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The Crystal Structure of $KCu_2(CN)_3.H_2O$*

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The crystal structure of $KCu_2(CN)_3.H_2O$ has been determined by single crystal X-ray methods. The unit cell is monoclinic, space group $P2_1/c$ with

$$a=12\cdot105,\ b=8\cdot200,\ c=7\cdot500\ \text{Å};\ \beta=97\cdot4°$$

and it contains four formula units. Intensities were measured with a Geiger counter. The structure was refined by the least-squares method and anisotropic thermal parameters were included. The principal feature of the structure is the existence of polymer sheets of composition $[Cu_2(CN)_3^-]_\infty$. The sheets are made up of a $(CuCN)_\infty$ spiral chain similar to that found in $KCu(CN)_2$ and a $(CuCN)_\infty$ zig-zag chain; the copper atoms in these two chains are linked by the third cyanide group. The water molecules lie within rings of composition $(CuCN)_6$ and apparently are present only to fill space. The sheets are held together by K^+ ions. Reasonable locations for the hydrogen atoms were found from a difference Fourier. Each copper atom has three ligands, in one case one carbon and two nitrogen atoms and in the other case one nitrogen and two carbon atoms. Cu-C bonds are 1·87, 1·89 and 1·90 Å; Cu–N bonds are 1·96, 1·98 and 2·02 Å.

Introduction

The crystal structure of $KCu(CN)_2$ was reported several years ago by Cromer (1957). This compound proved to be of considerable interest, for the copper atom was found to be in a threefold hybridized state, perhaps sp^2. This was the first observation of a Cu(I) atom so hybridized known to the present authors. The metal atoms in the analogous silver and gold compounds have been shown to form linear *sp* hybrids (Hoard, 1933; Rosenzweig & Cromer, 1959). As part of our continuing program of studying complex metal cyanides we have determined the structure of $KCu_2(CN)_3.H_2O$.

Experimental

The system KCN–CuCN–H_2O has been studied by Bassett & Corbet (1924). Of the four compounds in this system, $KCu(CN)_2$, $K_3Cu(CN)_4$, $K_3Cu(CN)_4.H_2O$ and $KCu_2(CN)_3.H_2O$, the last can be prepared in the most straightforward manner. Small crystals of $KCu_2(CN)_3.H_2O$ suitable for X-ray diffraction work were prepared by adding excess CuCN to a solution of KCN in water, filtering the undissolved CuCN and slowly evaporating the resulting solution.

Crystallographic data on this compound have been published by Walker & Staritzky (1956). The crystals are monoclinic and the systematic extinctions uniquely establish the space group to be $P2_1/c$. The cell dimensions as measured from resolved α_1–α_2 doublets on zero level Weissenberg films (Cu $K\alpha_1 \lambda=1\cdot54051$ Å), are $a=12\cdot105$, $b=8\cdot200$ and $c=7\cdot500$, all $\pm 0\cdot01$ Å and $\beta=97\cdot4\pm0\cdot1°$. There are four formula units per unit cell. These cell dimensions differ somewhat from the findings of Walker & Staritzky who reported $a=12\cdot11$, $b=8\cdot16$, $c=7\cdot44$ Å and $\beta=97\cdot5°$. Our calculated density of 2·359 g.cm.$^{-3}$ agrees well with their measured density of 2·365 g.cm.$^{-3}$.

Intensities were measured with a Geiger counter attachment on a Weissenberg camera (Evans, 1953) using Cu $K\alpha$ radiation. Data were obtained from *b* and *c* axis mountings for levels 0 through 5. The crystal mounted on the *b* axis had approximate dimensions of 0·21 (rotation axis) $\times 0\cdot05 \times 0\cdot025$ mm. and the one mounted on the *c* axis had approximate dimensions of 0·14 (rotation axis) $\times 0\cdot06 \times 0\cdot11$ mm. Lorentz-polarization corrections were applied but no absorption corrections were made. All data were placed on the same scale by comparing reflections that had been measured on two different levels. Of 1419 independent reflections investigated, 1219 were observed to have an intensity greater than zero.

Determination and refinement of the structure

The asymmetric portion of the unit cell contains one formula unit. The three-dimensional Patterson function was calculated and study of this enabled us to approximately locate the potassium atom and the two copper atoms. Further study of the Patterson might have led to the location of some or all of the light atoms but it seemed expedient to proceed directly to a three-dimensional Fourier synthesis. Such a Fourier was computed using as coefficients about two-thirds of the observed reflections. In this Fourier the oxygen atom and the three cyanide groups were easily located.

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However, there was uncertainty about the orientation of the cyanide groups, i.e., it was uncertain which atom of the two was nitrogen and which atom was carbon.

A least-squares refinement was then started using Maniac I, a computer that is now extinct. McWeeny's (1951) form factors for carbon, nitrogen and oxygen and Viervoll & Øgrim's (1949) form factors for potassium and copper were used. The copper form factor was reduced by 1·3 electrons to correct for anomalous dispersion (Wheeler & Bearden, 1934). Isotropic temperature factor parameters were assigned to each crystallographically different atom. The hydrogen atoms were ignored. Off-diagonal terms in the matrix were omitted. The original assignment of carbon and nitrogen atoms had cyanide groups 1 and 3 reversed from their final assignment.

