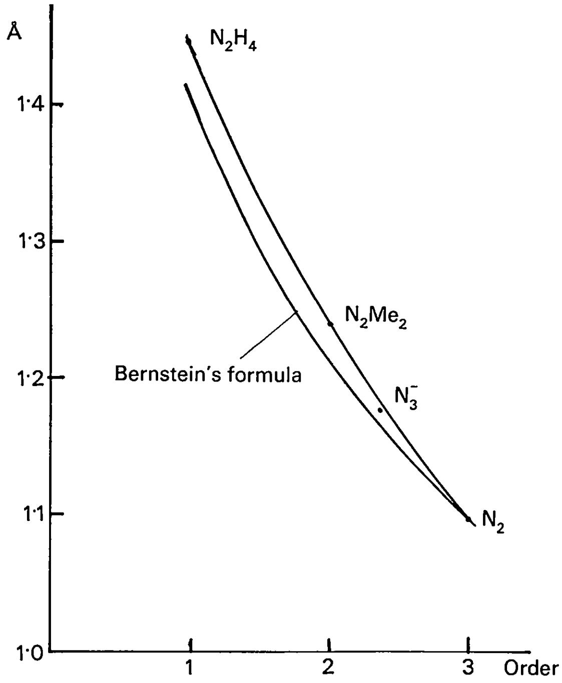

Fig. 7. Order and length of N–N bonds.

pyramidal (octahedral if we include nitrogen of the same ion); similarly in alkali halides, the higher of two coordination numbers is promoted by low temperatures or high pressure. The equivalence ratio of pressure and temperature is in reasonable accord with a thermodynamic estimate based on the postulate of an order-disorder mechanism.

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The Crystal Structure of $K_3Cu(CN)_4$*

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The crystal structure of $K_3Cu(CN)_4$ and the absolute configuration for the particular crystal used have been determined. The space group is $R3c$, rather than the previously reported space group of $R32$. The rhombohedral cell with two formula units has dimensions $a=8{\cdot}039$ Å and $\alpha=73°54'$; the hexagonal cell has $a=9{\cdot}665$ and $c=17{\cdot}361$ Å. Anomalous dispersion for copper and potassium was included in the calculations, and anisotropic least-squares refinement leads to a conventional R index of 0·0249 for the correct absolute orientation and 0·0431 for the incorrect, inverse structure. There are discrete $Cu(CN)_4^{3-}$ tetrahedra with three Cu–C distances of $1{\cdot}992 \pm 0{\cdot}007$ Å and one Cu–C distance of $2{\cdot}014 \pm 0{\cdot}011$ Å. These distances are about 0·1 Å longer than the Cu–C distances in trigonally bonded copper(I).

Introduction

As a continuation of our studies of complexes of CuCN (*e.g.* see Cromer & Larson, 1962; Cromer, Larson & Roof, 1966) we have determined the structure of $K_3Cu(CN)_4$. This compound was first studied by Cox, Wardlaw & Webster (1936) who reported a unit cell and space group but did no further work other than to deduce that the $Cu(CN)_4^{3-}$ ion must be tetrahedral. They also noted a strong pyroelectric effect. Staritzky & Ellinger (1956) reported morphological, optical and

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X-ray powder data and the existence of a strong piezoelectric effect. Both of these previous papers report the space group to be $R32$. However, we find that the space group is $R3c$.

Experimental

Small crystals were grown from aqueous solution of stoichiometric amounts of KCN and CuCN. Precession photographs showed the unit cell to be essentially as previously reported but that systematic extinctions were present for *hhl* (rhombohedral) with $l=2n+1$; hence the space group is $R3c$. The presence of strong piezoelectric and pyroelectric effects rules out a centrosymmetric space group. The lattice constants were obtained by least-squares analysis of nine reflections measured with Mo $K\alpha_1$ ($\lambda=0{\cdot}70926$ Å) radiation. A single-crystal orienter was used on a General Electric Co. XRD-5 spectrogoniometer. The values found are, for the hexagonal cell, $a=9{\cdot}665\pm0{\cdot}001$, $c=17{\cdot}361\pm0{\cdot}002$ Å. The rhombohedral cell has dimensions $a=8{\cdot}039$ Å and $\alpha=73°54'$. Cox *et al.* (1936) reported the values $a=8{\cdot}02$ Å and $\alpha=77°32'$; Staritzky & Ellinger (1956) found $a=8{\cdot}02$ Å and $\alpha=74°6'$ from a powder pattern and $\alpha=73°55'$ from morphological measurements. The density calculated from our rhombohedral unit cell with $Z=2$ is 2·021 g.cm^{-3} and Staritzky & Ellinger (1956) report a measured value of 2·021 g.cm^{-3}.

