Fluorescent Copper(I) Complexes: an *X*-Ray Diffraction Study of Complexes of Copper(I) Iodide and Pyridine Derivatives of Rhombic, $[Cu_2I_2(3Me\text{-}py)_4]$, and Polymeric Structure, $[\{CuI(2Me\text{-}py)\}_\infty]$ and $[\{CuI(2,4Me_2\text{-}py)\}_\infty]$†

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Three previously unreported forms of complexes of CuI with a pyridine derivative have been isolated and examined by single-crystal *X*-ray techniques: $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**) (3Me-py = 3-methylpyridine), stoicheiometry 1 : 1 : 2, monoclinic space group $P2_1$, a = 7.912(2), b = 19.390(6), c = 8.774(2) Å, β = 102.22(2)°, Z = 2, R = 0.047 for 2 072 observed reflections, crystallizes with isolated rhombohedra of Cu_2I_2, each Cu being co-ordinated to two ligand molecules *via* the nitrogen atoms; $[\{CuI(2Me\text{-}py)\}_\infty]$ (**2**) and $[\{CuI(2,4Me_2\text{-}py)\}_\infty]$ (**3**) (2,4Me$_2$-py = 2,4-dimethylpyridine), stoicheiometries 1 : 1 : 1, (**2**), monoclinic space group $P2_1/a$, a = 11.834(5), b = 14.914(6), c = 4.381(2) Å, β = 93.80(4)°, Z = 4, R = 0.078 for 1 082 reflections, (**3**), triclinic space group $P\bar{1}$, a = 11.648(8), b = 4.328(3), c = 10.198(4) Å, α = 77.64(5), β = 68.45(4), γ = 104.25(5)°, R = 0.063 for 1 731 reflections. Both (**2**) and (**3**) crystallize as edge-sharing Cu_2I_2 rhombs, with each copper atom bound to three iodide atoms and the nitrogen atom of a molecule of the Lewis base.

The complexes formed by copper(I) iodide with pyridine and its derivatives are notable for the variety of stoicheiometries and structural formats displayed.[1,2] Stoicheiometries of Cu:I:ligand of 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2, and 1:1:3 have been observed. Normally, complexes of stoicheiometry 1:1:3 are monomers,[3,4] those of stoicheiometry 1:1:2 are monomers[4] or rhombs,[4–6] and those of stoicheiometry 1:1:1.5 are chairs,[7] but complexes of stoicheiometry 1:1:1 may crystallize as cubes,[3,7–10] polymeric pleated sheets,[8] or rhombs.[2] The complex $[(CuI)_2(2Me\text{-}py)]$ (2Me-py = 2-methylpyridine) of stoicheiometry 1:1:0.5 is a polymer of chair forms linked side by side.[11]

Our interest in these complexes[12,13] focuses on families of complexes formed by CuI with a single ligand, varying in stoicheiometry or structural format and also in emission characteristics. While many compounds of this type emit in the visible range in the solid state, some complexes emit independent of temperature while others display temperature-dependent emission (thermochromism).[14–18] From a comparison of the structural and emission characteristics for members of these isoligand families, we are able to identify aspects of structure which give rise to components of the emission spectra.[12,13]

For example, CuI forms several solid-state complexes with quinoline. The complex $[Cu_2I_2(quin)_4]$ is of rhombic structure with a non-interactive Cu–Cu separation across the rhomb [3.364(5) Å] and packing of quinoline ligands in mutually perpendicular planes in the unit cell; and $[Cu_4I_4(quin)_4]$, which forms a variation of the chair structure with copper atoms grouped in two close pairs [Cu–Cu 2.558(10) Å], bridged by bi- and tri-dentate iodide atoms.[13] Ligated quinoline molecules project from the CuI framework in close [3.302(11) Å] and parallel planes. The packing of the complexes in the cell continues this parallel stacking of aromatic rings. The crystalline rhomb exhibits a broad, featureless emission at both room and low temperatures (λ 620 nm), a phenomenon assigned to metal-to-ligand charge-transfer (m.l.c.t.) excitation. The room-temperature emission of the second form is also broad and featureless (λ 625 nm), but the low-temperature spectrum (15 K) shows the fine structure of the spectrum of the quinoline ligand, which is assigned to interligand π—π^* transition phenomena. This fine structure does not appear for the rhombic form where the ligands are not closely packed.[13]

Another comparison study of the emission of the $[CuI(py)_x]$ polymeric pleated sheet and the $[Cu_4I_4(py)_4]$ cube[19] showed that the former [Cu–Cu 2.875(2) Å)] emits at 449 nm (due to metal-to-ligand, $d^{10} \longrightarrow d^9\ \pi^*$ excitation) whereas the latter [Cu–Cu 2.691(5) Å] emits at 436 nm due to m.l.c.t. and at 615 nm, assigned to the $d^{10} \longrightarrow d^9s^1$ transition.

