# Syntheses, Structures and Vibrational Spectroscopy of Some Mixed Pyridine/Triphenylphosphine Adducts of Copper(I) Cyanide

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 70$^{th}$ birthday*

Single crystal room temperature X-ray structure determinations are described for three adducts formed between copper(I) cyanide, pyridine ('py') and triphenylphosphine of (p : q : r =) 1:1:1, 1:1.5:0.5 and 1:0.5:2 (plus py hemisolvate) stoichiometry. The latter is binuclear [(Ph$_3$P)$_2$(py)Cu($\mu$-CN)Cu(PPh$_3$)$_2$(CN)]. py; the others are linear polymers with …Cu($\mu$-NC)Cu($\mu$-NC)Cu… spines with four-coordinate copper atoms, the coordination sphere of every copper atom in the first being completed by pendant py and Ph$_3$P ligands, while the second has those of alternate copper atoms coordinated by a pair of py ligands. Assignment of bridging CN in all cases is crystallographically ambiguous. The IR spectra of the infinite polymeric complexes show bands that are assigned to vibrations of the CuCN chains in the complexes: $\nu$(CN), $\nu$(CuC/N) (the CuC/N stretching mode, involving vibration of the CN group between its two neighbouring Cu atoms), $\delta$(CuCN) (the restricted rotation of the CN group) and $\delta$(NCuC) (the counter vibration of the Cu substructure against the CN substructure). The $\nu$(CN) and $\nu$(CuC/N) frequencies show correlations with the Cu-C/N bond lengths that are similar in form to those recently established for a range of AgCN complexes.

*Key words:* Copper Cyanide, Pyridine, Triphenylphosphine, Structure, Infrared Spectroscopy

## Introduction

As described in a number of earlier studies, the possibility of supplanting or augmenting the (nitrogen-base) ligand complement in adducts of the form MX : L (1:n) (M = Cu, Ag; X = Cl, Br, I) by the addition of unidentate ligands derivative of the higher pnictides, E, has been extensively explored, and is readily attainable, adducts of the form MX : L : L' (1:q:r) being readily achieved for L, L' = the parent pyridine ('py'), triphenylphosphine ligands for combinations q:r = 1:2, 1:1 [1 – 5], the former being mononuclear [(Ph$_3$P)$_2$(py)MX] [1, 2], and the latter binuclear [(Ph$_3$P)(py)M($\mu$-X)$_2$M(py)(PPh$_3$)] [3, 4]. The possibility of obtaining similar arrays with X = pseudohalogen, in particular SCN or CN, has been much less extensively studied, there being as yet no structurally characterized examples of complexes of the form MCN : N-base : tertiary pnictide ER$_3$ (p:q:r), as pertinent to the present context [6], described, apart from the adduct [Cu$_2$(CN)$_2$(PPh$_3$)$_4$('hppH')] recently reported, where 'hppH' is a pyrimidine base [7]. Extending the previous essays, copper(I) cyanide: triphenylphosphine mixtures have been crystallised from pyridine. Three distinct complexes have been obtained for which single crystals have been isolated and, as described hereunder, subjected to single crystal X-ray studies, reported herein as having 1:0.5:2 (plus py hemisolvate), 1:1:1 and 1:1.5:0.5 CuCN : py : PPh$_3$ stoichiometry, their structures, together with those previously determined for related species, forming a basis for interpretation of their vibrational spectroscopy.

## Experimental Section

*Synthesis*

These compounds were prepared by the dissolution of 0.1 mmol of copper(I) cyanide in a solution of 0.2, 0.1, or 0.05 mmol of triphenylphosphine in pyridine, by a combination of stirring and gentle warming. The reaction mixtures were allowed to stand until sufficient pyridine had evaporated to give colourless deposits of well-formed, albeit small crystals, which were isolated by filtration.

**CuCN : py : PPh$_3$ (:py solvent) (1:0.5:2(:0.5))-** C$_{82}$H$_{70}$Cu$_2$ N$_4$P$_4$ (1386.5): calcd. C 72.79, H 5.05, N 4.04, Cu 9.17; found C 73.2, H 4.9, N 3.7, Cu 8.9.

**CuCN : py : PPh$_3$ (1:1:1)**-C$_{24}$H$_{20}$CuN$_2$P (431.0): calcd. C 66.91, H 4.64, N 6.50, Cu 14.75; found C 67.1, H 4.7, N 6.7, Cu 14.5.

**CuCN : py : PPh$_3$ (1:1.5:0.5)**-C$_{35}$H$_{30}$Cu$_2$N$_5$P$_2$ (678.5): calcd. C 61.95, H 4.42, N 10.32, Cu 18.73; found: C 62.0, H 4.5, N 10.3, Cu 18.9.

*Spectroscopy*

General procedural details are given in an accompanying paper [6].

