmpip) (1.0 g) in dry distilled acetone (10 cm³). Cooling of the solution to −30 °C overnight resulted in deposition of small, needle-shaped, air-sensitive crystals of the complex. Recrystallization failed to increase crystal size.

[CuI(acr)] (4). This complex has previously been reported in the literature as brick red crystals, decomposition temperature 335 °C.[36] Crystals used in this experiment were prepared by the addition of copper(ı) iodide (0.4 g) to a solution of acridine (acr) (1.0 g) in acetonitrile (20 cm³). The brick red precipitate thus formed was refluxed for 2 d in acetonitrile, in which it was slightly soluble, resulting in the formation of large, ill formed deep red crystals of the complex.

[Cu₄I₄(2Me-py)₆] (5). The formation of this complex, rather than the 1 : 1 adduct of copper(ı) iodide and 2-methyl-

pyridine, (2), was observed with copper(ı) iodide : base ratios in the range 1 : 2—1 : 10 in acetone; the product obtained at the extremes of this range was contaminated with the 1 : 1 and what was subsequently shown to be the 1 : 2 adduct.[37] Typically, addition of copper(ı) iodide (0.5 g) to a solution of 2-methylpyridine (2 cm³) in acetone (10 cm³) resulted in complete dissolution; cooling to −30 °C resulted in the crystallization of the 1 : 1.5 complex as multifaceted colourless blocks. These crystals were stable indefinitely in the presence of air, but decomposed rapidly in the absence of mother-liquor.

Crystallography.—General crystallographic data and procedures for this and the following paper [37] are as follows. As a general rule, crystals were mounted in argon-filled capillaries, together with their mother-liquor in order to prevent oxidation and/or loss of ligand. For each compound a unique data set was measured to a 2θ limit predetermined from the scope of the data, using a Syntex P2₁ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 69 Å) and operating in conventional 2θ–θ scan mode at 295(1) K. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered ' observed ' and used in the (basically) 9 × 9 block-diagonal least-squares refinement after analytical absorption correction. Full-matrix refinement was used for the smaller structures. Reflection weights were [σ²(F_o) + 0.0005 (F_o)²]⁻¹. Residuals at convergence (R,R') are quoted on |F|. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[38] Hydrogen atoms were included in the refinements at calculated positions with U_H set at 1.25 $\bar{U}_{11}$ (parent C); anisotropic thermal parameters were refined for the other atoms. Computation used the X-RAY 76 program system [39] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Any departures from the above are noted as ' abnormal features ' for individual cases. Specific details for the present structures are given below.

Crystal data. [Cu₄I₄(NEt₃)₃], (1), C₁₈H₄₅Cu₄I₄N₃, M = 1 065, Trigonal, space group P3(C_3^1, no. 143), a = 19.46(2), c = 7.119(7) Å, U = 2 335(3) Å³, D_c (Z = 3) = 2.27 g cm⁻³, F(000) = 1 506, μ_Mo = 64 cm⁻¹. Specimen size: 0.40 × 0.40 × 0.55 mm. 2θ_max. = 60°; N,N_o = 3 875, 2 942; R,R' = 0.074, 0.103.

(2), C₂₄H₂₈Cu₄I₄N₄, M = 1 134, Tetragonal, space group *I*4*cm* (C_{4v}^{10}, no. 108), a = 20.10(2), c = 15.94(1) Å, U = 6 443(12) Å³, D_c (Z = 8) = 2.34 g cm⁻³, F(000) = 4 224, μ_Mo = 64 cm⁻¹. Specimen size: 0.10 × 0.10 × 0.30 mm. 2θ_max. = 50°; N,N_o = 1 554, 782; R,R' = 0.055, 0.069.

(3), C₁₈H₃₈Cu₂I₂N₂, M = 662, Orthorhombic, space group *Cmca* (D_{2h}^{18}, no. 64), a = 12.43(2), b = 9.964(7), c = 19.30(3) Å, U = 2 391(4) Å³, D_c (Z = 4) = 1.84 g cm⁻³, F(000) = 1 296, μ_Mo = 43 cm⁻¹. Specimen size: 0.20 × 0.09 × 0.09 mm. 2θ_max. = 40°; N,N_o = 598, 278; R,R' = 0.071, 0.070.

(4), C₁₃H₉CuIN, M = 369.7, Triclinic, space group *P*1̄, (*C*¹ᵢ, no. 2), a = 14.381(4), b = 9.888(3), c = 4.117(1) Å, α = 83.96(2), β = 81.57(2), γ = 86.03(2)°, U = 575.1(3) Å³, D_m = 2.17(1), Z = 2, D_c = 2.14 g cm⁻³, F(000) = 352, μ_Mo = 52 cm⁻¹. Specimen size: 0.43 × 0.20 × 0.07 mm. 2θ_max. = 55°; N,N_o = 3 369, 2 649; R,R' = 0.078, 0.101.

(5), C₃₆H₄₂Cu₄I₄N₆, M = 1 320, Triclinic, space group *P*1̄ (*C*¹ᵢ, no. 2), a = 12.856(8), b = 9.736(7), c = 9.472(7) Å, α = 105.38(5), β = 98.68(5), γ = 104.90(5)°, U = 1 074(1) Å³, D_c (Z = 1) 2.02 g cm⁻³, F(000) = 628, μ_Mo = 48 cm⁻¹. Specimen size: 0.15 × 0.40 × 0.08 mm. T = 295 K, 2θ_max. = 60°; N,N_o = 6 262, 4 010; R,R' = 0.034, 0.044.

Abnormal features. Structures (1)—(4) presented difficulties in processing. In (1), high residuals appear to be a consequence of disorder in one of the amine ligands; this was modelled as a pair of superimposed ligands with common nitrogen atoms

but with the three nitrogen substituents staggered relative to each other. Thermal motion in all ethyl systems is very high. In the case of (2) the nitrogen ligand 2 was disordered with the methyl groups found at the 2 or 6 sites; symmetry constrained the populations at 50% (the space group being assumed correct). Thermal motion on all the ligands was very high, and meaningful refinement was not possible for the ligand atoms; accordingly isotropic forms were used throughout for the ligands, with values for x, y, z, and U constrained at estimates obtained from difference-Fourier maps after location of the Cu_4I_4 molecular core. In the case of (3), the small specimen available limited the data accessible; isotropic thermal parameters were refined only for the ligand atoms in the structure; while in (4) the data were badly streaked, presumably a consequence of stacking faults in the polymer array. Atom numbering within the ligands is as follows:
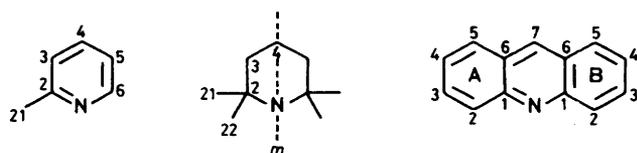
Discussion

Complex (1).—The structure determination establishes the overall stoicheiometry of the complex to be copper : iodide : triethylamine = 4 : 4 : 3. The space group $P3$ contains three independent crystallographic sites of 3 symmetry within the unit cell at ($\frac{2}{3}$, $\frac{1}{3}$, z), ($\frac{1}{3}$, $\frac{2}{3}$, z), and (0, 0, z). About each of these three-fold axes we find similar structural units which form the basis of the structure; these are Cu_4I_4 ' cubane ' entities, oriented such that the three-fold axis passes through the pair of copper and iodine atoms that lie at either end of a body diagonal of a ' cube '. The remaining three copper and iodine atoms, and the triethylamine ligands, are related by a three-fold rotation. Thus the asymmetric unit of the molecule is built up from equal contributions from each of the three sites of off-axis copper, and iodine atoms, one triethylamine molecule, and one third of the axial copper and iodine atoms giving the overall stoicheiometry $[Cu_4I_4(NEt_3)_3]$.