After several cycles of isotropic refinement R dropped to 13·1%. A final choice as to the identity of the carbon and nitrogen atoms had not yet been made. For $KCu(CN)_2$ a very important if not decisive factor in identifying the atoms was the bond angles. In the present structure only cyanide group 2 is oriented so that the bond angles serve to fix the atoms. Cyanide groups 1 and 3 lie approximately along lines joining two copper atoms so that either orientation is permissible insofar as the bond angles are concerned. As noted by Rossmann *et al.* (1959), and also in this laboratory, the behavior of temperature factors in a least squares refinement will often aid in distinguishing between atoms of similar atomic number. However, in this case the temperature factors did not offer much help, probably because in a cyanide group both atoms are so 'smeared out' that their electron densities become very similar. Interatomic distances appeared to be the best criterion to use, because, from the study of $KCu(CN)_2$ we expect the Cu–N distance to be of the order of 0·1 Å greater than the Cu–C distance. This order for bond lengths is reversed from that expected from the normal single bond radii but in these compounds the nitrogen atom uses an s orbital in the Cu–N bond and this orbital forms a weaker and longer bond than a p orbital would. On this basis C_1 and N_1 were definitely reversed, C_2 and N_2 were correct and C_3 and N_3 were indeterminate because the latter atoms were nearly equidistant from copper atoms. The atoms C_1 and N_1 were accordingly interchanged and the least-squares refinement was continued. After a few cycles R was reduced slightly to 13·0%. The distances of C_1, C_2, N_1 and N_2 from copper atoms were consistent with our identification of the atoms but C_3 and N_3 remained equidistant from copper atoms. At this point C_3 and N_3 were interchanged and after a few more least-squares cycles R became 12·9%. The changes in R were of course small but in the proper direction if the decisions were correct. More important, the positions of the atoms in cyanide group 3 changed so that now the Cu–N_3 distance was significantly larger than the Cu–C_3 distance. The final parameters from this isotropic refinement are given in Table 1.

Table 1. *Parameters of* $KCu_2(CN)_3.H_2O$ *as determined from the isotropic least-squares refinement*

Atom	x	y	z	B (Å^2)
K	0·3046 ± 0·0004	−0·0665 ± 0·0006	0·3432 ± 0·0006	3·5
Cu_1	0·1061 ± 0·0002	0·2866 ± 0·0004	0·1816 ± 0·0004	3·4
Cu_2	0·4328 ± 0·0002	0·3828 ± 0·0003	0·3826 ± 0·0004	3·0
C_1	0·0322 ± 0·0015	0·4809 ± 0·0023	0·2337 ± 0·0025	2·9
C_2	0·4563 ± 0·0014	0·5765 ± 0·0022	0·2587 ± 0·0024	2·7
C_3	0·2327 ± 0·0013	0·2621 ± 0·0021	0·5654 ± 0·0023	2·3
N_1	0·0210 ± 0·0014	0·0915 ± 0·0023	0·2415 ± 0·0025	4·0
N_2	0·4726 ± 0·0012	0·6907 ± 0·0019	0·1753 ± 0·0020	3·0
N_3	0·3075 ± 0·0013	0·3023 ± 0·0020	0·4983 ± 0·0021	3·2
O	0·1815 ± 0·0013	−0·2304 ± 0·0021	0·0536 ± 0·0022	4·8

Next, a three-dimensional Fourier synthesis was computed using all of the observed reflections. The peak electron densities are listed in Table 2. The nitrogen peaks are all higher than the corresponding carbon peaks although only for C_2 and N_2 is the

Table 2. *Electron densities in* e.Å^{-3} *at atom positions*

Atom	Fourier	Difference Fourier
K	34·0	−0·14
Cu_1	54·5	−0·16
Cu_2	58·3	−0·09
C_1	9·6	0·05
C_2	9·9	0·16
C_3	10·9	0·06
N_1	9·9	0·00
N_2	11·6	−0·10
N_3	11·3	0·00
O	11·1	0·01

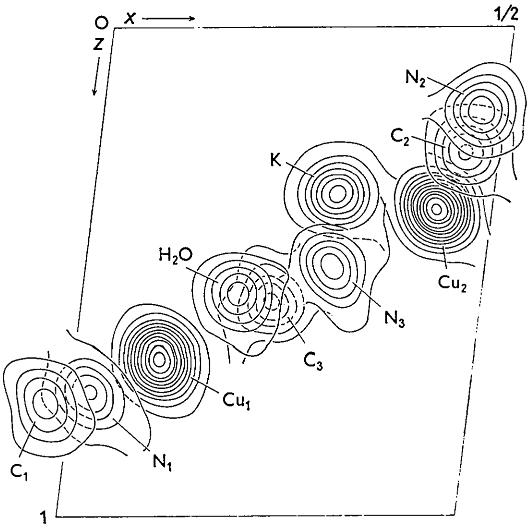

Fig. 1. Composite of electron density sections at constant y through the centers of the atoms. The contour intervals are arbitrary and the interval for the potassium and copper atoms is 2·5 times that for the other atoms.

difference significant. The standard deviation of the electron density is 0·24 e.Å^{-3} according to Cruickshank's (1949) formula.

