

# Syntheses, Structures and Vibrational Spectroscopy of Some Adducts of Copper(I) Cyanide with Unidentate Organic Nitriles

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 70<sup>th</sup> birthday*

A number of adducts of copper(I) cyanide, CuCN, have been synthesized by crystallization from its solutions in various unidentate organic nitriles, RCN. Low temperature single crystal X-ray structure determinations are recorded for a number of these, of the form CuCN : RCN (*m* : *n*) for R = Me, Et (*m* : *n* = 1 : 1), and Ph, *o*-tolyl (3:2). The 1 : 1 adduct with acetonitrile is a two-dimensional polymeric web, (CN)Cu( $\mu$ -CN)<sub>2</sub>Cu(NC) units being linked by the peripheral nitrogen and carbon atoms, with a fourth coordination site about each copper having MeCN pendant. The other three adducts are one-dimensional polymers, the propionitrile adduct being of the form ...Cu(NCEt)CNCu(NCEt)CN... with trigonal planar copper, the bridging cyanide groups being replaced in the benzo- and *o*-toluo nitrile adducts by linear Cu(CN)<sub>2</sub><sup>−</sup> moieties. The vibrational spectra of bulk samples are largely consistent with the single crystal structural results, but reveal the possible existence of adducts of higher CuCN content in the case of the CuCN/benzonitrile system.

**Key words:** Copper Cyanide, Nitrile, Structure, Infrared Spectroscopy, Raman Spectroscopy

## Introduction

Recent [1] and earlier [2] substantial studies have described synthetic, structural and spectroscopic studies defining a number of adducts of copper(I) cyanide (itself the subject of recent work [3,4]) with nitrogen bases, aliphatic and aromatic amines, ‘two-’ and ‘three-dimensional’ in profile, paralleling and extending earlier such work with similar adducts of copper(I) (pseudo-)halides. The latter studies [5] included the nitrogen base of ‘one-dimensional’ profile, acetonitrile, which exhibited distinctly different behaviour to its unhindered trigonal- and tetrahedral-nitrogen base counterparts, as also in the adducts of copper(I) perchlorate [6]. The nature of the interaction of copper(I) cyanide with organic nitriles in this manner is as yet undefined, an omission which this work goes some way towards rectifying. The adducts presented are obtained unproblematically by the crystallization of copper(I) cyanide from the parent nitrile, decomposition in ambience being averted by immediate transfer to the low temperature diffractometer stream or spectroscopic mull after rapid drying between filter paper.

## Experimental Section

General procedures for the structural and spectroscopic work have been outlined in a preceding paper [1]. Specific details are as follows:

*Crystal/refinement data (CCD instrument; T ca. 153 K)*

**CuCN : MeCN (1:1)**<sub>(∞|∞)</sub> ≡ C<sub>3</sub>H<sub>3</sub>CuN<sub>2</sub>, *M* = 130.6. Monoclinic, space group *P*2<sub>1</sub>/*c* (*C*<sub>2h</sub><sup>5</sup>, No. 14), *a* = 8.4227(9), *b* = 8.1522(9), *c* = 7.8525(8) Å, β = 116.607(2)°, *V* = 482.1 Å<sup>3</sup>. *Z* = 4; ρ<sub>calcd.</sub> = 1.772 g cm<sup>−3</sup>. μ<sub>Mo</sub> = 44 cm<sup>−1</sup>; specimen: 0.4 × 0.3 × 0.2 mm; *T*<sub>min/max</sub> = 0.55. 2θ<sub>max</sub> = 75°; *N*<sub>t</sub> = 9970, *N* = 2528 (*R*<sub>int</sub> = 0.034), *N*<sub>o</sub> = 2049; *R* = 0.033, *R*<sub>w</sub> = 0.040. |Δρ<sub>max</sub>| = 0.9(2) e Å<sup>−3</sup>. (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> refined.