In each of the cube units the polarity of the axial CuI pair is identical with respect to the three-fold axis, which is itself polar, but in a sense which is not determinable from the anomalous dispersion component and, presumably, peculiar to the crystal in question. Given this polarity, and the location of the three independent cubes, the question as to how the cell accommodates these, rather than reducing to a cell with a non-unique axis of one third the present length, is answered through consideration of the pseudo-mirror planes through the cube defined by the three-fold axes and the non-bonding Cu $\cdots$ I vector. It is evident from Figure 1(a) that the planes of this type which lie nearest to the plane defined by c and the long cell diagonal in the ab plane vary in their dihedral angle to it. Moreover, the z co-ordinates of the three axial iodine and copper atoms are significantly different and cannot be related to each other by any simple translational operation.

The c axial distance of 7.119(7) Å and the axial diagonal Cu $\cdots$ I distances of each cube [4.414(6), unit 1; 4.430(6), unit 2; and 4.445(6) Å, unit 3] mean that the copper and iodine atoms of adjacent cells related by the c translation lie within bonding distances of each other, generating from each cubane unit an infinite polymeric sequence of linked cubes. One such polymeric unit is illustrated in Figure 1(b). Consequently, only the off-axis copper atoms have the expected $CuI_3(NEt_3)$ tetrahedral co-ordination. The axial copper and iodine atoms

are similar to copper(i) iodide in being co-ordinated to four iodine and copper atoms respectively. However, the axial Cu$-$I bond length is considerably longer than the other Cu$-$I distances in the cube (average values: axial, 2.93 Å, non-axial, 2.60—2.74 Å).

This difference between the co-ordination environment of the axial and off-axial copper atoms (CuI_4 *vs.* CuI_3N) provides a useful comparator for the relative effects of the nitrogen base and the iodide ion on the tetrahedral geometry of the first co-ordination sphere surrounding the copper atom. Significant differences are observed. The N$-$Cu$-$I angle about CuI_3N is 110°; the I$-$Cu$-$I angle is 106°. With substitution of the iodide ion for the nitrogen base as the fourth ligand, the equivalent angles are 103 and 114° respectively. This result suggests that the principal factors influencing the detailed geometry of the complex are a complex combination of steric and electronic factors.

The high degree of disorder amongst the peripheral atoms of the nitrogen ligand and the unique polymeric configuration adopted by the molecule do not permit a direct, detailed comparison of the molecular geometries of copper(i) iodide–base adducts within the series triethylamine, triethylphosphine, and triethylarsine. However, a comparison of the internal Cu$-$I bond lengths [AsEt$_3$, 2.677(1); PEt$_3$, 2.684(1); NEt$_3$, 2.594(3)—2.808(5) Å] indicates that this parameter thus far does not correlate with the systematic changes in the steric and electronic factors of the bases involved. Trends in the values of I $\cdots$ I and Cu $\cdots$ Cu non-bonded interactions, or equivalent changes in I$-$Cu$-$I and Cu$-$I$-$Cu angles, are erratic and at variance with results from other structural work on copper(i) iodide–base adduct ' cubane ' systems showing a general increase in the I $\cdots$ I and a decrease in the Cu $\cdots$ Cu distances as the ligand varies from phosphorus or arsenic to nitrogen base systems (see below).

The CuI : L 1 : 1 *Complexes* (2)—(4).—Structural studies of coinage metal(i) halide–nitrogen-base adducts of 1 : 1 stoicheiometry have shown the formation principally of either tetrameric ' cubane ' or polymeric ' stair ' structures, whereas with tertiary phosphorus and arsenic bases the predominant structural types are the tetrameric ' cubane ' and ' step ' structures; for the last cases, it has been shown that crystallization in either of the tetrameric forms is dependent on the relative bulk of the metal, halide, and base. For the nitrogen system the unknown ' step ' structure is presumably subsumed into the polymeric ' stair ' structure as a consequence of different ligand profiles to those in the structurally defined phosphorus and arsenic systems. In all systems, introduction of extremely bulky ligand groups results in the formation of three-co-ordinate copper systems with disruption of the ' cubane ' or ' step ' structures to form dimeric di-μ-halide-bridged structures,[15,28] or of the ' stair polymer ' to form the single strand $(CuXL)_\infty$ ' split stair polymer '.[28]

In the nitrogen-base system, structurally defined representatives of the ' cubane ' system are provided only by bases unsubstituted in the 2 and 6 positions,[22–24] with the exception of the adduct formed between copper(i) bromide and 2-methylpyridine[25] in which abnormally wide ranges are observed for Cu $\cdots$ Cu and Cu $\cdots$ Br distances [2.836(2)—3.033(3) and 2.435(2)—2.624(2) Å respectively], with similarly large ranges in the equivalent angles, suggestive of an unusual degree of distortion. The ' stair polymer ' is observed for a diverse range of sterically hindered and unhindered nitrogen bases, and for all halide ions excepting fluoride. The 1 : 1 complex of copper(i) iodide with pyridine, is in fact, dimorphic, crystallizing in both ' cubane ' and ' stair ' forms.[23,27]

