Syntheses, Structures and Vibrational Spectroscopy of Some Adducts of Copper(I) Cyanide with Pyridine Bases

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Synthetic and room temperature single crystal X-ray structural characterizations are recorded for adducts of copper(I) cyanide formed by crystallization of copper(I) cyanide from (unidentate) pyridine ('py') bases L, of 1:2 (L = py; new phase), 1:1.5 (L = 2-methylpyridine, '2mp') and 1:1 (L = quinoline, 'quin') stoichiometries. All are single-stranded polymers, with successive copper atoms linked by single linear cyanide bridges (C,N disordered, individual components not resolved), with four- or three-coordinate $N_2Cu(CN)_2$ or $NCu(CN)_2$ copper environments in the 1:2 and 1:1 adducts, these alternating in the 1:1.5 (2:3) adduct. The present and previous related studies providing a basis for a systematic survey of their vibrational spectroscopy. The IR spectra of the infinite polymers show bands that are assigned to vibrations of the CuCN chains in these complexes: ν(CN), ν(CuC/N) (the CuC/CuN stretching mode, involving vibration of the CN group between its two neighbouring Cu atoms), δ(CuCN) (the restricted rotation of the CN group), and δ(NCuC) (the counter-vibration of the Cu substructure against the CN substructure). Gravimetric and vibrational spectroscopic studies following loss of the base molecules from these complexes show that ligand removal occurs in several stages *via* a series of well-defined adducts, some of which have unusual stoichiometries and structures. Conversely, solid CuCN may be "activated" towards adduct formation by prior reaction with pyridine bases.

Key words: Copper Cyanide, Pyridine, Structure, Infrared Spectroscopy, Raman Spectroscopy

Introduction

Despite the long history of transition metal cyanide chemistry, a considerable amount of research on this subject continues to be reported, with remarkable results in areas such as solid state chemistry and materials chemistry [1]. Many of the compounds concerned are polymeric, with unusual structures which derive from the linear bridging coordination mode of the cyanide ligand [1]. A number of complexes of copper(I) cyanide have been reported over the years [2], but recent studies [3 – 7] have shown that there is still much to be learnt about such systems. Copper(I) cyanide has shown promise in the assembly of zeolitic-type frameworks [8], and as a precursor in the synthesis of $YBa_2Cu_3O_{7-x}$ superconductors [9].

The structure and properties of copper(I) cyanide itself have been the subject of a number of studies over the years, and it is surprising to find that new information on the structure of this deceptively simple compound continues to emerge [10 – 14]. The most recently reported results show that solid CuCN can exist in two different crystalline forms, both of which contain one dimensional copper cyanide chains resulting from the common preference of both the copper(I) ion and the cyanide ligand for linear two-fold coordination. In the so-called "high temperature" form [12a], which is isomorphous with AgCN [15], the chains are parallel and exactly linear. In the "low temperature" form [12b], the chains contain five crystallographically distinct Cu atoms which form waves with a repeat corresponding to nine CuCN units. These chains are arranged in alternate layers in which the chain axes are rotated by 49° relative to each other. Despite the names given to these phases, they are interconvertible at room temperature *via* a reaction with aqueous potassium bromide that involves reversible insertion of KBr and water between the CuCN chains [12b, 16].

One of the interesting properties of transition metal cyanide compounds is the unusual inclusion behaviour

of compounds involving two- and three-dimensional polymeric structures [1]. The Group 11 metal(I) cyanides present a unique situation in which essentially one-dimensional metal cyanide structures occur as a result of the common preference of both the metal(I) ion and the cyanide ligand for linear two-coordination [10–12]. This can allow the inclusion of other molecules or ions between the-M-CN-M-CN-chains without disruption of the extended chain structure [16–18], although linkage of metal atoms in adjacent chains by these can be reasonable and feasible [19]. The resulting compounds differ from the clathrate-type inclusion compounds formed by two- or three- dimensional metal cyanide structures, in that the 'guest' molecule or ion can be bound to atoms in the chain. In this respect, they more closely resemble those intercalation compounds in which the guest molecule is coordinatively immobilized [20, 21]. In the Group 11 metal cyanide compounds, interaction of the guest molecule or ion with the metal atom may be relatively weak compared to the intra-chain bonding, giving rise to unusual properties and reactions. The conversion between the two forms of solid CuCN by a reversible reaction with aqueous KBr is an example of one such reaction [12b, 16]. Further examples of such interactions are explored in the present work.

In this paper, we further explore the interaction of pyridine bases with CuCN, which readily absorbs such bases from the gas or liquid phases to form adducts with a range of stoichiometries. Some of these compounds can also be prepared in crystalline form by dissolution of CuCN in a solution of the base in appropriate supporting solvent (acetonitrile is often suitable), or in the neat base itself. Single crystal studies for a number of such complexes with unidentate nitrogen bases, together with a complex with 1,10-phenanthroline ('phen') have been reported previously [17], building upon an earlier study of the 1:1 CuCN : NH_3 adduct [22]. In the latter, a two-dimensional structure is found, comprising motifs of varying complexity, but in the adducts with diethylamine, triethylamine, 4-methylpyridine, ('4mp'), phen, and 2,9-dimethylphenanthroline ('dmp'), single-stranded polymers were found, with single cyanide groups linking the metal atoms end-on, the metal atoms carrying base groups, the stoichiometry being 1:1 in almost all, with the copper atom three-coordinate planar in the adducts with unidentate bases, and four-coordinate in those with bidentate bases. The adduct of 1:1.5 stoichiometry, CuCN : 4mp (1:1.5), is also

a linear polymer, but with alternate three- and four-coordinate metal atoms carrying, respectively, one or two ligands. In much of our work of this type conveniently liquid pyridine bases have been used as both ligand and crystallization solvent, offering the capability of exploring the effects of steric hindrance by the introduction of one (or two) methyl groups in the 2- (and 6-) positions of their planar aromatic rings; in the previous study, because many such adducts were only obtained in microcrystalline form, the net was cast wider, including 'tetrahedral-donor' aliphatic N-bases such as NEt_3, as above.

With the recent availability of (a) more definitive structural data on the parent CuCN [10–12] (b) the advent of a new generation of (CCD/area detector) diffractometer technology, and (c) the possibility of complementing such work with definitive (semi-)quantitative vibrational spectroscopic studies, we have been encouraged to revisit this system, and also, in the following paper, its silver(I) counterpart, with a view to extending the range of cognate information. We record hereunder the structural characterization (by room temperature single crystal X-ray methods) of adducts of 1:1, 1:1.5 and 1:2 copper(I) cyanide : unidentate py-base L stoichiometry for L = quinoline (= 'quin'), 2-methylpyridine (= '2mp') and py, (previously described at 130 K [23], the present study at 300 K defining a new phase) together with a study of a wide range of such complexes by way of vibrational spectroscopy. We also report vibrational spectroscopic studies which, in the reverse process, follow the loss of the base molecules from these complexes. These studies show that in many cases ligand removal occurs in several stages *via* a series of well defined adducts, some of which have unusual stoichiometries and structures.