Fig. 1 is a composite of sections at constant y through the center of each atom. Anisotropic thermal motion is clearly indicated for many of the atoms. It has been our usual experience with counter data to have R of the order of 10% or less. This fact coupled with the obvious anisotropy suggested that further least-squares refinement with anisotropic thermal parameters would be profitable.

An anisotropic refinement was then carried out using an IBM-704 computer. The temperature factors were in the form

$$\exp\left(-B11h^2-B22k^2-B33l^2-B12hk-B13hl-B23kl\right)$$

and symmetry operations appropriate to space group $P2_1/c$ were included in calculating the structure factors. The entire matrix was now computed and solved for parameter shifts and inverted for standard deviation calculations. The formation and solution of a 91 × 91 matrix was therefore required, there being three position and six thermal parameters for each of ten atoms plus the scale factor. The hydrogen atoms were again ignored. The final position parameters are given in Table 3, the final thermal parameters in Table 4 and the final observed and calculated structure factors, for which $R = 7·5\%$ with $F_o = 0$ terms omitted, are given in Table 5. Comparison of Tables 1 and 3 shows that inclusion of anisotropic temperature factors has not significantly changed the atomic positions but has nearly halved their standard deviations.

Table 3. *Final position parameters after the anisotropic least-squares refinement*

Atom	x	y	z
K	0·3045 ± 0·0002	−0·0665 ± 0·0003	0·3432 ± 0·0004
Cu_1	0·1062 ± 0·0001	0·2866 ± 0·0002	0·1816 ± 0·0003
Cu_2	0·4327 ± 0·0001	0·3827 ± 0·0002	0·3826 ± 0·0002
C_1	0·0324 ± 0·0009	0·4810 ± 0·0014	0·2337 ± 0·0015
C_2	0·4559 ± 0·0009	0·5758 ± 0·0013	0·2598 ± 0·0015
C_3	0·2322 ± 0·0008	0·2617 ± 0·0013	0·5651 ± 0·0014
N_1	0·0213 ± 0·0009	0·0922 ± 0·0013	0·2396 ± 0·0016
N_2	0·4722 ± 0·0007	0·6919 ± 0·0011	0·1752 ± 0·0013
N_3	0·3076 ± 0·0008	0·3023 ± 0·0012	0·4996 ± 0·0012
O	0·1813 ± 0·0007	−0·2302 ± 0·0013	0·0529 ± 0·0012

A difference or $(F_o - F_c)$ Fourier, for which the parameters of Tables 3 and 4 were used to calculate F_c, was computed in the regions of the atoms. This Fourier is of particular interest at the carbon and nitrogen sites, for if these atoms have been incorrectly identified, the difference Fourier should show a positive value at the supposed carbon site and a negative value at the supposed nitrogen site. The difference Fourier was flat and near zero in these regions. The densities at the atom sites are also given in Table 2. Remembering that $\sigma(\varrho) = 0·24$ e.Å^{-3}, these values are not significantly different from zero. The difference Fourier therefore supports the atom selection as do the electron densities in the F_o Fourier, the bond lengths and, in the case of cyanide group 2, the bond angles.

The present analysis does not rule out the possibility of random orientation of cyanide groups 1 and 3 although if there is significant disorder the apparent Cu–C and Cu–N bond lengths ought to be nearly the same.

The difference Fourier was inspected in the vicinity of the oxygen atom for peaks that could possibly be hydrogen atoms. At about 1 Å from the oxygen atom there were only two peaks of possible significance. One peak of height 0·6 e.Å^{-3} was at $x_1 = 0·108$, $y_1 = -0·181$, $z_1 = -0·008$ and the other peak had height 0·5 e.Å^{-3} and was at $x_2 = 0·251$, $y_2 = -0·126$ and $z_2 = 0·041$. It is not unreasonable to believe that these peaks are hydrogen atoms for they result in the distances O–H_1 = 1·03 Å and O–H_2 = 1·21 Å and an H–O–H angle of 105°. These values are reasonably close to those expected for water.

The least-squares thermal parameters were transformed into parameters related to the principal axes of the ellipsoids of vibration. The magnitudes of these principal axes and their direction angles relative to the *crystallographic axes* are given in Table 6. This transformation was carried out on an IBM-704 computer by means of a program developed by one of us (A. C. L.).