The structure determination of complex (2) establishes the stoicheiometry to be copper : halide : base $=$ 1 : 1 : 1 with a
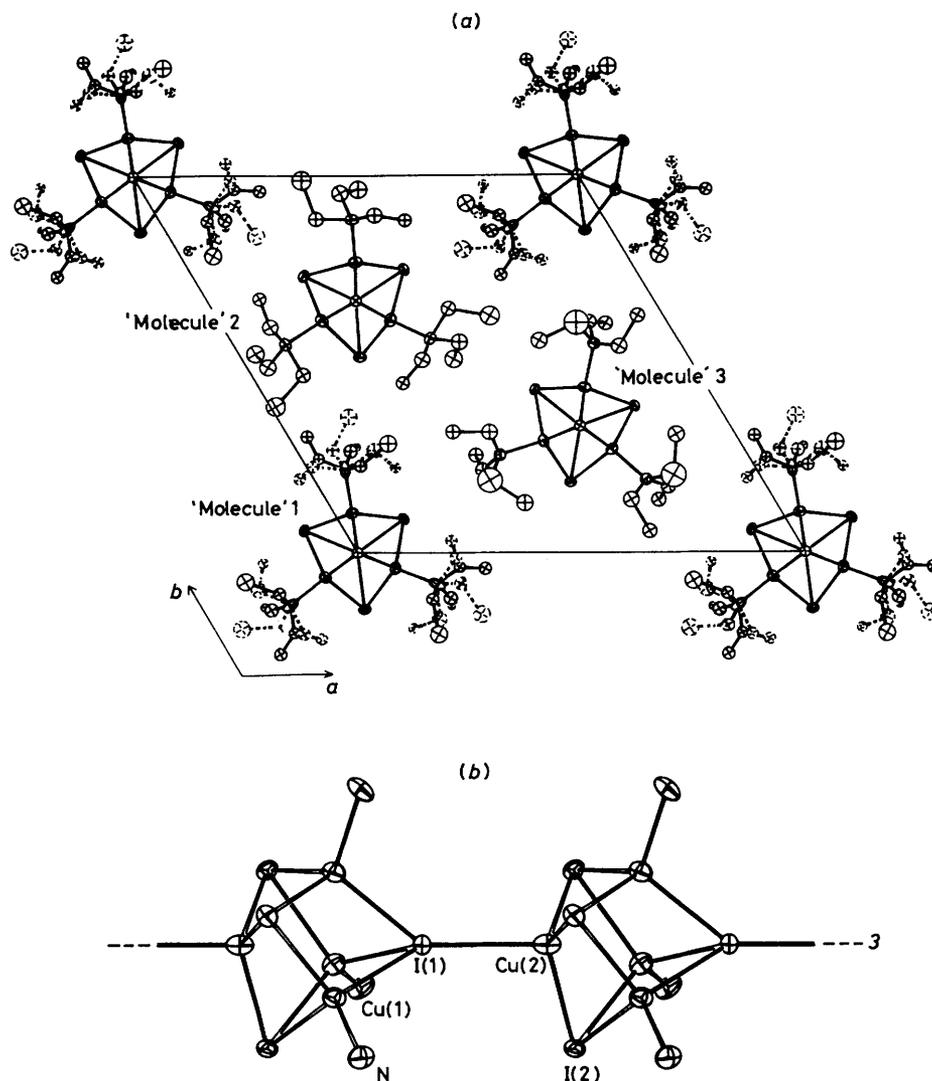
Figure 1. (a) Unit-cell contents of complex (1) projected down c; 20% thermal ellipsoids are shown for the non-hydrogen atoms. (In the case of carbon atoms these are spheres.) (b) A segment of polymeric string 3 in (1). In all polymer strings, I(1) and Cu(2) are axial and bonded to each other, thus lying in successive cubes. Cu(1) and I(2) are off-axis and are bonded to and lie in the same cubes as I(1) and Cu(2) respectively

tetrameric molecular unit crystallizing in a highly distorted ' cubane ' configuration. Significant geometric parameters for the structure, however, are available only for the Cu_4I_4 core. The ligand atoms exhibit an extremely high level of thermal motion and/or disorder and all attempts at least-squares refinement were unsuccessful. Consequently, ligand parameters are not significant and are not discussed further. This observed disorder contrasts with the level of precision for the parameters obtained for the structure of the complex of 2-methylpyridine with copper(i) bromide.[25]

A comparison of the Cu−I, Cu ··· Cu, and I ··· I distances in the Cu_4I_4 molecular core of this complex with those of other copper(i) iodide ' cubane ' structures and with the tri-ethylamine complex (1) (Table 7) shows that while Cu−I remains within the same range (ca. 2.6—2.8 Å) irrespective of whether the base ligand contains nitrogen, phosphorus, or arsenic, the Cu ··· Cu and I ··· I non-bonding contact distances are respectively shorter and longer in the nitrogen-base adducts when compared to adducts with phosphorus and arsenic (N, 2.6—2.7, 4.5—4.6; P/As, 2.8—3.0, 4.3—4.5 Å). Within each of the groups corresponding to different donor

types however, no real and systematic variation can be observed or correlated with electronic or steric properties of the ligands. This is particularly apparent if the pyridine and 2-methylpyridine complexes are compared; the increased basicity and steric influence of the 2-methyl-substituted ligand might be expected to have an observable effect on the above parameters. These results are consistent with the hypothesis that the nitrogen-base ligands, considered as a group, exert a considerably greater steric effect on the geometry of the Cu_4I_4 ' core.' In the present context it seems that the 2-methylpyridine ligand exists at the maximum level of steric requirement consistent with formation of the ' cubane ' structure, and any further increase in the relative effective bulk of the ligand should result in disruption of the ' cubane ' structure giving various other possible structures with more ' open ' geometries.

The structure determination of complex (3) establishes the stoicheiometry to also be copper : iodide : base = 1 : 1 : 1, but with the molecular unit a di-μ-iodo-bridged dimer rather than the ' cubane ' structure observed for (2). The Cu_2I_2 core of the dimer is contained within the plane of a crystallographically

Table 3. Non-hydrogen atom co-ordinates of [{(CuI)$_4$(NEt$_3$)$_3$}$_\infty$], (1)

		1 ^{a}			2			3	
Atom	x	y	z	x	y	z	x	y	z
I(1)	0	0	0 ^{b}	¼	¾	0.244 4(6)	¼	¼	0.636 8(5)
I(2)	−0.089 9(1)	0.059 0(1)	0.497 3(5)	0.483 7(1)	0.750 1(1)	0.736 2(5)	0.615 0(1)	0.429 7(1)	1.127 0(4)
Cu(1)	0.040 5(2)	0.104 8(2)	−0.286 0(7)	0.384 3(3)	0.769 9(2)	−0.043 7(8)	0.565 0(2)	0.293 9(2)	0.350 0(6)
Cu(2)	0	0	0.409 8(12)	¼	¾	0.657 3(11)	¼	¼	1.049 0(10)
N	0.082(2)	0.219(2)	−0.186(4)	0.434(2)	0.884(1)	0.074(3)	0.450(1)	0.258(1)	0.458(3)
C(11)	0.122(4)	0.229(4)	0.029(9)	0.491(3)	0.894(3)	0.224(7)	0.391(2)	0.218(2)	0.315(6)
C(12)	0.214(7)	0.288(7)	0.222(18)	0.552(2)	0.881(2)	0.221(5)	0.395(2)	0.257(2)	0.149(6)
C(21)	0.038(3)	0.248(3)	−0.140(8)	0.443(3)	0.954(3)	−0.077(7)	0.457(3)	0.318(2)	0.522(7)
C(22)	0.041(4)	0.306(4)	−0.251(9)	0.489(4)	0.963(4)	−0.276(9)	0.375(3)	0.319(2)	0.594(6)
C(31)	0.119(5)	0.268(4)	−0.325(11)	0.354(3)	0.885(3)	0.175(6)	0.393(7)	0.191(8)	0.612(21)
C(32)	0.138(2)	0.279(2)	−0.518(5)	0.374(4)	0.988(4)	0.268(11)	0.441(3)	0.131(3)	0.636(8)
C(41)	0.014(4)	0.227(4)	−0.021(9)						
C(42)	−0.032(4)	0.195(4)	0.025(8)						
C(51)	0.080(4)	0.271(4)	−0.322(9)						
C(52)	0.161(7)	0.358(7)	−0.433(16)						
C(61)	0.173(5)	0.270(5)	−0.158(12)						
C(62)	0.198(3)	0.224(3)	0.010(6)						

^{a} Carbon atom populations 0.5. ^{b} Defines origin.

