

## Lewis Base Adducts of Group 11 Metal(I) Compounds. Part 36.<sup>1</sup> The Synthesis and X-Ray Crystallographic Characterisation of Polymeric Copper(I) Iodide-Benzonitrile (2/1)\*

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Recrystallisation of copper(I) iodide from benzonitrile yields not the 1:1 adduct as with the chloride and bromide, but a novel 2:1 adduct, [(CuI)<sub>2</sub>(PhCN)], the nature of which has been established by single-crystal X-ray structure determination. Crystals are monoclinic, space group C2/c, *a* = 21.99(1), *b* = 15.109(6), *c* = 15.286(9) Å, β = 125.63(4)°, *Z* = 16, and *R* = 0.033 for 2 403 'observed' reflections. The compound is a novel infinite polymer based on chiral, interlocking arrays of extended 'step' motifs.

Recrystallisation of the copper(I) halides CuX (X = Cl, Br, or I) from acetonitrile yields 1:1 adducts which adopt the common 'stair polymer' configuration.<sup>2-6</sup> Similar complexes are obtained for the chloride<sup>7</sup> and bromide<sup>8</sup> with benzonitrile, but no copper(I) iodide-benzonitrile adduct has been characterised. We find that the reaction of copper iodide with benzonitrile under nitrogen does not yield 1:1 stair polymers but rather colourless crystals of stoichiometry [(CuI)<sub>2</sub>(PhCN)] (Found: C, 17.3; H, 1.05; I, 52.4; N, 2.90. Calc. for C<sub>7</sub>H<sub>5</sub>Cu<sub>2</sub>I<sub>2</sub>N: C, 17.3; H, 1.05; I, 52.4; N, 2.90%). The compound has been structurally characterised by a single-crystal X-ray study on a specimen mounted in a capillary along the needle axis as a unique, complex polymeric species (Figure).

The generators of the structure are a pair of extended Cu<sub>8</sub>I<sub>8</sub> step motifs, shown dissected from the cell [Figure (a)]. Both are centrosymmetric; one (α) is defined so that one half is the asymmetric unit of the structure, the other half being generated by the inversion at (-¼, ¼, 1). The Cu<sub>2</sub>I<sub>2</sub> planes within it are defined ABCDCBA as shown (Figure); the nitrogen atoms N(1) at either end differ in *y* by 0.36, so that through its length α achieves a substantial inclination in *y* through the cell, along *a*. In conjunction with its attached inversion image through (½, ½, 1), centred on (¼, -¼, 1), the entire *a* axis is traversed with ABCDCBA, ABCDCBA *in toto* descending through one unit of *b* from (0, 1, 1) to (1, 0, 1). The other, 'β', motif, running across the cell perpendicular to *a* through (½, ½, ½), is also centrosymmetric and traverses the whole cell encompassing a descent of ½ in *y* and connecting four α motifs in the process in a sequence CXAYAXC. Motifs 'β' are cross-linked by B units to give the cell contents, which can similarly be visualised as made up of motifs 'α' cross-linked by X and Y units.

One other polymeric compound with 2:1 copper(I) halide-base stoichiometry has been reported, that of [(CuI)<sub>2</sub>-(2Me-py)] (2Me-py = 2-methylpyridine).<sup>9</sup> However, the two compounds represent different structural classes and this is illustrated, together with the relationship between them and the 'stair' polymer, in the schematic diagrams (I)–(III). Both (II) and (III) can be considered to be derived from the stair polymer (I) in which iodide atoms on successive units replace two of the

Table 1. Non-hydrogen atom co-ordinates for [(CuI)<sub>2</sub>(PhCN)]