*Structure determinations*

General procedures are described in ref. [6], all determinations using a single counter instrument at *ca.* 295 K, $2\theta_{max}$ being 50°; specific crystal/refinement details are as follows:

**CuCN : py : PPh$_3$ (:py solvent) (1:0.5:2(:0.5))**$_{(\infty|\infty)}$. C$_{84}$H$_{70}$Cu$_2$N$_4$P$_4$, $M = 1386.5$. Triclinic, space group $P\bar{1}$ ($C_i^1$, No. 2), $a = 25.23(8)$, $b = 12.97(1)$, $c = 12.38(2)$ Å, $\alpha = 114.97(9)$, $\beta = 93.35(11)$, $\gamma = 101.45(12)°$, $V = 3554$ Å$^3$. $Z = 2$ dimers; $\rho_{calcd.} = 1.29_6$ g cm$^{-3}$. $\mu_{Mo} = 7.4$ cm$^{-1}$; specimen: $0.375 \times 0.225 \times 0.12$ mm; $T_{min,max} = 0.83, 0.91$. $N = 12576$, $N_o = 4812$; $R = 0.099$, $R_w = 0.11$. $|\Delta\rho_{max}| = 1.48(2)$ e Å$^{-3}$.

*Variata*. Weak and limited data resulted in a determination of inferior precision; the central CN group was modelled as disordered end for end with composite C/N atoms, while the peripheral was treated as C bound. 'Thermal motion' on the solvent pyridine was very high and refined using isotropic forms for the non-hydrogen atoms with site occupancy set at unity after trial refinement. The assignment of N is tentative.

**CuCN : py : PPh$_3$ (1:1:1)**. C$_{24}$H$_{20}$CuN$_2$P, $M = 431.0$. Monoclinic, space group $C2/c$ ($C_{2h}^6$, No. 15), $a = 8.979(9)$, $b = 27.617(9)$, $c = 9.038(8)$ Å, $\beta = 115.50(7)°$, $V = 2023$ Å$^3$. $Z = 8$; $\rho_{calcd.} = 1.41_5$ g cm$^{-3}$. $\mu_{Mo} = 11.7$ cm$^{-1}$; specimen: $0.30 \times 0.05 \times 0.13$ mm; $T_{min,max} = 0.82, 0.95$. $N = 3561$, $N_o = 1336$; $R = 0.064$, $R_w = 0.060$. $|\Delta\rho_{max}| = 0.74(3)$ e Å$^{-3}$.

**CuCN : py : PPh$_3$ (1:1.5:0.5)**$_{(\infty|\infty)}$. ($\times 2$) $\equiv$ C$_{35}$H$_{30}$Cu$_2$N$_5$P$_2$, $M = 678.5$. Monoclinic, space group $C2/c$, $a = 15.306(8)$, $b = 9.528(4)$, $c = 43.55(3)$ Å, $\beta = 91.10(5)°$, $V = 6350$ Å$^3$. $Z = 8$; $\rho_{calcd.} = 1.42_0$ g cm$^{-3}$. $\mu_{Mo} = 14.4$ cm$^{-1}$; specimen: $0.25 \times 0.45 \times 0.175$ mm; $T_{min,max} = 1.26, 1.40$. $N = 5683$, $N_o = 3287$; $R = 0.048$, $R_w = 0.048$. $|\Delta\rho_{max}| = 0.58(2)$ e Å$^{-3}$.

*Variata*. In the second compound the specimen size was small, with data correspondingly weak and limited. Problems with the third arose by virtue of the long axial length, data being recorded by an $\omega$ scan technique, with some evident profile overlap in certain areas, despite a nice specimen with narrow line width. (*Caveat*: This may cause systematic errors in derivative geometries.) In both, behaviour of the cyanide

groups, coordinating through both ends was such as to suggest a lack of ordering, and the two atoms accordingly were treated as C/N composites.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 246240–246242. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

## Discussion

*Structural studies*

In executing an array of structure determinations necessitating the aquisition of reasonably crystalline material for a variety of copper(I) salt : phosphine ligand adducts, we have often noted the difficulty (relative, *e.g.*, to their silver(I) counterparts) of obtaining adequately crystalline samples under conditions also yielding stoichiometric purity. In studying the present series of complexes, where the results obtained indicate an array of rather similar species differing in ligand ratio and aggregation by way of the use of potentially bridging ligands in a manner which would appear to lend itself to a widely and continuously variable array of coexisting species, we find each of the complexes described to be obtained as a highly crystalline, analytically pure species without undue precautions or synthetic difficulty. All contain, in various ratios, copper(I) cyanide, triphenylphosphine and pyridine in novel forms, and are obtained by the crystallisation of appropriate stoichiometric mixtures of copper(I) cyanide and triphenylphosphine from pyridine; one is binuclear and the others one-dimensional polymers, single-stranded with the cyanide linkages between the copper atoms bridging end-on, contrasting with other adducts of the form CuX : unidentate N-base: unidentate tertiary phosphorus base (p:q:r), which, for simple X = halide, are overwhelmingly mononuclear [XCu(N-base)$_q$(PR$_3$)$_r$] or binuclear [(R$_3$P)(N-base) Cu($\mu$-X)$_2$Cu(N-base)(PR$_3$)] arrays.