Previously reported CuI(L) complexes for which structural results are known include $[Cu_4I_4(py)_4]$ (cubic),[10] $[\{CuI(py)\}_x]$ (polymer),[8] and $[Cu_2I_2(py)_4]$ rhomb.[6] Polymeric pleated sheets where Cl or Br replaces I are also known.[2] The $[Cu_4I_4(2Me\text{-}py)_4]$ (cube),[7] $[Cu_4I_4(2Me\text{-}py)_6]$ (chair),[7] $[Cu_2I_2(2Me\text{-}py)_4]$ (rhomb),[4] and $[(CuI)_2(2Me\text{-}py)]$ (polymeric chair form)[11] are known, as well as the bromide analogue[7] of cubic format and the chloro and bromo rhombic forms.[5] The complexes $[CuI(3Me\text{-}py)_3]$, a monomer,[3] and $[Cu_4I_4(3Me\text{-}py)_4]$, a cube,[9] have been reported. Complexes with 2,4-dimethylpyridine are known of rhombic format $[Cu_2X_2(2,4Me_2\text{-}py)_4]$ (X = I, Br, or Cl).[5] The two known complexes of 2,6-dimethylpyridine involve trigonal, three-co-ordinate copper $[CuI(2,6Me_2\text{-}py)_2]$ (a monomer)[4] and $[Cu_2I_2(2,6Me_2\text{-}py)_2]$ (a rhomb).[2] The complex $[CuI(2,4,6Me_3\text{-}py)]$ forms a single-strand polymer involving three-co-ordinate copper atoms ligated to a single pyridine ligand.[2]

Variables in the synthesis of these complexes include the stoicheiometry of the reagents, temperature of crystallization, and the solvent of reaction. In general, large excesses of ligand such as Cu:I:L = 1:1:10 tend to favour formation of 1:1:3 monomeric and 1:1:2 rhombic forms, as do high temperatures of crystallization. Most of the cubic $[Cu_4I_4L_4]$ solids result from crystallization at −30 °C. Common synthetic procedures are: (1) addition of CuI to an excess of the hot ligand (liquid ligand) with further heating until crystallization ensues; (2) addition of CuI to a stoicheiometric amount of ligand in acetone or ethanol with crystallization at −30 °C; and (3) dissolution of CuI in saturated KI to which a stoicheiometric amount of

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† Di-μ-iodo-bis[bis(3-methylpyridine)copper(I)], poly[iodo(2-methylpyridine)copper(I)], and poly[(2,4-dimethylpyridine)iodocopper(I)].

Supplementary data available (No. SUP 56625, 8 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

ligand is added in an organic solvent. We have used method (3) followed by room-temperature crystallization to produce three new members of the known families of complexes, $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**), a rhomb, and the polymeric forms $[\{CuI(2Me\text{-}py)\}_x]$ (**2**) and $[\{CuI(2,4Me_2\text{-}py)\}_x]$ (**3**). Forms (**2**) and (**3**) display solid-state fluorescent thermochromism whereas the emission of (**1**) is visually the same at room temperature (r.t.) and 15 K.

Experimental

All chemicals used were freshly purchased reagent-grade materials used without further purification.

$[Cu_2I_2(3Me\text{-}py)_4]$ (**1**).—To a suspension of CuI (0.95 g, 5 mmol) in warm acetone (25 cm^3) was added a saturated solution of KI with stirring until a clear solution was obtained. To this solution, 3-methylpyridine (0.93 g, 10 mmol) in acetone (20 cm^3) was added and the mixture refluxed for 12 h, then left to crystallize at room temperature. Yellow needle-shaped crystals were formed after 24 h. These were collected by filtration.

$[\{CuI(2Me\text{-}py)\}_\infty]$ (**2**).—A saturated solution of KI in water was added to a suspension of CuI (0.95 g, 5 mmol) in acetone (25 cm^3) until a clear solution was obtained. 2-Methylpyridine (0.93 g, 10 mmol) was dissolved in acetone (25 cm^3) and added. The mixture was heated under reflux for 24 h and then allowed to cool to room temperature. The long colourless needle-shaped crystals formed were collected by filtration.