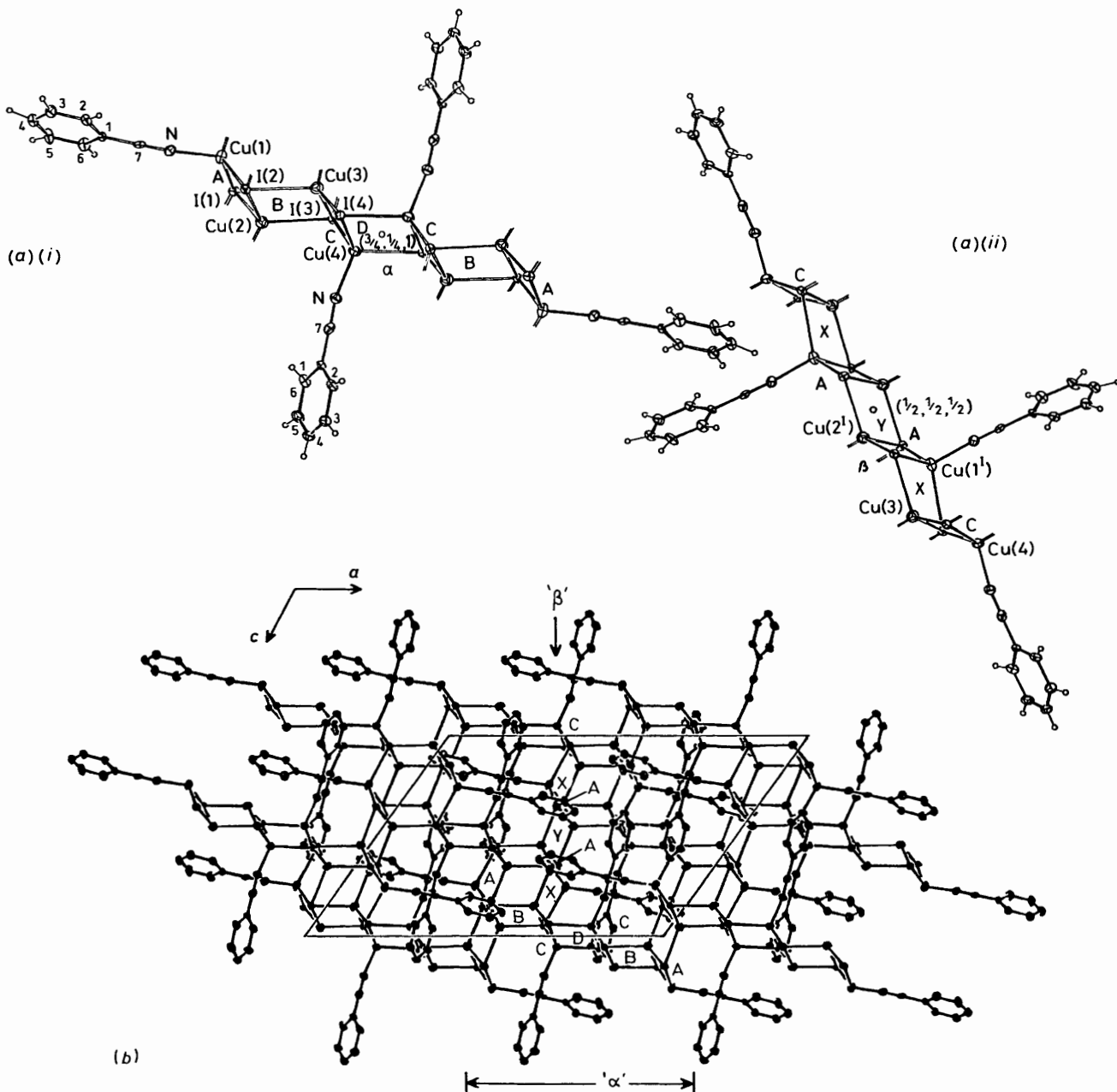
Atom	<i>x</i>	<i>y</i>	<i>z</i>
I(1)	0.439 09(4)	0.586 81(5)	0.853 00(6)
I(2)	0.455 72(4)	0.294 98(6)	0.847 48(6)
I(3)	0.645 31(4)	0.456 53(6)	0.948 42(6)
I(4)	0.654 36(4)	0.159 65(5)	0.938 65(6)
Cu(1)	0.374 63(8)	0.438 92(11)	0.746 64(13)
Cu(2)	0.524 25(9)	0.447 27(11)	0.951 45(12)
Cu(3)	0.579 36(9)	0.305 37(11)	0.850 81(12)
Cu(4)	0.722 26(9)	0.305 11(11)	1.048 98(11)
N(1)	0.277 4(5)	0.431 9(6)	0.723 5(7)
C(11)	0.141 8(6)	0.438 0(8)	0.676 2(8)
C(12)	0.093 9(8)	0.367 1(9)	0.624 2(11)
C(13)	0.021 7(7)	0.374 9(9)	0.594 8(11)
C(14)	0.000 6(7)	0.452 0(11)	0.620 0(11)
C(15)	0.048 0(8)	0.520 1(10)	0.670 8(12)
C(16)	0.120 0(7)	0.512 9(8)	0.699 6(11)
C(17)	0.217 2(6)	0.433 8(7)	0.702 9(8)
N(4)	0.744 8(5)	0.299 2(7)	1.192 6(7)
C(41)	0.798 0(6)	0.293 6(8)	1.396 1(8)
C(42)	0.840 6(8)	0.222 4(9)	1.457 5(11)
C(43)	0.870 8(7)	0.222 4(10)	1.566 3(11)
C(44)	0.859 5(7)	0.293 0(10)	1.611 5(9)
C(45)	0.817 9(8)	0.362 1(10)	1.550 6(11)
C(46)	0.786 9(7)	0.363 3(8)	1.440 9(11)
C(47)	0.768 8(6)	0.295 0(8)	1.284 2(10)