Table 4. Heavy-atom geometry of [{(CuI)$_4$(NEt$_3$)$_3$}$_\infty$], (1). A superscript denotes the transformation of the final atom in the string; where two superscripts are given, these denote the transformations of the two peripheral atoms of an angle

		Polymer			
		1	2	3	Mean
(a) Distances/Å					
	I(1)–Cu(1)	2.705(4)	2.689(6)	2.674(5)	2.69
	I(1)–Cu(2)	2.917(9)	2.940(10)	2.934(8)	2.93
	I(2)–Cu(2)	2.603(4)	2.600(3)	2.594(3)	2.60
	I(2)–Cu(1)	2.711(6^I)	2.662(7^I)	2.808(5^I)	}
	I(2)–Cu(1)	2.744(9^{II})	2.820(6^{VI})	2.686(8^{IX})	} 2.74
	Cu(1)–N	2.08(3)	2.10(2)	2.14(3)	2.11
	Cu(1)···Cu(2)	2.805(8)	2.749(8)	2.753(7)	2.77
	Cu(1)···Cu(1)	3.086(7)	3.013(7)	2.992(9)	3.03
	I(1)···I(2)	4.350(4^{III})	4.325(6)	4.313(5)	4.33
		4.381(4^{IV})	4.420(6^{IV})	4.426(5^{IV})	4.41
	I(2)···I(2)	4.377(7^{III})	4.397(6^{VII})	4.388(7^X)	4.39
(b) Angles/°					
	Cu(1)–I(1)–Cu(2)	138.8(1)	139.7(1)	139.8(1)	139.4
	Cu(1)–I(1)–Cu(1)	69.6(2^{III})	68.2(2^{VII})	68.0(2^X)	68.6
	Cu(2)–I(2)–Cu(1)	63.7(2^I)	63.0(2^I)	61.1(2^I)	}
	Cu(2)–I(2)–Cu(1)	63.2(2^{II})	60.8(2^{VI})	62.8(2^{IX})	} 62.4
	Cu(1)–I(2)–Cu(1)	68.9(2^{I,II})	66.6(2^{I,VI})	65.9(2^{I,IX})	67.1
	I(1)–Cu(1)–N	111.2(8)	106.7(7)	108.9(7)	108.9
	N–Cu(1)–I(2)	110.2(10^{IV})	113.7(8^{IV})	109.0(9^{VII})	}
	N–Cu(1)–I(2)	113.4(8^V)	111.6(10^{VIII})	113.7(7^{XI})	} 111.9
	I(1)–Cu(1)–I(2)	108.0(1^{IV})	111.4(2^{IV})	107.6(1^{IV})	}
	I(1)–Cu(1)–I(2)	107.0(2^V)	106.7(2^{VIII})	111.3(2^{XI})	} 108.7
	I(2)–Cu(1)–I(2)	106.7(2^{IV,V})	106.6(2^{IV,VIII})	106.0(2^{IV,XI})	106.4
	I(2)–Cu(2)–I(2)	114.5(2^{III})	115.5(2^{VII})	115.5(2^X)	115.2
	I(1)–Cu(2)–I(2)	103.9(2)	102.5(2)	102.4(2)	102.9

Transformations of the asymmetric unit: I $x, y, 1 + z$; II $\bar{y}, x - y, 1 + z$; III $\bar{y}, x - y, z$; IV $x, y, z - 1$; V $y - x, \bar{x}, z - 1$; VI $y - x, 1 - x, 1 + z$; VII $1 - y, 1 + x - y, z$; VIII $1 - y, 1 + x - y, z - 1$; IX $1 - x + y, 1 - x, 1 + z$; X $1 - y, x - y, z$; XI $1 - x, x - y, y - 1$.

imposed mirror symmetry element. The ligands are symmetrically disposed about this plane. Within the Cu$_2$I$_2$ core the I···I distance of 4.493(7) Å is longer than, but comparable with that of its 2,6-dimethylpyridine analogue [28] (4.414 Å), and at the lower end of the range observed for ' cubane ' structures (Table 7). This change in I···I distance might be expected to be partly a consequence of the decrease in Cu–I

bond length [2.505(9) and 2.652(8) Å] concomitant with the reduction of the co-ordination number of the copper atom from four to three.

The Cu···Cu distance in (3) is even shorter than in the 2,6-dimethylpyridine complex (2.53$_5$ vs. 2.58$_6$ Å) and represents one of the shortest Cu···Cu distances yet reported for non-anionic complexes. The shortness of this distance and the

Table 5. Non-hydrogen atom co-ordinates of [{CuI(2Me-py)}₄], (2)

Atom	x	y	z	Atom	x	y	z
I(1)	0.146 8(1)	0.195 1(1)	0	Ligand 2 ^{a}			
I(2)	0.109 0(1)	0.391 0(−)	0.130 0(3)	N(1)	0.133 5(−)	0.366 5(−)	−0.098 2(−)
I(3)	0.256 2(1)	0.243 8(−)	0.235 1(3)	C(2)	0.160 0(−)	0.424 6(−)	−0.130 1(−)
Cu(1)	0.261 1(2)	0.238 9(−)	0.070 4(5)	C(21) ^{b}	0.220 2(−)	0.451 6(−)	−0.083 6(−)
Cu(2)	0.175 2(2)	0.324 8(−)	0.002 2(6)	C(3)	0.139 2(−)	0.461 8(−)	−0.198 8(−)
Cu(3)	0.141 7(2)	0.261 4(2)	0.146 8(4)	C(4)	0.075 3(−)	0.424 7(−)	−0.229 0(−)
Ligand 1 ^{a}				Ligand 3 ^{a}			
N(1)	0.324 1(−)	0.175 9(−)	0.031 2(−)	N(1)	0.065 3(−)	0.217 3(−)	0.214 4(−)
C(2)	0.340 0(−)	0.160 0(−)	−0.045 0(−)	C(2)	0.001 3(−)	0.207 4(−)	0.180 6(−)
C(21)	0.298 5(−)	0.201 5(−)	−0.105 1(−)	C(21)	−0.030 0(−)	0.230 0(−)	0.095 0(−)
C(3)	0.380 0(−)	0.120 0(−)	−0.090 0(−)	C(3)	−0.051 3(−)	0.173 5(−)	0.222 8(−)
C(4)	0.410 0(−)	0.090 0(−)	−0.037 0(−)	C(4)	−0.037 0(−)	0.155 1(−)	0.298 9(−)
C(5)	0.410 0(−)	0.090 0(−)	0.040 0(−)	C(5)	0.031 6(−)	0.158 2(−)	0.337 3(−)
C(6)	0.365 0(−)	0.135 0(−)	0.075 0(−)	C(6)	0.077 0(−)	0.199 7(−)	0.294 9(−)

^{a} All ligand parameters estimated from difference maps and constrained in refinement. ^{b} Population: 0.5.