Table 1. Crystal data for $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**), $[\{CuI(2Me\text{-}py)\}_\infty]$ (**2**), and $[\{CuI(2,4Me_2\text{-}py)\}_\infty]$ (**3**)

	(**1**)	(**2**)	(**3**)
Formula	$C_{24}H_{28}Cu_2I_2N_4$	C_6H_7CuIN	C_7H_9CuIN
M	763.41	283.58	297.60
a/Å	7.912(2)	11.834(5)	11.648(8)
b/Å	19.390(6)	14.914(6)	4.328(3)
c/Å	8.774(2)	4.381(2)	10.198(4)
α/°	90.0	90.0	77.64(5)
β/°	102.22(2)	93.80(4)	68.45(4)
γ/°	90.0	90.0	104.25(5)
U/Å^3	1 315.4(6)	771.4(6)	436.21(46)
F(000)	728	528	280
μ(Mo-K)/cm^{-1}	39.63	67.13	59.413
λ(Mo-K)/Å	0.710 69	0.710 69	0.710 69
D_c/g cm^{-3}	1.902	2.44	2.265
Z	2	4	2
Space group	$P2_1$	$P2_1/a$	$P\bar{1}$

$[\{CuI(2,4Me_2\text{-}py)\}_\infty]$ (**3**).—To a suspension of CuI (0.76 g, 4 mmol) in acetone (10 cm^3) was added a saturated solution of KI in water with stirring until a clear solution was obtained. 2,4-Dimethylpyridine (0.43 g, 4 mmol) in acetone (25 cm^3) was added and the solution stirred for 12 h whereupon white needles were observed. The mixture was allowed to stand at room temperature undisturbed until crystallization was complete.

Crystallography.—Crystals of complexes (**1**)—(**3**) were mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions (Table 1) were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.710 69 Å). Data [3 229 (**1**), 3 060 (**2**), and 4 229 (**3**) reflections] were collected at room temperature using a variable scan rate, a θ—2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections

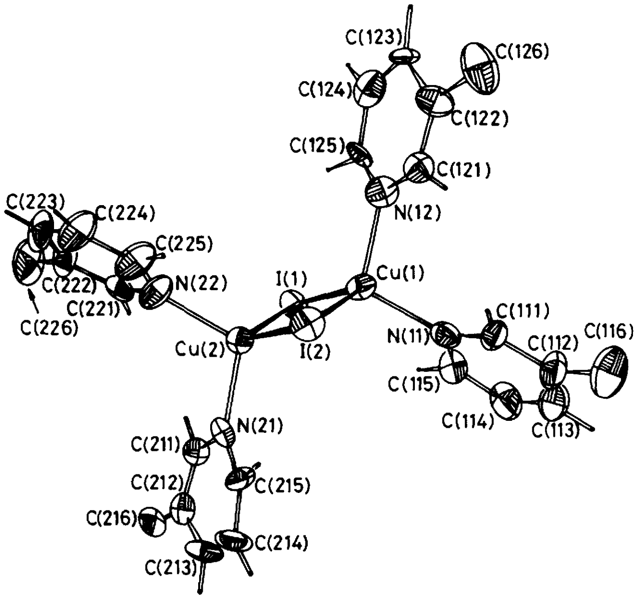

Figure 1. View of $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**)

Table 2. Positional parameters for $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**)

Atom	x	y	z
I(1)	0.444 0(1)	0.328 7(1)	0.294 4(1)
I(2)	0.944 8(2)	0.238 2(1)	0.213 4(1)
Cu(1)	0.780 2(3)	0.344 3	0.315 6(3)
Cu(2)	0.608 9(3)	0.224 9(1)	0.193 1(3)
N(11)	0.821 1(20)	0.433 3(9)	0.193 2(18)
N(12)	0.896 0(20)	0.359 4(9)	0.548 2(18)
N(21)	0.488 7(18)	0.212 8(8)	−0.037 2(17)
N(22)	0.567 8(21)	0.137 5(9)	0.317 1(18)
C(111)	0.981 9(27)	0.453 3(12)	0.184 1(26)
C(112)	1.012 9(30)	0.511 7(12)	0.094 2(27)
C(113)	0.871 8(34)	0.546 4(12)	0.017 6(29)
C(114)	0.709 3(32)	0.527 7(13)	0.027 6(31)
C(115)	0.680 5(26)	0.472 2(11)	0.117 7(27)
C(116)	1.196 9(37)	0.528 9(15)	0.085 9(37)
C(121)	1.068 1(23)	0.367 1(11)	0.588 9(22)
C(122)	1.157 2(23)	0.373 9(10)	0.737 9(21)
C(123)	1.059 2(26)	0.369 2(10)	0.864 8(19)
C(124)	0.885 4(32)	0.363 8(13)	0.813 3(29)
C(125)	0.808 7(23)	0.357 6(10)	0.656 0(21)
C(126)	1.354 6(31)	0.382 3(15)	0.785 6(34)
C(211)	0.315 4(24)	0.208 6(11)	−0.084 9(23)
C(212)	0.228 7(25)	0.199 5(10)	−0.238 2(22)
C(213)	0.328 4(26)	0.203 1(11)	−0.342 0(22)
C(214)	0.500 5(28)	0.208 4(12)	−0.308 1(23)
C(215)	0.583 0(26)	0.211 2(11)	−0.151 3(21)
C(216)	0.030 7(25)	0.192 0(12)	−0.279 5(25)
C(221)	0.407 4(28)	0.120 6(11)	0.336 5(23)
C(222)	0.370 3(32)	0.063 3(12)	0.412 1(28)
C(223)	0.510 0(45)	0.019 8(13)	0.475 0(35)
C(224)	0.674 4(35)	0.036 6(15)	0.458 2(33)
C(225)	0.694 0(30)	0.096 5(14)	0.382 9(29)
C(226)	0.183 5(35)	0.047 1(16)	0.424 5(36)

showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space-group-forbidden data [(**1**) and (**2**)], 2 072 (**1**), 1 082 (**2**), and 1 731 (**3**) reflections were considered observed [$I > 3.0\sigma(I)$]. The structures were solved using MULTAN 80[20] to locate the heavy-atom positions. Successive cycles of least-squares refinement followed by Fourier difference synthesis allowed location of the remainder of the non-hydrogen atoms.

Refinement of scale-factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Positions for those hydrogen atoms bonded to atoms of the aromatic rings were calculated for complexes (**1**) and (**2**). For (**3**), all hydrogen atoms were apparent from a final Fourier difference synthesis. Hydrogen-atom positions and assigned isotropic thermal parameters were included in the final cycles of refinement[21] but were held constant. The final cycle of refinement [function minimized $\Sigma(|F_o| - |F_c|)^2$] led to final agreement factors of $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100 = 0.047$ (**1**), 0.078 (**2**), and 0.063 (**3**). Anomalous dispersion corrections were made for Cu and I. Scattering factors were taken from ref. 22. Unit weights were used until the final cycles of refinement when $w = 1/F$ was introduced; $R' = 0.052$ (**1**), 0.099 (**2**), and 0.073 (**3**).

Table 3. Positional parameters for $[\{CuI(2Me\text{-}py)\}_\infty]$ (**2**)

Atom	*x*	*y*	*z*
Cu	0.527 0(3)	0.073 4(2)	0.338 2(9)
I	0.652 1(1)	0.028 7(1)	0.837 8(4)
N	0.502(2)	0.210(1)	0.313(6)
C(1)	0.416(2)	0.251(2)	0.441(6)
C(2)	0.402(3)	0.346(2)	0.400(8)
C(3)	0.478(4)	0.392(2)	0.235(9)
C(4)	0.566(3)	0.349(2)	0.112(8)
C(5)	0.577(2)	0.258(2)	0.163(7)
C(6)	0.337(3)	0.199(2)	0.620(8)

Table 4. Positional parameters for $[\{CuI(2,4Me_2\text{-}py)\}_\infty]$ (**3**)

Atom	*x*	*y*	*z*
I	0.868 7(1)	0.009 5(2)	0.197 3(1)
Cu	0.971 0(2)	0.352 8(5)	−0.095 4(2)
N	0.841 8(11)	0.306 2(30)	−0.189 7(12)
C(1)	0.725 5(14)	0.339 5(33)	−0.137 4(15)
C(2)	0.642 7(16)	0.292 5(39)	−0.205 6(18)
C(3)	0.684 2(15)	0.226 3(39)	−0.339 3(16)
C(4)	0.801 7(16)	0.189 6(43)	−0.393 1(17)
C(5)	0.879 0(15)	0.224 6(44)	−0.318 9(16)
C(12)	0.686 1(16)	0.427 9(44)	0.003 5(19)
C(32)	0.594 3(21)	0.181 2(53)	−0.416 1(22)

Discussion

The complex $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**) crystallizes as a rhomb of alternating copper and iodide atoms with two 3-methylpyridine groups ligated to each copper atom (Figure 1, Tables 2 and 3). While Cu_2I_2 rhombs are commonly observed, they display considerable variation in copper–copper separation, within the range 2.535(9)—3.576(2) Å if stoicheiometries of Cu:I:L = 1:1:1 and 1:1:2 are considered, as well as P or N donor ligands. It has been suggested that larger ligands cause an opening of the L–Cu–L angle accompanied by narrowing of the I–Cu–I angle and a resultingly larger Cu–Cu separation. The known structures with L = pyridine or pyridine derivatives display the expected decrease in Cu–Cu separation with ligands of smaller bulk: thus 3.024(2) Å is observed for L = 2,9-dimethyl-1,10-phenanthroline, 3.083(3) Å when L = 2-methylpyridine, 2.699(5) Å when L = pyridine, and 2.586(5) Å is the Cu–Cu separation in the $[Cu_2I_2L_2]$ system with L = 2,6-dimethylpyridine (one ligand per copper atom).