**CuCN : py : PPh$_3$ (1:1:2)**. This, [(Ph$_3$P)$_2$(py) Cu($\mu$-*CN*)Cu(PPh$_3$)$_2$(CN)].py, despite being the 'largest' of the three structures (and least precisely determined), is comprised of discrete binuclear species of CuCN : py : PPh$_3$ (1:0.5:2) stoichiometry with an additional 0.5 pyridine of solvation, with tentative N assignment; one formula unit makes up the asymmetric unit of the structure, the unsolvated residue being
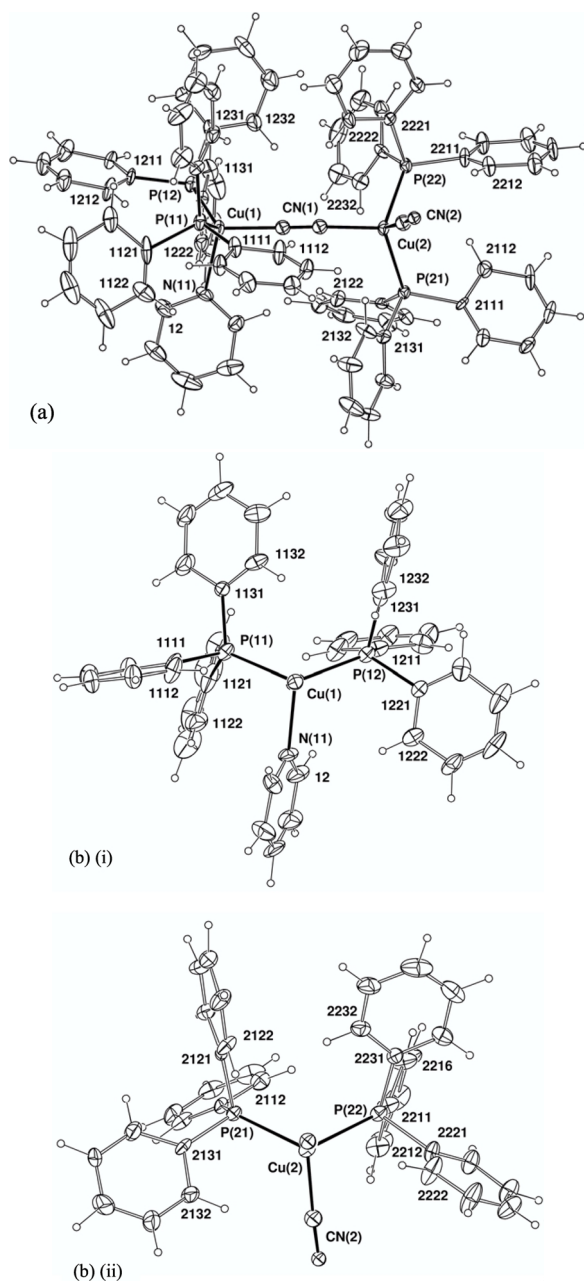
(a)

(b) (i)

(b) (ii)

Fig. 1. (a) The dimer of CuCN : py : PPh$_3$ (:py solvent) (1:0.5:2(:0.5)), [(Ph$_3$P$_2$(py)Cu($\mu$-*CN*)Cu(PPh$_3$)$_2$(CN)], viewed normal to the Cu...Cu line, and (b) (i),(ii) the two copper environments viewed, in each case down the central cyanide-Cu bond, showing the similar (but inverse) ligand conformations.

formally similar to the pyrimidine analogue recently reported [7]. The two copper atoms are linked by a cyanide group, terminally bound to each. Difference

map residues and thermal motion behaviour suggested end for end disordered cyanides to be superimposed: the aggregate and the structure was modelled with a pair of C/N composites, refined with isotropic displacement parameter forms converging to very similar values. The two copper atoms are both four-coordinate, each carrying a pair of triphenylphosphine ligands; the fourth site is occupied about Cu(1) by a pyridine ligand, and about Cu(2) by a cyanide, presumed on the basis of refinement behaviour and geometry to be C bound, but with the carbon atom thermal envelope possibly indicative of some insecurity in the assignment. The molecule is shown side-on to the Cu...Cu line in Fig. 1(a); from the latter it is evident that the ligand dispositions about the pair of copper atoms are almost eclipsed, (as is also the case in the polymers (see below)), with the pyridine and terminal cyanide ligands eclipsing triphenylphosphine ligands, and P(12) eclipsing P(22). Ligand-Cu(1)...Cu(2)-Ligand torsion angles are (specifying the relevant ligand atoms) P(11)...C(2), −1.1(4); N(11)...P(21), 14.7(4); P(12)...P(22), 23.0(2)$^\circ$. Interestingly the Cu-P(n2) distances associated with the eclipsed pair of phosphorus atoms, which might be expected to be the most sterically hindered phosphine ligands are, if anything, shorter than their Cu-P(n1) counterparts. Ligand dispositions about the two copper atoms are compared in Fig. 1(b), shown projected down the central cyanide-copper bond, showing very similar conformations, albeit mirror images.