Intensity measurements were made with the single-crystal orienter and Mo $K\alpha$ radiation by the stationary-crystal, stationary-counter technique with balanced Zr–Y filters. The crystal used was a rhombohedron which had a maximum dimension of about 0·3 mm. Absorption corrections were made by the Busing & Levy (1957) method using Burnham's (1962) program modified for the present geometry. The crystal was mounted on the {100} hexagonal reciprocal axis and the entire hemisphere of reflections with $2\theta\le50°$ was measured, a total of 1051 measurements. Thus, in general, $F(hkl)$ was measured twice and $F(\bar{h}\bar{k}\bar{l})$, the Friedel related reflection, was also measured twice. The quantity $R_F=\Sigma\,2(||F_1|-|F_2||)/(F_1+F_2)$, an estimate of the average agreement between *equivalent* reflections F_1 and F_2, is 0·021. A total of 549 independent reflections were measured and of these, 537 were observed greater than zero according to the criterion $(I-\text{Background})\ge2{\cdot}5(I+\text{Background})^{\frac{1}{2}}$. It should be noted that the 549 independent reflections include Friedel related pairs.

Determination and refinement of the structure

All calculations were based on the hexagonal cell and all results are given for this cell.

A Patterson function was calculated with the differences between $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ being temporarily ignored. $R3c$ is a polar space group, so the z parameter of one atom is arbitrary. The copper atoms were therefore placed in the sixfold set $00z$ with $z=0$. There remained to be located one potassium atom and one cyanide group in general positions and one cyanide group in position set $00z$. The potassium atom was easily found from the Patterson function and an F_{obs} electron density map phased on the copper and potassium position was computed. The two cyanide groups were readily found from this synthesis.

A full-matrix least-squares refinement was then made with the use of all of the independent reflections and with the dispersion terms $\Delta f'$ and $\Delta f''$ for potassium and copper (Cromer, 1965) included. Scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). The quantity minimized was $\Sigma\,w(|F_o|-|F_c^*|)^2$ where w is the weight based on counting statistics (Evans, 1961),

$$F_c^*=K|F_c|\left\{1+g\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]\text{Lp}\,.\,F_c^2\right\}^{-\frac{1}{4}},$$

K is a scale factor, F_c is the usual calculated structure factor, g is an extinction parameter (Zachariasen, 1963; Larson, 1967), and Lp is the Lorentz and polarization factor.

The explicit form used for the structure factor was

$$F_c(\mathbf{H})=\Sigma\,T_jf_j\cos2\pi\mathbf{H}\,.\,\mathbf{X}_j-\Sigma\,T_j\Delta f_j''\sin2\pi\mathbf{H}\,.\,\mathbf{X}_j$$
$$+i[\Sigma\,T_jf_j\sin2\pi\mathbf{H}\,.\,\mathbf{X}_j+\Sigma\,T_j\Delta f_j''\cos2\pi\mathbf{H}\,.\,\mathbf{X}_j]\,,$$

where the f_j include the real term $\Delta f_j'$,

$$T_j=\exp\left[-(h^2\beta_{11j}+k^2\beta_{22j}+l^2\beta_{33j}+hk\beta_{12j}+hl\beta_{13j}+kl\beta_{23j})\right]$$

and $\mathbf{H}$ and $\mathbf{X}_j$ have their usual meanings.

The expression $F_c(\mathbf{H})$ may be abbreviated as

$$F_c(\mathbf{H})=(A-B')+i(B+A')$$

and the phase angle α', as listed in Table 2 ,is

$$\alpha'=\tan^{-1}\left(\frac{B+A'}{A-B'}\right).$$

Refinement proceeded until all changes were less than about 2×10^{-5} times their standard deviations.

After several cycles of refinement, $R=\Sigma\,|\Delta F|/\Sigma\,|F_o|$, with unobserved reflections omitted, was reduced to 0·0249. At this point we did not know whether we had chosen the correct set of coordinates or the inverse set. Consequently the signs of all coordinates were reversed and the calculation repeated. For this reversed case $R=0{\cdot}0431$. The weighted R index, $R_w=[\Sigma\,w(\Delta F)^2/\Sigma\,wF_o^2]^{\frac{1}{2}}$, as used by Hamilton (1965), was 0·0179 for the first case and 0·0273 for the second and their ratio is 1·53. With 37 parameters and 537 observations the difference between the cases is significant at the 99·5% confidence level if the R_w ratio exceeds 1·008 (Hamilton, 1965). Consequently we can say almost certainly that the first set of parameters is correct. These parameters are listed in Table 1. The calculated and observed structure factors are given in Table 2.