Discussion of the structure

The structure in projection on (010) is shown in Fig. 2 and the interatomic distances and bond angles are given in Table 7. Certain features of the structure are similar to those found in $KCu(CN)_2$. The atoms Cu_2,

Table 4. *Final thermal parameters* × 10^4 *after the anisotropic least-squares refinement*

Atom	$B11$	$B22$	$B33$	$B12$	$B13$	$B23$
K	79 ± 2	104 ± 4	156 ± 5	−8 ± 5	4 ± 5	15 ± 8
Cu_1	46 ± 1	119 ± 3	212 ± 4	2 ± 3	60 ± 3	−23 ± 6
Cu_2	64 ± 1	75 + 2	168 ± 4	−8 ± 3	84 ± 3	16 ± 5
C_1	50 ± 8	114 ± 19	140 ± 23	17 ± 21	46 ± 21	24 ± 33
C_2	45 ± 7	79 ± 17	166 ± 24	14 ± 18	3 ± 21	−67 ± 33
C_3	30 ± 6	100 ± 17	125 ± 21	−22 ± 17	−1 ± 18	5 ± 30
N_1	84 ± 10	135 ± 19	233 ± 27	−41 ± 23	80 ± 26	−45 ± 37
N_2	51 ± 7	79 ± 14	162 ± 21	−28 ± 16	2 ± 18	−13 ± 28
N_3	56 ± 7	125 ± 16	140 ± 20	−26 ± 18	2 ± 19	−32 ± 30
O	63 ± 7	254 ± 22	186 ± 20	2 ± 20	29 ± 19	−21 ± 34

Table 5. *Final observed and calculated structure factors for* $KCu_2(CN)_3.H_2O$

The column headings are l, F_o and F_c. If $F_o = 0$, the reflection was obscured by the beam trap. If $F_o < 0$, it was unobserved and the minus sign should be interpreted as 'less than'