Experimental Section

Synthesis

The three adducts presently characterized by the single crystal X-ray work were obtained from solutions of copper(I) cyanide in the parent base by cooling and/or evaporation of a saturated solution. The colourless/off-white crystals were very small and were introduced, wet with mother liquor, into capillaries for the X-ray work. On exposure to the atmosphere, they lost solvent/ligand more or less rapidly, so that, generally, melting points are not recorded nor analyses attempted, except as given below.

The samples used in the IR spectroscopic studies were prepared in the above manner, and also *in situ* by adding an

excess of the liquid ligand to solid CuCN, removing the excess liquid, and then preparing the sample as a mull in the normal way. In the case of CuCN : py (1:2) and CuCN : 4mp (1:1.5), samples were also prepared by direct absorption of ligand vapour by solid CuCN. A weighed amount of CuCN in a glass tube was placed in a Schlenk tube containing an excess of the liquid ligand; the Schlenk tube was then closed, evacuated, and allowed to stand, the apparent volume of the solid CuCN increasing considerably as it absorbed the ligand vapour. The mass of the final products confirmed that uptake of 2 mole of py and 1.5 mole of 4mp per mole of CuCN had occurred, with the IR spectra of these products confirming that they were indeed the same as the compounds crystallized from the liquid ligand syntheses. These studies were extended with py and hexamethylenetetramine ('hmt'), as described below.

CuCN : py (1:0.8). Copper(I) cyanide (0.68 g) was dissolved in hot py (10 ml), and hot water (5 ml) was added to the resulting solution. The crystalline solid that formed upon cooling the solution was collected and washed with water. The yellow product, which smells strongly of py, gradually loses py as it dries to form a white solid (yield 1.15 g). $C_5H_4CuN_{1.8}$ (152.8): calcd. C 39.29, H 2.64, N 16.50; found C 39.3, H 2.4, N 16.4.

CuCN : hmt (1.5:1). A solution of hmt (2.2 g, 15.7 mmol) in water (5 ml) was added to solid copper(I) cyanide:py (1:0.8) (0.4 g, 2.6 mmol). The odour of py was apparent upon mixing. The white product was collected and washed with a little water (yield 0.47 g). $C_{15}H_{24}Cu_3N_{11}$ (549.1): calcd. C 32.81, H 4.41, N 28.06; found C 33.1, H 4.1, N 27.7.

Spectroscopy

Infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as Nujol mulls between KBr plates on a Perkin Elmer Spectrum 1000 Fourier-transform infrared spectrometer. Far-infrared spectra were recorded with 2 cm^{-1} resolution at room temperature as pressed Polythene disks or petroleum jelly mulls between Polythene plates on a Digilab FTS-60 Fourier-transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 lines/mm wire mesh beam splitter, a mercury lamp source and a pyroelectric triglycine sulfate detector. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a cooled photomultiplier (RCA C31034A) detector, with 514.8 nm argon-ion laser excitation (Spectra-Physics Model 2016). Fresh samples of the complexes obtained from the preparative procedures described above were used for all vibrational spectroscopic studies.

Structure determinations

The following general crystallographic procedure is appropriate to structure determinations recorded for all of the compounds studied in this and following papers; individual idiosyncrasies/difficulties/variations in procedure/abnormal features (*etc.*) are recorded specifically as appropriate ('*Variata*').

For most determinations recorded herein, unique sequential/single counter diffractometer data sets were measured on capillary mounted specimens within the specified $2\theta_{max}$ limits at room temperature ($\sim$ 295 K) (monochromatic Mo-K_α radiation, λ = 0.71073 Å; $2\theta/\theta$ scan mode). N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement on $|F|$. Unless otherwise stated, a gaussian absorption correction was applied. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, usually constrained at estimated values but refined, as noted, in some cases where the quality of the data was supportive. For a number of determinations, a Bruker AXS CCD area detector instrument was used at *ca.* 153 or 300 K, full spheres of data being measured, and N_t the total number of reflections. Data were processed using proprietary software with 'empirical'/multiscan 'absorption correction' for which $'T'_{min/max}$ are quoted; R_{int} for the merging of the data to N unique reflections is also quoted. Conventional residuals R, R_w on $|F|$ are quoted at convergence for N_o 'observed' reflections with $I > 3\sigma(I)$ (single counter data), $F > 4\sigma(F)$ (CCD data), statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Computation used the XTAL 2.*x* and 3.*x* program systems [24], neutral atom complex scattering factors being used. Pertinent results are given in the Tables (non-hydrogen atom parameters and geometries) and Figures; the latter show labelling (carbon atoms denoted by number only in the more crowded arrays), and 20% (room temperature; 50% 'low' temperature) displacement envelopes, normally anisotropic, for the non-hydrogen atoms, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å. Unit cell projections are given where there is evidence of interspecies packing /arrays of sufficient interest. Full cif. depositions (excluding structure factor amplitudes) have been made with the Cambridge Crystallographic Data Base. Where the space group is non-centrosymmetric, the chirality quoted is the preferred one, in terms of a ratio test or refinement of the 'absolute structure parameter' ('x_{abs}') where meaningful, 'Friedel pairs' $(\bar{h},\bar{k},\bar{l})$ being preserved distinct. Where significant non-trivial residues were found in final difference maps, their treatment is described, usually in terms of full or partial (refined population) 'solvent' occupancies, sometimes 'water' (oxygen). Where metal atom geometries are presented as a matrix, r is the metal-ligand atom distance (Å), the other entries being subtended by the relevant atoms at the head of the row and column.

For the following studies, a CCD instrument operating at *ca.* 300 K was used; crystals were small and weakly diffract-

ing. $(x, y, z, U_{\text{iso}})_H$ were constrained in refinement. In no case could C, N of the cyanide moieties be distinguished, each component being refined as a composite on a common unresolved site. Specific crystal/refinement details are as follows:

CuCN : py (1:2)$_{(\infty|\infty)}$. $C_{11}H_{10}CuN_3$, $M = 247.8$. Orthorhombic, space group $Fdd2$ (C_{2v}^{19}, No. 43), $a = 15.840(2)$, $b = 32.180(5)$, $c = 9.213(1)$ Å, $V = 4696$ Å^3. $Z = 16$; $\rho_{\text{calcd.}} = 1.40_2$ g cm^{-3}. $\mu_{\text{Mo}} = 18.3$ cm^{-1}; specimen: $0.33 \times 0.21 \times 0.22$ mm; $'T'_{\text{min/max}} = 0.78$. $2\theta_{\text{max}} = 58°$; $N_t = 13673$, $N = 1426$ ($R_{\text{int}} = 0.035$), $N_o = 866$; $R = 0.062$, $R_w = 0.065$. $x_{\text{abs}} = 0.15(8)$. $|\Delta\rho_{\text{max}}| = 0.75(1)$ e Å^{-3}.

