Acta Cryst. (1972). B28, 1052

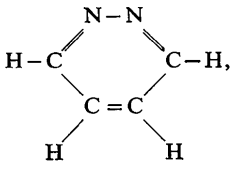
The Structures of the 1:1 Complex of CuCN with Pyridazine and with 4-Cyanopyridine*

BY DON T. CROMER AND ALLEN C. LARSON

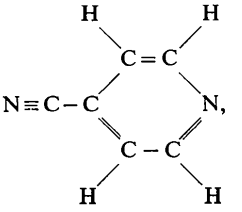
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, *U.S.A.*

(*Received* 11 *June* 1971)

The crystal structures of the 1:1 complexes of CuCN with pyridazine (PAZ):



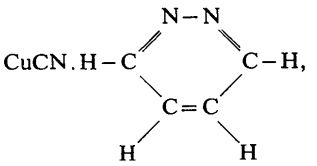
and 4-cyanopyridine (4CP):



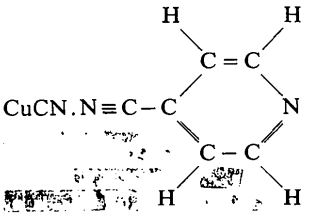
have been determined using graphite monochromated Mo $K\alpha$ X-rays and an automated diffractometer. CuCN.PAZ is monoclinic, space group $P2_1/m$, $Z=4$, $a=6{\cdot}833\,(3)$, $b=11{\cdot}960\,(6)$, $c=7{\cdot}958\,(4)$ Å, and $\beta=107{\cdot}2\,(1)°$. CuCN.4CP is orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=8{\cdot}519\,(4)$, $b=13{\cdot}576\,(7)$, and $c=6{\cdot}076\,(3)$ Å. Refinement was by least-squares methods with anisotropic thermal parameters on heavy atoms and isotropic hydrogen atoms. Hydrogen atoms were in constrained positions. Final conventional R indices are 0·049 for CuCN.PAZ and 0·032 for CuCN.4CP. Both compounds have zigzag CuCN chains linked *via* the nitrogen atoms of the organic molecules. The copper atoms in both compounds are approximately tetrahedrally coordinated to three nitrogen atoms and one carbon atom. The cyanide ions are probably ordered. No unusual bond lengths were observed.

Introduction

In continuation of our work at this laboratory on complexes of CuCN with KCN, or with nitrogen-containing compounds, we have prepared and determined the structure of the 1:1 complex with pyridazine (CuCN.PAZ),



and with 4-cyanopyridine (CuCN.4CP),



For references to earlier work see Williams, Cromer & Larson (1971) and additional references therein.

These complexes generally contain infinite zigzag chains of CuCN linked together *via* the organic ligands and/or CN groups to form interesting three-dimensional polymeric structures.

Experimental

Dark red crystals of CuCN.PAZ were prepared by dissolving a small amount of CuCN in warm pyridazine and allowing the solution to cool. Photographs of CuCN.PAZ showed *mmm* symmetry, but with the peculiar feature that reflections in one zone were almost entirely absent. The crystals proved to be monoclinic twins, each member comprising approximately one-half of the crystal. The crystals are twinned by a rotation of 180° about the $[10\bar{1}]^*$ reciprocal lattice vector, and the cell is of such a size and shape that if $h+l=5n$, reflections for the two halves exactly superimpose.

The space group of CuCN.PAZ is $P2_1/m$, as shown by the systematic extinctions ($0k0$ absent if $k=2n+1$) and by the structure determination. The twinned pseudo-orthorhombic cell with $A=8{\cdot}92$, $B=11{\cdot}94$, $C=29{\cdot}5$ Å is related to the true monoclinic cell by the transformation:

$$(a,b,c)=\begin{pmatrix}\frac{2}{5} & 0 & -\frac{1}{5}\\ 0 & 1 & 0\\ \frac{3}{5} & 0 & \frac{1}{5}\end{pmatrix}\begin{pmatrix}A\\B\\C\end{pmatrix}$$

Crystallographic data for CuCN.PAZ are shown in Table 1(*a*).

* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Crystallographic data*

(*a*)	(*b*)
CuCN.PAZ	CuCN.4CP
Dark red crystals	Orange crystals
$P2_1/m$	$P2_12_12_1$
$a=$ 6·883 (3) Å	$a=$ 8·519 (4) Å
$b=$11·960 (6)	$b=$13·576 (7)
$c=$ 7·958 (4)	$c=$ 6·076 (3)
$\beta=$107·2 (1)°	
$Z=4$	$Z=4$
$d_{calc}=1·798$ g.cm^{-3}	$d_{calc}=1·830$ g.cm^{-3}
$\mu=33$ cm^{-1}	$\mu=29$ cm^{-1}
$R_F=0·021$	$R_F=0·017$ (Friedel pairs considered equivalent)
	$R_F=0·011$ (for 426 centric zonal reflections)
Maximum transmission 0·81	Maximum transmission 0·76
Minimum transmission 0·74	Minimum transmission 0·64

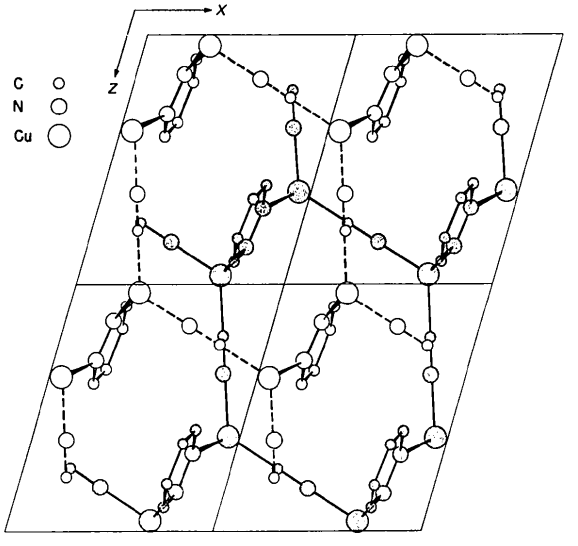


Fig. 1. Four unit cells of the CuCN.PAZ structure viewed along the *b* axis. Solid Cu, C, and N circles lie on the mirror at $y=\frac{1}{4}$ and the solid rings point up. Open Cu, C, and N circles are on the mirror at $y=\frac{3}{4}$ with the open rings pointing down. Another ring is directly below or above the rings shown.

CuCN.4CP was prepared in two ways, and powder photographs showed the products to be identical. In the first method, a small amount of CuCN was added to a solution of 4-cyanopyridine in either dimethylformamide or dimethyl sulfoxide. A yellow solution formed first, and after a few seconds orange crystals of the complex precipitated. These crystals were too small to be used in single-crystal work and could not be redissolved by heating. In the second method, six drops of a saturated solution of 4-cyanopyridine in water were added to 10 ml of a KCN–CuCN–water solution (5 gm KCN in 200 ml H_2O saturated with CuCN). Again, a yellow solution formed immediately, and soon afterwards the complex crystallized, but at a slower rate than in the first method. Suitable crystals were obtained by this second method. Heating this solution dissolved the crystals. With KCN present, there are evidently two competing, complex-forming reactions, the desired reaction being slower and reversible by heating. Preliminary precession photographs of CuCN.4CP showed the space group to be $P2_12_12_1$ (systematic absences $h00$, $0k0$, $00l$ for $h, k, l\neq 2n$). Crystallographic data for CuCN.4CP are given in Table 1*b*.

Lattice constants were obtained from a least-squares analysis of the settings of 12 reflections measured with graphite monochromated Mo $K\alpha_1$ radiation ($\lambda=$ 0·70926 Å) on an automated Picker diffractometer. The orientation least-squares and data-collection programs were local versions of the Oak Ridge system (Busing, Ellison, Levy, King & Roseberry, 1968). A θ–2θ scan technique was used with steps of 0·05° over a 2°, 2θ, range and a 2-sec count at each step. The background was measured for 20 sec at each end of the scan range and assumed to vary linearly over the range. Absorption corrections were made by the method of Busing & Levy (1957) using a modified version of Burnham's (1962) program.

For CuCN.PAZ, reflections were measured for $h\geq 0$, $\pm k$, $\pm l$ to a maximum $2\theta=55°$. After deleting all data for which $h+l=5n$ and then averaging equivalent reflections, there were 1208 unique data of which 702