Formally, the environment of Cu(1) here may be regarded as analogous to those of the previously studied mononuclear [(Ph$_3$P)$_2$(py)CuX] [1], all X therein Cl, Br, I, *cf.* the present end-on bridging (disordered?) cyanide. Cu-P in those complexes are shortest for X = Cl (2.256(1), 2.272(1)), and longest for X = I (2.283(2), 2.292(2) Å), with associated P-Cu-P 125.82(5), 125.95(6)$^\circ$; the present example (Table 1) has values corresponding rather well with those for the intermediate bromide (isomorphous with the chloride) (2.277(3), 2.286(4) Å); 123.6(1)$^\circ$, perhaps rather a surprising finding in view of the different bonding characteristics of cyanide *cf.* the halides, as demonstrated in other related studies [8]. The Cu-N(py) distances in the three halide complexes (2.130(2), 2.145(9), 2.131(5) Å) are also similar to the present.

**CuCN:py:PPh$_3$ (1:1:1)**. This is the simplest of the three complexes stoichiometrically and stereochemically, one formula unit compris-

Table 1. Metal atom environments. (a) CuCN : py : PPh$_3$ (:py) (1:0.5:2:(0.5)). The two values in each entry are for Cu(1,2) respectively; C/N is associated with the central cyanide while X is the pyridine nitrogen for Cu(1) and the cyanide carbon for Cu(2). *r* is the metal-ligand atom distance (Å); other entries are the angles subtended by the relevant atoms at the head of the row and column.

| Atom | *r* | P(2) | C/N | X |
|---|---|---|---|---|
| P(1) | 2.289(7) | 122.2(2) | 110.8(5) | 102.5(5) |
|  | 2.295(8) | 118.0(2) | 104.6(5) | 112.9(4) |
| P(2) | 2.274(5) |  | 107.3(5) | 110.9(4) |
|  | 2.273(7) |  | 103.7(5) | 104.0(6) |
| C/N | 1.98(2) |  |  | 101.1(7) |
|  | 1.98(1) |  |  | 113.7(6) |
| X | 2.12(2) |  |  |  |
|  | 1.98(1) |  |  |  |

Cu...Cu is 5.073(7) Å.

(b) Cu : CN : py (1:1:1). C/N belongs to the copper atom of the asymmetric unit, while (C/N)' is symmetry generated. N(2) is the pyridine nitrogen atom.

| Atom | *r* | (C/N)' | N(2) | P |
|---|---|---|---|---|
| C/N | 1.97(1) | 123.6(5) | 100.4(5) | 109.3(4) |
| (C/N)' | 1.99(1) |  | 99.1(5) | 116.5(3) |
| N(2) | 2.19(1) |  |  | 103.5(4) |
| P | 2.284(4) |  |  |  |

Cu...Cu are 5.025(5) Å.

(c) CuCN : py : PPh$_3$ (2:3:1). N(lm1) are the nitrogen atoms of pyridine l.

| Cu(1) | *r* | N/C(1') | N(111) | P |
|---|---|---|---|---|
| N/C(1) | 1.950(5) | 117.5(2) | 100.0(2) | 122.2(2) |
| N/C(1') | 1.977(5) |  | 97.1(2) | 109.0(1) |
| N(111) | 2.196(5) |  |  | 106.5(1) |
| P | 2.257(2) |  |  |  |

| Cu(2) | *r* | N/C(2') | N(211) | N(221) |
|---|---|---|---|---|
| N/C(2) | 1.946(5) | 134.4(2) | 107.3(2) | 105.4(2) |
| N/C(2') | 1.943(3) |  | 105.8(2) | 102.2(2) |
| N(211) | 2.148(5) |  |  | 94.8(2) |
| N(221) | 2.228(5) |  |  |  |

Cu(1)...Cu(2) ($x, y, z; x - \frac{1}{2}, \frac{1}{2} + y, z$) are 4.922(2), 5.033(2) Å.



(a)



(b)

Fig. 2. (a),(b) Sections of the CuCN : py : PPh$_3$ (1:1:1) and (2:3:1) polymers.