H= 0 K= 0		
2	82	-87
4	54	-53
6	27	26
8	-9	4
H= 1 K= 0		
-8	24	-26
-6	46	46
-4	75	72
-2	69	-68
0	0	-30
2	34	-34
4	54	54
6	30	-28
8	12	-13
H= 2 K= 0		
-8	16	17
-6	28	-28
-4	62	-59
-2	89	84
0	60	65
2	243	-244
4	38	35
6	13	-13
8	-9	5
H= 3 K= 0		
-8	22	24
-6	48	47
-4	76	-69
-2	18	-14
0	30	-24
2	12	-8
4	85	88
6	18	-17
8	-8	-4
H= 4 K= 0		
-8	9	-10
-6	47	-45
-4	17	17
-2	53	54
0	17	-13
2	18	-18
4	11	18
6	-10	-3
8	20	20
H= 5 K= 0		
-8	19	23
-6	34	-32
-4	7	-7
-2	3	3
0	67	-68
2	85	91
4	16	13
6	58	-57
8	-7	5
H= 6 K= 0		
-8	-9	-6
-6	23	-23
-4	83	81
-2	48	45
0	49	-48
2	16	-15
4	7	7
6	19	18
H= 7 K= 0		
-8	10	13
-6	-10	0
-4	5	5
-2	70	-67
0	75	74
2	42	42
4	55	-55
6	-10	3
H= 8 K= 0		
-8	17	-30
-6	-10	6
-4	69	69
-2	87	-81
0	52	-49
2	26	25
4	-8	-1
6	-9	-2
H= 9 K= 0		
-8	-6	1
-6	10	-10
-4	32	-32
-2	12	10
0	70	73
2	52	-52
4	6	-5
H= 9 K= 0		
6	11	10
H= 10 K= 0		
-6	51	53
-4	13	-11
-2	45	-43
0	34	32
2	-6	4
4	-6	0
6	10	9
H= 11 K= 0		
-6	-8	-4
-4	19	-17
-2	29	29
0	10	9
2	36	-36
4	10	11
H= 12 K= 0		
-6	11	16
-4	38	-38
-2	17	17
0	9	-9
2	6	6
4	13	12
H= 13 K= 0		
-4	3	-2
-2	35	39
0	8	-11
2	14	-14
H= 14 K= 0		
-4	8	-10
-2	7	8
0	16	-15
2	16	18
H= 0 K= 1		
1	23	21
2	11	-10
3	41	36
4	64	65
5	39	-38
6	29	-29
7	-10	-3
8	-9	-7
9	10	15
H= 1 K= 1		
-9	-7	-8
-8	-9	-1
-7	9	11
-6	13	-14
-5	8	7
-4	44	-42
-3	27	22
-2	106	117
-1	41	-37
0	70	-75
1	50	-52
2	83	-97
3	24	24
4	47	46
5	32	31
6	-10	-1
7	-10	-11
8	-9	2
9	10	-12
H= 2 K= 1		
-9	-7	2
-8	18	18
-7	9	-8
-6	6	-8
-5	14	-11
-4	14	-11
-3	25	-20
-2	48	43
-1	45	41
0	43	-45
1	48	46
2	116	139
3	68	-70
4	5	-4
5	27	-26
6	41	-41
7	28	29
8	17	17
H= 3 K= 1		
-2	-7	-4
-8	-9	2
-7	-7	2
-6	29	-26
-5	40	37
-4	66	65
-3	6	2
-2	84	83
-1	122	-122
0	103	-119
1	64	64
2	21	20
3	56	58
4	31	29
5	16	-16
6	7	-8
7	14	-12
8	6	-4
H= 4 K= 1		
-9	-7	6
-8	9	9
-7	16	-15
-6	27	-26
-5	28	-26
-4	-6	-1
-3	45	41
-2	28	-29
-1	77	76
0	20	-19
1	75	-79
2	37	40
3	29	-26
4	84	-87
5	32	32
6	-10	-1
7	-10	3
8	8	10
H= 5 K= 1		
-9	-6	-8
-8	11	-14
-7	25	28
-6	16	15
-5	7	6
-4	72	88
-3	85	-84
-2	112	-111
-1	-5	-0
0	38	-36
1	84	88
2	46	47
3	38	-35
4	13	-11
5	7	-7
6	14	12
7	-7	1
8	-7	2
H= 6 K= 1		
-8	-8	-6
-7	21	-20
-6	21	-19
-5	30	28
-4	7	5
-3	38	36
-2	7	-5
-1	18	-16
0	48	50
1	39	-39
2	10	10
3	17	18
4	17	-17
5	6	4
6	27	25
7	-9	1
H= 7 K= 1		
-8	9	-13
-7	13	14
-6	37	37
-5	39	-37
-4	28	-23
-3	8	-5
-2	70	-67
-1	35	34
0	75	75
1	7	6
2	10	-9
3	5	-5
4	4	2
5	5	3
6	-10	5
7	10	-9
H= 8 K= 1		
-8	-7	-17
-7	-9	7
-6	10	10
-5	14	12
-4	7	-6
-3	7	-4
-2	40	37
-1	5	-4
0	30	28
1	32	-30
2	46	-45
3	7	5
4	8	-6
5	14	12
6	6	4
7	3	-1
H= 9 K= 1		
-8	-6	10
-7	-8	-6
-6	33	33
-5	15	-16
-4	39	-36
-3	10	6
-2	11	10
-1	7	7
0	21	19
1	22	20
2	16	-18
3	12	-12
4	14	11
5	14	-11
6	7	-8
H= 10 K= 1		
-7	-8	4
-6	-9	-0
-5	10	9
-4	19	-18
-3	10	10
-2	41	40
-1	27	-28
0	49	-49
1	7	-6
2	27	-26
3	28	28
4	25	24
5	6	-1
H= 11 K= 1		
-7	-6	-10
-6	8	-10
-5	13	-12
-4	35	-35
-3	12	14
-2	16	15
-1	16	15
0	5	-4
1	7	-8
2	13	11
3	17	-16
4	-6	-1
5	7	7
H= 12 K= 1		
-6	-7	-10
-5	8	10
-4	22	21
-3	20	-21
-2	19	18
-1	12	-13
9	33	-32
1	24	24
2	27	27
3	-7	-1
4	10	9
H= 13 K= 1		
-5	8	10
-4	11	11
-3	14	15
-2	14	14
-1	5	-6
0	6	-5
1	9	-7
2	7	7
3	5	3
H= 14 K= 1		
-4	9	15
-3	11	-12
-2	22	-23
-1	8	10
0	10	-9
1	6	5
2	-5	8
H= 0 K= 2		
0	79	-73
1	89	91
2	32	-27
3	74	73
4	8	-8
5	54	-52
6	19	-17
7	-10	-3
8	16	17
9	-6	3
H= 1 K= 2		
-9	3	4
-8	-9	-1
-7	32	-38
-6	21	-24
-5	3	-1
-4	45	45
-3	83	80
-2	76	-73
-1	26	-22
0	65	-60
1	71	-76
2	97	103
3	31	-31
4	4	-4
5	29	28
6	-10	-5
7	7	7
8	14	16
H= 2 K= 2		
-9	-7	4
-8	-9	5
-7	21	30
-6	41	-45
-5	-5	0
-4	56	53
-3	115	-118
-2	8	1
-1	108	108
0	20	17
1	63	71
2	55	60
3	25	-23
4	15	13
5	10	-10
6	-10	-7
7	-10	-1
8	-8	4
H= 3 K= 2		
-9	5	-15
-8	6	-8
-7	10	-15
-6	-10	4
-5	58	58
-4	31	29
-3	16	15
-2	72	-70
-1	36	-31
0	90	95
1	25	-25
2	11	-9
3	5	-4
4	50	-49
5	28	28
6	14	16
7	-10	5
8	8	-2
H= 4 K= 2		
-8	-9	-14
-7	-10	5
-6	18	20
-5	42	-40
-4	45	41
-3	48	-46
-2	75	-72
-1	84	84
0	65	62
1	19	-17
2	32	-30
3	17	-17
4	31	-30
5	23	-23
6	-10	5
7	-9	-4
8	5	6
H= 5 K= 2		
-8	-8	-3
-7	11	13
-6	18	19
-5	19	17
-4	4	3
-3	6	5
-2	44	-41
-1	22	-20
0	45	44
1	66	-69
2	34	-33
3	48	47
4	19	17
5	26	26
6	10	7
7	15	-16
8	-6	-2
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3	17	17
4	38	38
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4	8	8
H=	4 K=	8
-5	5	6
-4	-5	-3
-3	17	17
-2	33	34
-1	31	-31
0	-8	-2
1	14	14
2	28	-28
3	4	4
4	7	8
H=	5 K=	8
-5	-6	1
-4	13	-15
-3	-7	4
-2	19	-24
-1	9	-9
0	36	36
1	24	24
2	11	11
3	14	-14
4	12	-12
H=	6 K=	8
-4	15	20
-3	7	-7
-2	8	6
-1	13	-14
0	21	-22
1	7	14
2	9	-7
3	5	-7
H=	7 K=	8
-4	16	-21
-3	-5	-7
-2	5	6
-1	10	11
0	8	8
1	5	4
2	-6	-2
3	14	-19
H=	8 K=	8
-3	17	-20
-2	-5	1
-1	5	7
0	-7	-6
1	-5	3
2	-5	-5
H=	9 K=	8
-1	4	9
0	5	8
H=	0 K=	9
1	19	19
2	15	15
3	-6	-7
4	7	-8
H=	1 K=	9
-4	7	10
-3	17	17
-2	7	5
-1	44	-41
0	-7	-6
1	-5	0
2	-5	0
3	-6	23
H=	2 K=	9
-4	12	-15
-3	16	18
-2	11	-10
-1	5	5
0	18	19
1	-7	-0
2	9	-9
3	14	-14
H=	3 K=	9
-3	17	-20
H=	3 K=	9
-2	4	-4
-1	18	-19
0	-7	-0
1	20	21
2	-5	1
3	-5	2
H=	4 K=	9
-3	4	5
-2	7	8
-1	-5	3
0	11	11
1	7	8
2	7	-7
3	17	-20
H=	5 K=	9
-3	15	-19
-2	8	9
-1	-5	2
0	13	-14
1	13	13
2	-5	-5
H=	6 K=	9
-2	-5	1
-1	10	13
0	-5	6
1	18	-21
H=	0 K=	10
0	14	16
1	14	18
H=	1 K=	10
-1	-5	4
0	-5	-1
1	-5	-1
H=	2 K=	10
-1	7	-12
0	13	16