*Variata.* In all determinations, the assignment of C vs N in the cyanide moieties is of varying uncertainty, being defined on the basis of refinement statistics of varying definitiveness; in all cases, the acceptance of the assignment should be appropriately circumspect. Here, the assignment appears definitive, a result not unreasonable in view of the quite different ambiances of the two ends of the grouping.

**CuCN : EtCN (1:1)**<sub>(∞|∞)</sub> ≡ C<sub>4</sub>H<sub>5</sub>CuN<sub>2</sub>, *M* = 144.6. Orthorhombic, space group *Pnma* (*D*<sub>2h</sub><sup>16</sup>, No. 62), *a* = 8.6847(8),

$b = 6.4457(6)$ ,  $c = 9.5910(9)$  Å,  $V = 536.9$  Å<sup>3</sup>.  $Z = 4$ ;  $\rho_{\text{calcd.}} = 1.789$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 39$  cm<sup>-1</sup>; specimen:  $0.4 \times 0.1 \times 0.08$  mm;  $T'_{\text{min/max}} = 0.50$ .  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 11068$ ,  $N = 1512$  ( $R_{\text{int}} = 0.047$ ),  $N_o = 1187$ ;  $R = 0.046$ ,  $R_w = 0.055$ .  $|\Delta\rho_{\text{max}}| = 2.0(1)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}$ )<sub>H</sub> constrained.

*Variata*. C, N as assigned are differentiated from N, C but not C/N composite models.

**CuCN : PhCN (3:2)**<sub>(∞|∞)</sub>  $\equiv$  C<sub>17</sub>H<sub>10</sub>Cu<sub>3</sub>N<sub>5</sub>,  $M = 474.9$ . Triclinic, space group  $P\bar{1}$  ( $C_i^1$ , No. 2),  $a = 6.880(2)$ ,  $b = 7.304(2)$ ,  $c = 9.575(2)$  Å,  $\alpha = 96.128(4)$ ,  $\beta = 93.529(4)$ ,  $\gamma = 114.245(3)^\circ$ ,  $V = 433.3$  Å<sup>3</sup>.  $Z = 1$ ;  $\rho_{\text{calcd.}} = 1.820$  cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 37$  cm<sup>-1</sup>; specimen:  $0.12 \times 0.10 \times 0.08$  mm;  $T'_{\text{min/max}} = 0.73$ .  $2\theta_{\text{max}} = 58^\circ$ ;  $N_t = 4220$ ,  $N = 2113$  ( $R_{\text{int}} = 0.023$ ),  $N_o = 1667$ ;  $R = 0.040$ ,  $R_w = 0.047$ .  $|\Delta\rho_{\text{max}}| = 0.83(6)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}$ )<sub>H</sub> constrained.

*Variata*. Refinement statistics favoured modelling of the cyanide moieties as (C/N) ( $\times 2$ ) composites in this and the following compound:

**CuCN : *o*-tolCN (3:2)**<sub>(∞|∞)</sub>  $\equiv$  C<sub>19</sub>H<sub>14</sub>Cu<sub>3</sub>N<sub>5</sub>,  $M = 503.0$ . Monoclinic, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14, variant),  $a = 11.999(1)$ ,  $b = 6.6364(7)$ ,  $c = 12.815(1)$  Å,  $\beta = 110.683(2)^\circ$ ,  $V = 955$  Å<sup>3</sup>.  $Z = 2$ ;  $\rho_{\text{calcd.}} = 1.750$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 33$  cm<sup>-1</sup>; specimen:  $0.10 \times 0.06 \times 0.04$  mm;  $T'_{\text{min/max}} = 0.78$ .  $2\theta_{\text{max}} = 50^\circ$ ;  $N_t = 18902$ ,  $N = 1639$  ( $R_{\text{int}} = 0.073$ ),  $N_o = 1382$ ;  $R = 0.023$ ,  $R_w = 0.028$ .  $|\Delta\rho_{\text{max}}| = 0.42(5)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}$ )<sub>H</sub> constrained.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 246248–246251. 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

