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## Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 17.\* Synthesis and Crystal Structures† of Adducts of Copper(I) Cyanide with Nitrogen Bases

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Compounds of the type  $[\text{Cu}(\text{CN})_n\text{L}_n]$  [ $\text{L}$  = diethylamine, (1), triethylamine, (2), 4-methylpyridine, (3), or 1,10-phenanthroline, (4)] have been synthesized by recrystallization of copper(I) cyanide from (or with) the parent base and their crystal structures have been determined by single-crystal X-ray diffraction methods;  $n = 1$  except in the case of (3) where  $n = 1.5$ . Crystals of (1) are monoclinic, space group  $P2_1/n$ , with  $a = 15.108(7)$ ,  $b = 7.321(5)$ ,  $c = 13.699(6)$  Å,  $\beta = 103.00(4)^\circ$ , and  $Z = 8$ ;  $R$  was 0.044 for  $N_o = 871$  independent 'observed' reflections. For (2), crystals are orthorhombic, space group  $Pnma$ , with  $a = 9.501(4)$ ,  $b = 8.921(4)$ ,  $c = 11.279(5)$  Å, and  $Z = 4$ ;  $R = 0.039$ ,  $N_o = 369$ . For (3), crystals are monoclinic, space group  $Cc$ , with  $a = 9.587(3)$ ,  $b = 16.326(4)$ ,  $c = 14.022(4)$  Å,  $\beta = 109.38(2)^\circ$ , and  $Z = 4$ ;  $R = 0.031$ ,  $N_o = 1\ 070$ . For (4), crystals are trigonal, space group  $P3_1$ , with  $a = 9.175(5)$ ,  $c = 11.753(8)$  Å, and  $Z = 3$ ;  $R = 0.041$ ,  $N_o = 812$ . All complexes are one-dimensional polymers, that in (2) being disposed completely in a mirror plane except for the substituent alkyl groups. Copper atoms in (1) and (2) are trigonally planar co-ordinated by C,N(cyanide) and N(base), as is one of the two copper atoms in (3); the other copper atom in (3) is unusual, being four-co-ordinated pseudo-tetrahedrally by C,N(cyanide) and two N(base). A similar copper environment is found in (4).

Elsewhere<sup>1</sup> we have reported the synthesis and single-crystal X-ray structure determinations of adducts of copper(I) thiocyanate with a variety of pyridine bases. In the present report we extend the study to the cyanide species. The complexes were prepared by the reaction of copper(I) cyanide with the pure parent base (L) yielding precipitates from which colourless crystals of the 1:1 CuCN:L adduct were obtained for L = diethylamine, (1), by recrystallization from tetrahydrofuran (thf), and L = triethylamine, (2), by recrystallization from dichloromethane, and the 1:1.5 adduct with 4-methylpyridine (4Me-py), (3), by slow recrystallization from the hot parent base. The 1:1 CuCN:phen adduct, (4), (phen = 1,10-phenanthroline),<sup>2</sup> was obtained as orange crystals from acetonitrile solvent. Stoichiometries and structures were established by single-crystal X-ray diffraction studies on crystals generally encapsulated in capillaries.

### Experimental

**Crystallography.**—General procedural details are given in a previous paper.<sup>3</sup>

**Crystal data for  $[\text{Cu}(\text{CN})(\text{NHEt}_2)]$  (1).**  $\text{C}_5\text{H}_{11}\text{CuN}_2$ ,  $M = 162.7$ , monoclinic, space group  $P2_1/n$  ( $C_{2h}^2$ , no. 14, variant),  $a = 15.108(7)$ ,  $b = 7.321(5)$ ,  $c = 13.699(6)$  Å,  $\beta = 103.00(4)^\circ$ ,  $U = 1\ 476(1)$  Å<sup>3</sup>,  $D_c$  ( $Z = 8$ ) =  $1.47$  g cm<sup>-3</sup>,  $F(000) = 672$ . Specimen:  $0.36 \times 0.11 \times 0.11$  mm;  $\mu_{\text{Mo}} = 30$  cm<sup>-1</sup>,  $2\theta_{\text{max.}} = 45^\circ$ ;  $N, N_o = 1\ 663, 871$ ;  $R, R' = 0.044, 0.047$ .

**Crystal data for  $[\text{Cu}(\text{CN})(\text{NEt}_3)]$  (2).**  $\text{C}_7\text{H}_{15}\text{CuN}_2$ ,  $M = 190.8$ , orthorhombic, space group  $Pnma$  ( $D_{2h}^{10}$ , no. 62),  $a = 9.501(4)$ ,  $b = 8.921(4)$ ,  $c = 11.279(5)$  Å,  $U = 956.0(7)$  Å<sup>3</sup>,  $D_c$  ( $Z = 4$ ) =  $1.33$  g cm<sup>-3</sup>,  $F(000) = 400$ . Specimen:  $0.16 \times$

$0.10 \times 0.05$  mm;  $\mu_{\text{Mo}} = 21.5$  cm<sup>-1</sup>,  $2\theta_{\text{max.}} = 45^\circ$ ;  $N, N_o = 601, 369$ ;  $R, R' = 0.039, 0.041$ .