However, the flexibility of these systems is demonstrated by the variation of Cu–Cu distances seen in three solid-state observations of the $[Cu_2I_2(quin)_4]$ rhombohedra which differ in the presence and identity of included molecules of solvent. Without included solvent, Cu–Cu is 3.364(5) Å.[10] With MeCN in the crystalline lattice,[23] Cu–Cu is 3.137(2) Å, which narrows to 2.866(3) Å when the included organic molecule is quinoline.[4]

Complex (**1**) with a value of 2.782(3) Å thus displays an intermediate Cu–Cu separation. The rhombohedron is planar (standard deviation 0.003 Å) and displays a non-crystallographic centre of symmetry. The two rhombohedra per unit cell are thus related by $-x, \frac{1}{2} + y, -z$ of space group $P2_1$. A

Table 5. Bond angles (°) and distances (Å) for $[Cu_2I_2(3Me\text{-}py)_4]$ (**1**)

I(1)–Cu(1)	2.644(3)	C(124)–C(125)	1.39(3)	Cu(1)–I(1)–Cu(2)	63.3(1)	C(123)–C(122)–C(126)	118(2)
I(1)–Cu(2)	2.652(4)	Cu(2)–N(21)	2.06(1)	Cu(1)–I(2)–Cu(2)	62.9(1)	C(122)–C(123)–C(124)	114(2)
I(2)–Cu(1)	2.688(3)	Cu(2)–N(22)	2.08(2)	I(1)–Cu(1)–I(2)	116.1(1)	C(123)–C(124)–C(125)	122(2)
I(2)–Cu(2)	2.638(3)	N(21)–C(211)	1.35(2)	I(1)–Cu(1)–N(11)	108.7(4)	C(124)–C(125)–N(12)	123(2)
Cu(1)–N(11)	2.09(2)	N(21)–C(215)	1.37(3)	I(1)–Cu(1)–N(12)	108.3(5)	Cu(2)–N(21)–C(211)	123(1)
Cu(1)–N(12)	2.07(2)	C(211)–C(212)	1.39(3)	I(2)–Cu(1)–N(11)	108.7(5)	Cu(2)–N(21)–C(215)	121(1)
N(11)–C(111)	1.35(3)	C(212)–C(213)	1.33(3)	I(2)–Cu(1)–N(12)	107.0(5)	C(211)–N(21)–C(215)	117(2)
N(11)–C(115)	1.39(3)	C(212)–C(216)	1.54(3)	N(11)–Cu(1)–N(12)	107.8(6)	N(21)–C(211)–C(212)	125(2)
C(111)–C(112)	1.43(3)	C(213)–C(214)	1.34(3)	Cu(1)–N(11)–C(111)	121(1)	C(211)–C(212)–C(213)	115(2)
C(112)–C(113)	1.35(3)	C(214)–C(215)	1.39(3)	Cu(1)–N(11)–C(115)	120(1)	C(211)–C(212)–C(216)	121(2)
C(112)–C(116)	1.51(4)	N(22)–C(221)	1.36(3)	C(111)–N(11)–C(115)	119(2)	C(213)–C(212)–C(216)	125(2)
C(113)–C(114)	1.35(4)	N(22)–C(225)	1.31(3)	N(11)–C(111)–C(112)	122(2)	C(212)–C(213)–C(214)	125(2)
C(114)–C(115)	1.38(4)	C(221)–C(222)	1.36(3)	C(111)–C(112)–C(113)	116(2)	C(213)–C(214)–C(215)	118(2)
N(12)–C(121)	1.34(2)	C(222)–C(223)	1.40(4)	C(111)–C(112)–C(116)	119(2)	C(214)–C(215)–N(21)	121(2)
N(12)–C(125)	1.28(3)	C(222)–C(226)	1.54(4)	C(113)–C(112)–C(116)	125(2)	Cu(2)–N(22)–C(221)	121(1)
C(121)–C(122)	1.35(2)	C(223)–C(224)	1.38(5)	C(112)–C(113)–C(114)	122(2)	Cu(2)–N(22)–C(225)	122(2)
C(122)–C(123)	1.49(3)	C(224)–C(225)	1.36(4)	C(113)–C(114)–C(115)	121(2)	C(221)–N(22)–C(225)	116(2)
C(122)–C(126)	1.54(3)	Cu(1)–Cu(1)	2.782(3)	C(114)–C(115)–N(11)	119(2)	N(22)–C(221)–C(222)	124(2)
C(123)–C(124)	1.36(3)			Cu(1)–N(12)–C(121)	119(1)	C(221)–C(222)–C(223)	117(2)
				Cu(1)–N(12)–C(125)	122(1)	C(221)–C(222)–C(226)	121(2)
				C(121)–N(12)–C(125)	119(2)	C(223)–C(222)–C(226)	123(2)
				N(12)–C(121)–C(122)	124(2)	C(222)–C(223)–C(224)	120(3)
				C(121)–C(122)–C(123)	118(2)	C(223)–C(224)–C(225)	117(2)
				C(121)–C(122)–C(126)	124(2)	C(224)–C(225)–N(22)	125(2)