ing the asymmetric unit of the structure. The complex is an infinite one-dimensional polymer (glide plane as generator), with successive copper atoms linked by end-bonded cyanide groups, modelled with disordered C/N composite atoms, ...{Cu(py)(PPh$_3$)}(CN){Cu(py)(PPh$_3$)}(CN)... The copper atoms are again four-coordinate, with the phosphine and pyridine nitrogen atoms making up the coordination sphere. A view of a section of the polymer is shown in Fig. 2. The N(py)-Cu...Cu-N(py) torsion angle is −5(2)°. A formal analogy with previously studied CuX : py : PPh$_3$ (1:1:1) arrays
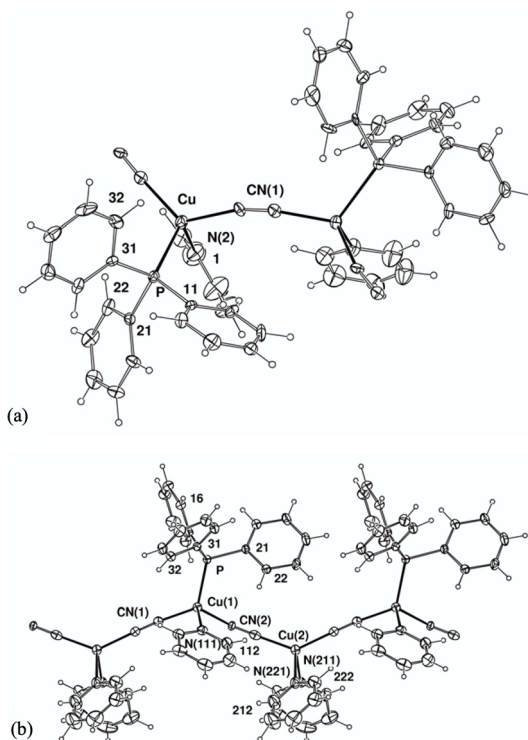
is less pertinent in this case, since, although the copper environment is indeed P$_2$CuX$_2$, the bridging nature of the attached X species differs considerably, being components of a single-stranded polymer in the cyanide, while in the halides the ($\mu$-X)$_2$ array, constrained by the binuclear nature of the complexes with their Cu($\mu$-X)$_2$Cu cores, with diminished X-Cu-C angles, may be considered to comprise a bidentate ligand of small 'bite'.

**CuCN:py:PPh$_3$ (2:3:1)**. Here, one formula unit (containing two copper atoms) makes up the asymmetric unit of the structure. Like the preceding, the complex is an infinite one-dimensional polymer, generated by the *C*-translation, with four-coordinate copper atoms, two of the coordination sites being occupied by the end-bonded bridging cyanides, again modelled with disordered composite atoms. The remaining coordination sites about the copper atoms are alternately a pair of pyridine nitrogen atoms, and a pyridine nitrogen and a triphenylphosphine phosphorus, ...{Cu(py)(PPh$_3$)}(CN){Cu(py)$_2$}(CN)... The N(111)-Cu(1)...Cu(2)-N(221) torsion angle is 15.1(2)°. The environment of Cu(1) is similar to that of

Table 2. Torsion angles (degrees). Where values are italicized read 6 instead of 2 for the ortho ring carbon.

| (C/N implicit) Atoms | C/N-Cu-P(N)-C(lmn1) | Cu-P-C(lmn1)-C(lmn2) |
|---|---|---|
| CuCN : py : PPh$_3$ (:py) (1:0.5:2(:0.5)) | | |
| Cu(1), P(11), C(1111) | −34(1) | 29(2) |
| C(1121) | −149.0(8) | 71(2) |
| C(1131) | 86.3(9) | −13(1) |
| P(12), C(1211) | −178.8(9) | 15(2) |
| C(1221) | 60.4(9) | 37(1) |
| C(1231) | −58.6(9) | 60(2) |
| Cu(1), N(11), (C(12)) | 18(2) | – |
| Cu(2), P(21), C(2111) | 172.2(8) | −52(1) |
| C(2121) | 48.2(9) | −49(2) |
| C(2131) | −66.0(7) | −12(1) |
| P(22), C(2211) | −172.0(8) | −47(2) |
| C(2221) | 70.9(8) | −44(2) |
| C(2231) | −44.1(8) | −17(2) |
| CuCN : py : PPh$_3$ (1:1:1) | | |
| Cu, P, C(11) | −12.0(5), −158.2(6) | −37(1) |
| C(21) | −131.4(5), 82.5(6) | −37(1) |
| C(31) | 108.1(7), −38.1(7) | 36(2) |
| Cu, N(2), C(2) | 64(1), 8(1) | – |
| CuCN : py : PPh$_3$ (2:3:1) | | |
| Cu(1), P, C(11) | −38.8(3), 103.8(2) | −34.4(5) |
| C(21) | −158.6(3), −16.0(3) | −38.8(5) |
| C(31) | 82.5(3), −134.9(2) | −40.7(5) |
| Cu(1), N(111), C(112) | −35.5(4), 17.4(5) | – |
| Cu(2), N(211), C(212) | −8.6(6), 28.8 (6) | – |
| N(221), C(222) | 44.8(6), 13.9(6) | – |

the preceding compound, the environment about both of the copper atoms being PNCu(end-on cyanide)$_2$; the entries of Table 1 show that in detail, the correspondence is only approximate with the Cu-P distances differing by nearly 0.03 Å, and divergences in counterpart angles of up to *ca.* 6°. A variety of complexes of copper(I) cyanide with unidentate pyridine bases have been recorded, the most relevant to the present purposes being the 1:2 complexes with pyridine [6] and 4-methylpyridine [9], both one- dimensional linear polymers with four-coordinate copper atoms archetypical of those found in the 2:3:1 adduct. Their Cu-N(py base) distances are 2.148(5), 2.228(5) Å, *cf.* values of 2.12(2) Å in the binuclear species and 2.19(1) Å in the 1:1:1 adduct. In CuCN: py, 4mp (1:2) Cu-N(py base) are 2.10(1), 2.25(2) Å and 2.097(2), 2.161(7) Å; N-Cu-N in these latter are 94.8(6) and 96.4(3)°, *cf.* the counterpart value of 94.8(2)° in the 2:3:1 adduct. These latter values, lying well below the tetrahedral norm are consistent with the Cu-N(py base) interactions being among the weakest in the structures studied.