Table 2. *Final parameters for* CuCN.PAZ

Values except for the rational positional parameters are multiplied by 10^4

	x	*y*	*z*	β_{11} or *B*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	3164 (2)	$\frac{3}{4}$	0370 (1)	217 (5)	96 (1)	101 (2)		75 (6)	
Cu(2)	0568 (2)	$\frac{3}{4}$	3802 (1)	204 (5)	91 (1)	99 (3)		85 (6)	
C(1)	7753 (19)	$\frac{3}{4}$	2495 (11)	185 (34)	72 (9)	118 (20)		92 (47)	
C(2)	2204 (16)	$\frac{3}{4}$	7851 (11)	212 (32)	65 (8)	74 (15)		31 (40)	
N(1)	6041 (17)	$\frac{3}{4}$	1733 (10)	262 (33)	108 (9)	107 (17)		98 (45)	
N(2)	1668 (14)	$\frac{3}{4}$	6335 (11)	252 (32)	111 (9)	130 (17)		148 (43)	
N(3)	2330 (9)	6052 (5)	1535 (7)	202 (19)	75 (6)	126 (10)	−4 (17)	114 (25)	−14 (12)
N(4)	2049 (9)	6094 (5)	3131 (7)	189 (19)	72 (5)	126 (11)	4 (17)	145 (25)	1 (12)
C(3)	2713 (15)	5068 (7)	0922 (11)	397 (36)	84 (9)	233 (21)	−47 (28)	313 (47)	−67 (21)
C(4)	2239 (14)	5161 (7)	4068 (10)	292 (29)	87 (8)	210 (19)	−16 (26)	223 (42)	29 (21)
C(5)	2666 (18)	4146 (8)	3499 (14)	547 (45)	79 (9)	366 (29)	51 (31)	507 (66)	65 (27)
C(6)	2925 (18)	4101 (8)	1886 (15)	609 (48)	56 (8)	455 (33)	−28 (31)	562 (73)	−60 (27)
H(1)	287 (2)	508 (5)	−028 (2)	4·6 (1·9) Å^2					
H(2)	203 (2)	531 (5)	524 (3)	4·5 (1·7)					
H(3)	277 (3)	351 (4)	434 (7)	8·7 (2·7)					
H(4)	322 (2)	343 (4)	127 (8)	9·2 (2·8)					

were observed to have an intensity greater than $3\sigma(I)$, where $\sigma(I)=[I+B+(kI)^2]^{1/2}$, I is the intensity, B is the background, and $k=0{\cdot}02$ (a constant derived from the variation of a periodically measured standard reflection). For CuCN.4CP, two octants were measured to a maximum of 65° 2θ: the octant with h, k, l all ≥ 0 and the one with h, k, l all ≤ 0. Considering hkl and $\bar{h}\bar{k}\bar{l}$ as being different (except for the zonal reflections), 2551 unique reflections were measured and 2073 were observed greater than $3\sigma(I)$.

The average agreement between equivalent reflections was estimated by forming the index:

$$R_F=\sum_n\sum_i|\bar{F}-F_{i,n}|/\sum_n\sum_i F_{i,n},$$

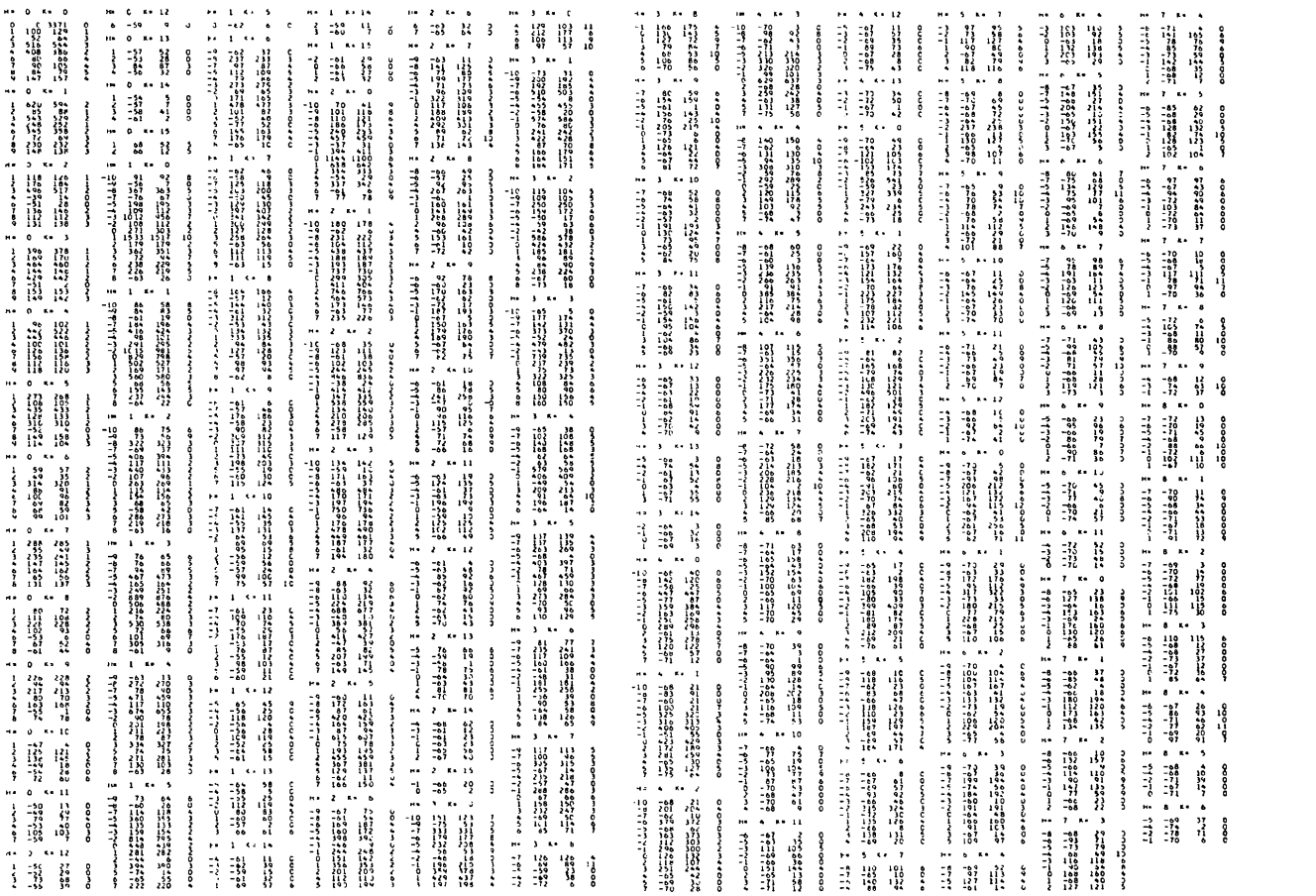
where $\bar{F}=\sum_i w_iF_i/\sum w_i$, w_i is the weight of the F_i as derived from $\sigma(I)$ (see Stout & Jensen, 1968), and the summation is taken over all n sets of i equivalent F_i's. The values of R_F are given in Table 1. For CuCN.4CP, the difference between the two R_F values indicates the fact that Friedel pairs are not truly equivalent in noncentric space groups when anomalous dispersion is appreciable.