C_2 and N_2 form an infinite spiral chain about the screw axis at $x=\frac{1}{2}$ with distances and angles close to those found in $KCu(CN)_2$. The atoms Cu_1, C_1 and N_1 form an infinite zig-zag chain about the screw axis at $x=0$. The distinction between these two
can be most easily seen by noting in Fig. 2
of the Cu_1, C_1 and N_1 atoms are essentially c
These two chains are linked by cyanide gr

Table 6. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the vibration ellipsoids*

Atom	Axis i	B_i (Å^2)	α	β	γ
K	1	4·8 ± 0·1	18 ± 4°	96 ± 3°	114 ± 4°
	2	2·8 ± 0·1	87 ± 4	13 ± 7	103 ± 7
	3	3·4 ± 0·1	73 ± 4	78 ± 8	28 ± 5
Cu_1	1	2·4 ± 0·1	16 ± 3	99 ± 4	110 ± 1
	2	3·2 ± 0·1	79 ± 4	13 ± 3	84 ± 3
	3	4·8 ± 0·1	79 ± 1	99 ± 2	21 ± 2
Cu_2	1	2·6 ± 0·1	46 ± 3	113 ± 5	133 ± 2
	2	1·9 ± 0·1	73 ± 4	23 ± 5	107 ± 3
	3	4·6 ± 0·1	49 ± 2	89 ± 1	48 ± 2
C_1	1	2·5 ± 0·3	31 ± 29	101 ± 54	126 ± 50
	2	2·8 ± 0·4	99 ± 62	37 ± 28	124 ± 46
	3	3·7 ± 0·3	60 ± 21	56 ± 25	54 ± 22
C_2	1	2·5 ± 0·4	24 ± 17	86 ± 22	74 ± 15
	2	1·7 ± 0·4	103 ± 22	24 ± 11	69 ± 12
	3	4·2 ± 0·5	110 ± 14	113 ± 10	27 ± 12
C_3	1	1·5 ± 0·3	25 ± 13	70 ± 16	82 ± 15
	2	3·1 ± 0·3	115 ± 14	52 ± 53	44 ± 58
	3	2·7 ± 0·3	86 ± 30	136 ± 52	47 ± 58
N_1	1	4·2 ± 0·4	47 ± 17	105 ± 22	139 ± 15
	2	3·2 ± 0·4	65 ± 20	26 ± 17	88 ± 16
	3	6·0 ± 0·4	54 ± 14	110 ± 8	50 ± 15
N_2	1	3·1 ± 0·3	43 ± 24	119 ± 14	67 ± 29
	2	1·8 ± 0·3	63 ± 13	29 ± 14	83 ± 10
	3	3·8 ± 0·4	121 ± 26	85 ± 15	24 ± 28
N_3	1	2·4 ± 0·2	57 ± 15	57 ± 14	56 ± 20
	2	3·8 ± 0·3	132 ± 57	42 ± 49	89 ± 64
	3	3·5 ± 0·3	121 ± 61	112 ± 65	34 ± 20
O	1	3·6 ± 0·4	1 ± 15	91 ± 8	97 ± 41
	2	6·9 ± 0·6	89 ± 7	6 ± 9	95 ± 9
	3	4·1 ± 0·4	91 ± 41	85 ± 9	9 ± 32

form a two-dimensional polymer sheet of composition $[Cu_2(CN)_3^-]_\infty$. The direction of maximum thermal motion is more or less normal to these sheets. The