Table 6. Molecular core geometry of [{CuI(2Me-py)}₄], (2); distances in Å, angles in degrees

Cu(1)-I(1)	2.704(6)	Cu(2)-I(2)	2.774(8)	Cu(3)-I(3)	2.720(6)	Cu(2)···Cu(3)	2.720(10)
Cu(1)-I(3)	2.628(9)	Cu(2)-N(2)	1.99(−)	Cu(3)-N(3)	2.07(−)	I(1)···I(2)	4.515(4)
Cu(1)-N(1)	1.90(−)	Cu(3)-I(1)	2.695(6)	Cu(1)···Cu(2)	2.674(7)	I(1)···I(3)	4.453(5)
Cu(2)-I(1)	2.670(3)	Cu(3)-I(2)	2.702(5)	Cu(1)···Cu(3)	2.729(7)	I(2)···I(3)	4.508(4)

Cu(1)-I(1)-Cu(2)	59.7(1)	I(1)-Cu(1)-I(3)	113.3(2)	I(2)-Cu(2)-N(2)	100(−)
Cu(1)-I(1)-Cu(3)	60.7(2)	I(1)-Cu(1)-I(1¹)	112.4(2)	I(1)-Cu(3)-I(2)	113.5(2)
Cu(2)-I(1)-Cu(3)	60.9(2)	I(1)-Cu(1)-N(1)	102(−)	I(1)-Cu(3)-I(3)	110.7(2)
Cu(2)-I(2)-Cu(3)	59.6(2)	I(3)-Cu(1)-N(1)	112(−)	I(1)-Cu(3)-N(3)	106(−)
Cu(3)-I(2)-Cu(3¹)	61.3(1)	I(1)-Cu(2)-I(2)	112.1(2)	I(2)-Cu(3)-I(3)	112.5(2)
Cu(1)-I(3)-Cu(3)	61.3(2)	I(1)-Cu(2)-N(2)	108(−)	I(2)-Cu(3)-N(3)	106(−)
Cu(3)-I(3)-Cu(3¹)	60.9(2)	I(1)-Cu(2)-I(1¹)	114.6(1)	I(3)-Cu(3)-N(3)	108(−)

Transformation of the asymmetric unit: I ½ − y, ½ − x, z.

Table 7. Comparative data for the Cu₄I₄ core of tetrameric copper(I) iodide adducts with nitrogen, phosphorus, and arsenic ligands, (CuIL)₄

L	Ref.	Distance/Å		
		Cu-I	Cu···Cu	I···I
AsEt₃	2	2.677(1)	2.783(2)	4.424(1)
PEt₃	2	2.684(1)	2.927(2)	4.380(1)
PMePh₂	9	2.644(1)—2.733(1)	2.839(1)—3.009(1)	4.297(1)—4.488(1)
AsPh₃	10	2.667(2)—2.698(2)	2.784(3)—2.900(3)	4.314(2)—4.471(2)
py	23	2.629(4)—2.794(4)	2.619(5)—2.722(5)	4.482(3)—4.479(3)
2Me-py	^{a}	2.628(9)—2.774(8)	2.674(7)—2.729(7)	4.508(4)—4.515(4)
piperidine	24	2.696(1)—2.717(2)	2.630(2)—2.671(2)	4.488(2)—4.571(2)
NEt₃	^{b}	2.594(3)—2.820(6)	2.749(8)—3.086(7)	4.313(5)—4.426(5)

^{a} This work, [{CuI(2Me-py)}₄] (2). ^{b} This work, [{(CuI)₄(NEt₃)₃}∞] (1).

low values of Cu···Cu in nitrogen-base ligand complexes in general cannot readily be explained. The low electronegativity of the iodide, the high electron density on the nitrogen, and the absence of either d orbitals or low-lying, unoccupied π* orbitals on the aliphatic nitrogen all serve to increase the electron density on the two metal atoms, leading, presumably to an increase in Cu–Cu repulsion forces and the Cu···Cu bond length. Delocalization of electron density via the formation of a direct metal–metal bond would mitigate the non-bonding effect and arguably lead to a reduction in the Cu···Cu distance. However, the available evidence [40] suggests that copper–copper bonding, if present at all in these systems, is very weak. A further possibility is that excess of electron density on the copper can be transferred to the lowest unoccupied orbitals of the iodide atom via a 'back-bonding' effect. The resultant decrease in copper electron density,

increase in iodide electron density, and increase in the Cu–I bond order might be expected to provide a mechanism that could lead to the effects observed for this structure. The general validity of such a hypothesis does, however, depend on further testing by either the accumulation of more, relevant structural data or on the future determination of electron-density parameters by other spectroscopic methods.

The asymmetry of the Cu–I distances in complex (3) [2.505(9) and 2.652(8) Å] is considerable when compared to that of the 2,6-dimethylpyridine dimer [2.583(5) and 2.576(5) Å]; there is also an increased asymmetry in the N–Cu–I angular geometry [122.8(7) and 116.8(7)° (2,6Me₂-py derivative), cf. 131.9(12) and 106.9(12)° (present compound)]. This appears to result from the unsymmetrical interaction of the ligand methyl substituents with the two iodine atoms; because of the presence of a tetrahedral rather than a trigonal

(a)

(b)

Figure 2. (a) Unit-cell contents of complex (2) projected down c; 20% thermal ellipsoids are shown for the non-hydrogen atoms, only those for Cu and I being anisotropic. (b) A projection of the molecule of (2) showing the ligand numbering

Table 8. Non-hydrogen atom co-ordinates of [{CuI(tmpip)}₂], (3)

Atom	x	x	z
I	¼	0.146 1(4)	0.911 4(2)
Cu	¼	0.102 2(6)	1.039 1(4)
N	¼	0.233(4)	1.125(2)
C(2)	0.395(3)	0.302(3)	1.134(2)
C(21)	0.369(3)	0.383(4)	1.071(2)
C(22)	0.308(4)	0.197(4)	1.142(2)
C(3)	0.398(3)	0.378(4)	1.201(2)
C(4)	¼	0.453(5)	1.208(3)

Table 9. Molecular non-hydrogen geometry of [{Cu(tmpip)}₂], (3); distances in Å, angles in degrees

Cu–I	2.505(9)	C(2)–C(22)	1.51(5)
Cu–I^I	2.652(8)	C(2)–C(3)	1.50(5)
Cu–N	2.12(4)	C(3)–C(4)	1.47(5)
N–C(2)	1.49(4)	Cu···Cu^I	2.535(9)
C(2)–C(21)	1.50(5)	I···I^I	4.493(7)
I–Cu–I^I	121.2(3)	N–C(2)–C(21)	110(3)
I–Cu–N	131.9(12)	N–C(2)–C(22)	108(3)
I^I–Cu–N	106.9(12)	C(3)–C(2)–C(21)	116(3)
Cu–I–Cu	58.8(2)	C(3)–C(2)–C(22)	106(3)
Cu–N–C(2)	112(2)	C(21)–C(2)–C(22)	108(3)
C(2)–N–C(2)	123(3)	C(2)–C(3)–C(4)	111(4)
N–C(2)–C(3)	108(3)	C(3)–C(4)–C(3^{II})	118(4)

Transformations of the asymmetric unit: I $1 - x$, $\bar{y}$, $2 - z$; II $1 - x, y, z$.

the tetrahedral value. The ligand, within the precision of the structure determination, assumes the expected chair geometry.