Variata. The structure of this adduct has been previously described [23] at 130 K in monoclinic space group Cc ($a =$
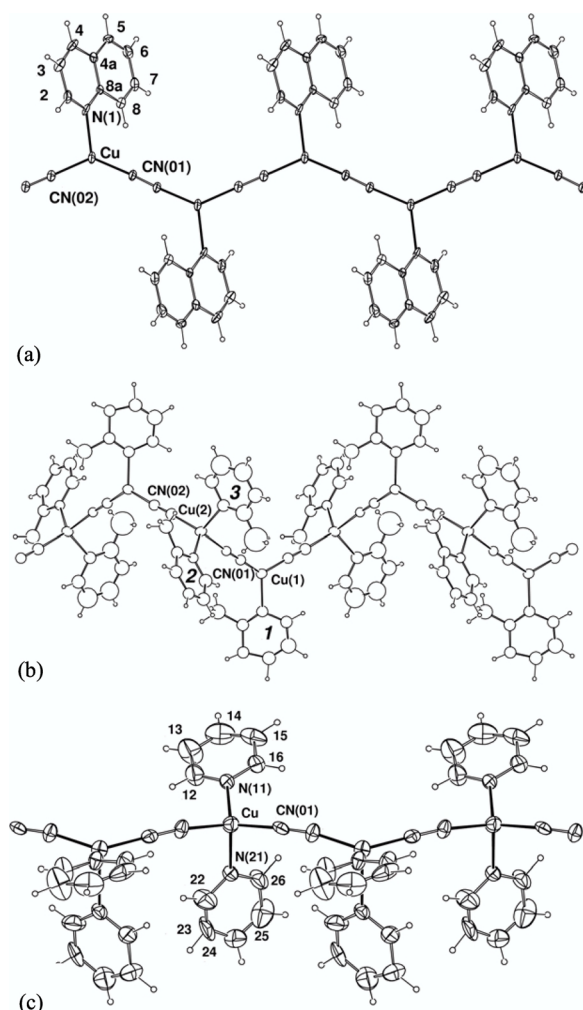

(a)

(b)

(c)

Fig. 1. Projections of the polymer strands normal to their propagation axes in (a) CuCN : quin (1:1), (b) CuCN : 2mp (2:3) (isotropic envelopes; see Experimental Section), and (c) CuCN : py (1:2).

$9.082(2)$, $b = 31.835(7)$, $c = 9.000(2)$ Å, $\beta = 119.44(1)°$, $V = 2266$ Å^3. On examining the nature of the crystals deposited from pyridine solution at room temperature on a capillary mounted specimen, in the context of the gravimetric studies, we were intrigued to find the apparent symmetry to be orthorhombic, verified ultimately by measurement of the full sphere of data (for which R_{int} was 0.035) and successful refinement of the structure in space group $Fdd2$ as above, the symmetry seemingly degraded at the lower temperature (see below).

CuCN : 2mp (2:3)$_{(\infty|\infty)}$. $C_{20}H_{21}Cu_2N_5$, $M = 458.5$. Monoclinic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 11.126(2)$, $b = 13.908(3)$, $c = 13.917(3)$ Å, $V = 2154$ Å^3. $Z = 4$; $\rho_{\text{calcd.}} = 1.41_4$ g cm^{-3}. $\mu_{\text{Mo}} = 19.9$ cm^{-1}; specimen: $0.43 \times 0.08 \times 0.04$ mm; $'T'_{\text{min/max}} = 0.68$. $2\theta_{\text{max}} = 50°$; $N_t = 24998$, $N = 2055$ ($R_{\text{int}} = 0.046$), $N_o = 538$; $R = 0.067$, $R_w = 0.076$. $x_{\text{abs}} = 0.02(16)$. $|\Delta\rho_{\text{max}}| = 0.67(2)$ e Å^{-3}.

Variata. The geometry of the ring of ligand 3 was constrained during refinement. Isotropic displacement parameter forms were refined for C, N.

CuCN : quin (1:1)$_{(\infty|\infty)}$. $C_{10}H_7CuN_2$, $M = 218.7$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 6.389(5)$, $b = 7.762(6)$, $c = 9.041(7)$ Å, $\alpha = 81.54(1)$, $\beta = 83.69(1)$, $\gamma = 81.86(1)°$, $V = 437._2$ Å^3. $Z = 2$; $\rho_{\text{calcd.}} = 1.66_1$ g cm^{-3}. $\mu_{\text{Mo}} = 24.4$ cm^{-1}; specimen: $0.8 \times 0.04 \times 0.04$ mm; $'T'_{\text{min/max}} = 0.29$. $2\theta_{\text{max}} = 50°$; $N_t = 4675$, $N = 1496$ ($R_{\text{int}} = 0.083$), $N_o = 1038$; $R = 0.091$, $R_w = 0.096$. $|\Delta\rho_{\text{max}}| = 1.35(7)$ e Å^{-3}.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 246119 – 246121. 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

Previous studies concerning substituted-pyridine base adducts of various copper(I) salts have shown considerable capacity for steric control of the coordination environment of the metal atom by variation of the substitution pattern of the base at the 2- (and 6-) positions. With copper(I) cyanide, structural data on its nitrogen base adducts has been considerably restricted by greater difficulty of access of crystals of adequate quality, perhaps arising from their generally polymeric nature. Nevertheless, it is of interest that to date, when crystallized from the bases $HNEt_2$,
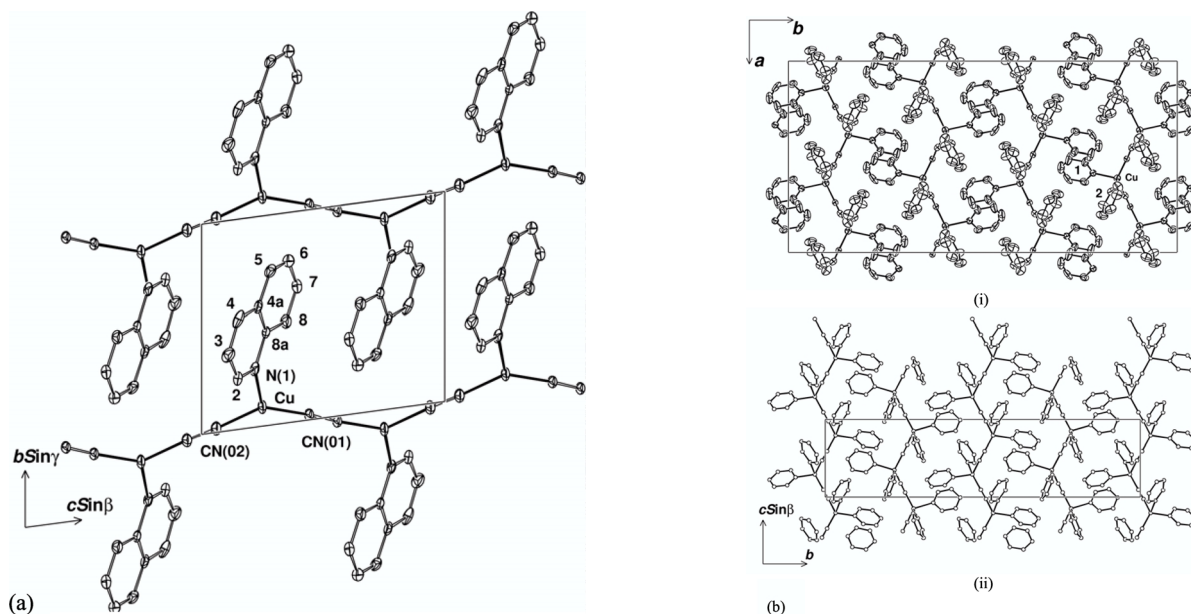
Fig. 2 (a) Projection of the unit cell contents of CuCN : quin (1:1), showing the inversion related stacking of the ligand planes between the polymer strands. (b) (i) Unit cell contents of CuCN : py (1:2) (300 K study) projected down *c*. (ii) The counterpart projection for the 130 K study, for comparison.