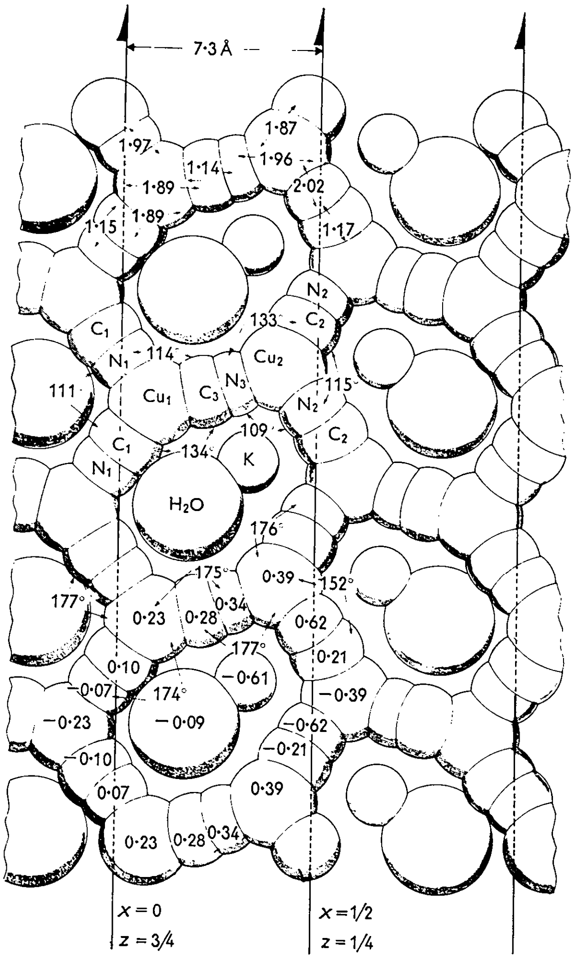

Fig. 3. Drawing of one of the polymer sheets of composition $[Cu_2(CN)_3^-]_\infty$.

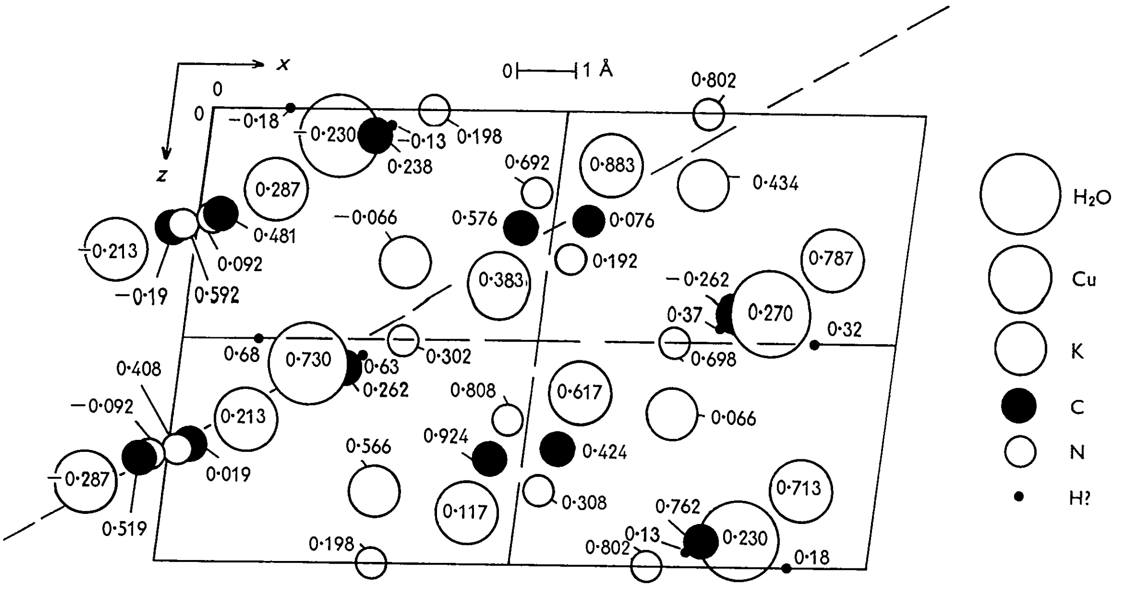

Fig. 2. Projection of the structure of $KCu_2(CN)_3.H_2O$ on (010). The numbers indicate the y coordinate of the particular atom.

sheets are parallel to and centered between the (202) planes; hence the 202 reflection is very strong. A portion of one of the sheets is shown in Fig. 3. The plane of Fig. 3 is the plane halfway between the (202) crystallographic planes and the trace of this plane is shown as a dashed line in Fig. 2. The number in the center of some of the atoms in Fig. 3 is the distance in Å from the plane. The important bond distances and angles are also shown in Fig. 3. These sheets are held together by the K^+ ions. If cyanide group 3 were inverted, the Cu_2 spiral chain would be virtually identical to that found in $KCu(CN)_2$.