Solution and refinement of the structures

Both structures were solved without difficulty by direct methods. Least-squares refinements minimized $\sum w(F_o-KF_c)^2$, where K is a scale factor. Anisotropic thermal parameters used were of the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Scattering factors for copper and nitrogen were taken from Doyle & Turner (1968), for hydrogen from Stewart, Davidson & Simpson (1965), and a Hartree–Fock valence state scattering factor for carbon was taken from Cromer (1968). Both real and imaginary anomalous dispersion terms were used for all atoms except hydrogen (Cromer & Liberman, 1970). R indices quoted are $R=\sum|\Delta F|/\sum F_o$ and $R_w=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$, with unobserved data omitted. Secondary extinction was very small and hence neglected.

Table 3. *Observed and calculated structure factors for* CuCN.PAZ

Column headings are l, $10F_o$, $10Fc$ and $10\sigma(F_o)$. A minus sign preceding F_o means 'less than', and the value given is that derived from $3\sigma(I)$. $\sigma(F_{obs})$ is given as zero for these unobserved reflections.



Discussion

Structure of CuCN.PAZ

Final parameters for this compound are given in Table 2. Observed and calculated structure factors are listed in Table 3. The hydrogen atoms were included in constrained positions in the final refinements (Waser, 1963; Rollett, 1970). They were required to be about 1·0 Å, with a standard deviation of 0·05 Å, from the carbon atoms of the ring. Also, to keep them in the plane of the ring their distances to a null atom, at a point 10 Å from the ring on the normal through the center of the ring, were fixed. Without hydrogen, $R=0{\cdot}055$ and $R_w=0{\cdot}048$. With hydrogen, $R=0{\cdot}049$ and $R_w=0{\cdot}039$. Evidently, the hydrogen atoms make a small but significant contribution to the total scattering.

The structure is shown in Fig. 1, and a stereo drawing is in Fig. 2. Thermal ellipsoids are shown in Fig. 3. The ring-numbering system used is presented in Fig. 4. Two crystallographically different CuCN groups lie on the mirror to form infinite zigzag chains. These chains are linked by Cu–N bonds to the pyridazine ring on both sides of the mirror. The result is a layering of two-dimensional polymers, adjacent layers being related to each other by the screw axis. The interleaved rings are nearly normal to these layers and all are oriented nearly parallel to the (100) planes. The copper atoms are each approximately tetrahedrally coordinated to three nitrogen atoms and one carbon atom.

The cyanide groups appear to be ordered. Any other arrangements increased R_w by a small but significant amount and produced extremes in thermal parameters.

The bond lengths and angles for CuCN.PAZ are given in Table 4. The addition of the four hydrogen atoms to the model produced a marked shrinkage of the ring, particularly in the C(5)–C(6) distances. The ring dimensions and angles obtained from the model, without hydrogen, are also given in Table 4. Addition of hydrogen to the model had no appreciable effect on

Table 4. *Bond distances and angles in* CuCN.PAZ

Values in brackets are for the model without hydrogen.