NEt_3, which, by comparison, being tetrahedrally substituted, could be considered 'bulky', polymeric complexes of 1:1 stoichiometry are achieved, analogous to the 'split-stair' and 'extended split-stair' arrays found with halide [25] and thiocyanate [26] adducts with bulky ligands. In the present work, we have been unable to access useful crystals from bases substituted in both 2- and 6- positions of pyridine; nevertheless, the three complexes which have been usefully amenable to study are of interest, despite the limited precision of the determinations, providing adducts of all of the 1:1, 1.5, 2 range of stoichiometry, broadly paralleling the degree of hindrance about the pyridine nucleus. Whereas other CuX : unidentate *N*-base (1:n) adducts hitherto defined for X = halide (Cl, Br, I) may be discrete mono- or oligo-, or poly-nuclear species depending on circumstances, the pseudo-halide SCN and CN adducts so far studied have shown an essentially invariable propensity towards single-stranded polymer formation, which is continued here. All of the present arrays are single-stranded polymers, Fig. 1, comprising sequences of copper(I) atoms, linked by single end-coordinated cyanides, with one or two pyridine ligands appended, with associated copper atom coordination numbers of three or four. As is often the case, assignment of carbon and nitrogen atoms within cyanide

groups is ambiguous, perhaps a consequence of genuinely indiscriminate coordination or longer range disorder (in respect of which the vibrational spectroscopy is also generally unhelpful), and/or in circumstances such as the present, a consequence of limited data quality with consequent limited resolution.

In the quinoline adduct, **CuCN : quin (1:1)**$_{(\infty|\infty)}$, one formula unit comprises the asymmetric unit of the structure, the polymer being propagated along *c*, by inversion centres located at the CN bond centres, and translations, the ligands disposed to either side of the chain, interleaving with adjacent polymer strands and overlapping with inversion related equivalents (Fig. 2(a)), all ligand planes being necessarily parallel, and, in such a model, the C, N atoms of the cyanide (unresolved) obligate composites. The copper atom is bound to two cyanide groups and one quin ligand, the environment being three-coordinate and planar; parameters are compared with those of the CuCN : $HNEt_2$, NEt_3 adducts in Table 1. The copper atom lies 0.15(1) Å out of the quin C_9N plane, the latter lying at 51.0(3)° to the $N(L)Cu((C/N)Cu)_2$ plane. The most profound variation is found in the angles about the copper(I) atom; those of the (1:1) quin and $HNEt_2$ adducts differ only slightly if at all, but those of the NEt_3 differ dramatically. This ligand is presumably the

L/stoichiometry	quin (1:1)	HNEt$_2$ [a] (1:1)	NEt$_3$ [a] (1:1)	4mp[a] (1:1.5)	2mp (1:1.5)
Distances [Å]:					
Cu-N(L)	2.07(1)	2.09(1), 2.11(1)	2.21(1)	2.097(7)	2.10(3)
Cu-C/N(CN) (1)	1.89(1)	1.95(1), 1.96(1)	1.89(1)	1.909(8)	1.82(3)
(2)	1.89(1)	*1.87(1), 1.87(1)*	*1.86(1)*	*1.865(9)*	1.84(4)
Angles [°]:					
(L)N-Cu-C/N(CN) (1)	120.2(4)	99.9(4), 98.4(4)	101.6(4)	104.3(8)	128(2)
(2)	107.3(4)	*126.9(5), 128.3(4)*	*109.6(4)*	*108.7(3)*	104(2)
(CN)C/N-Cu-C/N(CN)	132.5(5)	133.2(5), 133.3(5)	148.9(8)	146.8(3)	128(2)
Σ	360.$_0$	360.$_0$, 360.$_0$	360.$_1$	359.$_8$	360

Table 1. Three-coordinate (L)NCu(CN)$_2$ environmental parameters in CuCN : L (1:1). (Counterpart environments in 1:1.5 complexes are also recorded for comparison; italicized values correspond to cyanide *C* atoms, where recorded as (tentatively) distinguished).

[a] Ref. [17]; C,N of the cyanide were tentatively 'distinguished' in these structures. In the L = quin structure, Cu-N-C (2,8a) are 119.1(8), 122.9(8)°.

bulkiest of the three and it may be that expansion of the angle between the cyanides is a reflection of increased Cu-N(L). Or it may reflect the difference in base characteristics of NEt$_3$ *vs.* HNEt$_2$.

The same three-coordinate copper(I) environment is found in the adducts with *n*-methylpyridine ($n = 2, 4$) of 1:1.5 stoichiometry, that of the present adduct of 2mp, **CuCN : 2mp (2:3)**$_{(\infty|\infty)}$, perhaps surprisingly being the same as that of its less hindered 4-substituted counterpart, previously recorded [17]. In the latter polymer, the repeating unit is the (CuCN) 2L 3 asymmetric unit, propagated by the *b*- (*not c*-, as ref. [17] states) translation in monoclinic space group *Cc*; here, with a similar asymmetric unit of alternating 3- and 4-coordinate copper atoms coordinated by one and two ligands pendant to the polymer chain, respectively, the propagator is a 2$_1$-screw axis in space group $P2_12_12_1$. Here, less surprisingly, perhaps, since both ligands are unsymmetrically hindered by the presence of 2-substituents, we find the environment of the three-coordinate copper atom in the 2mp adduct most nearly resembling that of the 1:1 quin adduct in respect of distances and (cyanide)-Cu-(cyanide) angle, the relatively minor difference perhaps arising out of a difference in the nature of the 2-substituent, but that is less certain. By contrast, the corresponding (cyanide)-Cu-(cyanide) angle in the 4mp adduct is enlarged to a value comparable to that observed in the 1:1 NEt$_3$ adduct.