**Crystal data for  $[\text{Cu}_2(\text{CN})_2(4\text{Me-py})_3]$  (3).**  $\text{C}_{20}\text{H}_{21}\text{Cu}_2\text{N}_5$ ,  $M = 458.5$ , monoclinic, space group  $Cc$  ( $C_s^2$ , no. 9),  $a = 9.587(3)$ ,  $b = 16.326(4)$ ,  $c = 14.022(4)$  Å,  $\beta = 109.38(2)^\circ$ ,  $U = 2\ 070(1)$  Å<sup>3</sup>,  $D_c$  ( $Z = 4$ ) =  $1.47$  g cm<sup>-3</sup>,  $F(000) = 936$ . Specimen:  $0.05 \times 0.10 \times 0.25$  mm;  $\mu_{\text{Mo}} = 26.6$  cm<sup>-1</sup>,  $2\theta_{\text{max.}} = 45^\circ$ ;  $N, N_o = 1\ 225, 1\ 070$ ;  $R, R' = 0.031, 0.035$  (preferred chirality).

**Crystal data for  $[\text{Cu}(\text{CN})(\text{phen})]$  (4).**  $\text{C}_{13}\text{H}_8\text{CuN}_3$ ,  $M = 269.8$ , trigonal, space group  $P3_1$  ( $C_3^2$ , no. 144),  $a = 9.175(5)$ ,  $c = 11.753(8)$  Å,  $U = 856.6(9)$  Å<sup>3</sup>,  $D_c$  ( $Z = 3$ ) =  $1.57$  g cm<sup>-3</sup>,  $F(000) = 408$ . Specimen:  $0.20 \times 0.20 \times 0.24$  mm;  $\mu_{\text{Mo}} = 19.6$  cm<sup>-1</sup>,  $2\theta_{\text{max.}} = 45^\circ$ ;  $N, N_o = 908, 812$ ;  $R, R' = 0.041, 0.047$ .

**Abnormal Features.**—All structures. Assignment of the cyanide was on the basis of reasonable thermal parameters and significant changes in  $R$  were not possible for the less precise structures. In conformity with the more precise structures, in cases of doubt, atoms assigned as carbon are those with the shortest bonds to copper. Atomic co-ordinates are in Tables 1—4 and the structures are shown in Figures 1—4.

**Compound (4).** It will be evident from inspection of the co-ordinates (Table 4) and Figure 4 that the structure contains additional symmetry over and above that of space group  $P3_1$ , conforming closely to that of space group  $P3_121$  (no. 152), the only potential deviant from ideal symmetry being the cyanide. Refinement of the structure in  $P3_121$  resulted in a residual of 0.044 (reverse chirality, 0.047); the atoms of the cyanide were modelled by a disordered C,N composite. With ordered cyanide components in space group  $P3_1$ , the residual falls significantly to 0.041, and the structure is therefore finally described in those terms. It is of interest that in the process, the most significant change in the structure consists of movement of the atoms of the cyanide to give a model consistent with the significant geometrical discrepancy expected for Cu—C and Cu—N bonds. The overall difference, however, is relatively minor and co-

\* Part 16 is ref. 3.

† Supplementary data available (No. SUP 56150, 18 pp.): thermal parameters, H-atom parameters, ligand geometries and planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

**Table 1.** Non-hydrogen atom co-ordinates for (1)\*

Atom	x	y	z
Cu(1)	0.164 3(1)	0.396 0(2)	0.490 5(1)
Cu(2)	0.489 2(1)	0.331 3(2)	0.662 3(1)
Cyanides			
C(1)	0.367 8(9)	0.351 9(15)	0.595 1(8)
N(1)	0.292 0(7)	0.363 5(14)	0.554 7(7)
C(2)	0.092 7(8)	0.320 2(17)	0.367 2(9)
N(2)	0.049 6(7)	0.269 5(14)	0.292 7(8)
Amine ligand			
N(3)	0.122 0(6)	0.549 5(14)	0.600 8(7)
C(3)	0.149 8(9)	0.458 7(20)	0.700 5(8)
C(4)	0.113 0(11)	0.270 8(23)	0.698 1(12)
C(5)	0.157 0(9)	0.738 8(21)	0.602 7(10)
C(6)	0.115 0(10)	0.840 9(19)	0.506 3(12)
N(4)	0.605 6(6)	0.421 2(14)	0.615 3(6)
C(7)	0.656 1(9)	0.553 0(19)	0.688 2(9)
C(8)	0.603 6(11)	0.716 7(22)	0.695 2(12)
C(9)	0.666 2(9)	0.266 1(21)	0.602 6(10)
C(10)	0.617 3(11)	0.147 7(20)	0.517 4(12)