Discussion

The parameters which resulted from the second refinement were only slightly different from those of the first refinement and the structures resulting from both cases are essentially the same. For the present compound the only significance to the absolute configuration is the direction in which the $Cu(CN)_4^{3-}$ tetrahedra point in the *particular crystal used, i.e.* 'which way is up'. However, if the coordinates are chosen correctly, agreement between calculated and observed data is better and thus a better structure determination is achieved. It is also of interest that a rather striking difference between the R indices can be noted even where the $\Delta f''$ terms are small ($\Delta f''_{Cu} = 1{\cdot}36$ and $\Delta f''_{K} = 0{\cdot}30$ for Mo radiation).

Table 1. *Final least-squares parameters for* $K_3Cu(CN)_4$

	x	y	z	$\beta_{11}\times 10^4$	$\beta_{22}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}=10^4$	$\beta_{13}\times 10^4$	$\beta_{23}\times 10^4$
Cu	0·0	0·0	0·0	78 ± 1	β_{11}	21 ± 1	β_{11}	0	0
K	0·4204 ± 2	0·0363 ± 2	0·0548 ± 1	135 ± 3	139 ± 3	18 ± 1	196 ± 5	14 ± 2	11 ± 2
C(1)	0·0	0·0	−0·1159 ± 6	82 ± 10	β_{11}	13 ± 4	β_{11}	0	0
N(1)	0·0	0·0	−0·1811 ± 6	90 ± 10	β_{11}	36 ± 5	β_{11}	0	0
C(2)	0·2020 ± 8	0·1862 ± 8	0·0378 ± 3	114 ± 11	95 ± 11	14 ± 2	136 ± 20	0 ± 8	2 ± 8
N(2)	0·3235 ± 7	0·2880 ± 6	0·0543 ± 4	92 ± 9	84 ± 9	25 ± 2	52 ± 15	−10 ± 7	−7 ± 7

$g = 9{\cdot}89 \pm 20 \times 10^{-7}$

Table 2. *Observed and calculated structure factors for* $K_3Cu(CN)_4$

The column headings are h, k, l, $|F_o|/K$, $|F_c^*|/K$, and α' (°).