Table 7. *Important interatomic distances and bond angles in* $KCu_2(CN)_3.H_2O$

$\mathrm{Cu_1–C_1}$	1·893 ± 0·020 Å	∠ $\mathrm{C_1–Cu_1–N_1}$	111·2 ± 0·9°
$\mathrm{–C_3}$	1·895 ± 0·018	∠ $\mathrm{C_1–Cu_1–C_3}$	134·5 ± 0·8
$\mathrm{–N_1}$	1·975 ± 0·020	∠ $\mathrm{C_3–Cu_1–N_1}$	113·9 ± 0·8
$\mathrm{Cu_2–C_2}$	1·871 ± 0·019	∠ $\mathrm{C_2–Cu_2–N_2}$	115·1 ± 0·7
$\mathrm{–N_2}$	2·022 ± 0·016	∠ $\mathrm{C_2–Cu_2–N_3}$	132·7 ± 0·8
$\mathrm{–N_3}$	1·960 ± 0·016	∠ $\mathrm{N_2–Cu_2–N_3}$	109·2 ± 0·7
$\mathrm{C_1–N_1}$	1·153 ± 0·028	∠ $\mathrm{Cu_1–C_1–N_1}$	173·8 ± 1·7
		∠ $\mathrm{Cu_1–N_1–C_1}$	176·4 ± 1·7
$\mathrm{C_2–N_2}$	1·175 ± 0·025	∠ $\mathrm{Cu_2–C_2–N_2}$	176·3 ± 1·6
		∠ $\mathrm{Cu_2–N_2–C_2}$	152·0 ± 1·3
$\mathrm{C_3–N_3}$	1·140 ± 0·024	∠ $\mathrm{Cu_1–C_3–N_3}$	175·0 ± 1·5
		∠ $\mathrm{Cu_2–N_3–C_3}$	176·9 ± 1·4
$\mathrm{O–H_1}$ (?)	1·03	∠ $\mathrm{H_1–O–H_2}$	105
$\mathrm{–H_2}$ (?)	1·21		
–K	2·816 ± 0·018		
–K	2·843 ± 0·018		

The Cu–C and Cu–N distances appear to be slightly shorter in $KCu_2(CN)_3.H_2O$ than in $KCu(CN)_2$ where they were 1·92 and 2·05 Å respectively. Only Cu_1–N_1 and Cu_2–N_3 are significantly shorter, however.

The sheets are made up of puckered hexagons of composition $(CuCN)_6$, all edges being shared. Of the 18 atoms in the ring, 13 of them are not far from being coplanar; one Cu_2, two C_2 and two N_2 atoms are not included in the plane. The maximum deviation of the 13 atoms from the least squares plane is 0·13 Å and the mean deviation is 0·06 Å. The equation for this least squares plane, in orthogonal coordinates, is $0{\cdot}08999x + 0{\cdot}00077y + 0{\cdot}18993z = 1{\cdot}0$.

The water molecules lie within the hexagons and apparently are present only to fill up space within the structure. The nitrogen *s* electrons are used for bonding with copper and, therefore, are not available to form hydrogen bonds.

The copper atoms form approximately planar groups with their bonded neighbors. Cu_1 is 0·07 Å from the plane of its three neighbors and Cu_2 is 0·19 Å from the plane of its three neighbors. Cu_2 has a non-bonded Cu_2 neighbor in an adjacent sheet at 2·95 Å. In $KCu(CN)_2$ there is a short non-bonded Cu–Cu distance of 2·84 Å. This point was overlooked in the discussion of that structure. The copper atoms are perhaps in an sp^2 hybridized state, although the bond structure is unusual and may be complicated by double-bond formation, partial ionic character and weak intermetallic bonding.

The bond distances in the three cyanide groups agree well with those observed in other organic and inorganic cyanide compounds. The potassium ion has two near oxygen neighbors at an average distance of 2·83 Å. Other potassium neighbors closer than 4·0 Å, besides hydrogen atoms, are five carbon atoms ranging from 3·30 to 3·55 Å, and six nitrogen atoms from 3·81 to 3·99 Å.

The oxygen atom has two potassium neighbors at an average distance of 2·83 Å. Other oxygen neighbors closer than 4·0 Å, besides hydrogen atoms, are one Cu_1 atom at 3·72 Å, six carbon atoms varying from 3·37 to 3·89 Å, five nitrogen atoms varying from 3·27 to 3·87 Å and two oxygen atoms at 3·76 Å.

Added note: The crystal structure of the cuprous chloride azomethane complex has recently been published by Brown & Dunitz (1960). In this compound the copper atom has four ligands in a distorted tetrahedral arrangement. The largest angle about the copper atom is 132·1°, a value close to the largest angles about the copper atoms in the two cyanide complexes, which are 134·5° and 132·7° in $KCu_2(CN)_3.H_2O$ and 134·2° in $KCu(CN)_2$. The nature of the Cu–N bond is the same in all three compounds. Brown & Dunitz found 1·993 Å for this bond and the average of the four different Cu–N bonds in the two cyanide complexes is 2·002 Å.

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