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

**Table 2.** Non-hydrogen atom co-ordinates for (2)

Atom	x	y	z
Cu	0.270 6(1)	0.25	0.193 0(1)
Cyanide			
C	0.459 0(11)	0.25	0.239 3(11)
N	0.578 1(11)	0.25	0.263 9(10)
Amine ligand			
N(1)	0.257 2(8)	0.25	-0.002 2(8)
C(11)	0.397 7(13)	0.25	-0.056 3(13)
C(12)	0.422 5(19)	0.25	-0.189 9(16)
C(21)	0.177 1(9)	0.118 1(14)	-0.037 7(9)
C(22)	0.238 3(10)	-0.029 3(13)	0.005 9(12)

ordinates and thermal parameters for the  $P3_121$  disordered model are given in SUP 56150.

## Results and Discussion

Previous structural work on copper(I) cyanide systems is limited in quantity and scope. The structure of the parent copper(I) cyanide still seemingly remains undetermined by single-crystal methods, and the bulk of work carried out on the system appears to have been on double salts, containing polymeric complex anions in the solid, or on ammonia and hydrazine derivatives. The dominant feature thus far is the trigonal-planar copper(I) atom surrounded by three cyanide ligands linearly co-ordinated through either carbon or nitrogen, or two cyanide groups and a base, resulting in two-dimensional network structures or one-dimensional polymers. Cyanide carbon atoms are generally more tightly bound than cyanide nitrogen atoms and this is reflected correspondingly in inequivalences in the trigonal angles in the plane. Individual examples, however, provide interesting variations in the above pattern.  $\text{Na}[\text{Cu}(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ <sup>4</sup> and  $\text{K}[\text{Cu}(\text{CN})_2]$ <sup>5</sup> have one-dimensional polymeric  $[\text{Cu}(\text{CN})_2]_\infty$  chains with C,N-bridging and C-bonded terminal cyanides about trigonal copper atoms.  $\text{K}[\text{Cu}_2(\text{CN})_3] \cdot \text{H}_2\text{O}$ <sup>6</sup> has a two-dimensional sheet structure consisting of  $\text{Cu}_6(\text{CN})_6$  rings linked as in graphite.  $\text{K}_3[\text{Cu}(\text{CN})_4]$ <sup>7</sup> has

**Table 3.** Non-hydrogen atom co-ordinates for (3)

Atom	x	y	z
Cu(1)	0	0.547 13(6)	0.5
Cu(2)	0.373 4(2)	0.323 68(6)	0.583 5(1)
Cyanides			
C(1)	0.144 9(10)	0.466 2(5)	0.524 6(6)
N(1)	0.225 8(9)	0.411 2(5)	0.540 5(6)
C(2)	0.421 4(9)	0.222 6(5)	0.535 3(7)
N(2)	0.456 5(9)	0.159 5(5)	0.515 6(6)
Pyridine ligands			
N(11)	-0.208 0(8)	0.492 2(4)	0.435 9(5)
C(12)	-0.333 1(13)	0.533 8(6)	0.394 8(8)
C(13)	-0.467 9(12)	0.501 1(6)	0.354 6(8)
C(14)	-0.485 0(10)	0.417 0(6)	0.354 0(6)
C(141)	-0.633 0(12)	0.375 3(8)	0.310 9(8)
C(15)	-0.357 8(12)	0.371 4(5)	0.396 0(8)
C(16)	-0.223 1(11)	0.411 4(5)	0.434 5(7)
N(21)	0.576 1(7)	0.393 7(4)	0.632 9(5)
C(22)	0.706 6(11)	0.355 7(5)	0.679 6(7)
C(23)	0.837 5(9)	0.397 3(5)	0.716 9(7)
C(24)	0.842 7(10)	0.480 7(5)	0.704 0(6)
C(241)	0.983 8(12)	0.528 1(6)	0.744 0(7)
C(25)	0.710 2(12)	0.518 1(5)	0.656 7(7)
C(26)	0.581 4(10)	0.473 7(5)	0.622 8(7)
N(31)	0.361 8(8)	0.299 8(4)	0.736 3(6)
C(32)	0.261 6(11)	0.335 9(5)	0.770 3(8)
C(33)	0.271 0(11)	0.338 0(5)	0.868 7(8)
C(34)	0.388 9(14)	0.301 9(6)	0.941 8(8)
C(341)	0.404 4(15)	0.303 4(7)	1.050 8(10)
C(35)	0.491 6(12)	0.263 8(6)	0.908 0(9)
C(36)	0.476 0(11)	0.264 2(6)	0.807 8(10)