Table 2. Polymer geometry: distances in Å

Cu(1)		Cu(2)		Cu(3)		Cu(4)	
N(1)	1.96(1)	I(1)	2.633(2)	I(3)	2.650(1)	N(4)	1.95(1)
I(1)	2.638(1)	I(2)	2.702(2)	I(4)	2.606(1)	I(3)	2.726(2)
I(2)	2.661(2)	I(3)	2.693(3)	I(2)	2.694(3)	I(4)	2.640(2)
I(3 <sup>I</sup> )	2.762(2)	I(1 <sup>II</sup> )	2.654(3)	I(2 <sup>I</sup> )	2.661(2)	I(4 <sup>III</sup> )	2.662(2)
Cu(2)	2.940(3)	Cu(2 <sup>II</sup> )	2.779(3)	Cu(4)	2.822(3)	Cu(4 <sup>III</sup> )	2.938(3)
Cu(3 <sup>I</sup> )	3.012(3)	Cu(3)	3.257(3)	Cu(3 <sup>I</sup> )	3.025(3)		
		I(1)		I(3)		I(4)	
Cu(1)	2.638(1)	Cu(1)	2.661(2)	Cu(2)	2.693(3)	Cu(3)	2.606(1)
Cu(2)	2.633(2)	Cu(2)	2.702(2)	Cu(3)	2.650(2)	Cu(4)	2.640(2)
Cu(2 <sup>II</sup> )	2.654(3)	Cu(3)	2.694(3)	Cu(1 <sup>I</sup> )	2.762(2)	Cu(4 <sup>III</sup> )	2.662(2)
		Cu(3 <sup>I</sup> )	2.661(2)	Cu(4)	2.726(2)		

Transformations of the asymmetric unit: I 1 - *x*, *y*, ½ - *z*; II 1 - *x*, 1 - *y*, 2 - *z*; III ½ - *x*, ½ - *y*, 2 - *z*.

\* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue, 1, pp. xvii–xx.

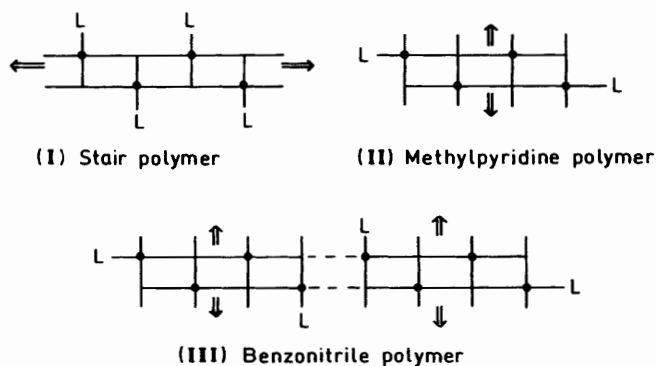


**Figure.** (a) (i), (ii) The extended 'step' structure motifs in orientation corresponding to Figure (b); interplanar dihedral angles are: ( $\alpha$ ) A/B, 62.7(7), B/C, 64.2(8), C/D, 66.9(8), ( $\beta$ ) C/X, 59.3(8), X/A, 59.5(8), and A/Y, 61.9(8) $^\circ$ . (b) The unit-cell contents of the 2:1 copper(I) iodide-benzonitrile adduct. The polymer is 'grown' from the centre of the cell, ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), discontinuities arising because of its helical structure

base ligands L in the  $\text{Cu}_4\text{I}_4$  in each of the two arrangements that are consistent with polymer generation.

The benzonitrile ligands occupy voids in the structure, being sited around the  $2_1$  screw axis to give rise to a lattice generating helical array. The benzonitrile ligands disrupt the close-packed structure of the iodide atoms. However, the iodide...phenyl ring distances of 4.0–4.2 Å are the same as the iodide...iodide distances and in this compound the phenyl groups occupy sites in the iodide lattice; it is this feature of the steric profile of both the anion and the ligand that results in this unusual polymeric system.