h	k	l	$\|F_o\|/K$	$\|F_c^*\|/K$	α'
0	3	0	253	249	0
0	6	0	125	123	46
0	9	0	51	51	62
1	1	0	58	56	0
1	4	0	137	135	0
1	7	0	79	79	346
2	2	0	96	98	0
2	5	0	128	128	0
2	8	0	69	70	355
3	3	0	104	104	0
3	6	0	56	56	36
4	1	0	140	136	0
4	4	0	66	64	0
4	7	0	25	26	351
5	2	0	131	130	12
5	5	0	93	92	0
6	3	0	53	53	334
7	1	0	80	81	23
7	4	0	27	27	23
8	2	0	70	71	15
1	3	1	123	122	88
3	1	-1	131	124	95
1	6	1	59	58	77
6	1	-1	63	59	105
1	9	1	11	9	204
9	1	-1	-9	9	347
2	1	1	149	161	308
1	2	-1	171	162	233
2	4	1	64	64	288
4	2	-1	65	64	255
2	7	1	10	11	268
7	2	-1	12	11	267
3	2	1	82	83	193
2	3	-1	85	83	351
3	5	1	45	44	240
5	3	-1	45	45	304
3	8	1	10	10	308
8	3	-1	11	10	240
4	3	1	92	92	65
3	4	-1	92	91	117
4	6	1	21	23	44
6	4	-1	22	22	139
5	1	1	25	27	313
1	5	-1	29	28	230
5	4	1	25	24	177
4	5	-1	26	24	8
6	2	1	34	34	242
2	6	-1	34	34	301
6	5	1	11	11	244
5	6	-1	11	11	302
7	3	1	46	46	1
3	7	-1	45	46	180
8	1	1	26	26	194
1	8	-1	26	26	350
0	1	2	106	105	0
1	0	-2	105	107	0
0	4	2	52	51	55
4	0	-2	45	45	314
0	7	2	73	70	6
7	0	-2	71	69	0
1	2	2	131	139	331
2	1	-2	149	146	35
1	5	2	121	120	340
5	1	-2	122	124	27
1	8	2	38	37	349
8	1	-2	40	40	24
2	0	2	180	194	0
0	2	-2	197	197	0
2	3	2	144	146	0
3	2	-2	148	148	0
2	6	2	32	29	0
6	2	-2	29	32	19
3	1	2	46	45	313
1	3	-2	54	53	55
3	4	2	61	60	18
4	3	-2	46	59	354
3	7	2	67	64	0
7	3	-2	50	65	12
4	2	2	95	99	312
2	4	-2	106	106	54
4	5	2	76	76	326
5	4	-2	78	80	42
5	0	2	175	183	0
0	5	-2	184	184	0
5	3	2	57	56	0
3	5	-2	57	58	3
5	6	2	13	11	26
6	5	-2	13	11	5
6	1	2	58	56	2
1	6	-2	58	56	0
6	4	2	74	70	19
4	6	-2	69	69	350
7	2	2	29	29	324
2	7	-2	34	34	49
8	0	2	76	79	330
0	8	-2	82	85	37
8	3	2	39	39	320
3	8	-2	42	44	48
9	1	2	43	41	28
1	9	-2	42	39	344
1	1	3	71	74	165
1	1	-3	72	73	22
1	4	3	58	58	284
4	1	-3	58	56	259
1	7	3	70	69	284
7	1	-3	68	69	259
2	2	3	51	48	316
2	2	-3	52	49	227
2	5	3	61	60	97
5	2	-3	61	60	87
2	8	3	24	26	71
8	2	-3	24	26	114
3	3	3	31	31	139
3	3	-3	31	31	43
3	6	3	15	13	196
6	3	-3	12	12	349
4	1	3	53	52	23
1	4	-3	54	53	160
4	4	3	26	25	338
4	4	-3	26	25	207
4	7	3	14	14	209
7	4	-3	13	14	333
5	2	3	61	60	202
2	5	-3	60	60	341
5	5	3	-8	9	338
5	5	-3	9	9	207
6	3	3	-8	7	109
3	6	-3	8	8	79
7	1	3	62	63	13
1	7	-3	65	64	171
7	4	3	12	13	77
4	7	-3	12	12	105
8	2	3	26	27	226
2	8	-3	25	27	319
0	2	4	150	147	59
2	0	-4	136	139	306
0	5	4	150	152	50
5	0	-4	141	145	315
0	8	4	13	15	73
8	0	-4	-8	8	310
1	0	4	160	161	0
0	1	-4	159	159	0
1	3	4	129	129	358
3	1	-4	132	131	17
1	6	4	78	78	4
6	1	-4	79	76	0
1	9	4	54	53	23
9	1	-4	50	51	347
2	1	4	47	51	0
1	2	-4	52	52	12
2	4	4	48	49	316
4	2	-4	56	54	53
2	7	4	44	42	340
7	2	-4	46	45	31
3	2	4	108	108	44
2	3	-4	105	102	323
3	5	4	65	65	9
5	3	-4	65	65	0
4	0	4	170	178	0
0	4	-4	181	177	0
4	3	4	92	93	7
3	4	-4	94	91	0
4	6	4	64	65	40
6	4	-4	59	61	328
5	1	4	41	43	28
1	5	-4	38	39	345
5	4	4	12	12	6
4	5	-4	14	12	26
6	2	4	69	69	0
2	6	-4	73	70	11
6	5	4	53	54	351
5	6	-4	58	55	20
7	0	4	67	68	18
0	7	-4	68	66	355
7	3	4	36	36	53
3	7	-4	32	32	318
8	1	4	35	36	0
1	8	-4	40	37	10
1	2	5	147	147	0
2	1	-5	141	146	180
1	5	5	29	29	349
5	1	-5	30	28	194
1	8	5	21	20	110
8	1	-5	21	21	75
2	3	5	71	71	104
3	2	-5	73	71	79