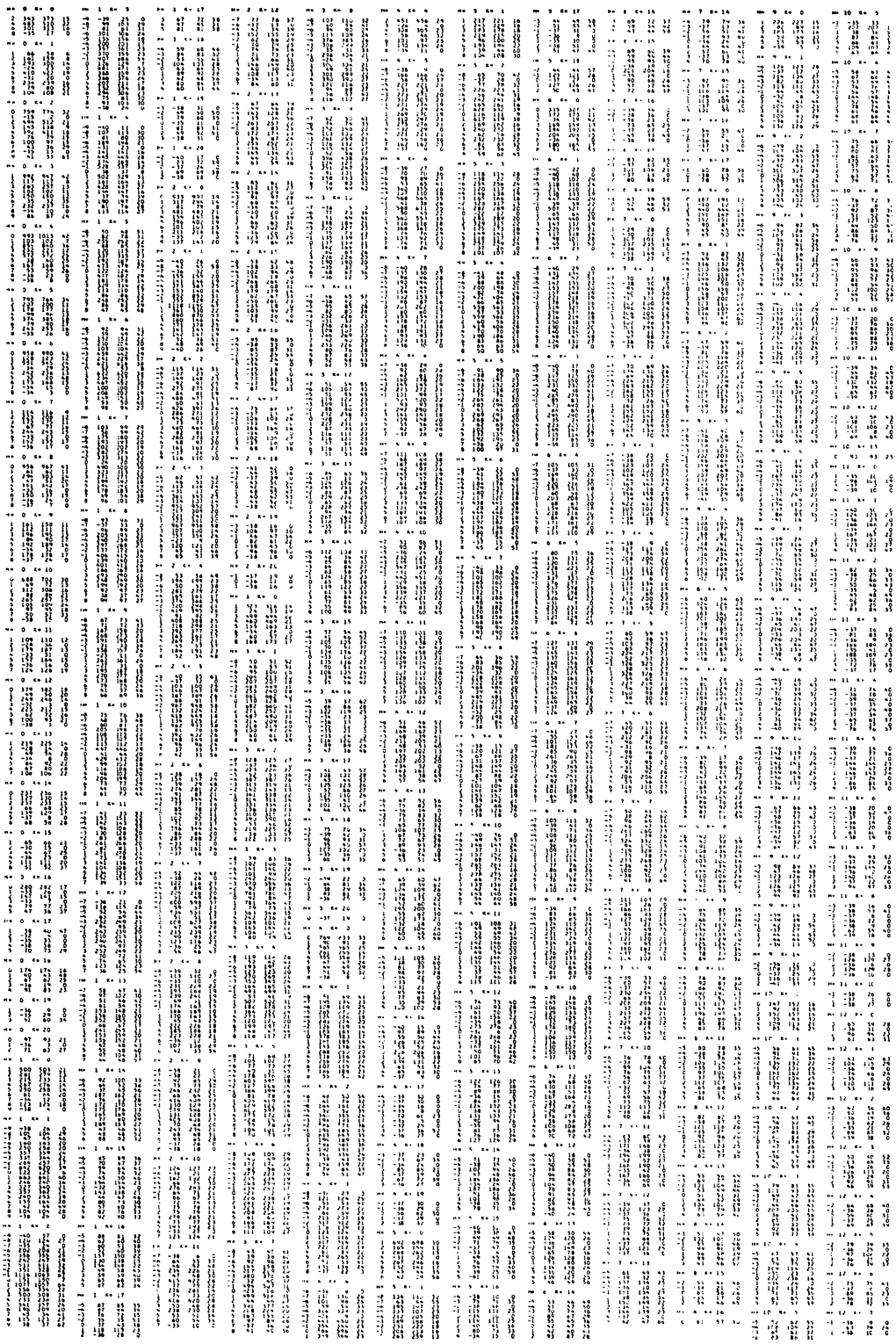
Cu(1)–N(1)	1·956 (11) Å			N(1)—Cu(1)–C(2)	124·0 (5)°
–C(2)	1·915 (8)		2	N(1)—Cu(1)–N(3)	96·8 (2)
–2N(3)	2·122 (6)		2	C(2)—Cu(1)–N(3)	113·8 (2)
				N(3)—Cu(1)–N(3)	109·4 (3)
Cu(2)–N(2)	1·932 (8)			C(1)—Cu(2)–N(2)	126·1 (5)
–C(1)	1·909 (12)		2	C(1)—Cu(2)–N(4)	110·5 (2)
–2N(4)	2·115 (6)		2	N(2)—Cu(2)–N(4)	101·2 (2)
				N(4)—Cu(2)–N(4)	105·3 (3)
C(1)—N(1)	1·155 (11)			Cu(2)–C(1)—N(1)	178·8 (9)
C(2)—N(2)	1·153 (9)			Cu(1)–N(1)—C(1)	178·1 (8)
				Cu(1)–C(2)—N(2)	178·6 (10)
N(3)—N(4)	1·341 (7)	[1·346]		Cu(2)–N(2)—C(2)	175·8 (10)
N(3)—C(3)	1·330 (8)	[1·348]		Cu(1)–N(3)—C(3)	117·0 (6)
N(4)—C(4)	1·327 (8)	[1·349]		Cu(1)–N(3)—N(4)	121·1 (4)
C(4)—C(5)	1·358 (12)	[1·377]		Cu(2)–N(4)—C(4)	120·1 (5)
C(5)—C(6)	1·348 (12)	[1·398]		Cu(2)–N(4)—N(3)	119·0 (4)
C(6)—C(3)	1·372 (11)	[1·409]			
C(3)—H(1)	1·00			N(4)—N(3)—C(3)	118·7 (6) [120·4]
C(4)—H(2)	1·00			N(3)—N(4)—C(4)	118·9 (6) [119·8]
C(5)—H(3)	1·00			N(3)—C(3)—C(6)	122·8 (9) [121·2]
C(6)—H(4)	0·99			N(4)—C(4)—C(5)	124·0 (8) [122·9]
				C(4)—C(5)—C(6)	117·2 (9) [117·6]
				C(5)—C(6)—C(3)	118·5 (10) [118·0]