While direct, quantitative comparisons are not possible with the copper(I) chloride–tricyclohexylphosphine adduct because of the change in halide, these structures assume the same configuration and indicate that the three ligands might be grouped in a growing class of molecules with similar steric requirements during the formation of such Lewis acid–base adducts.

The structure determination of complex (4) establishes the stoicheiometry to be 1 : 1 : 1 also as expected. Rather than an oligomeric structure as is found for (2) and (3), however, we observe the formation of a one-dimensional polymer with a –Cu–I–Cu–I– backbone running parallel to c, and with one CuI(acr) unit comprising the asymmetric unit of the structure. The acridine ligands form a series of parallel planes (Figure 4). We ascribe the unusual deep red colour of the complex to the presence of charge-transfer interactions between the copper and acridine. Cu···Cu and I···I are the repeat c translation [4.117(1) Å].

The structural type is the ' split-stair ' polymer, only known so far for the CuI adduct of 2,4,6-trimethylpyridine (collidine). (The terminology is derived from the obvious topological derivation of the structure from the ' stair ' or ' ribbon ' polymer observed for CuCl·py and similar compounds.) In the collidine adduct,[28] crystallizing in an orthorhombic cell, the repeat lattice distance is 4.159(1) Å, very similar to the present, with Cu–I 2.474(4) and 2.611(4) Å and angles at the Cu and I atoms of 109.7(1) and 109.7(1)°; the last values are also similar to the parameters of the present system but with a greater asymmetry in the Cu–I bond lengths.

The present complexes, together with those previously studied, suggest that a hierarchy of structural types exist in the CuXL 1 : 1 : 1 nitrogen-base systems which is dependent on the steric rather than the electronic properties of the individual ligands. Where steric hindrance is small, the ' stair polymer '

nitrogen atom, and the disposition of the ligand across the mirror plane which contains the Cu₂I₂ core, one of the iodine atoms is necessarily more crowded than the other, and in consequence exhibits a longer copper–iodine bond. The Cu–N–C(2) angle, however, does not differ significantly from
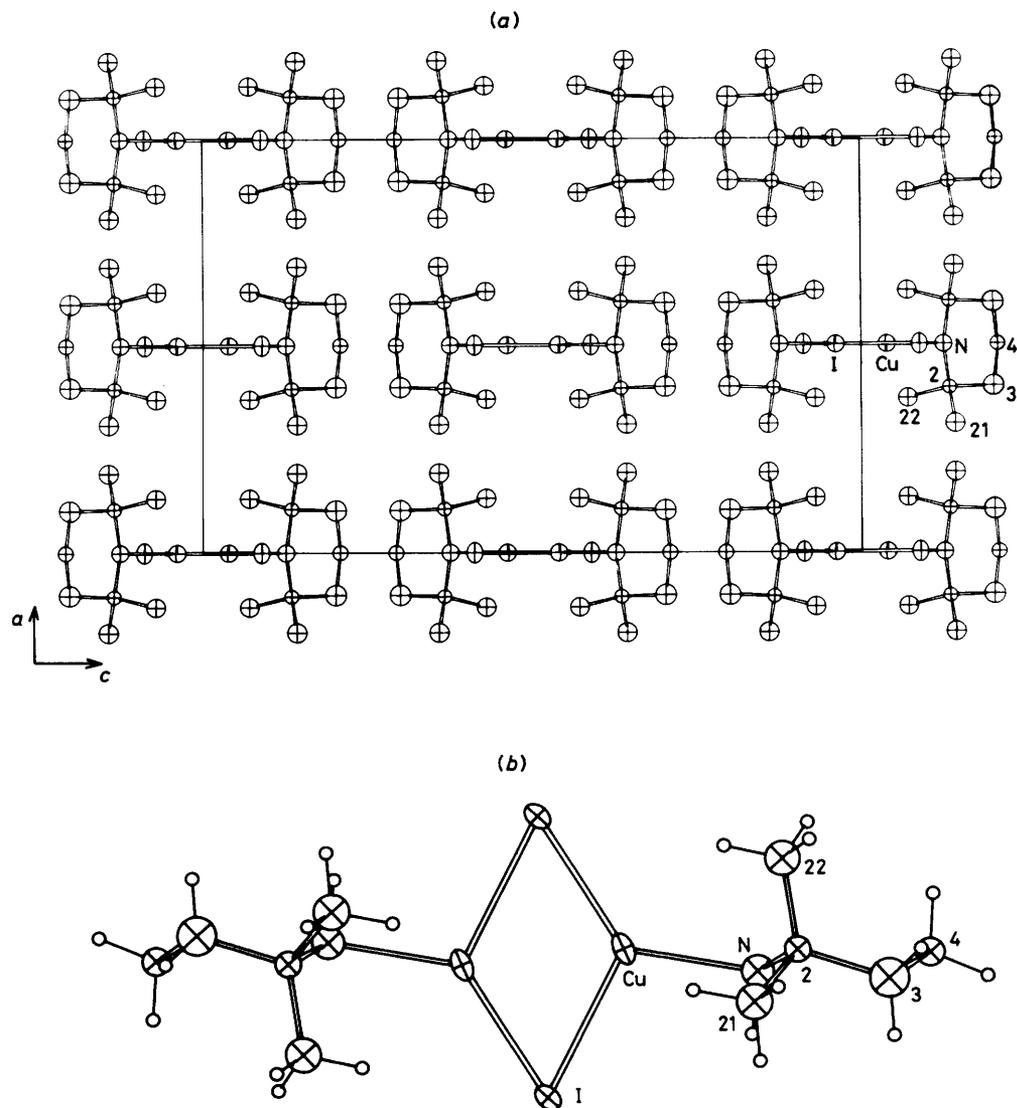
Figure 3. (a) Unit-cell contents of complex (3) projected down b. (b) A projection of the dimer of (3) normal to the Cu_2I_2 ring plane

Table 10. Non-hydrogen atom co-ordinates of $[\{CuI(acr)\}_\infty]$, (4)