2	6	5	25	26	51
6	2	-5	26	26	133
3	1	5	116	118	213
1	3	-5	120	117	330
3	4	5	68	72	231
4	3	-5	74	73	312
3	7	5	40	42	294
7	3	-5	41	42	249
4	2	5	53	55	17
2	4	-5	57	54	166
4	5	5	22	23	134
5	4	-5	23	24	50
5	3	5	42	44	62
3	5	-5	44	43	122
5	6	5	10	10	67
6	5	-5	-9	9	119
6	1	5	55	57	222
1	6	-5	58	56	321
6	4	5	18	20	266
4	6	-5	17	20	278
7	2	5	11	11	337
2	7	-5	9	10	203
9	1	5	11	11	127
1	9	-5	14	11	61
0	0	6	264	258	89
0	3	6	104	101	73
3	0	-6	94	92	290
0	6	6	47	48	306
6	0	-6	56	53	63
0	9	6	35	36	301
9	0	-6	40	41	67
1	1	6	193	194	0
1	1	-6	189	197	0
1	4	6	125	129	0
4	1	-6	128	127	0
1	7	6	70	73	18
7	1	-6	71	72	352
2	2	6	128	132	0
2	2	-6	138	135	14
2	5	6	89	93	26
5	2	-6	93	91	342
2	8	6	47	48	33
8	2	-6	47	45	336
3	0	6	152	153	50
0	3	-6	146	147	315
3	3	6	89	91	0
3	3	-6	93	91	3
3	6	6	42	45	325
6	3	-6	48	48	44
4	1	6	81	83	0
1	4	-6	86	83	3
4	4	6	66	68	359
4	4	-6	71	70	14
5	2	6	35	36	32
2	5	-6	33	33	342
5	5	6	49	50	48
5	5	-6	48	46	320
6	0	6	154	159	0
0	6	-6	163	156	0
6	3	6	81	79	0
3	6	-6	78	79	0
7	1	6	28	29	345
1	7	-6	32	32	28
8	2	6	23	23	45
2	8	-6	18	19	331
9	0	6	-51	87	2
0	9	-6	86	86	0
1	3	7	96	95	213
3	1	-7	105	96	330
1	6	7	46	47	198
6	1	-7	47	48	346
2	1	7	114	113	56
1	2	-7	116	114	127
2	4	7	58	58	49
4	2	-7	59	58	134
2	7	7	13	12	344
7	2	-7	12	12	193
3	2	7	66	66	314
2	3	-7	70	67	229
3	5	7	37	36	0
5	3	-7	39	36	182
4	3	7	82	83	180
3	4	-7	66	83	0
4	6	7	21	23	168
6	4	-7	21	23	15
5	1	7	19	20	81
1	5	-7	20	21	103
5	4	7	24	22	302
4	5	-7	22	21	243
6	2	7	32	33	351
2	6	-7	34	33	192
7	3	7	37	40	120
3	7	-7	38	40	64
8	1	7	26	26	307
1	8	-7	24	25	236
0	1	8	125	124	0
1	0	-8	119	124	0
0	4	8	99	98	325
4	0	-8	102	103	43
0	7	8	31	29	12
7	0	-8	31	28	5
1	2	8	118	121	0
2	1	-8	126	121	0
1	5	8	102	99	26
5	1	-8	97	96	342
1	8	8	39	39	0
8	1	-8	40	40	10
2	0	8	75	75	51
0	2	-8	69	69	316
2	3	8	52	53	35
3	2	-8	50	50	335
2	6	8	60	60	339
6	2	-8	63	62	29
3	1	8	127	128	347
1	3	-8	132	131	22
3	4	8	50	49	331
4	3	-8	54	54	39
3	7	8	33	32	42
7	3	-8	31	29	330
4	2	8	114	118	0
2	4	-8	119	117	0
4	5	8	73	76	22
5	4	-8	75	74	347
5	0	8	64	65	82
0	5	-8	58	58	281
5	3	8	40	40	0
3	5	-8	41	40	12
6	1	8	51	52	351
1	6	-8	53	54	21
6	4	8	16	15	69
4	6	-8	12	10	307
7	2	8	55	56	352
2	7	-8	59	58	18
8	0	8	67	67	26
0	8	-8	64	65	342
1	1	9	73	70	282
1	1	-9	68	69	263
1	4	9	44	45	42
4	1	-9	44	44	141
1	7	-9	45	47	52
1	7	9	60	59	37
2	2	9	35	33	49
2	2	-9	36	35	134
2	5	9	46	45	213
5	2	-9	44	45	331
3	3	9	20	21	235
3	3	-9	21	22	307
3	6	9	15	15	303
6	3	-9	12	15	241
4	1	9	39	38	154
1	4	-9	38	39	30
4	4	9	25	24	104
4	4	-9	24	23	81
5	2	9	45	45	320
2	5	-9	46	46	223
5	5	9	-8	8	108
5	5	-9	9	8	78
6	3	9	-8	4	279
3	6	-9	-8	4	279
7	1	9	45	46	133
7	1	-9	60	59	147
0	2	10	66	66	315
2	0	-10	69	71	51
0	5	10	-9	6	273
5	0	-10	-10	12	92
0	8	10	53	53	334
8	0	-10	56	56	34
1	0	10	130	127	23
0	1	-10	120	123	344
1	3	10	120	120	16
3	1	-10	117	118	355
1	6	10	54	52	17
6	1	-10	51	51	354
2	1	10	129	127	0
1	2	-10	126	129	8
2	4	10	117	118	0
4	2	-10	118	118	0
2	7	10	57	57	6
7	2	-10	58	57	0
3	2	10	47	47	333
2	3	-10	49	51	35
3	5	10	47	47	11
5	3	-10	46	47	0
4	0	10	112	113	44
0	4	-10	106	107	322