A number of adducts of copper(I) cyanide with organic nitriles of CuCN : RCN ( $m : n$ ) stoichiometry have been synthesized by its crystallization from solution in the conveniently liquid organic nitrile as solvent as well as ligand and characterized by vibrational spectroscopy and low temperature single crystal X-ray structure determinations. Adducts defined structurally of copper(I) cyanide with various unidentate amines are all single stranded polymers [1, 2], successive copper atoms catenated by ambidentate cyanide linkages coordinated end-on as 'rod' motifs; the copper atoms may be planar three- or tetrahedral four-coordinated by one or two additional bases, the stoichiometry following appropriately. The parent copper(I) cyanide polymer itself is uni-dimensional [3, 4], although an ear-

Table 1. Interatomic distances [Å] and angles [°], CuCN : MeCN (1 : 1)<sub>(∞|∞)</sub>. The second, italicised entry is for the CuCN : NH<sub>3</sub> (1 : 1)<sub>(∞|∞)</sub> counterpart.

Atoms	Distance	Atoms	Angle
Cu-N(1)	2.014(3), 2.070(7)	N(1)-Cu-N	109.9(1), 107.6(3)
Cu-N	1.947(3), 1.984(8)	N(1)-Cu-C <sup>i</sup>	114.3(1), 110.6(3)
Cu-C <sup>i</sup>	1.998(3), 2.09(1)	N(1)-Cu-C <sup>ii</sup>	100.2(1), 105.2(4)
Cu-C <sup>ii</sup>	2.205(3), 2.13(1)	N-Cu-C <sup>i</sup>	114.6(1), 111.2(4)
N(1)-C(1)	1.134(4), –	N-Cu-C <sup>ii</sup>	107.3(1), 112.0(4)
C(1)-C(2)	1.456(5), –	C <sup>i</sup> -Cu-C <sup>ii</sup>	109.5(1), 110.1(3)
N-C	1.153(4), 1.13(1)	Cu-N(1)-C(1)	176.3(3), –
		Cu-N-C	177.8(2), 177.2(8)
Cu...Cu <sup>v</sup>	2.4327(4), 2.417(2)	N-C-Cu <sup>iii</sup>	155.1(2), 146.7(8)
C...C <sup>v</sup>	3.434(4), 3.46(1)	N-C-Cu <sup>iv</sup>	134.2(2), 143.4(8)
		Cu <sup>iii</sup> -C-Cu <sup>iv</sup>	70.5(1), 69.9(3)

Transformations of the asymmetric unit: <sup>i</sup>  $2 - x, y - 1/2, 1/2 - z$ ; <sup>ii</sup>  $x, 3/2 - y, 1/2 + z$ ; <sup>iii</sup>  $2 - x, 1/2 + y, 1/2 - z$ ; <sup>iv</sup>  $x, 3/2 - y, z - 1/2$ ; <sup>v</sup>  $2 - x, 1 - y, 1 - z$ .

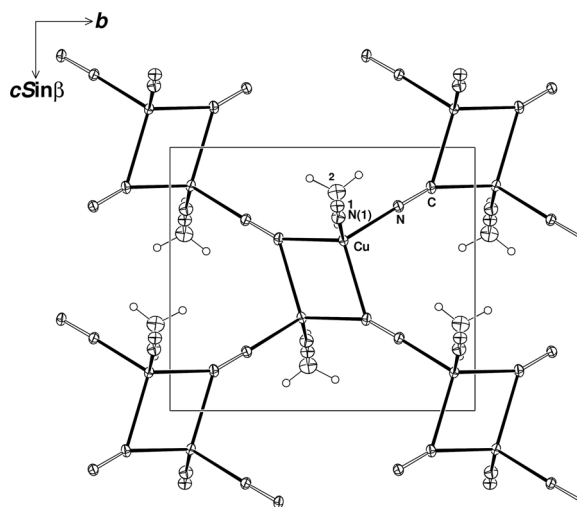


Fig. 1. Projection of the two-dimensional polymeric structure of CuCN : MeCN(1 : 1)<sub>(∞|∞)</sub> down  $a$ .

lier single crystal study of a presumed closely related species shows a cross-linked web [7].