The **CuCN : py (1:2)** adduct has been the subject of a previous study at 130 K [23]; revisitation at 300 K has surprisingly disclosed a simpler orthorhombic structure in space group *Fdd*2 in which one formula unit comprises the asymmetric unit of the structure, the symmetry seemingly degrading to monoclinic *Cc* at 130 K, with two formula units defining independent polymer strands comprising the asymmetric unit; the relationship between the two structures is shown

in Fig. 2(b). Apparently the compound undergoes a phase transition from a high-temperature to a low-temperature form upon cooling from 300 to 130 K. For the present spectroscopic purposes, as those measurements were also made at room temperature, we adopt that structure, to which tabulated data and comparative comments below pertain; for most other purposes the data of the 130 K study is obviously to be preferred.

This pyridine adduct provides the parent member of the above family, **CuCN : py (1:2)**$_{(\infty|\infty)}$, of the maximal CuCN : N-base stoichiometry hitherto achieved (1:2); whether this is because it is an unhindered planar ('two-dimensional') *N*-base, *cf.* more bulky 'three-dimensional' *N*-bases incorporating tetrahedral nitrogen, is unclear, remembering that the 4mp ligand, yielding an adduct of 2:3 stoichiometry, should have a similar steric profile. Whatever the reason, it retains the same form of a single-stranded …Cu(cyanide)Cu(cyanide)… polymer, but now with two N-bases being coordinated to each copper atom, which thus is in a four-coordinate ((L)N)$_2$Cu(cyanide)$_2$ environment. Similar environments have been previously recorded in the CuCN : phen/dmp adducts, but there the (ligand N)$_2$Cu angle is diminished because of the 'bite' constraint of the ligand; they are also found in the 2/4mp adducts of 1:1.5 stoichiometry, the totality of these environments being summarized in Table 2. Here again, the feature which varies most between structures is the (cyanide)-Cu-(cyanide) angle; the associations are less mysterious in that the angles for the environments in the CuCN : py (1:2) and CuCN : 4mp (1:1.5) are similar as might be expected. These are larger than in CuCN : 2mp (1:1.5), where the change in steric profile may have an effect, and in CuCN : phen (1:1), where, despite ligand constraints, Cu-N(phen) are short, in respect of which the angle might be expected to be diminished

Table 2. Four-coordinate $((L)N)_2Cu(CN)_2$ environmental parameters in CuCN : L (1:2), L = unidentate. Counterpart environments in $L_2 = N,N'$-bidentate are also included, as are those from complexes of 1:1.5 stoichiometry. X (1,2) are the cyanide atoms, 1 being the carbon, *italicized* (where 'resolved'). Values for the 1:2 py complex pertain to the present 300 K study.

L Stoichiometry	py (1:2)	2mp (1:1.5)	4mp (1:1.5)[a]	phen (1:1)[a]	dmp (1:1)[b]
Distances [Å]:					
Cu-N(1)	2.10(1)	2.16(4)	2.161(7)	2.12(2)	2.121(9)
Cu-N(2)	2.25(2)	2.16(3)	2.215(9)	2.11(1)	2.131(9)
Cu-X(1)	1.86(2)	1.96(5)	*1.898(9)*	*1.88(1)*	*1.90(1)*
Cu-X(2)	1.91(2)	2.00(3)	1.960(8)	1.94(2)	2.01(1)
Angles [°]:					
N(1)-Cu-N(2)	94.8(6)	95(1)	96.4(3)	79.7(5)	79.1(3)
N(1)-Cu-X(1)	107.3(6)	118(2)	*106.0(3)*	*106.7(5)*	*125.9(4)*
N(1)-Cu-X(2)	110.3(6)	103(1)	101.2(3)	115.9(7)	107.5(4)
N(2)-Cu-X(1)	101.9(7)	112(2)	*106.7(3)*	*114.9(5)*	*116.0(4)*
N(2)-Cu-X(2)	100.0(6)	105(1)	99.5(4)	107.1(4)	112.6(4)
X(1)-Cu-X(2)	134.2(7)	121(1)	139.5(3)	124.1(6)	111.9(5)

[a] Ref. [17]; [b] ref. [27].

with similar factors operative, together with increased steric profile; (cyanide)-Cu-(cyanide) in CuCN : dmp (1:1) is diminished even further to the smallest value recorded in this array of complexes. In the context of aromatic *N,N'*-base adducts with CuCN, mention should also be made of the adducts of stoichiometry less than 1:1, achieved by the incorporation of additional CuCN units in the spacers, such as the spectacular CuCN : bpy (7:2), (the record of which also refers to unpublished CuCN : bpy (1:1)) [6b], as well as CuCN : biquinolyl (4:1) [6a], and others, these species, although more complex, having a similar motivic constitution to the present. Indeed, in respect of adducts of MX with $N,N'(N''(etc.)$ bi-(oligo-)dentate ligand adducts more generally, it is cause for some wonder that, while a considerable body of data exists on complexes involving quite arcane and complex ligands of considerable synthetic difficulty, consequent upon various 'supramolecular'/'crystal engineering' rationales underpinning their study, the most basic motifs involving quite the simplest of these ligand types often remain neglected, yet, as we see in this and subsequent contributions, which go some way towards rectifying this deficiency, these frequently offer equally fascinating and more accessible fundamental insight into such arrays.

Vibrational spectra

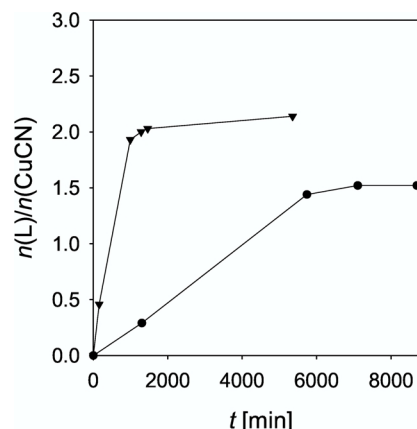Since the complexes involving the unidentate ligands readily lose ligand upon exposure to air, more

Fig. 3. The time dependence of the composition (ligand (L) : CuCN mole ratio) of the solid formed during the addition of ligand from the vapour phase to a fixed amount of solid CuCN at ambient temperature (L = py, ▼; 4mp, ●).

generally than other M : L (1:n) adducts of bases such as those with X = other halide, in keeping with their description above in 'clathrate' terms, in most cases it was not possible to check the identity and homogeneity of the bulk samples prepared for IR spectroscopy by the more usual melting point determinations or elemental analysis. However, the composition of the bulk samples was established in two cases by gravimetric monitoring of the addition of ligand from the vapour phase to a known amount of CuCN (see Experimental Section). The progress of the addition of py and 4mp to CuCN with time is shown in Fig. 3. In both cases the rate of addition of the ligand to the solid is constant up to the point where the reaction essentially ceases, at 2 mol of py and 1.5 mol of 4mp per mol of CuCN. These ratios correspond to the stoichiometries of the solids obtained in the crystallization of the adducts from liquid ligand solution and characterized crystallographically (see above). Fig. 3 also shows that the rate of addition of 4mp under these conditions is considerably slower than that for py. The rate of addition seems to be a very sensitive function of the particular ligand, quin vapour undergoing no reaction at all with CuCN under similar conditions, and an IR study showing that the reaction of neat liquid quin with solid CuCN at ambient temperature required several weeks to go to completion.