Substantial differences may be noted in the geometries, presented comparatively in Table 1, in particular, for the copper atoms with common environments suggestive that more general conclusions concerning geometry across the whole series may need to be considered circumspectly. The following further points may be noted:

(i) Cu-P distances range between 2.257(2) to 2.295(8) Å, broadly corresponding to values in the four-coordinate mononuclear copper(I) analogues [1]. Except for ligand 1 of the binuclear array, all phosphine ligands conform reasonably, (and quite closely throughout the others) to three-fold symmetry about Cu-P (Table 2).

(ii) The parent copper(I) cyanide can exist in two different crystalline phases, both of which contain one dimensional copper cyanide chains with the cyanide ambiguous in respect of end-for-end disorder [10–12]. The structures of the chains in the two phases are sufficiently similar that they cannot easily be distinguished by magnetic resonance or vibrational spectroscopy [11–13]. Single crystal data for a (possibly) hydrated adduct is available [14]; that complex, like most other copper(I) cyanide species structurally authenticated, has cyanide moieties bridging successive copper atoms in poly-( or oligo-) meric arrays, the copper atom normally having a coordination number other than four, and the cyanide ambiguous in respect of end-for-end disorder. Potentially, the most valuable piece of single crystal information providing unambiguously coordinated cyanide to copper(I) bonding is the determination of the mononuclear anion in K$_3$[Cu(CN)$_4$] [15]; in that determination, old, but nevertheless of very acceptable precision, the anion lies on a 3-fold axis in space group *R*3*c* with two independent Cu-C distances of 2.01(1) (unique) and 1.992(7) Å (×3). Although unambiguous, perhaps because of the unique array in this complex, these distances appear to be rather longer than other (possibly disordered) typical Cu-C distances in C-bound cyanide which would appear to be of the order of 1.85–1.95 Å, a range in keeping with present estimates of 1.95–2.0 Å for disordered species, the one (presumably) terminally coordinated cyanide being bound at 1.98(1) Å in the less precise determination of the binuclear species.
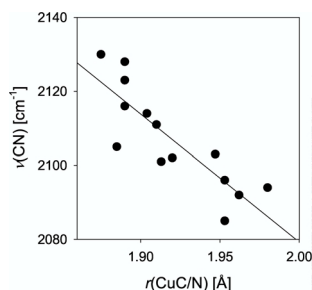
*Vibrational spectra*

The infrared spectra of the complexes reported in the present study were recorded in order to establish

Table 3. The IR $v(CN)$ wavenumbers $(cm^{-1})$ and related Cu-C/N bond lengths [Å].

| Compound | $v(CN)$ | $r(Cu - C/N)$ |
|---|---|---|
| CuCN : py : PPh$_3$ (1:0.5:2) | 2116 | 1.98(1) |
| | 2098 | 1.98(2), 1.99(1) |
| CuCN : py : PPh$_3$ (1:1:1) | 2094 | 1.97(1), 1.99(1) |
| CuCN : py : PPh$_3$ (2:3:1) | 2103 | 1.950(5), 1.943(3) |
| | 2092 | 1.977(5), 1.946(5) |



Fig. 3. Plot of the wavenumber of the $v(CN)$ band against the mean Cu-C/N bond length for compounds that have infinite chain structures.

correlations between the vibrational frequencies of the CuCN entities and their structures as revealed in the X-ray study. The IR spectra of all of the compounds studied showed strong $v(CN)$ bands, whose frequencies are listed in Table 3. We have recently shown that a correlation exists between the $v(CN)$ frequencies and the Ag-C/N bond lengths in a number of AgCN complexes, such that $v(CN)$ increases with decreasing Ag-C/N bond length [16]. Considering first the two complexes that have infinite -CuCNCuCN-chain structures, a similar trend is evident in the data for these complexes presented in Table 3. In the cases where two $v(CN)$ bands are observed, corresponding to the presence of two inequivalent CN groups in the structure, the higher wavenumber band has been assigned to the CN group with the shorter Cu-C/N bond length (the average of the two bond lengths has been used in the case of the linearly bridging CN groups). The relationship between $v(CN)$ and $r(Cu - C/N)$, using data for the two complexes in the present study that have infinite -CuCNCuCN- chain structures (together with data for the CuCN : amine base complexes with similar structure from ref. [6]), is shown in Fig. 3. Although the plot shows a significant degree of scatter, which arises mainly from the two compounds that have two inequivalent CN groups in their infinite chains, the relationship is similar to that observed previously for analogous AgCN complexes [16]. For a 0.1 Å decrease in the M-C/N bond length, the increase in $v(CN)$ is about 35 cm$^{-1}$ for M = Cu, compared with about 20 cm$^{-1}$ for M = Ag [16]. In addition to the sharp bands listed in Table 3, the two polymers each showed one weaker but broader $v(CN)$ band, at 2113 and 2118 cm$^{-1}$ respectively. The origin of these bands is not known with certainty at present, but one possibility is that they arise from partial loss of pyridine from the CuCN polymer chains.