4	3	10	46	47	18
3	4	-10	46	47	354
5	1	10	79	77	357
1	5	-10	80	78	15
5	4	10	63	63	348
4	5	-10	66	64	21
6	2	10	49	51	23
2	6	-10	49	51	347
7	0	10	45	45	6
0	7	-10	44	45	0
8	1	10	45	43	0
1	8	-10	44	43	7
1	2	11	92	90	98
2	1	-11	89	90	85
1	5	11	24	23	100
5	1	-11	23	23	82
2	3	11	46	47	223
3	2	-11	46	46	321
2	6	11	14	15	166
6	2	-11	15	16	19
3	1	11	85	85	335
1	3	-11	83	83	209
3	4	11	41	44	351
4	3	-11	42	44	194
4	2	11	40	40	140
2	4	-11	37	39	43
4	5	11	20	19	257
5	4	-11	18	20	287
5	3	11	32	35	180
3	5	-11	30	35	5
6	1	11	43	45	337
1	6	-11	43	44	206
7	2	11	14	12	57
2	7	-11	13	11	126
0	0	12	153	150	252
0	3	12	97	94	300
3	0	-12	104	101	64
0	6	12	90	89	0
6	0	-12	90	90	11
1	1	12	124	120	19
1	1	-12	115	118	349
1	4	12	40	39	18
4	1	-12	38	38	357
1	7	12	17	15	352
7	1	-12	19	17	28
2	2	12	90	87	0
2	2	-12	88	88	0
2	5	12	22	22	333
5	2	-12	26	25	41
3	0	12	63	58	286
0	3	-12	67	65	78
3	3	12	58	58	0
3	3	-12	60	60	9
3	6	12	61	60	0
6	3	-12	61	61	7
4	1	12	70	68	0
1	4	-12	69	70	11
4	4	12	46	46	2
4	4	-12	47	47	5
5	2	12	59	59	324
2	5	-12	62	63	44
6	0	12	45	47	94
0	6	-12	38	40	271
6	3	12	22	24	41
3	6	-12	22	22	335
7	1	12	59	58	343
1	7	-12	54	60	26
1	3	13	54	63	341
3	1	-13	63	63	203
1	6	13	32	33	321
6	1	-13	33	33	223
2	1	13	56	56	180
1	2	-13	55	57	5
2	4	13	42	43	168
4	2	-13	43	43	15
3	2	13	43	42	72
2	3	-13	42	43	112
3	5	13	25	25	122
5	3	-13	26	25	63
4	3	13	58	59	290
3	4	-13	56	59	253
5	1	13	14	15	212
1	5	-13	14	15	332
6	2	13	25	25	99
2	6	-13	25	25	84
0	1	14	64	63	33
1	0	-14	58	59	337
0	4	14	85	82	22
4	0	-14	82	80	347
0	7	14	34	33	342
7	0	-14	37	36	30
1	2	14	36	38	18
2	1	-14	36	36	357
1	5	14	14	14	90
5	1	-14	-8	7	272
2	0	14	55	58	324
0	2	-14	63	62	46
2	3	14	49	46	333
3	2	-14	50	49	38
2	6	14	47	47	25
6	2	-14	45	45	346
3	1	14	77	77	35
1	3	-14	71	74	333
3	4	14	61	60	0
4	3	-14	61	60	0
4	2	14	32	33	73
2	4	-14	26	28	295
5	0	14	45	43	297
0	5	-14	50	50	72
5	3	14	34	33	0
3	5	-14	33	33	16
6	1	14	43	42	15
1	6	-14	41	41	358
1	1	15	52	51	39
1	1	-15	48	50	147
1	4	15	27	30	158
4	1	-15	28	29	25
2	2	15	19	19	147
2	2	-15	20	21	36
2	5	15	28	29	331
5	2	-15	27	29	214
3	3	15	11	12	331
3	3	-15	11	12	211
4	1	15	26	26	283
1	4	-15	26	26	262
5	2	15	28	29	79
2	5	-15	28	29	105
0	2	16	104	101	0
2	0	-16	99	101	1
0	5	16	69	68	339
5	0	-16	69	69	30
1	0	16	30	28	14
0	1	-16	27	27	0
1	3	16	30	29	32
3	1	-16	28	27	341
2	1	16	78	77	26
1	2	-16	74	74	341
2	4	16	56	55	53
4	2	-16	51	51	314
3	2	16	76	75	0
2	3	-16	74	74	9
4	0	16	11	11	304
0	4	-16	15	15	71
4	3	16	38	39	354
3	4	-16	39	39	16
5	1	16	46	47	29
1	5	-16	43	45	341
1	2	17	48	47	209
2	1	-17	46	48	335
1	5	17	17	16	210
5	1	-17	16	16	334
2	3	17	29	28	344
3	2	-17	27	28	201
3	1	17	52	54	88
1	3	-17	53	53	95
4	2	17	28	28	259
2	4	-17	26	27	284
0	0	18	133	132	0
0	3	18	85	84	0
3	0	-18	84	85	0
1	1	18	10	8	6
1	1	-18	10	10	31
1	4	18	34	32	330
4	1	-18	35	36	40
2	2	18	30	32	12
2	2	-18	29	31	0
3	0	18	81	82	353
0	3	-18	81	83	15
4	1	18	26	28	11
1	4	-18	25	28	3
1	3	19	41	41	102
3	1	-19	39	41	82
2	1	19	25	25	300
1	2	-19	25	26	245
0	1	20	12	15	321
1	0	-20	17	19	52
2	0	20	55	53	15
0	2	-20	53	53	356