The IR band assignments for the vibrations of the extended -CuCN-CuCN- chains that are present in all of the compounds examined in the present study structurally characterized herein and elsewhere [17, 27] are

Compound	ν(CN)	ν(CuC/N)	δ(CuCN)	δ(NCuC)	r(Cu − C/N)	Structure ref.
CuCN[a]	2170	591	326	168	1.846	12b
CuCN : Et$_3$N (1:1)	2130	531	328	173	1.86(1), 1.89(1)	17
CuCN : quin (1:1)	2128, 2123	501	322, 295	171, 147	1.89(1)	b
CuCN : phen (1:1)	2111	c	324	163	1.88(1), 1.94(1)	17
CuCN : dmp (1:1)	2096, 2085	425	318, 302		1.90(1), 2.01(1)	26
CuCN : 4mp (1:1.5)	2114 2101	c	327, 312	177, 139	1.909(8), 1.898(9) 1.865(9), 1.960(8)	17
CuCN : 2mp (1:1.5)	2116 2102	c	313, 300	179, 142	1.82(3), 1.96(5), 1.84(4), 2.00(3)	b
CuCN : 2mp (1:1)	2126	497	320, 295	183, 144		
CuCN : py (1:2)	2105	d	313	185, 146	1.86(2), 1.91(2)	b
CuCN : py (1:0.8)	2131, 2125, 2086	520 − 440	317	180, 149		

Table 3. IR band assignments (wavenumber [cm^{-1}]) and related Cu-C/N bond lengths [Å].

[a] Vibrational frequencies from Ref. [10]; [b] this work; [c] obscured by strong bands due to the coordinated ligand; [d] no ν(CuC/N) band unambiguously assigned.
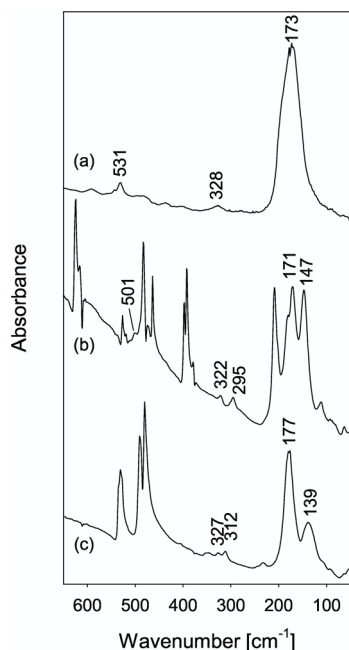
Fig. 4. Far-IR spectra of (a) CuCN : NEt$_3$ (1:1), (b) CuCN : quin (1:1), and (c) CuCN : 4mp (1:1.5). Bands assigned to vibrations of the CuCN chains are labelled with their wavenumbers.

given in Table 3. The IR spectra showed strong ν(CN) bands, whose frequencies are listed in Table 3. We have shown elsewhere that a correlation exists between the ν(CN) frequencies and the Ag-C/N bond lengths in a number of AgCN complexes, such that ν(CN) increases with decreasing Ag-C/N bond length [28]. A similar trend is evident in the data for the CuCN complexes in Table 3. In the case of the 4mp complex where two ν(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 average Cu-C/N bond length. The results show a trend of de-

creasing ν(CN) with increasing r(Cu-C/N) similar to that observed previously for analogous AgCN complexes [28].

Solid CuCN contains extended linear -CuCN-CuCN- chains, with ν(CN) = 2170 cm^{-1} [10]. The ν(CN) frequencies for the chain polymers in Table 3 are lower than this, a result of the fact that the binding of the py donor ligands to the copper weakens the Cu-C/N bonds, thus lowering ν(CN).

The far-IR spectra of a selection of the complexes are shown in Figs. 4 and 5. The following low-frequency vibrational modes have previously been assigned in the extended linear -CuCN-CuCN- chains present in solid CuCN: ν(CuC/N) = 591 cm^{-1}, involving vibration of the CN group between its two neighbouring Cu atoms: δ(CuCN) = 326 cm^{-1}, which can be described as a restricted rotation of the CN group, and δ(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 [10]. In the infinite-chain compounds, in which the copper atoms are coordinated to the py ligands, shifts in the above frequencies and splitting of the bending modes (which are doubly degenerate in the isolated linear chains) are expected. For the ν(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 ν(CuC/N) is observed as a weak band in the IR at 531 cm^{-1} (Fig. 4). In CuCN : quin (1:1) ν(CuC/N) is observed as a weak band in the IR at 501 cm^{-1} (Fig. 4); despite the large number of stronger and potentially interfering ligand bands, a definitive assignment is possible by comparison with the spectrum of the AgCN : quin (1:2) complex [29]. In the case of CuCN : phen (1:1), however, the ligand bands do obscure the ν(CuC/N) region. The IR spec-
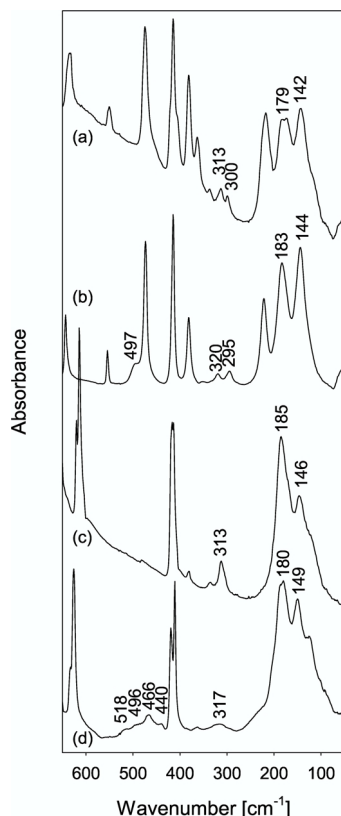
Fig. 5. Far-IR spectra of (a) CuCN : 2mp (1:1.5), (b) CuCN : 2mp (1:1), (c) CuCN : py (1:2), and (d) CuCN : py (1:0.8). Bands assigned to vibrations of the CuCN chains are labelled with their wavenumbers.