**CuCN : MeCN(1 : 1)**<sub>(∞|∞)</sub>. The 'simplest' of the present structurally characterized array of adducts, which are all polymeric, may in fact be considered the most complex. The adducts with the aliphatic nitriles, aceto- and propio-nitrile, are both of 1 : 1 stoichiometry. Unlike the above and the propionitrile adduct, the acetonitrile adduct (Table 1, Fig. 1) is a two-dimensional polymer, disposed as a wrinkled web of copper and cyanide groups about the  $bc$  plane, the acetonitrile moieties projecting and interlocking to either side. One formula unit (CuCN : MeCN (1 : 1)) devoid of crystallographic symmetry comprises the

Table 2. Interatomic distances [Å] and angles [°], CuCN : EtCN (1 : 1)<sub>(∞|∞)</sub>.

Atoms	Distance	Atoms	Angle
Cu-N(11)	1.970(3)	N(11)-Cu-C	124.9(1)
Cu-C	1.895(4)	N(11)-Cu-N <sup>i</sup>	112.0(1)
Cu-N <sup>i</sup>	1.928(3)	N <sup>i</sup> -Cu-C	123.1(1)
C-N	1.164(5)	Cu-C-N	173.3(3)
N(11)-C(11)	1.139(5)	C-N-Cu <sup>ii</sup>	179.5(3)
C(11)-C(12)	1.460(5)	Cu-N(11)-C(11)	175.4(3)

Transformations of the asymmetric unit: <sup>i</sup> 1/2 - x, 1/2 - y, 1/2 - z;  
<sup>ii</sup> 1/2 + x, 1/2 - y, 1/2 - z.

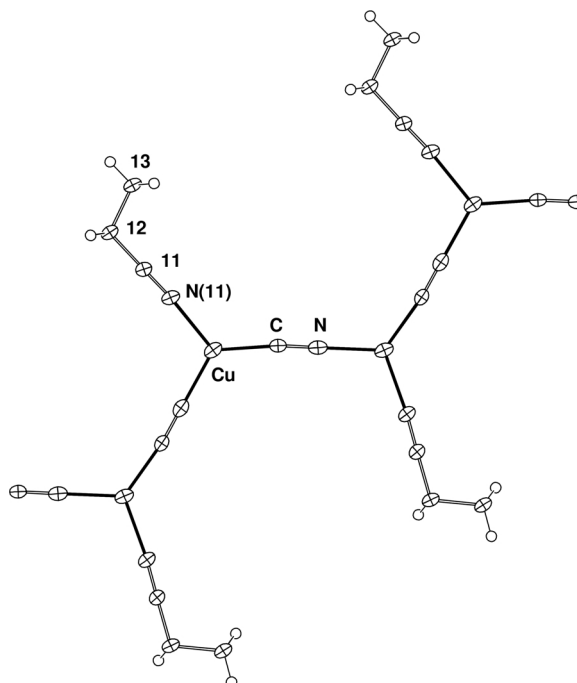
asymmetric unit of the structure. Refinement behaviour defines C, N components of the cyanide reasonably definitively, the differentiation being not unexpected, and as expected on the basis of the different terminations of the ambidentate, end-on coordinated C-N 'rod'. The structure is built up around four-membered motifs comprising (obligate planar) centrosymmetric rings made up of pairs of copper atoms, bridged by the carbon atoms of a pair of cyanide moieties, the rings disposed about the cell origins and centre. The CN nitrogen atoms projecting outwards coordinate to the copper atoms of other motifs, creating the two-dimensional web of the polymer, while the four-coordinate coordination environment of each copper is completed by the unidentate acetonitrile. The structure is remarkably similar to, although not isomorphous with, that of CuCN : NH<sub>3</sub> (1 : 1)<sub>(∞|∞)</sub> [8]. The counterpart geometry of the latter is presented in Table 1 also, despite the considerable difference in donor characteristics between ammonia and acetonitrile; the four-membered ring motif is also found in ref. [7] and more "complex" arrays [9].