Atom	x	y	z	Atom	x	y	z
Cu	0.246 39(9)	0.410 26(11)	−0.283 55(29)	C(6)	0.329 4(6)	0.821 3(9)	−0.406 2(20)
I	0.249 83(4)	0.257 14(5)	0.260 52(12)	C(7)	0.256 6(7)	0.893 6(9)	−0.217 1(24)
Ligand section A				**Ligand section B**			
N	0.246 9(5)	0.611 0(7)	−0.273 4(16)	C(1)	0.175 8(6)	0.680 7(8)	−0.094 5(19)
C(1)	0.322 1(6)	0.680 4(8)	−0.427 4(19)	C(2)	0.096 5(6)	0.608 4(10)	0.065 3(23)
C(2)	0.396 1(7)	0.608 1(10)	−0.617 6(24)	C(3)	0.023 1(7)	0.678 7(11)	0.243 2(25)
C(3)	0.472 0(7)	0.678 0(11)	−0.771 1(25)	C(4)	0.026 9(8)	0.817 3(11)	0.272 2(26)
C(4)	0.479 3(7)	0.818 5(11)	−0.748 5(26)	C(5)	0.101 6(8)	0.889 4(11)	0.126 4(26)
C(5)	0.409 4(7)	0.888 9(11)	−0.572 8(26)	C(6)	0.178 7(6)	0.822 7(9)	−0.059 5(21)

appears to occur in preference to the ' step ' structure which is the common structural type among the phosphine and arsine analogues. With increased ligand size we pass through the ' cubane ' to the dimer form, which becomes unsymmetrical as the hindrance increases further (e.g. on passing from the CuI adduct of 2,6-dimethylpyridine to that of 2,2,6,6-tetramethylpiperidine). A further degree of steric hindrance is

presumably represented by acridine, in which the hydrogen atoms in closest proximity to the metal–ligand bond are fixed and, also, with 2,4,6-trimethylpyridine in which a similar situation may obtain in consequence of the higher degree of substitution relative to 2,6-dimethylpyridine; for both of these cases, the ' split-stair polymer ' is found. The ultimate stage, the linear monomer, LCuI, has not yet been achieved.

(a)

(b)(i)

(b) (ii)

Figure 4. (a) Unit-cell contents of complex (4) projected down c. (b) A projection of the polymer of (4), (i) normal to the (CuI)$_\infty$ plane, (ii) through the bisector of I–Cu–I

Table 11. Non-hydrogen interatomic distances (Å) and angles (°) of [{CuI(acr)}$_\infty$], (4). Where two entries are given these are for ligand sections A,B respectively

Cu–I	2.573(1)		C(2)–C(3)	1.37(1), 1.38(1)
Cu–I^I	2.526(2)		C(3)–C(4)	1.41(2), 1.39(2)
Cu–N	1.990(7)		C(4)–C(5)	1.35(1), 1.36(2)
N–C(1A,B)	1.36(1), 1.36(1)		C(5)–C(6)	1.42(1), 1.42(1)
C(1)–C(2)	1.42(1), 1.43(1)		C(6)–C(7)	1.41(1), 1.40(1)
C(1)–C(6)	1.42(1), 1.43(1)			

I–Cu–I^I	107.70(5)		C(2)–C(3)–C(4)	122.7(9),
Cu–I–Cu^{II}	107.70(5)			120.8(9)
I–Cu–N	118.5(2)		C(3)–C(4)–C(5)	119.8(10),
I^I–Cu–N	133.8(2)			122.0(10)
Cu–N–C(1)	120.4(5),		C(4)–C(5)–C(6)	119.9(10),
	121.2(5)			119.6(10)
C(1A)–N–C(1B)	118.2(7)		C(1)–C(6)–C(5)	120.4(8),
N–C(1)–C(2)	118.4(8),			119.2(8)
	118.4(8)		C(1)–C(6)–C(7)	119.3(8),
N–C(1)–C(6)	122.7(7),			119.4(8)
	122.2(7)		C(5)–C(6)–C(7)	120.3(8),
C(2)–C(1)–C(6)	118.9(8),			121.4(8)
	119.4(7)		C(6A)–C(7)–C(6B)	118.2(8)
C(1)–C(2)–C(3)	118.3(9),			
	118.9(9)			

Transformations of the asymmetric unit: I $x, y, z - 1$; II $x, y, z + 1$.

metal, halide, and base are such that the bulk of the base and halide is large, but not so great as to lead to complete disruption of the tetrameric structure. In the present example the different properties of nitrogen bases compared to phosphorus or arsenic bases become apparent with co-ordination of not one but two of the 2-methylpyridine ligands at the peripheral metal positions, which thereby become four- rather than three-co-ordinate. The central copper atom is also four-co-ordinate, while the halide bridges, as usual in this type of structure, are two- and three-co-ordinate.

Of the known Cu$_4$X$_4$L$_4$ complexes with the ' step ' structure, one has a Cu$_4$I$_4$ core, namely [Cu$_4$I$_4$(PPh$_3$)$_4$],[14] and it is of interest to consider the relative Cu$_4$I$_4$ core geometry of that species (also centrosymmetric) in relation to the present complex (Table 13). Variations within the geometry of the central Cu$_2$I$_2$ ring are minor; the greatest variations, as might be expected, are to be found about the peripheral copper atom at which a change in co-ordination number occurs. The two Cu–I distances are lengthened by more than 0.1 Å and the angle between the two bonds is accordingly diminished by some 6°. In [Cu$_4$I$_4$(PPh$_3$)$_4$] the dihedral angle between the two Cu$_2$I$_2$ planes is 64.9°; in the present complex it is 65.7°.

This structure encompasses two differing copper environments: CuI$_3$L and CuI$_2$L$_2$. Comparison of the molecular geometry of the two co-ordination environments (Table 13) shows no systematic variation in Cu–I [range 2.661(2)—2.721(2) Å] or in Cu–N bond lengths [range 2.045(5)—2.059(5) Å]. The increased steric interactions of the two 2-methylpyridine ligands in the CuI$_2$L$_2$ configuration opens up the N–Cu–N angle to 124° with a concomitant reduction in the N–Cu–I angles compared with the CuI$_3$L configuration. In this context, it is of interest to note that the I–Cu–I angle is *not* reduced in comparison (Cu$_2$I$_2$L$_2$, 111; CuI$_3$L, 101, 103, and 112°); the repulsive N · · · I interactions are, presumably, countered by stronger I · · · I repulsive interactions.