**Table 4.** Non-hydrogen atom co-ordinates for (4)

Atom	x	y	z
Cu	-0.000 1(2)	0.191 0(1)	0.000 0(-)
Cyanide			
C	-0.095(1)	0.048(1)	0.126(1)
N	-0.140(1)	-0.042(1)	0.203(1)
Ligand			
N(1)	-0.160(1)	0.289(2)	-0.039(1)
C(11)	-0.318(2)	0.206(2)	-0.073(1)
C(12)	-0.412(2)	0.292(4)	-0.088(1)
C(13)	-0.329(3)	0.459(4)	-0.069(2)
C(14)	-0.167(3)	0.553(2)	-0.036(1)
C(15)	-0.087(2)	0.453(2)	-0.020(1)
C(16)	-0.087(5)	0.723(3)	-0.018(2)
N(2)	0.160(1)	0.447(1)	0.040(1)
C(21)	0.320(2)	0.525(2)	0.074(1)
C(22)	0.412(3)	0.699(3)	0.091(1)
C(23)	0.340(4)	0.794(3)	0.071(2)
C(24)	0.171(3)	0.718(2)	0.036(1)
C(25)	0.086(2)	0.540(1)	0.019(1)
C(26)	0.081(5)	0.803(3)	0.016(2)

discrete  $[\text{Cu}(\text{CN})_4]^{3-}$  tetrahedral anions.  $\text{Cu}(\text{CN}) \cdot \text{NH}_3$ <sup>8</sup> has a two-dimensional network/sheet structure with a spiral  $-\text{CuCN}(\text{CN})\text{Cu}-$  chain backbone and crosslinking/bridging  $\text{Cu}-\text{Cu}(\text{CN})$  contacts leading to very short (2.42 Å)  $\text{Cu}-\text{Cu}$  distances, so that with the ammonia, each copper atom has five near neighbours.  $[\text{Cu}_3(\text{CN})_4(\text{NH}_3)_3]$ <sup>9</sup> has the copper(I) atoms trigonally planar, co-ordinated by three cyanide groups in a one-dimensional polymer, successive segments of which are closed by  $\text{Cu}^{\text{II}}(\text{NH}_3)_3$  units co-ordinated to cyanides at the 1,4- and 2,3-

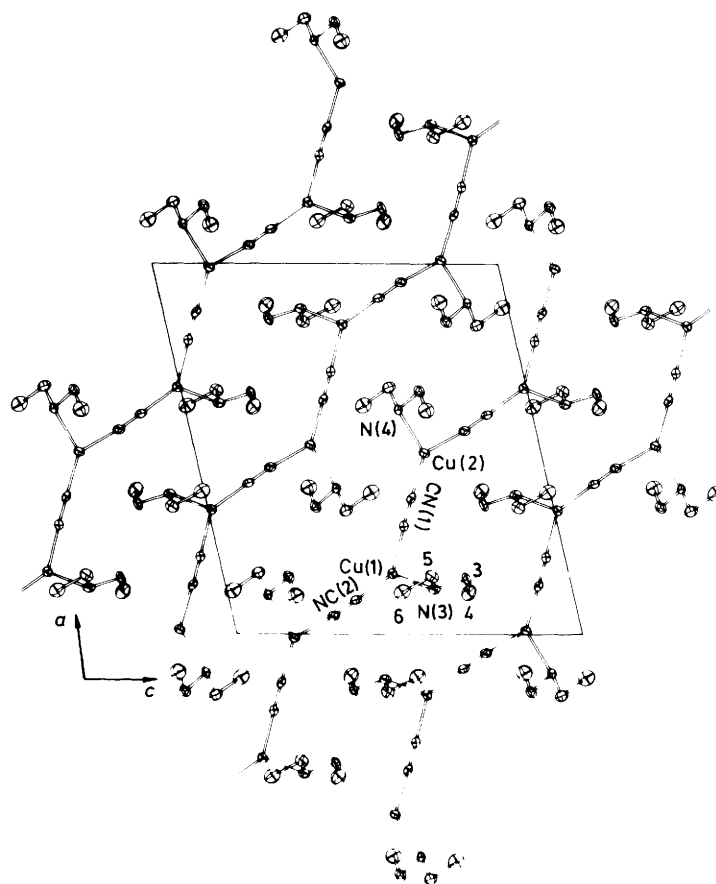


Figure 1. Unit-cell contents of (1), projected down *b*, showing the atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms

positions of the chain.  $\text{Cu}(\text{CN})\cdot\text{N}_2\text{H}_4$  has  $-\text{CNCuCNCuCNCu}-$  parallel chains crosslinked by  $\text{H}_2\text{N}-\text{NH}_2$  molecules so that the copper atoms are four-co-ordinate.<sup>10</sup> Mixed-valence compounds,  $[\{\text{Cu}^{\text{I}}_4(\text{CN})_6\text{Cu}^{\text{II}}(\text{NH}_3)_2\}_n]$ <sup>11</sup> and  $[\{\text{Cu}^{\text{I}}_3(\text{CN})_5\text{Cu}^{\text{II}}(\text{NH}_3)_2(\text{OH}_2)\}_n]$ <sup>11</sup> show co-ordination numbers of three and two for the  $\text{Cu}^{\text{I}}$  atoms in a complex polymeric network. A contemporary study of the adduct  $\text{Cu}(\text{CN})\text{-dmphen}$ <sup>12</sup> shows a  $-\text{CuCNCuCN}-$  linear polymer with bidentate 2,9-dimethyl-1,10-phenanthroline (dmphen) ligands to each copper making up four-co-ordination about that atom. In the context of this history of variety, we therefore turn to consider the present results.