In the case of the binuclear array, the only discrete molecular species in Table 3, the IR spectrum shows two well-resolved $v(CN)$ bands, in agreement with the structure [(Ph$_3$P$_2$)(py)Cu($\mu$-CN)Cu(PPh$_3$)$_2$(CN)], which contains one linearly bridging and one terminal CN group. The assignment of the higher frequency band to the terminal group is tentatively made on the basis of the shorter Cu-C/N bond length for this group, although it should be noted that the rate of increase of $v(CN)$ with decreasing M-C/N was found to be greater for linear bridging CN than for terminal CN in the case of M = Ag [16]. At present there are insufficient experimental data for complexes with terminal Cu-CN bonds to allow a comparison with the results for the linear bridging case for copper(I) complexes.

It has recently been shown by vibrational spectroscopy that for the infinite linear -CuCN-CuCN-chains in solid CuCN, $v(CN) = 2170$ cm$^{-1}$ [13]. The $v(CN)$ frequencies for the chain polymers in Table 3 are lower than this, as a result of the fact that the binding of the Group 15 donor ligand to the copper weakens the Cu-C/N bonds, and thus lowers the $v(CN)$. The trend in Fig. 3 thus reflects the increased strength of binding of copper(I) by PPh$_3$ relative to the nitrogen bases.

The far-IR spectra of the three CuCN : py : PPh$_3$ complexes were recorded in an attempt to observe the other vibrational modes of the dimeric and polymeric CuCN groups that they contain. The spectra are shown in Fig. 4. The following low-frequency vibrational modes have previously been assigned in the infinite linear -CuCNCuCN- chains present in solid CuCN : $v(CuC/N) = 591$ cm$^{-1}$, involving vibration of the CN group between its two neighbouring Cu atoms; $\delta(CuCN) = 326$ cm$^{-1}$, which can be described as a restricted rotation of the CN group; $\delta(NCuC) = 168$ cm$^{-1}$, which can be described as a counter-vibration of the Cu substructure against the CN substructure, in a direction perpendicular to the CuCN chains [13]. In the infinite chain compounds in which the copper atoms are coordinated to the Group 15 donor ligand, shifts in the above frequencies and
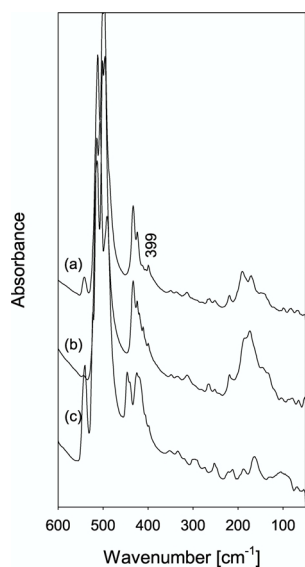
Fig. 4. Far-IR spectra of (a) CuCN : py : PPh$_3$ (1:1:1), (b) CuCN : py : PPh$_3$ (2:3:1), and (c) CuCN : py : PPh$_3$ (1:0.5:2).

splitting of the bending modes (which are doubly degenerate in the isolated linear chains) are expected. For the $\nu$(CuC/N) mode, a downward frequency shift is expected because the binding of the Group 15 ligand weakens the Cu-C/N bonds, and this is observed in CuCN : NEt$_3$ (1:1), where $\nu$(CuC/N) is observed as a weak band in the IR at 531 cm$^{-1}$ [6]. Still lower frequencies are expected for the CuCN : py : PPh$_3$ complexes, but unfortunately the appropriate region of the IR spectra (between 400 and 550 cm$^{-1}$) is obscured by strong bands due to the PPh$_3$ and pyridine ligands. However, in the case of the 1:1:1 compound, there is a weak but sharp band at 399 cm$^{-1}$ that appears to be in the right position to be assigned to the single $\nu$(CuC/N) mode expected for this complex. Strong support for this assignment is obtained from the $\nu$(CuC/N) *vs.* $r$(CuC/N) relationship found previously for a wide range of CuCN... amine base complexes with infinite -CuCNCuCN-structures [6]. This suggests that a similar relationship exists for the CuCN complexes, as would be expected. The two other CuCN : py : PPh$_3$ arrays (1:0.5:2(:0.5 py), and 2:3:1) have more complicated structures with two distinct CN environments, compared with the 1:1:1 complex, which has only one CN environment. The Cu-C/N distances in the former two complexes are similar to those in the latter, so that similar $\nu$(CuC/N) frequencies would be expected. The spectra show evidence of weak

bands in the 400 cm$^{-1}$ region, but there is severe overlap with ligand bands so that no definite assignments can be made in these cases.