The proven existence of both ' step ' and ' cubane ' structures for this ligand might suggest that the steric influence of the 2-methylpyridine molecule is slightly less than that of triphenylphosphine, for which no ' cubane ' structure has been

The CuI : L 1 : 1.5 *System* (5).—Structure determination establishes the stoicheiometry of this complex to be Cu$_2$I$_2$-(2Me-py)$_3$, the first example of metal : halide : base stoicheiometry of 1 : 1 : 1.5 to be structurally characterized in a nitrogen-base system. Unlike the complex of the same stoicheiometry previously established in the system [Cu$_2$Cl$_2$(PPh$_3$)$_3$], the present complex is tetranuclear and centrosymmetric, being disposed about a crystallographic inversion centre, and with a Cu$_4$I$_4$ core which conforms not to the ' cubane ' type structure so far observed in tetranuclear (CuXL)$_4$ species such as [{CuI(2Me-py)}$_4$] but rather the ' step ' structure which, as discussed earlier, has not been previously observed in nitrogen-base systems. In complexes of copper halides with phosphine or arsine bases, where the occurrence of the ' step ' structure has been previously established, the relative sizes of

Figure 5. (a) Unit-cell contents of complex (5) projected down c; 20% thermal ellipsoids are shown for the non-hydrogen atoms. (b) Projection of a single molecule of (5)

Table 12. Non-hydrogen atom co-ordinates of [{(CuI)₂(2Me-py)₃}₂], (5)

Atom	x	y	z	Atom	x	y	z
I(1)	0.418 89(3)	−0.086 58(4)	0.173 67(4)	Ligand 2a			
Cu(1)	0.040 05(6)	0.177 74(9)	0.129 67(9)	N(1)	0.301 4(3)	0.194 7(5)	0.475 8(5)
I(2)	0.243 34(3)	0.358 20(4)	0.166 43(4)	C(2)	0.406 3(4)	0.281 9(6)	0.546 8(6)
Cu(2)	0.247 74(6)	0.113 41(9)	0.245 78(8)	C(21)	0.488 0(5)	0.295 5(9)	0.449 2(8)
				C(3)	0.435 8(5)	0.354 2(7)	0.699 7(7)
Ligand 1				C(4)	0.358 8(5)	0.334 8(7)	0.786 5(6)
N(1)	−0.051 7(4)	0.265 3(5)	0.266 2(5)	C(5)	0.253 2(5)	0.242 7(7)	0.716 7(6)
C(2)	−0.083 8(5)	0.384 6(7)	0.261 0(7)	C(6)	0.226 8(4)	0.176 1(7)	0.562 1(6)
C(21)	−0.060 8(6)	0.448 5(8)	0.138 6(8)				
C(3)	−0.139 7(5)	0.446 7(7)	0.366 9(8)	Ligand 2b			
C(4)	−0.158 0(6)	0.385 3(8)	0.479 4(7)	N(1)	0.318 5(4)	−0.013 7(5)	0.103 5(5)
C(5)	−0.125 5(6)	0.262 5(8)	0.483 0(7)	C(2)	0.344 6(5)	−0.131 4(7)	0.126 5(7)
C(6)	−0.073 8(5)	0.207 6(7)	0.377 6(7)	C(21)	0.338 1(7)	−0.159 9(9)	0.271 5(9)
				C(3)	0.374 2(6)	−0.228 6(8)	0.014 8(9)
				C(4)	0.379 1(6)	−0.203 8(9)	−0.120 1(9)
				C(5)	0.357 6(6)	−0.081 2(9)	−0.140 0(7)
				C(6)	0.324 6(5)	0.009 7(7)	−0.030 0(7)

isolated with a Cu₄I₄ molecular core, a hypothesis supported by the presence of three-co-ordinate copper at the periphery of the tetrameric copper(I) iodide–triphenylphosphine step structure compared to the four-co-ordinate species found in this complex. This view is countered somewhat, however, by

the reported synthesis of the tetrakis(triphenylphosphine) complex [Cu(PPh₃)₄]ClO₄;[41] attempts to prepare the analogous 2-methylpyridine complex have resulted only in the three-co-ordinate species, [CuL₃]ClO₄.[42]

Preliminary structural results on the structure of [Cu-

Table 13. Molecular non-hydrogen geometry of [{(CuI)$_2$(2Me-py)$_3$}$_2$], (5); distances in Å, angles in degrees

(a) The Cu$_4$I$_4$N$_4$ core; primed atoms are generated by the intramolecular inversion centre. Values in square brackets are for the Cu$_4$I$_4$ core of [Cu$_4$I$_4$(PPh$_3$)$_4$] ('step' structure)

Cu(1)-I(1)	2.719(2) [2.728(2)]	Cu(2)-I(1)	2.713(2) [2.591(2)]
Cu-I(2)	2.661(2) [2.620(2)]	Cu(2)-I(2)	2.694(2) [2.527(2)]
Cu(1)-I(1')	2.721(2) [2.707(2)]	Cu(2)-N(2a)	2.050(4)
Cu(1)-N(1)	2.045(5)	Cu(2)-N(2b)	2.059(5)

I(1)-Cu(1)-I(1')	101.04(4) [102.45(7)]	Cu(2)-I(1)-Cu(1')	109.35(3) [108.29(7)]
I(1)-Cu(1)-N(1)	106.8(2)	Cu(1)-I(2)-Cu(2)	68.46(5) [66.80(7)]
I(1)-Cu(1)-I(2)	112.07(6) [110.10(8)]	I(1)-Cu(2)-I(2)	111.23(5) [117.85(9)]
I(1')-Cu(1)-N(1)	118.1(1)		
I(1')-Cu(1)-I(2)	103.02(4) [104.20(7)]	I(1)-Cu(2)-N(2a)	108.5(1)
		I(1)-Cu(2)-N(2b)	98.5(1)
N(1)-Cu(1)-I(2)	115.1(1)	I(2)-Cu(2)-N(2a)	103.9(2)
Cu(1)-I(1)-Cu(2)	67.34(4) [64.34(7)]	I(2)-Cu(2)-N(2b)	109.7(2)
Cu(1)-I(1)-Cu(1')	78.97(4) [77.55(7)]	N(2a)-Cu(2)-N(2b)	124.9(2)

(b) The ligand geometries

	Ligand		
	1	2a	2b
N(1)-C(2)	1.339(9)	1.351(6)	1.335(10)
N(1)-C(6)	1.353(9)	1.359(8)	1.353(9)
C(2)-C(3)	1.417(10)	1.376(8)	1.391(10)
C(2)-C(21)	1.487(11)	1.504(10)	1.481(12)
C(3)-C(4)	1.374(11)	1.386(10)	1.369(13)
C(4)-C(5)	1.370(13)	1.368(8)	1.345(14)
C(5)-C(6)	1.351(11)	1.383(8)	1.374(11)
Cu-N(1)-C(2)	124.2(4)	122.7(4)	123.2(5)
Cu-N(1)-C(6)	118.3(5)	119.4(3)	118.3(5)
C(2)-N(1)-C(6)	117.3(6)	117.5(4)	117.8(6)
N(1)-C(2)-C(3)	121.2(6)	121.5(6)	120.8(7)
N(1)-C(2)-C(21)	117.9(6)	116.2(5)	118.9(6)
C(21)-C(2)-C(3)	120.9(7)	122.3(5)	120.3(7)
C(2)-C(3)-C(4)	118.9(7)	120.5(5)	120.6(8)
C(3)-C(4)-C(5)	119.3(7)	118.6(5)	118.4(7)
C(4)-C(5)-C(6)	118.8(7)	118.8(6)	119.7(8)
C(5)-C(6)-N(1)	124.4(7)	123.2(5)	122.6(7)

(PPh$_3$)$_4$]ClO$_4$,[43] however, reveal that the ligand system is highly distorted with one ligand forming a weaker bond than the others.

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