**Compound (1).**—The structure determination shows the stoichiometry of the copper(I) cyanide–diethylamine adduct recrystallized from tetrahydrofuran to be 1:1. Unlike the stoichiometrically similar  $\text{Cu}(\text{CN})\cdot\text{NH}_3$  adduct, however,<sup>8</sup> where the  $\text{Cu}(\text{CN})$  molecules link to form a two-dimensional network/sheet structure, in the present case, the asymmetric unit comprises a pair of  $\text{Cu}(\text{CN})(\text{base})$  units which, in sequence, make up the repeat unit of a one-dimensional  $\dots\text{Cu}(\text{CN})\text{-Cu}(\text{CN})\text{Cu}(\text{CN})\dots$  polymer, with the base units attached at the copper atoms. The co-ordination of the copper atoms is trigonal in each case, the co-ordination environment being made up of carbon and nitrogen atoms from independent cyanide linkages and the base nitrogen. Angle sums about the copper atoms in the co-ordination environments are both  $360.0^\circ$ , with the angle opposite the carbon being smallest and the angle opposite the base nitrogen being largest [ $133.2(5)$ ,  $133.3(5)^\circ$ ; Table 5].

The  $\text{Cu}-\text{N}(\text{base})$  distances [ $2.09(1)$ ,  $2.11(1)$  Å] are slightly longer than those reported for the ammonia complex [ $2.07(1)$

Å], reflecting the different steric profiles of  $\text{NH}_3$  and the alkyl-substituted base.

**Compound (2).**—The structure determination establishes the stoichiometry of the complex to be that of a 1:1 one-dimensional polymeric adduct of  $\text{Cu}(\text{CN})$  with triethylamine. The polymer is oriented parallel to the *a* axis and lies in the mirror plane parallel to the *ac* plane at  $y = 0.25$ . All atoms except one of the ethyl substituents on the ligand lie on Wyckoff *c* sites at  $y = 0.25$  in the space group *Pnma*. Each unit of polymer is generated by the two-fold screw axis at  $y = 0.25$ . The polymeric structure and the unit-cell contents are shown in Figure 2. The shortest  $\text{Cu}\cdots\text{Cu}$  distance is  $4.922(2)$  Å, slightly greater than the half-unit *a* translation (which is the repeat polymeric distance), because of the oblique orientation of the  $\text{Cu}-\text{N}-\text{C}-\text{Cu}$  moiety relative to *a*. The copper atom is in a distorted trigonal-planar geometry, bonded with one C atom from a cyanide group [ $1.86(1)$  Å, Table 6] and two nitrogen atoms from a ligand and another cyanide group:  $\text{Cu}-\text{N}(1)$   $2.21(2)$ ,  $\text{Cu}-\text{N}(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$   $1.89(1)$  Å. The long  $\text{Cu}-\text{N}(\text{base})$  distance [ $2.21(1)$  Å] lies in between the covalent sum ( $1.17 + 0.74 = 1.91$  Å) and ionic sum ( $0.96 + 1.71 = 2.67$  Å), and is indicative of very weak co-ordination to the copper atom, as is the large angle opposite,  $\text{N}(\text{C})-\text{Cu}-\text{C}$  being  $148.9(5)^\circ$ . The angles  $\text{N}(1)-\text{Cu}-\text{N}, \text{C}$  are  $< 120^\circ$  [ $101.6(4)$  and  $109.6(4)^\circ$ ], but the sum of the three angles is  $360.0^\circ$ , within experimental error.