Fig. 6. Plots of wavenumber of ν(MC/N) against M-C/N bond length for M = Ag (● = terminal CN, ■ = bridging CN; data from ref. [28]) and M = Cu (▲ = bridging CN; data for CuCN (s), CuCN : NEt$_3$ (1:1), CuCN : quin (1:1), CuCN : dmp (1:1) from Table 3).

trum of CuCN : dmp (1:1) has been reported previously, and the assignments ν(CuC) = 425, ν(CuN) = 318, 302 cm^{-1} have been proposed [27]. We have previously shown that separate ν(CuC) and ν(CuN) bands are not observed in the linear -CuCN-CuCN- chains in CuCN itself; rather a single ν(CuC/N) band is observed whose frequency is determined by the combined force constants for the Cu-C and Cu-N bonds [10]. The present results for the complex CuCN : NEt$_3$ (1:1), which gives a much simpler spectrum than the dmp complex, show that this is the case for infinite-chain CuCN complexes as well. Also, the presence of two ν(CuN) bands at 318, 302 cm^{-1} in the dmp complex was not explained. In the present study, these are assigned to δ(NCuC) (Table 3), the splitting into two bands being the result of a lowering of the symmetry of the chains as a result of complex formation (see below). It is clear from Table 3 that this assignment agrees very well with those for the other compounds
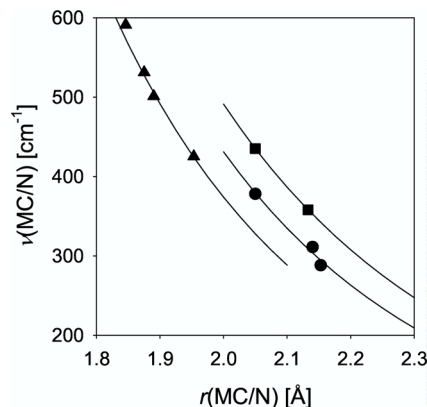
studied in this work. We therefore make this reassignment here, and assign ν(CuC/N) = 425 cm^{-1}.

Strong support for the above ν(CuC/N) assignments is obtained from Fig. 6, which compares the ν(CuC/N) *vs.* r(CuC/N) relationship for the three CuCN complexes discussed above with those established recently for several AgCN complexes [28]. This suggests that a similar relationship exists for the CuCN complexes, as would be expected.

According to the relationship shown in Fig. 6, ν(CuC/N) bands for CuCN : 4mp (1:1.5), for CuCN : 2mp (1:1.5), and CuCN : py (1:2) are expected at 480, 485 and 513 cm^{-1} respectively. In the case of the CuCN : 2mp and CuCN : 4mp (1:1.5), strong bands in the 470–490 cm^{-1} region completely obscure the expected ν(CuC/N) bands. In the case of the py complex, only extremely weak bands are observed in the expected region. However, stronger ν(CuC/N) bands occur in the range 440–520 cm^{-1} as py is partially removed from the solid (see below).

The far-IR spectra also contain bands below 400 cm^{-1}, some of which can be assigned to vibrations of the CuCN chains: weak bands in the range 295–330 cm^{-1} are assigned to δ(CuCN), and stronger bands in the range 170–190 cm^{-1} are due to δ(NCuC). These doubly degenerate (perpendicular) modes gives rise to a single band in the linear chains of CuCN [10], but this symmetry is lost in the present complexes. The observed multiplicity of these bands (Figs 4, 5) is probably due to this loss of axial symmetry.
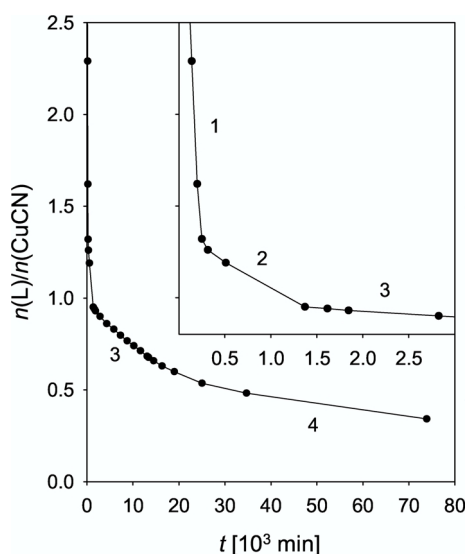
Fig. 7. The time dependence of the composition (ligand (L) : CuCN mole ratio) during the ligand loss from an initial 1:4 CuCN : 2mp mixture by standing in the air at ambient temperature. The numbered regions 1–4 are discussed in the text.

Fig. 8. Raman spectra of CuCN : 2mp complexes in the $v(CN)$ region using different Ar$^+$ laser 514.8 nm excitation powers (a) 1:1.5 complex, 10 mW excitation, (b) 1:1 complex, 10 mW excitation, (c) 1:1 complex, 20 mW excitation.

Examination of the materials that remain when complexes involving volatile ligands such as py and 2mp are allowed to stand in the air shows that ligand loss occurs in several stages *via* a series of well defined adducts, some of which have unusual stoichiometries and structures. The results of a gravimetric study of ligand loss from a mixture that initially had a 4:1 ratio of 2mp to CuCN are shown in Fig. 7. Four distinct regions are evident in this graph. Region 1 corresponds to the loss of excess ligand from the 1:1.5 complex, while region 2 corresponds to conversion of the 1:1.5 compound to a 1:1 complex. The IR spectrum of the 1:1 complex (Table 3, Fig. 5) shows that this, like the 1:1.5 complex, contains infinite CuCN chains, so that its formation simply involves the loss of one 2mp molecule from the copper atoms that bear two such molecules in the 1:1.5 complex. This ligand loss is apparently accompanied by a strengthening of the bonding within the CuCN chain, as is evidenced by the increase in the $v(CN)$ frequency (Table 3). This is also evident from the observation of a $v(CuC/N)$ band at 497 cm^{-1} (Fig. 5); the corresponding band in the 1:1.5 complex is predicted to occur at 485 cm^{-1}, and is apparently obscured by the strong ligand band at 471 cm^{-1}. Regions 3 and 4 in Fig. 7 possibly correspond to the conversion of the 1:1 to the 1:0.5 and the 1:0.5 to uncomplexed CuCN respectively. The long times required for
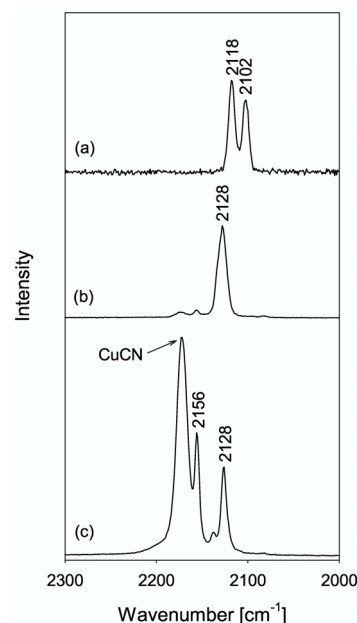
this conversion under ambient conditions, and the indistinct nature of the change between the two regions preclude a more definitive determination of the composition of the intermediate phase involved. However, the existence of such a phase is evidenced by the presence of a $v(CN)$ band at 2156 cm^{-1} in the IR spectrum of samples that have compositions corresponding to region 3. The removal of ligand molecules is also effected by the local heating produced by a laser beam, as shown in the Raman spectra of CuCN : 2mp compounds in the $v(CN)$ region (Fig. 8); at 10 mW laser power, the spectrum of the 1:1 complex is dominated by a single band at 2128 cm^{-1} due to this complex, but at 20 mW laser power, the spectrum also shows strong bands at 2156 cm^{-1}, tentatively assigned to a 1:0.5 complex, and at 2172 cm^{-1}, due to uncomplexed CuCN.