consideration of the co-ordinates of the copper atoms shows that a movement of the origin so as to place the rhombs on centres of symmetry in centric space group $P2_1/m$ is not consistent with the packing of the rhombs in the unit-cell volume.

One can view the three known complexes of copper(I) iodide and 3-methylpyridine, [Cu$_4$I$_4$(3Me-py)$_4$] (cube), [Cu$_2$I$_2$(3Me-py)$_4$] (**1**) (rhomb), and [CuI(3Me-py)$_3$] (monomer), as a series in which the number of iodide atoms ligated to a copper atom decreases from 3 to 2 to 1 while the number of Cu–N bonds increases from 1 to 2 to 3. Within the series, the average Cu–I distances are 2.694(3), 2.655(3), and 2.710(3) Å respectively. The corresponding average Cu–N distances are 2.04(3), 2.07(2), and 2.046(14) Å. Thus the Cu–I and Cu–N bond distances display no clearly discernible trends. Copper displays tetrahedral geometry in all three structures, with ranges of angles at copper of 98.7—118.0, 107.0(5)—116.1(1), and 105.9(2)—112.8(4)° respectively. Thus the environment at any single copper atom is relatively constant in the series, with the exception of the non-bonded Cu $\cdots$ Cu distances (av.) of 2.686 Å in the cube and 2.782(3) Å in the rhomb. There are no close Cu–Cu interactions in the monomer.

The complexes isolated from saturated aqueous potassium iodide solutions with copper(I) iodide and 2-methylpyridine or 2,4-dimethylpyridine are polymeric pleated sheets of stoicheiometry 1:1:1 [{CuI(2Me-py)}$_x$] (**2**) and [{CuI(2,4Me$_2$-py)}$_x$] (**3**). They crystallize with rhombs of alternating copper and iodide atoms, sharing edges in infinite series to form polymeric pleated sheets with one nitrogen-donor group ligated to each copper atom, the ligands projecting away from the polymeric chains (Figures 2 and 3, Tables 4—7). Three different Cu–I distances are observed in each pleated sheet, 2.646(4), 2.681(4), 2.806(4) (**2**) and 2.644(3), 2.675(2), 2.782(3) Å (**3**), with the distances at the folds of the polymeric sheets being the intermediate ones and those at the edge of the pleated sheets alternating between longer and shorter distances. Thus every other rhomb is formed of four short Cu–I distances [av. side 2.664(4) (**2**); 2.660(3) Å (**3**)] and these rhombs are linked to adjacent ones by longer Cu–I distances [2.806(4) (**2**); 2.782(3) Å (**3**)].

The Cu–Cu distances across the rhombs alternate between short [2.708(5) (**2**), 2.734(4) Å (**3**)] and long [3.706(5) (**2**),

Table 6. Bond angles (°) and distances (Å) for [{CuI(2Me-py)}$_\infty$] (**2**)

Cu(1)–Cu(1^{II})	2.708(5)	C(1)–C(2)	1.44(4)
Cu(1)–Cu(1^{IV})	3.706(5)	C(1)–C(6)	1.48(4)
Cu(1)–I(1)	2.646(4)	C(2)–C(3)	1.38(6)
Cu(1)–I(1^{I})	2.806(4)	C(3)–C(4)	1.36(6)
Cu(1)–I(1^{II})	2.681(4)	C(4)–C(5)	1.39(4)
Cu(1)–N(1)	2.07(2)	C(5)–N(1)	1.33(4)
N(1)–C(1)	1.34(4)		