The far-IR spectra also contain bands below 400 cm$^{-1}$, some of which can be assigned to vibrations of the CuCN entities. We consider first the two polymers, both of which contain infinite CuCN chains. Weak bands at about 310 cm$^{-1}$ are assigned to $\delta$(CuCN), and stronger bands in the range 170–190 cm$^{-1}$ are due to $\delta$(NCuC). These doubly degenerate (perpendicular) modes give rise to a single band in the linear chains of CuCN itself, but the axial symmetry of the chains is lost in the present complexes. The observed multiplicity of these bands (Fig. 4) is probably due to this loss of symmetry. In the binuclear complex, the spectrum is complicated by the presence of both terminal and linear bridging CN bonding modes, and again no specific assignments of the low frequency modes are possible. It is noteworthy that the relatively strong bands in the range 170–190 cm$^{-1}$ due to $\delta$(NCuC) in the chain polymer structures are absent in the spectrum of the binuclear complex. The presence of such bands appears to be characteristic of the chain polymer structure.

## Conclusions

Unlike their counterpart CuX : py : PPh$_3$ (p:q:r) halide (X = Cl, Br, I) adducts, which are discrete mono- or bi-nuclear species, the latter with the molecular core of the form M($\mu$-X)$_2$M, X = CN adducts of this form which have been isolated and structurally characterized take the aspect of solvated strands of (CuCN)$_{(\infty|\infty)}$ or fragments thereof, with characteristic IR spectra. The polymeric adducts may be viewed as developments of the polymeric CuCN : py (1:2) array, recorded in a preceding paper [6], which is a single-stranded copper(I) cyanide polymer, each copper atom becoming four-coordinate by the coordination of a pair of py ligands; in the present pair of adducts, one py ligand, firstly on alternating/successive copper atoms replaced by PPh$_3$, then one ligand on each copper atom. Further increased substitution by PPh$_3$ results in fragmentation of the chain into dimers, one of the cyanides at the (Ph$_3$P)$_2$Cu unit becoming terminal. This presents an interesting contrast with CuCN : PPh$_3$ (1:2) which has a cyclic hexameric (CuCN)$_6$ core, the phosphines appended at the four-coordinate atoms [17]. Interestingly, there appears as yet to be no structural authentication of any CuCN : PPh$_3$ (1:3) adduct.

[1] L. M. Engelhardt, P. C. Healy, J. D. Kildea, A. H. White, Aust. J. Chem. **42**, 895 (1989).

[2] L. M. Engelhardt, P. C. Healy, J. D. Kildea, A. H. White, Aust. J. Chem. **42**, 907 (1989).

[3] L. M. Engelhardt, P. C. Healy, J. D. Kildea, A. H. White, Aust. J. Chem. **42**, 913 (1989).

[4] S. Gotsis, L. M. Engelhardt, P. C. Healy, J. D. Kildea, A. H. White, Aust. J. Chem. **42**, 923 (1989).

[5] Effendy, L. M. Engelhardt, P. C. Healy, B. W. Skelton, A. H. White, Aust. J. Chem. **44**, 1585 (1991), (corrigenda to refs. [2 – 4]).

[6] G. A. Bowmaker, K. C. Lim, B. W. Skelton, A. H. White, Z. Naturforsch. **59b**, 1264 (2004).

[7] M. P. Coles, P. B. Hitchcock, Polyhedron **20**, 3027 (2001).

[8] (e.g.) Effendy, J. D. Kildea, A. H. White, Aust. J. Chem. **50**, 587 (1997).

[9] J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, A. H. White, J. Chem. Soc., Dalton Trans. 839 (1985).

[10] S. J. Hibble, S.M. Cheyne, A.C. Hannon, S.G. Eversfield, Inorg. Chem. **41**, 4990 (2002).

[11] S. J. Hibble, S. G. Eversfield, A. R. Cowley, A. M. Chippindale, Angew. Chem. Int. Ed. **43**, 628 (2004).

[12] S. Kroeker, R. Wasylishen, J. V. Hanna, J. Am. Chem. Soc. **121**, 1582 (1999).

[13] G. A. Bowmaker, B. J. Kennedy, J. C. Reid, Inorg. Chem. **37**, 3968 (1998).

[14] J. D. Kildea, B. W. Skelton, A. H. White, Aust. J. Chem. **38**, 1329 (1985).

[15] R. B. Roof, A. C. Larson, D. T. Cromer, Acta Crystallogr., Sect. B **24**, 269 (1968).

[16] G. A. Bowmaker, Effendy, J. C. Reid, C. E. F. Rickard, B. W. Skelton, A. H. White, J. Chem. Soc., Dalton Trans. 2139 (1998).

[17] Y. Zhao, M. Hong, W. Su, R. Cao, Z. Zhou, A. S. C. Chan, J. Chem. Soc., Dalton Trans. 1685 (2000).