The adduct with propionitrile, **CuCN : EtCN (1 : 1)<sub>(∞|∞)</sub>**, although of the same stoichiometry, takes the simpler linear form, planar three-coordinate copper atoms linked by ambidentate single cyanide 'rods' (Table 2, Fig. 2). Refinement statistics favour an ordered arrangement of the cyanide component atoms, although, given the nature of the behaviour of such species, we would not wish to regard that assignment as beyond revision by some more definitive technique. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, the polymer lying within the mirror plane of space group *Pnma*, substituent hydrogen atoms excepted, successive elements being generated by the associated two-fold screw axis. Bond lengths about the copper atom are in keeping with the assignment of ordered cyanide

Table 3. Selected geometries, CuCN : RCN(3 : 2)<sub>(∞|∞)</sub>, R = Ph, *o*-tol. The two values in each entry are for R = Ph, *o*-tol respectively. C, N(1,2<sup>(i)</sup>) are composites.

Atoms	Distance [Å]	Atoms	Angle [°]
Cu(1)-C(2)	1.919(3), 1.895(2)	N(11)-Cu-C(1')	124.5(1), 110.4(1)
Cu(1)-C	1.904(4)	N(11)-Cu(1)-C(2)	111.8(1), 106.78(9)
Cu(1)-N(11)	1.960(3), 2.049(3)	C(1')-Cu(1)-C(2)	123.3(2), 142.8(1)
C(1)-Cu(2)	1.839(3), 1.841(2)	Cu(1)-N(11)-C(11)	170.3(3), 163.0(2)
N(11)-C(11)	1.147(5), 1.141(4)	Cu(1)-N(1)-C(1)	170.2(3), 175.8(2)
C(1)-N(1)	1.155(5), 1.157(3)	Cu(1)-C/N(2)-C/N(2')	176.1(4), 178.1(2)
C(2)-N(2 <sup>i</sup> )	1.170(5), 1.159(3)	Cu(2)-N(1')-C(1')	172.8(3), 177.6(2)

Transformations of the asymmetric unit: <sup>i</sup>  $\bar{x}$ ,  $\bar{y}$ ,  $2 - z$ .

Fig. 2. A single strand of the polymer of CuCN : EtCN(1 : 1)<sub>(∞|∞)</sub>, all atoms except some substituent hydrogen atoms being contained within the mirror plane.

and concomitantly shorter as expected *vis-à-vis* those of the four-coordinate environment of the acetonitrile adduct. The N-Cu-N angle, opposed to the short Cu-C bond, is the smallest about the copper atom.

**CuCN : PhCN (3 : 2)<sub>(∞|∞)</sub>, CuCN : *o*-tolCN (3 : 2)<sub>(∞|∞)</sub>.** The two structures found with the aromatic cyanides are also one-dimensional polymers, also with

Table 4. Comparative trigonal (Base-N)Cu(cyanide)<sub>2</sub> geometries.  $\theta$  is the angle opposed to the base nitrogen,  $\phi_{1,2}$ , N-Cu-X<sub>1,2</sub>, the other pair of N-Cu-(cyanide)<sub>2</sub> angles.  $r$  is the Cu-N(Base) distance,  $s_{1,2}$  the Cu-cyanide donor distances Cu-X<sub>1,2</sub>.