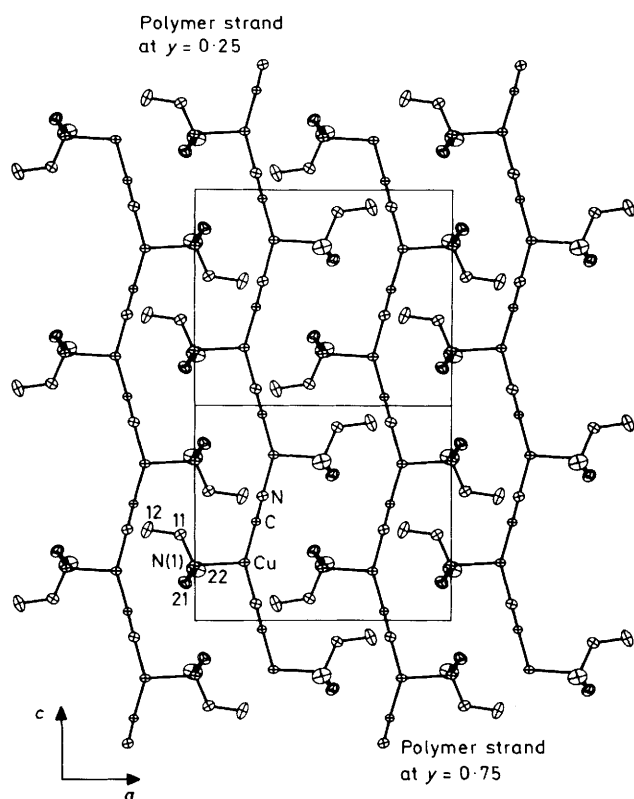
The cyanide group is presumed to be bonded through its carbon atom (comparing thermal parameters and *R* values between C and N). However, the difference between  $\text{Cu}-\text{C}$  and  $\text{Cu}-\text{N}$  is only  $0.03$  Å and  $\text{N}(1)-\text{Cu}-\text{C}, \text{N}$  angles differ by  $8^\circ$ .

**Table 5.** Copper–cyanide geometries in (1); italicized atoms are generated by  $(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$ 

Distances (Å)			
Cu(1)–N(1)	1.95(1)	Cu(2)–N(2)	1.96(1)
Cu(1)–C(2)	1.87(1)	Cu(2)–C(1)	1.87(1)
Cu(1)–N(3)	2.09(1)	Cu(2)–N(4)	2.11(1)
C(1)–N(1)	1.16(2)	C(2)–N(2)	1.14(2)

Angles (°)			
N(1)–Cu(1)–C(2)	133.2(5)	N(2)–Cu(2)–C(1)	133.3(5)
N(1)–Cu(1)–N(3)	99.9(4)	N(2)–Cu(2)–N(4)	98.4(4)
C(2)–Cu(1)–N(3)	126.9(5)	C(1)–Cu(2)–N(4)	128.3(4)
Cu(1)–N(1)–C(1)	176.8(10)	Cu(2)–N(2)–C(2)	173.1(11)
Cu(1)–C(2)–N(2)	178.2(12)	Cu(2)–C(1)–N(1)	178.9(13)

**Figure 2.** Unit-cell contents of (2), projected down *b*

Moreover, the thermal parameters of all atoms in the mirror plane,  $U_{22}$  for Cu, CN, N(1), and C(22) are high and more than double the corresponding  $U_{11}$  and  $U_{33}$ . Since the only atoms which protrude from the plane are the pair of symmetry-related ethyl groups, and the polymer disposition is such that  $U_{22}$  would probably be the largest diagonal component of these thermal tensors, it may also be the case that disorder is present which generates the high  $U_{22}$  components. Photography of the crystals shows no evidence for the presence of a superlattice. The cyanide group is linear with Cu–C–N 177.5(11) and Cu–N–C 178.9(11)°.

**Compound (3).**—The structure determination establishes the stoichiometry of the compound obtained by recrystallization

**Table 6.** Copper–cyanide geometry in (2); italicized atoms are generated by  $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$ 

Distances (Å)			
Cu–C	1.86(1)	Cu–N(1)	2.21(1)
Cu–N	1.89(1)	C–N	1.16(2)

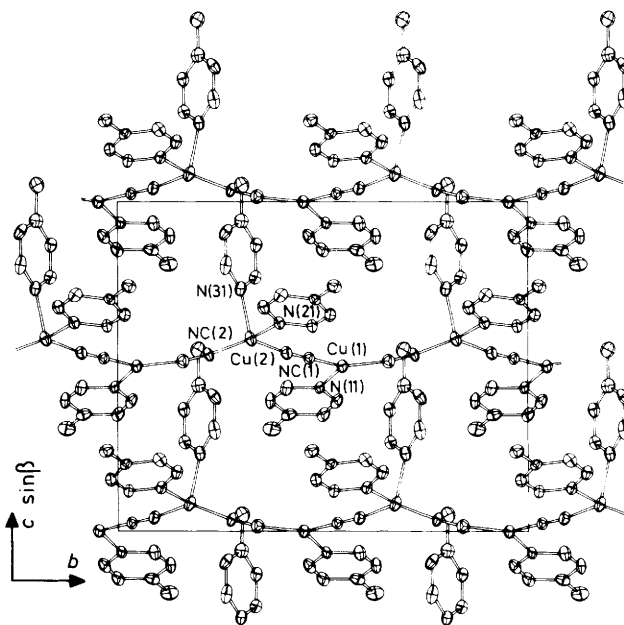
Angles (°)			
N(1)–Cu–C	109.6(4)	Cu–C–N	177.5(11)
N(1)–Cu–N	101.6(4)	Cu–N–C	178.9(11)
C–Cu–N	148.9(5)		