The distances and angles are listed in Table 3 and the thermal ellipsoids are given in Table 4. A stereo view of the structure is shown in Fig. 1.

Table 3. *Interatomic distances and bond angles in* $K_3Cu(CN)_4$

Bonds	
Cu—K	3·773 ± 0·002 Å
Cu—C(1)	2·014 ± 0·010
Cu—C(2)	1·992 ± 0·006
K—C(1)	3·235 ± 0·001
-N(1)	3·451 ± 0·004
K—C(1)	3·878 ± 0·008
-N(1)	3·152 ± 0·006
K—C(2)	3·667 ± 0·006
-N(2)	2·822 ± 0·005
K—C(2)	3·019 ± 0·006
-N(2)	3·067 ± 0·006
K—C(2)	3·289 ± 0·006
-N(2)	2·924 ± 0·006
K—C(2)	3·115 ± 0·006
-N(2)	3·013 ± 0·006
C(1)-N(1)	1·129 ± 0·014
C(2)-N(2)	1·128 ± 0·008
Angles	
Cu—C(1)-N(1)	180°
Cu—C(2)-N(2)	173·7 ± 0·6
C(1)-Cu—C(2)	109·2 ± 0·2
C(2)-Cu—C(2)	109·7 ± 0·2

The structure is clearly composed of potassium ions and discrete $Cu(CN)_4^{3-}$ tetrahedra. The six nearest neighbors of the potassium ion are nitrogen atoms or cyanide groups belonging to five different $Cu(CN)_4^{3-}$ tetrahedra. These neighbors form a somewhat distorted octahedron. A seventh cyanide group is at a somewhat larger distance (more than 4·0 Å) and might be considered a neighbor. The immediate surroundings of the potassium ion are shown in the stereo drawing of Fig. 2. In Fig. 2 dotted lines are drawn from the potassium ion to the six nearest nitrogen atoms but four of these lines more properly might be drawn to the midpoint of the cyanide group because the K–C and K–N distances are not greatly different.

The Cu–C distances are about 0·1 Å longer than the Cu–C distances in $KCu(CN)_2$ (Cromer, 1957) and in $KCu_2(CN)_3.H_2O$ (Cromer & Larson, 1962). In these latter two compounds the copper has three ligands, whereas there are four in the present compound. The C–N distances in the cyanide groups are a little shorter than the value of 1·15 Å usually reported but only for C(2)–N(2) is this difference of possible significance. Perhaps the longer Cu–C bonds allow a smaller C–N bond. The Cu–C(1)–N(1) angle is fixed by symmetry to be 180°. The Cu–C(2)–N(2) angle departs significantly from linearity, presumably because of steric factors.

The thermal ellipsoids do not agree well with what one might expect *a priori*. For example the copper atom has a larger motion along the *c* axis than C(1), and N(1) has a larger motion parallel to than perpendicular to **c**. Furthermore, the major axis of the C(2) ellipsoid makes an angle of only 21° with the Cu–C(2) bond. The N(2) major axis is more reasonable; it makes an angle of 81·5° with the Cu–N(2) vector.

Least-squares runs were made with the data terminated at $2\theta_{\max}=45°$ and 40°. The anomalies in the thermal ellipsoids showed no appreciable change and are thus not likely to have been caused by systematic

Table 4. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the thermal vibration ellipsoids*