Base <sup>Ref</sup>	$r$	$s_{1,2}$	$\theta$	$\phi_{1,2}$
EtCN <sup>a</sup>	1.970(3)	1.895(4), 1.928(3)	123.1(1)	124.9(1), 112.0(1)
PhCN <sup>a</sup>	1.960(3)	1.904(4), 1.919(3)	123.3(2)	111.8(1), 124.5(1)
<i>o</i> -tol CN <sup>a</sup>	2.049(3)	1.889(2), 1.895(2)	142.8(2)	106.78(9), 110.4(1)
Et <sub>2</sub> NH <sup>b</sup>	2.09(1)	1.87(1), 1.95(1)	133.2(5)	126.9(5), 99.9(4)
Et <sub>3</sub> N <sup>b</sup>	2.21(1)	1.86(1), 1.89(1)	148.9(5)	109.6(4), 101.6(4)
4Me-py <sup>b</sup>	2.097(7)	1.865(9), 1.909(8)	146.8(3)	108.7(3), 104.3(3)

<sup>a</sup> This work; <sup>b</sup> ref. [2]; Me-py  $\equiv$  methylpyridine.

three coordinate copper atoms associated with the nitrile, but with a different stoichiometry, the polymer being expanded by the insertion of Cu(CN)<sub>2</sub><sup>−</sup> rods alternately in place of successive simple cyanide groups, as are often found in other lower adducts of CuCN which frequently occur with the larger oligodentate aromatic polypyridine donors [10, 11], perhaps indicative of more wide-ranging structural effects in such systems. While it might be expected that the two types of copper atoms may lead to discrimination in coordination between the different ends of each cyanide moiety, in both structures refinement behaviour is such that a scrambled (C/N)-(C/N) model is the preferred option within the postulated cells and symmetries. In each case, one half of the CuCN : RCN (3 : 2) formula unit comprises the asymmetric unit of the structure, the copper atom of the Cu(CN)<sub>2</sub> moiety lying on an inversion centre in each case; the centre of the discrete cyanide linker is disposed likewise, so that its component atoms are obligate scrambled in this model. Given that the two complexes are not isomorphous and that the nitrile substituent is so well removed from the spine of the polymer that its steric effect might be expected to be relatively minor, it is interesting that the present structural type obtains with both, with closely consistent distances throughout except for the Cu-(nitrile-)N distances, which might be expected to be well-removed from the effects of disorder and other intra-polymer electronic effects, and which, nonetheless, are significantly different. The angular geometries of the polymer are also, concomitantly, different about Cu(I) with a gross difference in the angles opposed to the nitrile group. While some difference might be expected electronically between R = Ph, *o*-tol, it is difficult to envisage a change of sufficient magnitude to influence the distances and associated angles to this extent, and an explanation of the origin of this effect in terms of

Table 5. Infrared and Raman band assignments.

Compound	$\nu$ (CN)		$\nu$ (CuC/N)	
	IR	Raman	IR	Raman
CuCN/MeCN (1:1)	2098	2110	422	447
CuCN/CD <sub>3</sub> CN (1:1)	2098	2107	419	444
CuCN/EtCN (1:1)	2123, 2128	2132	472, 485	485
CuCN/PhCN (3:2)	2129, 2140	2132, 2142	<sup>a</sup>	<sup>a</sup>

<sup>a</sup> Obscured by PhCN bands.

different structural forces is more appealing. Similar excursions are observed in previously studied systems (Table 4), wherein values exalted above 140° for the angles between the cyanide donors are not uncommon and perhaps indicative of a tendency towards a linear Cu(CN)<sub>2</sub> species, perturbed by the base approach where other energetic considerations are favourable. Of those bases relevant to Table 4, it is of interest to note pK<sub>a</sub> values for di- and tri-ethylamine which are almost identical (10.9, 10.7) and considerably different to 4-methylpyridine (6.0) [12] although there is an aliphatic/aromatic dichotomy here.