Table 5. *Final parameters* ($\times 10^4$) *for* CuCN.4CP

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	3874·7 (3)	7482·2 (3)	2215·4 (5)	76·2 (4)	36·6 (2)	155·2 (8)	1·8 (7)	−19·0 (10)	19·1 (11)
C(1)	1905 (3)	7561 (2)	0732 (4)	76 (3)	32 (1)	138 (5)	12 (5)	11 (7)	11 (8)
N(1)	0805 (2)	7574 (2)	−0351 (4)	79 (3)	44 (1)	169 (6)	7 (5)	4 (6)	−3 (7)
N(2)	4262 (3)	6290 (2)	4408 (5)	77 (4)	29 (1)	125 (6)	6 (3)	−10 (9)	17 (5)
N(3)	5622 (3)	3541 (2)	0419 (5)	120 (5)	31 (1)	193 (9)	5 (4)	−24 (11)	16 (7)
C(2)	3512 (3)	6259 (2)	6341 (5)	82 (4)	29 (1)	166 (7)	17 (4)	4 (9)	0 (5)
C(3)	3791 (3)	5543 (2)	7906 (5)	101 (4)	34 (1)	143 (6)	−5 (4)	31 (11)	9 (5)
C(4)	4907 (3)	4830 (2)	7431 (6)	93 (4)	26 (1)	152 (7)	−15 (4)	−53 (8)	8 (6)
C(5)	5700 (4)	4845 (2)	5438 (5)	107 (4)	32 (1)	169 (8)	35 (4)	25 (10)	2 (6)
C(6)	5341 (3)	5601 (2)	3994 (5)	109 (4)	35 (1)	128 (7)	21 (4)	40 (10)	3 (5)
C(7)	5296 (3)	4088 (2)	9071 (5)	107 (4)	30 (1)	176 (8)	0 (4)	−9 (10)	6 (6)
H(1)	283	678	665	2·9 (6) Å^2					
H(2)	320	559	932	2·6 (6)					
H(3)	644	432	495	3·3 (8)					
H(4)	591	559	252	5·5 (9)					

Table 6. *Observed and calculated structure factors for* CuCN.4CP

Column headings are l, $10F_{obs}$, $10F_{calc}$ and $10\sigma(F_{obs})$. A minus sign preceding F_o means 'less than', and the given value is that derived from $3\sigma(I)$. $\sigma(F_{obs})$ is given as zero for these unobserved reflections.



any part of the structure other than the ring. The ring is planar, and the maximum deviation of any atom from the least-squares plane is 0·013 Å. The thermal parameters of the carbon atoms in the ring increase as the atoms get farther from the nitrogen atoms. The thermal motion is probably such that the ring rocks back and forth along an axis through the nitrogen atoms, or through the copper atoms to which the ring is attached. The thermal ellipsoids of N(3) and N(4) are not far from spherical, C(3) and C(4) are somewhat anisotropic, and C(5) and C(6) are markedly anisotropic. The major axes of the C(3), C(4), C(5), and C(6) thermal ellipsoids make angles of 25 to 37° with the normal to the plane of the ring.

It is of interest to compare this structure with that of the hydrazine complex, $CuCN.N_2N_4$ (Cromer, Larson & Roof, 1966, Fig. 1). In $CuCN.N_2H_4$, there are also zigzag CuCN chains lying on mirrors. Adjacent

Table 7. *Bond distances and angles in* CuCN.4CP

Values in brackets are for the model without hydrogen.