I(1)–Cu(1)–I(1^{I})	106.9(1)	Cu(1)–N(1)–C(5)	117(2)
I(1)–Cu(1)–I(1^{II})	118.9(1)	N(1)–C(1)–C(2)	119(3)
I(1^{I})–Cu(1)–I(1^{II})	95.1(1)	N(1)–C(1)–C(6)	121(2)
I(1)–Cu(1)–N(1)	111.3(7)	C(2)–C(1)–C(6)	120(3)
I(1^{I})–Cu(1)–N(1)	105.8(7)	C(1)–C(2)–C(3)	119(3)
I(1^{II})–Cu(1)–N(1)	116.1(6)	C(2)–C(3)–C(4)	121(3)
Cu(1)–I(1)–Cu(1^{II})	61.1(1)	C(3)–C(4)–C(5)	118(3)
Cu(1)–I(1)–Cu(1^{III})	106.1(1)	C(4)–C(6)–N(1)	123(3)
Cu(1^{II})–I(1)–Cu(1^{III})	84.9(1)	C(5)–N(1)–C(1)	121(2)
Cu(1)–N(1)–C(1)	122(2)		

Symmetry transformations: I $x, y, -1 + z$; II $1 - x, -y, 1 - z$; III $x, y, 1 + z$; IV $1 - x, -y, -z$.

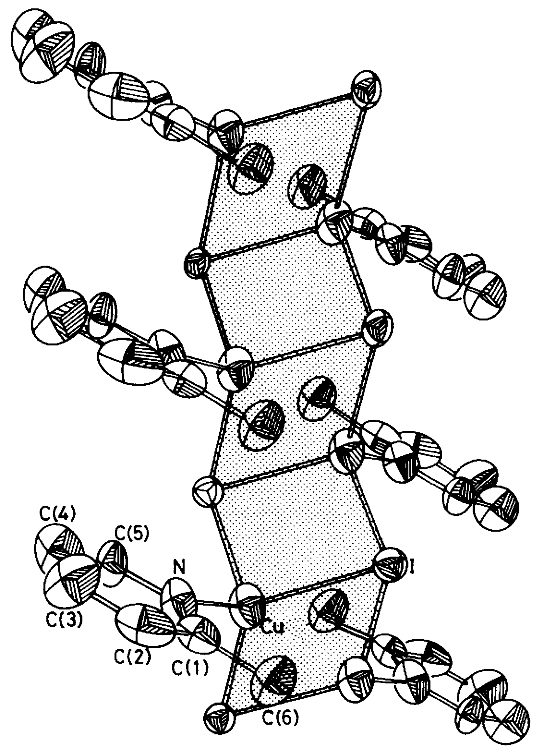

Figure 2. View of [{CuI(2Me-py)}$_x$] (**2**) showing polymeric repeat

Table 7. Bond distances (Å) and angles (°) for [{CuI(2,4Me$_2$-py)}$_\infty$] (**3**)

I(1)–I(1^{I})	4.328(3)	Cu(1)–N(1)	2.05(2)	C(2)–H(2)	0.79(2)	C(12)–H(121)	1.02(2)
I(1)–I(1^{II})	4.096(3)	N(1)–C(1)	1.32(2)	C(3)–C(4)	1.34(3)	C(12)–H(122)	0.97(2)
I(1)–Cu(1)	2.675(2)	N(1)–C(5)	1.38(2)	C(3)–C(32)	1.52(3)	C(12)–H(123)	0.94(2)
I(1)–Cu(1^{III})	2.644(3)	C(1)–C(2)	1.38(3)	C(4)–C(5)	1.37(3)	C(32)–H(321)	0.98(2)
I(1)–Cu(1^{II})	2.782(3)	C(1)–C(12)	1.50(2)	C(4)–H(4)	0.96(2)	C(32)–H(322)	1.00(2)
Cu(1)–Cu(1^{III})	2.734(4)	C(2)–C(3)	1.39(3)	C(5)–H(5)	0.99(2)	C(32)–H(323)	0.98(2)