**Table 7.** Copper–cyanide geometry in (3); N(2) is generated by  $(x - \frac{1}{2}, \frac{1}{2} - y, z)$ , Cu(1) is generated by  $(x + \frac{1}{2}, y - \frac{1}{2}, z)$ 

Distances (Å)			
Cu(1)–C(1)	1.865(9)	Cu(2)–C(2)	1.898(9)
Cu(1)–N(2)	1.909(8)	Cu(2)–N(1)	1.960(8)
Cu(1)–N(11)	2.097(7)	Cu(2)–N(21)	2.161(7)
C(1)–N(1)	1.16(1)	Cu(2)–N(31)	2.215(9)
C(2)–N(2)	1.15(1)		

Angles (°)			
C(1)–Cu(1)–N(2)	146.8(3)	N(1)–Cu(2)–N(31)	99.4(3)
C(1)–Cu(1)–N(11)	108.7(3)	N(21)–Cu(2)–N(31)	96.4(3)
N(2)–Cu(1)–N(11)	104.3(3)	Cu(2)–N(1)–C(1)	173.1(7)
C(2)–Cu(2)–N(1)	139.5(3)	Cu(1)–C(1)–N(1)	174.1(9)
C(2)–Cu(2)–N(21)	106.0(3)	Cu(1)–N(2)–C(2)	169.7(9)
C(2)–Cu(2)–N(31)	106.7(3)	Cu(2)–C(2)–N(2)	173.6(8)
N(1)–Cu(2)–N(21)	101.2(3)		

**Figure 3.** Unit-cell contents (3), projected down *a*

of copper(I) cyanide from 4-methylpyridine to be that of the 1:1.5 complex. The asymmetric unit of the structure is two copper atoms and a pair of cyanide groups arranged in the familiar linear polymeric  $-\text{Cu}(\text{CN})\text{Cu}(\text{CN})\text{Cu}(\text{CN})-$  array, generated by the *c* translation. The structure is novel, however, in that different numbers of base molecules are co-ordinated to the two independent copper atoms. Cu(1) has one base nitrogen

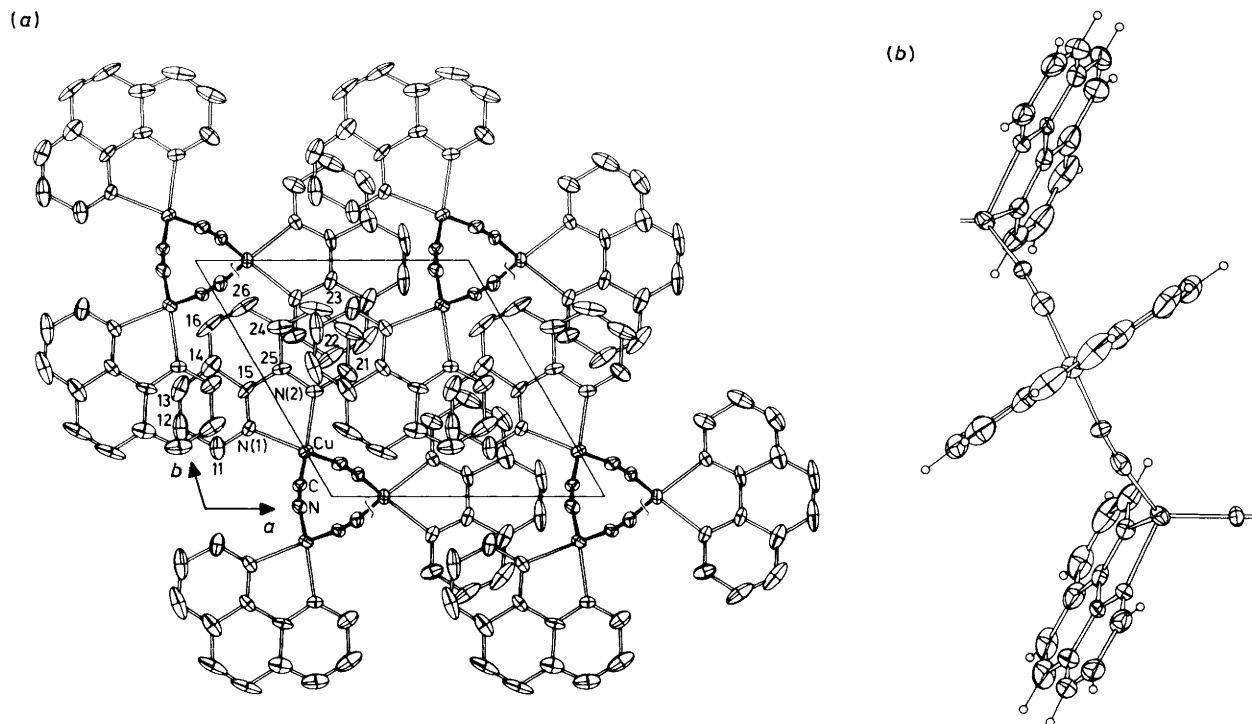


Figure 4. (a) Unit-cell contents (4), projected down  $c$ ; (b) a single polymer strand of (4)