As was found to be the case for the formation of these compounds (*e.g.* see Fig. 3), the compositions of the products that result from ligand loss depend strongly on the nature of the ligand. Thus CuCN : 2mp (1:1.5) converts to the 1:1 complex, whose structural simplicity is reflected in the observation of a single $v(CN)$ band in the IR and Raman spectra. However, this is not the case for the CuCN/py system. Gravi-
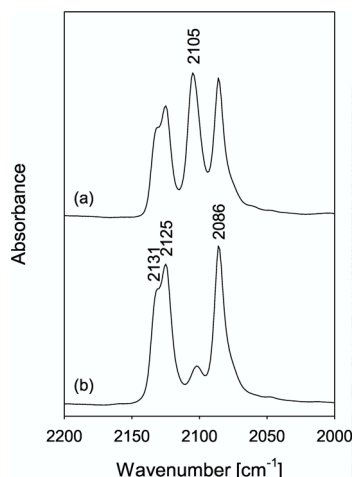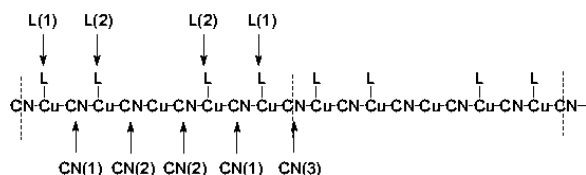
Fig. 9. IR spectra of the CuCN : py system during the conversion of the 1:2 to the 1:0.8 adduct (a) mid way through, and (b) towards the end of the conversion. The band labelled in (a) is that of the 1:2 complex; those in (b) are due to the 1:0.8 complex.

Scheme.

metric and elemental analysis (see Experimental Section) indicate that CuCN : py (1:2) converts directly to a phase of 1:0.8 stoichiometry, and the IR spectrum of this phase in the $v(\text{CN})$ region shows three bands at 2131, 2125 and 2086 cm^{-1} (Fig. 9). Some of the IR bands due to the py ligand are split into two bands (*e. g.* the band at 419, 412 cm^{-1}; Fig. 5(d)). These observations are consistent with an ordered chain structure in which one in every five copper atoms does not bear a py molecule (Scheme). Such a structure would give rise to two inequivalent pyridine sites L(1), L(2) and three inequivalent CN sites CN(1), CN(2), CN(3), in agreement with the observed IR spectrum.

Such a structure should show several different $v(\text{CuC/N})$ bands, in agreement with the observed far-IR spectrum, in which a group of incompletely resolved bands occur in the range 520–440 cm^{-1} (Fig. 5). An obvious parallel may be drawn between the type of complex proposed here and the structurally more well-defined AgCN : py (10:9) described in the following paper [29], as well as the more complex

species with spacers expanded by the incorporation of additional CuCN units, as in ref. [6e]. However, the presence of the relatively low frequency $v(\text{CN})$ band at 2086 cm^{-1} suggests that there could be some cross-linking between the chains, as has been observed in two other CuCN adducts [19, 30]. The same questions concerning the presence or absence of C/N disorder that were discussed in the structural section presumably arise for all of the compounds studied here, but vibrational spectroscopy gives no further information on this matter.

The synthesis and characterization of a number of complexes of CuCN with diamines and tetramines has recently been described [4, 5]. A systematic synthetic method was developed which involves a "thiosulfate-assisted" dissolution of the highly insoluble CuCN to allow reaction with the water-soluble amine. This resulted, for example, in the successful synthesis of CuCN : hmt (3:2) whereas all attempts to synthesise this compound by direct combination of CuCN and hmt in various solvents failed [4b]. The adducts described in the present work provide easy alternative routes to such compounds. Thus, the reaction of CuCN : py (1:0.8) with an aqueous solution of hmt under ambient conditions results in the quantitative formation of CuCN : hmt (3:2) (see Experimental Section). The IR spectrum shows $v(\text{CN})$ at 2112, 2132 cm^{-1}, differing significantly from the values 2070, 2088 cm^{-1} previously reported [4a]. However, the IR spectrum of the product prepared in the present study from CuCN : py (1:0.8) by the py-displacement method was found to be identical to that of a sample prepared by the previously reported method [4b]. This compound contains infinite -Cu-CN-Cu-CN- chains, with average Cu-C/N bond lengths of 1.88 and 1.91 Å for the two different types of copper atom in the chain [4a], and according to a recently established correlation for a range of compounds containing similar chain structures [31], $v(\text{CN})$ should lie above 2100 cm^{-1} in this compound in agreement with the present results. Other features of the IR spectrum of this compound are consistent with the previously reported structure [4a]. Thus the assignment of a weak $v(\text{CuC/N})$ band at 482 cm^{-1} is consistent with the average Cu-C/N bond length of 1.9 Å (Fig. 6). The $\delta(\text{CuCN})$ mode produces two bands at 332, 303 cm^{-1}, the positions and splitting of these bands being similar to those of the other compounds with comparable infinite-chain structures (Table 3). It may be that the presence of the py molecules in CuCN:py (1:0.8) "opens" the solid CuCN structure by separating the –Cu-CN-Cu-CN- chains and permitting the entry of other molecules that can displace the

py molecules, perhaps in the manner of the AgCN : py (10:9) complex described in the following paper [29]. The CuCN is thus "activated" for adduct formation by prior reaction with pyridine base. In this respect, these compounds behave in a similar manner to intercalation compounds, where intercalation by a particular species into a structure occurs much more readily by displacement of existing intercalated molecules than by direct intercalation [20].

Conclusions

Relatively weak inter-chain bonding in solid CuCN can be broken by amine bases, which coordinate to the metal atoms about an infinite -Cu-CN-Cu-CN- chain structure. The adducts so obtained have well-defined stoichiometries and structures, which depend on the steric profile and the base strength of the amine ligand: the maximum ligand to metal ratio for a particular ligand decreases as the size of the ligand increases. In a number of cases removal of base molecules has been shown to occur in several stages *via* a series of well defined adducts, some of which have unusual stoichiometry and structure. Finally, we note that solid CuCN may be "activated" towards adduct formation by prior reaction with pyridine bases.

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