### Vibrational Spectra

Since the complexes readily lose ligand upon exposure to air, it was not possible to check the homogeneity of the compounds by the usual methods of melting point determination or elemental analysis. The compounds were therefore examined by vibrational spectroscopy to check that the features expected on the basis of the single crystal structure determinations were present in the bulk samples. The spectra of the MeCN and EtCN adducts are consistent with the crystal structures, and show no evidence of other compounds in the bulk solid. The spectra of the PhCN adduct are more complex, as discussed in more detail below. The assignments of the bands due to the  $\nu$ (CN) and  $\nu$ (CuC/N) modes [3] for these compounds are given in Table 5.

The structural differences between the 1:1 CuCN/MeCN and CuCN/EtCN adducts are readily apparent in the vibrational spectra. For the MeCN adduct, which shows cross-linking between adjacent CuCN chains,  $\nu$ (CN) is about 30 cm<sup>−1</sup> lower than in the EtCN adduct, which has no cross-linking. The cross-linking apparently weakens the CN bond strength, resulting in a lowering of  $\nu$ (CN). A similar effect is seen in  $\nu$ (CuC/N), which is lowered by up to 60 cm<sup>−1</sup> by the cross-linking. A small splitting of two of the bands in the EtCN complex may be relevant

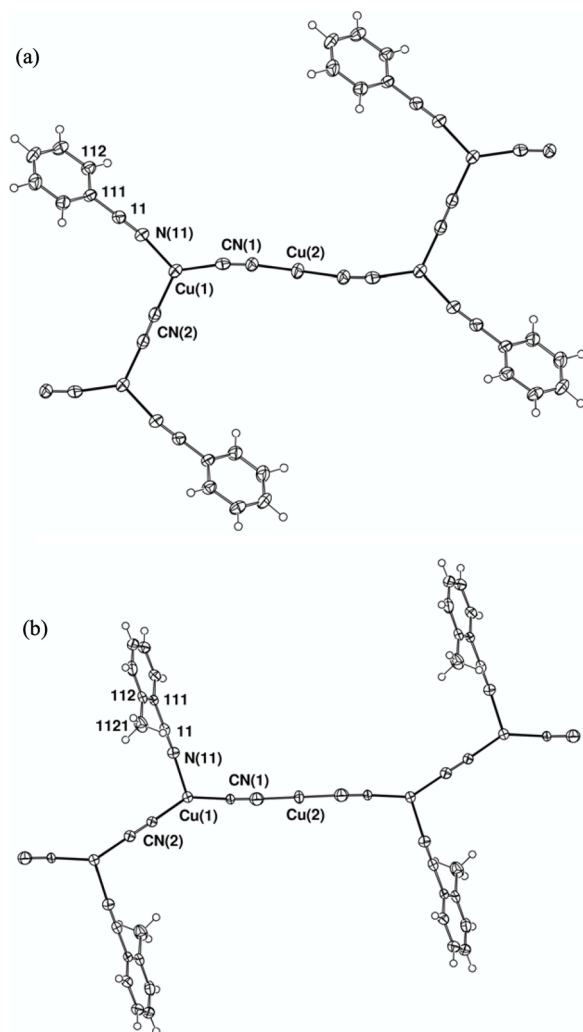


Fig. 3. (a,b) Single strands of the polymers of CuCN : RCN(3 : 2), R = (a), Ph, (b) *o*-tolyl.

to the question of the relative orientation of the CN groups (see above), but no definitive conclusion is possible as yet. The CD<sub>3</sub>CN adduct shows very similar  $\nu(\text{CN})$  and  $\nu(\text{CuC/N})$  to the MeCN adduct (Table 5).