Table 8. Copper-cyanide geometry in (4);  $N$  is generated by  $(y - x, \bar{x}, z - \frac{1}{4})$ ;  $Cu$  by  $(\bar{y}, x - y, \frac{1}{4} + z)$

Distances (Å)			
Cu-C	1.875(11)	Cu-N(2)	2.108(10)
Cu-N	1.944(17)	C-N	1.16(2)
Cu-N(1)	2.122(15)		
Angles (°)			
C-Cu-N	124.1(6)	N-Cu-N(2)	107.1(4)
C-Cu-N(1)	106.7(5)	N(1)-Cu-N(2)	79.7(5)
C-Cu-N(2)	114.9(5)	Cu-C-N	174(1)
N-Cu-N(1)	115.9(7)	Cu-N-C	173(1)

attached, making up a trigonal-planar array (angle sum in the co-ordination sphere,  $359.8^\circ$ ); the angle opposite the co-ordinated base is large and comparable with that observed in (2). Nevertheless, the Cu-N(base) distance in (3) is shorter than in (2) and comparable with the value found in (1), although the co-ordinated cyanide distances more nearly resemble the values of (2). Cu(2), by contrast, has two base nitrogen atoms attached; although both distances are longer than the corresponding distance for the single base of (1), N(31) is less strongly bound than N(21), and, as expected, the smallest angle in the co-ordination sphere lies between them. The angle between the cyanide linkages is still high, being  $139.5(3)^\circ$  (Table 7), a value greater than that observed in the trigonal co-ordination environment of (1).

**Compound (4).**—The stoichiometry of the 1,10-phenanthroline adduct of copper(I) cyanide is 1:1. The structure closely resembles that of the recently studied dmphen adduct,<sup>12</sup> being a single stranded polymer, with a single Cu(CN)(base) group as the repeating unit. Interestingly, however, whereas

both polymers are generated by crystallographic screw axes, that relevant to the dmphen compound is the  $2_1$  screw of space group  $P2_1/n$ , whereas in the present case it is the  $3_1$  screw of space group  $P3_1$ . The copper environment is four-co-ordinated by cyanide carbon and nitrogen atoms and a bidentate, fairly symmetrically co-ordinated phen ligand. Cu-N(phen) distances are both relatively short and the co-ordination environment more nearly tetrahedral than for Cu(2) in (3), the angle subtended at the copper atom by the two cyanide linkages being reduced to  $124.1(6)^\circ$  (Table 8).

In all four complexes, the cyanide is linearly co-ordinated; no angle at any cyanide carbon or nitrogen is less than  $169^\circ$ , and no tendency toward multiple co-ordination by either atom is observed. All copper-carbon distances lie in the range 1.86–1.88 Å and show no significant differences; Cu-N(cyanide) distances range from 1.89(1) in (2) (possibly unrealistically low because of disorder) to 1.94(2) Å in (4), the range again being of doubtful significance. The angle between the cyanide groups, by contrast, appears to be much more sensitive to changes in the co-ordination environment of the copper, and its variations have been noted above. Infrared absorption bands assignable to bridging  $-C\equiv N-$  stretching modes are observed for all four complexes in the region  $2100-2160\text{ cm}^{-1}$ : (1), 2160w (br), 2100s (br); (2), 2140, 2110w (sharp); (3) 2100s (br); (4) 2100s (sharp).

Given the occurrence of three-co-ordinate copper(I) in three of the complexes, the observation that no Cu-N(base) distance is less than 2.09 Å is convincing evidence that, relative to the cyanide, the bases are very weakly co-ordinated indeed {cf. the value of 1.99 Å for the Cu-N distance in  $[Cu(2Me-py)_3]^+$ }.<sup>13</sup> We note also, that in the thiocyanate complexes discussed elsewhere,<sup>1</sup> four-co-ordination of the copper in the context of one-dimensional polymer formation is the norm, except in cases of extreme steric hindrance by the ligand, leading normally to complexes of stoichiometry  $Cu(SCN)L_2$ . In the latter complexes, the angle subtended at the copper by the two

thiocyanate ligands is much closer to the tetrahedral norm than is the case in the present cyanide complexes. In the present series of experiments we observed no reaction between sterically hindered bases and Cu(CN), again illustrating the stability of the polymeric  $[\text{Cu}(\text{CN})]_{\infty}$  chain structure in these complexes.

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