Cu(1)–I(1)–Cu(1^{III})	61.85(8)	C(5)–N(1)–Cu(1)	117.1(1)	C(1)–C(12)–H(121)	106(1)	C(3)–C(2)–H(2)	101(1)
I(1)–Cu(1)–I(1^{III})	118.15(10)	N(1)–C(1)–C(2)	123.1(1)	C(1)–C(12)–H(122)	109(1)	C(2)–C(3)–C(4)	118(1)
I(1)–Cu(1)–I(1^{II})	97.27(9)	N(1)–C(1)–C(12)	116(1)	C(1)–C(12)–H(123)	118(2)	C(2)–C(3)–C(32)	120(1)
I(1^{II})–Cu(1)–I(1^{III})	112.75(10)	C(4)–C(3)–C(32)	122(1)	H(121)–C(12)–H(122)	106(1)	C(3)–C(32)–H(321)	109(2)
N(1)–Cu(1)–I(1)	116.4(4)	C(3)–C(4)–C(5)	120(1)	H(121)–C(12)–H(123)	106(1)	C(3)–C(32)–H(322)	108(2)
N(1)–Cu(1)–I(1^{III})	110.0(3)	C(3)–C(4)–H(4)	128(2)	H(122)–C(12)–H(123)	111(2)	C(3)–C(32)–H(323)	122(2)
N(1)–Cu(1)–I(1^{II})	107.3(4)	C(5)–C(4)–H(4)	110(1)	C(2)–C(1)–C(12)	121(1)	H(321)–C(32)–H(322)	106(2)
N(1)–Cu(1)–Cu(1^{III})	139.9(4)	N(1)–C(5)–C(4)	122(2)	C(1)–C(2)–C(3)	120(1)	H(321)–C(32)–H(323)	106(2)
C(1)–N(1)–C(5)	116(1)	N(1)–C(5)–H(5)	119(2)	C(1)–C(2)–H(2)	114(1)	H(322)–C(32)–H(323)	104(2)
C(1)–N(1)–Cu(1)	126(1)	C(4)–C(5)–H(5)	119(2)				

Symmetry operations: I x, $1.0 + y$, z; II $2.0 - x$, $-y$, $-z$; III $2.0 - x$, $1.0 - y$, z.

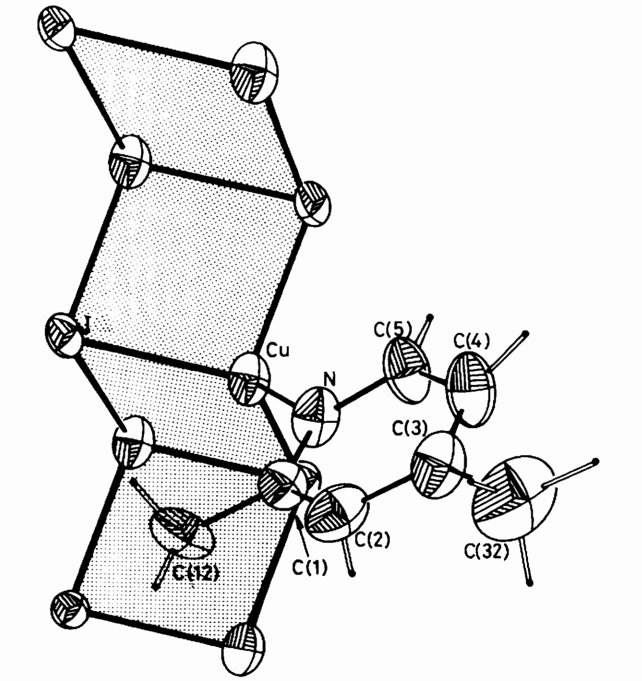

Figure 3. View of [{CuI(2,4Me$_2$-py)}$_\infty$]. For clarity, only one ligand molecule is shown

3.606(4) Å (3)] and both are shorter than those across the pleats of the polymer, 4.381(5) (**2**) and 4.328(4) Å (**3**). The dihedral angles between successive rhombs are respectively 67.5 and 67.7°. Thus the skeleton of the polymer is similar to that of [{CuI(py)}$_x$] which shows Cu–I distances of 2.646(2) and 2.806(2) Å alternating along the edges of the polymeric pleated sheets, Cu–I distances at shared edges of 2.681(2) Å, Cu–Cu distances of 2.708(2) and 3.706(2) Å across alternating rhombs and 4.381(2) Å across folds, and a dihedral angle of 67.5° between folds of the polymeric pleated sheet. Thus the steric bulk of the ligand has little influence on the geometry of the polymer.

The Cu–N distances are 2.07(2) in (**2**) and 2.05(2) Å in (**3**), similar to those observed for (**1**).

Variation of synthetic procedures has thus allowed isolation of three new members of the families of complexes formed by copper(I) iodide and pyridine derivatives. Within the families there are differences in the numbers of Cu–I bonds at each copper atom, Cu–Cu distances, numbers of Cu–N bonds at each Cu, and packing of the planes of aromatic ligands. These structural differences may now be correlated with difference in emission behaviour.[24]

Acknowledgements

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