Atomic co-ordinates are given in Table 1, motif geometries in Tables 2 and 3. As expected, the geometries around the copper atoms are not unusual. It is worth noting, however, that, as for



**Table 3.** Polymer geometry: angles in ° (transformations as for Table 2)

Cu(1)		Cu(2)		Cu(3)		Cu(4)	
N(1)I(1)	107.2(3)	I(1)I(2)	112.23(7)	I(2)I(3)	106.03(8)	N(4)I(3)	109.9(3)
N(1)I(2)	110.7(3)	I(1)I(3)	109.25(9)	I(2)I(4)	106.82(8)	N(4)I(4)	111.1(3)
N(1)I(3 <sup>b</sup> )	109.9(3)	I(1)I(1 <sup>h</sup> )	116.57(9)	I(2)I(2 <sup>b</sup> )	110.81(6)	N(4)I(4 <sup>h</sup> )	110.4(3)
I(1)I(2)	113.39(7)	I(2)I(3)	104.62(8)	I(3)I(4)	117.61(7)	I(3)I(4)	113.84(7)
I(1)I(3 <sup>b</sup> )	105.90(8)	I(2)I(1 <sup>h</sup> )	101.34(8)	I(3)I(2 <sup>b</sup> )	113.11(8)	I(3)I(4 <sup>h</sup> )	98.31(8)
I(2)I(3 <sup>b</sup> )	109.59(9)	I(3)I(1 <sup>h</sup> )	112.01(8)	I(4)I(2 <sup>b</sup> )	102.33(8)	I(4)I(4 <sup>h</sup> )	112.69(8)
I(1)		I(2)		I(3)		I(4)	
Cu(1)Cu(2)	67.79(9)	Cu(1)Cu(2)	66.74(7)	Cu(2)Cu(3)	75.09(7)	Cu(3)Cu(4)	65.07(7)
Cu(1)Cu(2 <sup>h</sup> )	103.38(7)	Cu(1)Cu(3)	106.96(8)	Cu(2)Cu(4)	104.00(7)	Cu(3)Cu(4 <sup>h</sup> )	100.41(7)
Cu(2)Cu(2 <sup>h</sup> )	63.43(7)	Cu(1)Cu(3 <sup>b</sup> )	68.92(7)	Cu(2)Cu(1 <sup>b</sup> )	118.47(6)	Cu(4)Cu(4 <sup>h</sup> )	67.31(7)
		Cu(2)Cu(3)	74.24(7)	Cu(3)Cu(4)	63.29(7)		
		Cu(2)Cu(3 <sup>b</sup> )	108.18(7)	Cu(3)Cu(1 <sup>b</sup> )	67.58(7)		
		Cu(3)Cu(3 <sup>b</sup> )	68.77(6)	Cu(4)Cu(1 <sup>b</sup> )	100.60(7)		

[(CuI)<sub>2</sub>(2Me-py)], the two  $\mu_4$  iodide atoms exhibit marginally longer I-Cu distances on average than the two  $\mu_3$  atoms: 2.694(13) Å vs. 2.639(8) Å. Within each rhomb the internal Cu-I-Cu angles are significantly greater for I<sub>2</sub>CuI<sub>2</sub>CuI<sub>2</sub> compared to either the I<sub>2</sub>CuI<sub>2</sub>CuIL or ILCuI<sub>2</sub>LI dimeric units: 74.24(7)—75.09(7) vs. 63.29(7)—68.77(6)°.

### Experimental

**Crystallography.**—*Crystal data.* C<sub>7</sub>H<sub>5</sub>Cu<sub>2</sub>I<sub>2</sub>N, *M* = 484, monoclinic, space group *C2/c* (*C*<sub>2h</sub><sup>6</sup>, no. 15), *a* = 21.99(1), *b* = 15.109(6), *c* = 15.286(9) Å,  $\beta$  = 125.63(4)°, *U* = 4 128(4) Å<sup>3</sup>, *D*<sub>c</sub> = 3.11 g cm<sup>-3</sup> (*Z* = 16), *F*(000) = 3 488, monochromatic Mo-K $\alpha$  radiation ( $\lambda$  = 0.710 69 Å,  $\mu$  = 102.6 cm<sup>-1</sup>). Specimen: 0.10 × 0.10 × 0.50 mm; transmission factors = 1.32 (minimum), 1.63 (maximum).

**Structure determination.** A unique data set was measured to  $2\theta_{\max}$  = 50° using a Syntex P2<sub>1</sub> four-circle diffractometer in conventional  $2\theta$ - $\theta$  scan mode. 3 639 Independent reflections were obtained, 2 403 with *I* > 3 $\sigma$ (*I*) being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> were included at estimated values. Conventional *R*, *R'* on |*F*| were 0.033, 0.027 [statistical weights derived from  $\sigma^2(I) = \sigma^2(I_{\text{diff.}}) + 0.0005\sigma^4(I_{\text{diff.}})$ ]. Neutral atom complex scattering factors were used.<sup>10</sup> Computation employed the XTAL program system<sup>11</sup> implemented by S. R. Hall on a Perkin-Elmer 3241 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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