Cu—C(1)	1·907 (2) Å		N(1)–Cu—C(1)	117·3 (1)°	
–N(1)	1·999 (2)		N(1)–Cu—N(2)	101·5 (1)	
–N(2)	2·122 (2)		N(1)–Cu—N(3)	104·4 (1)	
–N(3)	2·077 (3)		C(1)–Cu—N(2)	118·5 (1)	
C(1)–N(1)	1·145 (3)		C(1)–Cu—N(3)	118·0 (1)	
N(2)–C(2)	1·338 (4)	[1·344]	N(2)–Cu—N(3)	93·5 (1)	
N(2)–C(6)	1·335 (3)	[1·347]	Cu—N(1)–C(1)	177·0 (3)	
C(2)–C(3)	1·380 (4)	[1·395]	Cu—C(1)–N(1)	172·8 (2)	
C(3)–C(4)	1·387 (4)	[1·411]			
C(4)–C(5)	1·387 (4)	[1·405]	C(2)–N(2)–C(6)	118·1 (3)	[119·3]
C(5)–C(6)	1·385 (4)	[1·386]	C(3)–C(2)–N(2)	123·1 (2)	[122·3]
C(4)–C(7)	1·455 (4)		C(2)–C(3)–C(4)	117·8 (3)	[117·5]
C(7)–N(3)	1·140 (4)		C(3)–C(4)–C(5)	120·3 (3)	[120·0]
C(2)–H(1)	0·94		C(4)–C(5)–C(6)	117·2 (3)	[117·9]
C(3)–H(2)	1·00		C(5)–C(6)–N(2)	123·5 (3)	[122·4]
C(5)–H(3)	0·99		C(3)–C(4)–C(7)	119·8 (3)	[120·0]
C(6)–H(4)	1·02		C(5)–C(4)–C(7)	119·8 (3)	[119·9]
			N(3)–C(7)–C(4)	176·9 (3)	

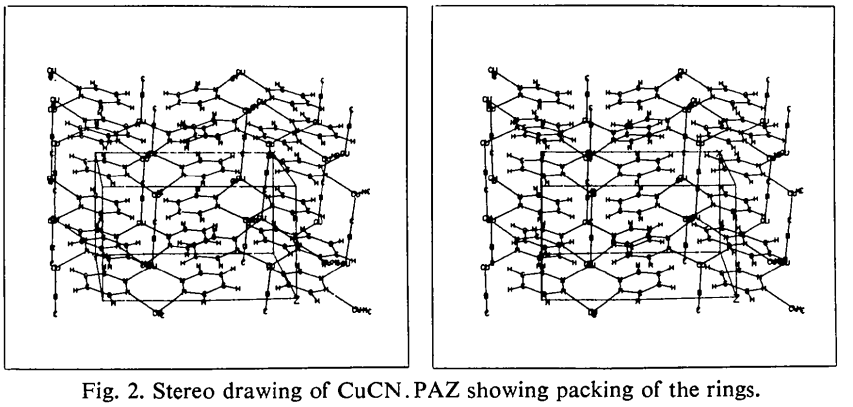


Fig. 2. Stereo drawing of CuCN.PAZ showing packing of the rings.

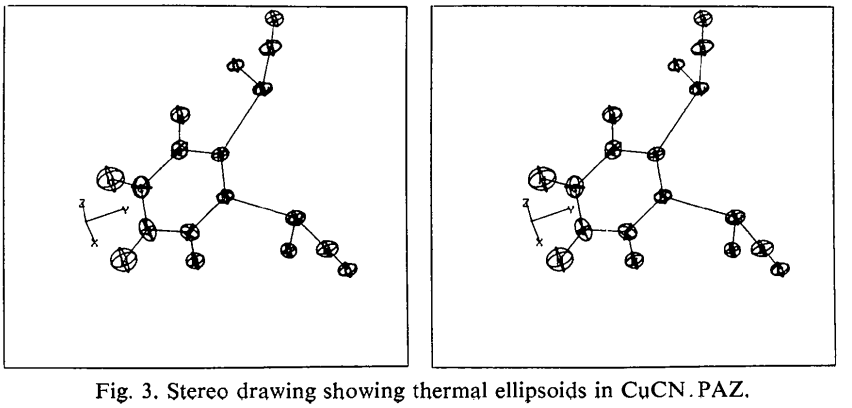


Fig. 3. Stereo drawing showing thermal ellipsoids in CuCN.PAZ.

chains are parallel, or in phase with each other, and the hydrazine molecule links copper atoms on neighboring mirrors. In CuCN.PAZ, adjacent chains on a mirror zigzag out of phase, and two copper atoms on the *same* mirror are linked by the pyridazine molecule.