Atom	Axis i	r.m.s. amplitude	B_i	α	β	γ
Cu	1	0·167 ± 0·001 Å	2·20 ± 0·03 Å^2	0°	120°	90°
	2			90	30	90
	3	0·179 ± 0·002	2·53 ± 0·06	90	90	0
K	1	0·170 ± 0·003	2·29 ± 0·07	51 ± 10	136 ± 8	52 ± 11
	2	0·238 ± 0·002	4·47 ± 0·09	62 ± 2	59 ± 2	80 ± 2
	3	0·162 ± 0·003	2·06 ± 0·06	128 ± 9	62 ± 10	40 ± 11
C(1)	1	0·171 ± 0·011	2·30 ± 0·29	0	120	90
	2			90	30	90
	3	0·141 ± 0·020	1·58 ± 0·44	90	90	0
N(1)	1	0·179 ± 0·010	2·54 ± 0·29	0	120	90
	2			90	30	90
	3	0·234 ± 0·015	4·31 ± 0·57	90	90	0
C(2)	1	0·159 ± 0·011	2·00 ± 0·29	46 ± 14	158 ± 24	105 ± 35
	2	0·205 ± 0·010	3·31 ± 0·33	46 ± 14	74 ± 10	90 ± 8
	3	0·145 ± 0·012	1·66 ± 0·26	80 ± 26	105 ± 34	15 ± 35
N(2)	1	0·211 ± 0·009	3·52 ± 0·29	25 ± 8	142 ± 14	101 ± 19
	2	0·160 ± 0·010	2·03 ± 0·25	65 ± 8	59 ± 10	71 ± 13
	3	0·193 ± 0·008	2·93 ± 0·26	88 ± 19	110 ± 19	22 ± 15

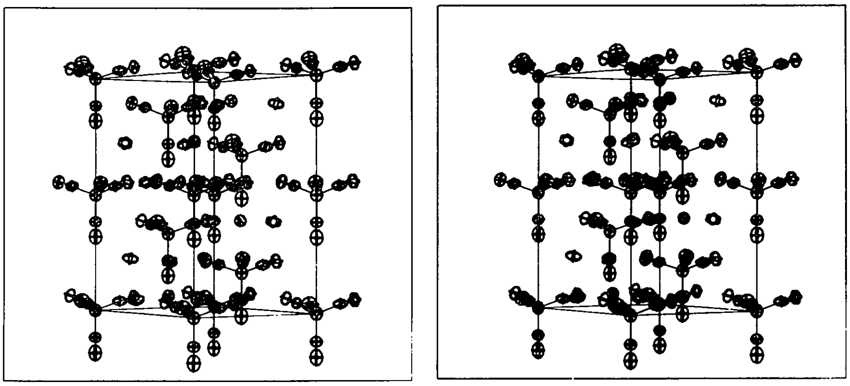

Fig. 1. A stereo view of the structure of $K_3Cu(CN)_4$. The hexagonal *c* axis is vertical and the view direction is perpendicular to the 120 plane. The origin is at the lower rear center.

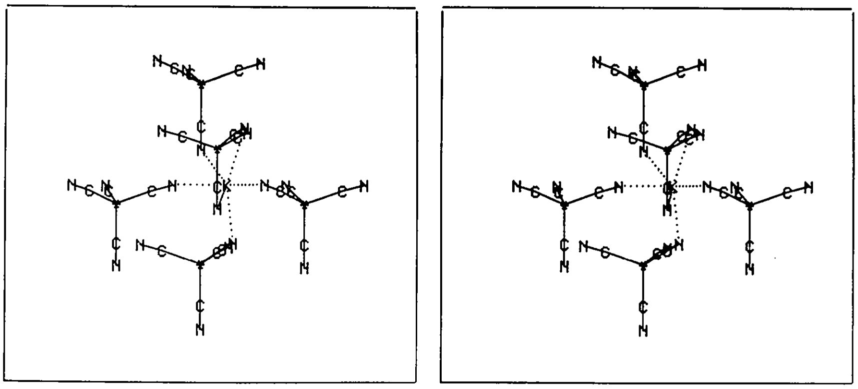

Fig. 2. A stereo view of the environment about the K atom. The hexagonal *c* axis is vertical and the view direction is perpendicular to the $\bar{1}50$ plane.

errors that are a function only of θ. A more probable reason for these anomalies is the inadequacy of free atom scattering factors for describing the scattering of cyanide groups.

Because anisotropic thermal parameters have a notorious tendency to interact with systematic errors one is usually tempted to believe them only when they agree with one's preconceived ideas. Consequently an independent study of this compound is desirable. A neutron diffraction study would be of particular value, for the smearing of the electrons in the cyanide group would then be of no consequence.

All calculations were performed on an IBM-7094 with programs written by the authors (Larson, Roof & Cromer, 1963, 1964, 1965).

Note added in proof (13 December 1967):– It has come to our attention that a paper on the structure of $K_3Cu(CN)_4$ has been published by Giuseppetti & Tadini (1966). These authors used film data and did not include anomalous dispersion corrections. Their results are essentially the same as ours but some of the bond distances differ by several standard deviations.

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