The IR spectrum of the 3:2 CuCN/PhCN adduct shows two well-separated  $\nu(\text{CN})$  bands in the IR and Raman spectra at about 2130 and 2140  $\text{cm}^{-1}$  (Fig. 4), as expected for the two different CN environments in the structure of this compound (see above). However, the IR spectrum also shows a weaker band at 2154  $\text{cm}^{-1}$ . If the compound is allowed to stand in the air, it gradually loses PhCN and the intensity of the 2154  $\text{cm}^{-1}$  band increases, and a further band

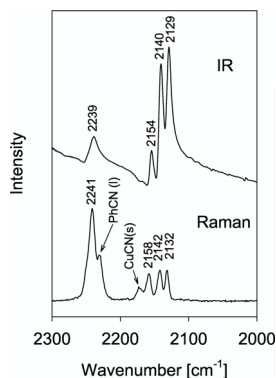


Fig. 4. IR and Raman spectra of CuCN/PhCN mixtures in the  $\nu(\text{CN})$  region.

at 2165  $\text{cm}^{-1}$  assigned to uncomplexed CuCN appears. These additional bands are also apparent in the Raman spectrum, even in the presence of an excess of liquid PhCN (Fig. 4). This suggests that loss of PhCN can be caused by the local heating effect of the laser beam used to excite the Raman spectrum, as has been observed previously for CuCN adducts with pyridine bases [1]. These results suggest that CuCN/PhCN adducts of higher CuCN content may exist, as has been shown in the case of adducts of CuCN with several pyridine bases [1]. Unfortunately, the  $\nu(\text{CuC/N})$  bands in the PhCN complex are obscured by bands due to PhCN, so no further information on the nature of the adducts of higher CuCN content could be obtained by this means.

## Conclusions

Relatively weak inter-chain bonding in solid CuCN can be broken by organic nitriles, which coordinate to the metal atoms about an infinite  $-\text{Cu}-\text{CN}-\text{Cu}-\text{CN}-$  chain structure. The adducts so obtained have well-defined compositions and structures, which depend on the steric profile and the base strength of the nitrile ligand: the maximum ligand to metal ratio for a particular ligand decreases as the size of the ligand increases, and comparison with the results for analogous complexes with pyridine bases shows that this ratio decreases as the donor strength of the ligand decreases. In the case of the complex with acetonitrile, the smallest ligand studied in the present series, cross-linking of the CuCN chains is observed. The vibrational spectra of bulk samples are largely consistent with the single crystal structural results, but reveal the possible existence of adducts of higher CuCN content in the case of the CuCN/benzonitrile system.

- [1] G. A. Bowmaker, K. C. Lim, B. W. Skelton, A. H. White, *Z. Naturforsch.* **59b**, 1264 (2004).
- [2] J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, A. H. White, *J. Chem. Soc., Dalton Trans.* 839 (1985).
- [3] G. A. Bowmaker, B. J. Kennedy, J. C. Reid, *Inorg. Chem.* **37**, 3968 (1998).
- [4] a) S. J. Hibble, S. M. Cheyne, A. C. Hannon, S. G. Eversfield, *Inorg. Chem.* **41**, 4990 (2002); b) S. J. Hibble, S. G. Eversfield, A. R. Cowley, A. M. Chippindale, *Angew. Chem. Int. Ed.* **43**, 628 (2004).
- [5] P. C. Healy, J. D. Kildea, B. W. Skelton, A. H. White, *Aust. J. Chem.* **42**, 79 (1989) and accompanying papers.
- [6] G. A. Bowmaker, D. S. Gill, B. W. Skelton, N. Somers, A. H. White, *Z. Naturforsch.* **59b**, 1307 (2004).
- [7] J. D. Kildea, B. W. Skelton, A. H. White, *Aust. J. Chem.* **38**, 1329 (1985).
- [8] D. T. Cromer, A. C. Larson, R. B. Roof, *Acta Crystallogr.* **19**, 192 (1965).
- [9] D. J. Chesnut, D. Plewak, J. Zubieta, *J. Chem. Soc., Dalton Trans.* 2567 (2001).
- [10] G. A. Bowmaker, Effendy, P. C. Junk, B. W. Skelton, A. H. White, *Z. Naturforsch.* **59b**, 1277 (2004).
- [11] D. J. Chesnut, A. Kusnetzow, R. Birge, J. Zubieta, *J. Chem. Soc., Dalton Trans.* 2581 (2001).
- [12] NIST Standard Reference Database 46, Version 4.0.