Structure of CuCN.4CP

Final parameters for CuCN.4CP are given in Table 5. Observed and calculated structure factors are listed in Table 6. Hydrogen atoms are also included with constraints in the final refinements. They were required to be about 1·0 Å from the carbon atoms, but no further constraints were needed to keep them in reasonable positions in the plane of the ring. Without hydrogen, $R=0{\cdot}038$ and $R_w=0{\cdot}047$; with hydrogen, $R=0{\cdot}032$ and $R_w=0{\cdot}033$. For the opposite absolute configuration, hydrogen included, $R=0{\cdot}043$ and $R_w=0{\cdot}043$. The orientation of the cyano group on the pyridine ring is, of course, known. The orientation of the cyanide ion is reasonably well determined by the bond lengths and thermal parameters. Reversing the cyanide ion also increased R_w by a significant amount.

Fig. 5 shows the CuCN.4CP structure as viewed down the *c* axis. Anisotropy of the thermal motion is not large for any of the atoms. Bond lengths and angles are given in Table 7. Again, there is a zigzag CuCN chain that is nearly planar, at $y=\frac{1}{4}, \frac{3}{4}$, but it is not required to be so by symmetry. Because of the long distance between the two nitrogen atoms in this bidentate organic molecule, the linkage is between two copper atoms in adjacent unit cells. The resulting structure is a very tangled array. There are three distinct interpenetrating three-dimensional polymers. Starting with the copper atom at $z=0{\cdot}22$ (Fig. 5) and following the chain around the screw axis at $x=\frac{1}{4}$, $y=\frac{1}{2}$, three unit cells are traversed in the z direction before the starting point is reached. This structure probably explains the facts noted in preparing the compound. Once formed, the structure cannot be dissolved except by the chemical action of the KCN–CuCN solution, in which the two competing, complex-forming reactions can be reversed by heating.

Again, the copper atom is approximately tetrahedrally coordinated to three nitrogen atoms and one carbon atom. The ring is planar, the maximum deviation from the least-squares plane being 0·007 Å, but C(7) is 0·07 Å and N(3) is 0·17 Å from the plane. The cyano group makes an angle of 2°40′ with the plane of the ring. When hydrogen was added to the model, the ring shrank, although the shrinkage was slightly less than that observed for the pyridazine ring. Ring dimensions without hydrogen in the model are also given in Table 7.

All calculations were performed on CDC-6600 and 7600 computers using the Los Alamos system of programs.

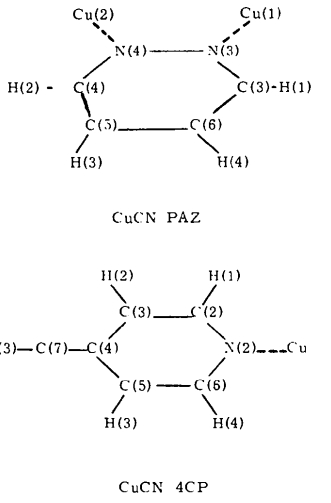


Fig. 4. Ring numbering system used.

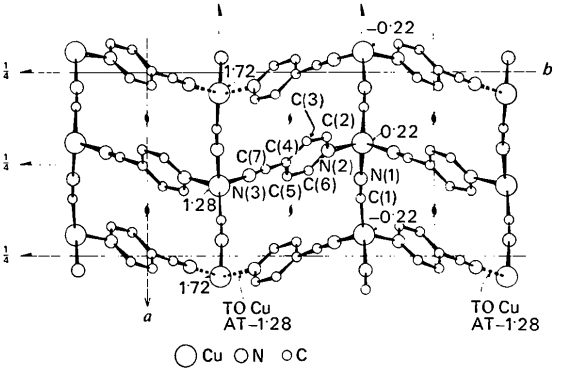


Fig. 5. The structure of CuCN.4CP viewed along the *c* axis.

References

BURNHAM, C. W. (1962). *IUCr World List of Crystallographic Computer Programs*. Program 338.

BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). ORNL Report 4143, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.

CROMER, D. T. (1968). Unpublished work.

CROMER, D. T., LARSON, A. C. & ROOF, R. B. JR (1966). *Acta Cryst.* **20**, 279.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390.

ROLLETT, J. S. (1970). *Crystallographic Computing*, p. 167. Copenhagen: Munksgaard.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination – A Practical Guide*, p. 457. New York: Macmillan.

WASER, J. (1963). *Acta Cryst.* **16**, 1091.

WILLIAMS, R. J., CROMER, D. T. & LARSON, A. C. (1971). *Acta Cryst.* B**27**, 1701.