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The Crystal Structure of $KAu(CN)_2$*

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$KAu(CN)_2$ is rhombohedral, space group $R\overline{3}$, with $a=9{\cdot}74$ Å and $\alpha=43{\cdot}9°$. The structure is similar to that of $KAg(CN)_2$ and consists of layers of linear $Au(CN)_2^-$ ions alternating with layers of K^+ ions. However, the stacking of the layers differs in the two compounds, so that $KAg(CN)_2$ is hexagonal and $KAu(CN)_2$ is rhombohedral. A refinement of the structure was made by least-squares analysis of counter data. The Au–C bond is $2{\cdot}12\pm0{\cdot}14$ Å, the C–N bond is $1{\cdot}17\pm0{\cdot}20$ Å and the average K–N distance is $2{\cdot}78$ Å. Twinned crystals of $KAu(CN)_2$ often occur and the nature of this twinning is discussed in detail.

Introduction

As part of a study of complex metal cyanides, which is being conducted in this laboratory (see Cromer, 1957, for further references), the crystal structure of $KAu(CN)_2$, has been determined. This compound has essentially the same structure as that of $KAg(CN)_2$ (Hoard, 1933) but, because of a different stacking sequence, the $KAu(CN)_2$ lattice is rhombohedral rather than hexagonal.

The space group of $KAu(CN)_2$ was reported by Staritzky & Ellinger (1956) to be $R3$ with $a=9{\cdot}74$ Å and $\alpha=43{\cdot}9°$. They reported the measured density to be $3{\cdot}55$ g.cm.$^{-3}$ and calculated $3{\cdot}56$ g.cm.$^{-3}$ with 3 formula units in the rhombohedral unit cell. Staritzky (1956) also reported the space group of $KAg(CN)_2$ to be $P31c$ rather than $P\overline{3}1c$ as reported by Hoard (1933). The assignment of non-centrosymmetric space groups to these compounds was based entirely on the habit of the crystals, no piezoelectric effect having been observed. Newnham (1954) also failed to observe a piezoelectric effect in these compounds.

Because of the disagreement between Staritzky and Hoard as to the space group of $KAg(CN)_2$, Hoard's structure was critically re-examined. Several of the key intensities that Hoard used to establish his structure were measured with a Geiger counter. No inconsistencies were found, and it was concluded that Hoard's structure is correct insofar as the evidence from diffraction intensities is concerned.

There is, however, a slight modification of Hoard's structure which would give the non-centrosymmetric space group $P31c$. If the linear complex ion is slightly rotated out of the plane of the a and c axes, the center of symmetry no longer exists. Jones (1958) has examined thin plates of $KAg(CN)_2$ with polarized infrared radiation, and has concluded that if such a rotation exists it cannot be more than about 2°. Because this rotation would involve only a small shift in positions of the carbon and nitrogen atoms, the effect on the X-ray intensities would be too small to observe experimentally. However, such a rotation could have a profound effect on the habit displayed by the crystals.

Experimental

A large number of crystals of $KAu(CN)_2$ were grown from water solution and from water solutions containing various amounts of acetone or ethyl alcohol. No marked change in habit was observed with changes in the proportions of these solvents. The usual habit was that of a steep rhombohedron $\{10{\cdot}1\}$, sometimes modified by the pinacoid $\{00{\cdot}1\}$, and the rhombohedron $\{01{\cdot}2\}$. It was not uncommon, however, to find crystals with an apparent trigonal dipyramidal habit. Goniometric measurements showed that these forms have the same polar angle as the rhombohedron $\{10{\cdot}1\}$. Crystals that were grown rapidly from saturated solutions formed long spike-like structures having numerous re-entrant angles and what appeared to be polysynthetic twin lamellae perpendicular to the c axis. Attempts to determine the true symmetry by the addition of dyes to the solution or by means of etch patterns were unsuccessful.

Precession photographs taken with Mo $K\alpha$ radiation of the $h0{\cdot}l$ zone of crystals with rhombohedral habit were indexed on a hexagonal cell with the systematic restriction $-h+k+l=3n$ indicating that the lattice is rhombohedral. Crystals with trigonal dipyramidal habit gave $h0{\cdot}l$ photographs which showed extra reflections that could not be indexed within the above restriction, but could be indexed with the restriction $h-k+l=3n$. Opposite ends of crystals of this habit yielded different photographs, one of which could be indexed according to $-h+k+l=3n$ and the other according to $h-k+l=3n$. Obviously these crystals are twins, and *all* such crystals investigated were found to be twins. Twinning of this type cannot

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be detected by optical methods. Because Staritzky & Ellinger (1956) did not use single crystal X-ray techniques in their work, they were unaware that the non-centric crystals they observed were invariably twinned. Therefore, their selection of $R3$ as the space group of $KAu(CN)_2$ is not necessarily correct.

Attempts to grind spheres from single crystals of $KAu(CN)_2$ were not successful, spheroids elongated in the direction of the c axis being the usual result. Such a prolate spheroid, 94μ in diameter and 134μ long was used to obtain the intensity data. It was mounted on the c axis, and intensities were measured with a scintillation counter attached to a Weissenberg camera. Levels for $l=0$ through 17 were recorded, using Cu $K\alpha$ radiation. The three equivalent reflections (six on the zero level) were measured and their average value was taken as the observed intensity. Of the 364 non-equivalent reflections accessible with the instrument, 350 were observed to be greater than zero. Absorption corrections for a sphere of diameter 114μ were applied (Evans & Ekstein, 1952).

Determination of the structure

Conversion of Staritzky & Ellinger's (1956) lattice constants for $KAu(CN)_2$ to a hexagonal cell gives $a=7{\cdot}28$ and $c=26{\cdot}36$ Å. For the silver compound $a=7{\cdot}40$ and $c=17{\cdot}59$ Å (Staritzky, 1956). The a axes are nearly the same and the ratio of the c axes is $ca.\frac{3}{2}$. The similarity of the two hexagonal cells suggests that the structures are the same except for stacking of the layers. This guess is supported by the work of Jones (1954) who, by using polarized infrared radiation, found that the complex $Au(CN)_2^-$ ion makes an angle of about $28\pm1{\cdot}8°$ with the c axis, a value close to that found by Hoard for the $Ag(CN)_2^-$ ion (27°).

Of the rhombohedral space groups having no systematic extinctions, only $R3$ or $R\overline{3}$ can have configurations of linear complex ions that correspond to the layer configuration of $KAg(CN)_2$. As a trial structure, 9 formula units were placed in space group $R\overline{3}$ as follows (hexagonal cell):

$$(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})+$$

$$\begin{array}{llll}
3\,K_1 & \text{in} & a: & (0,0,0)\\
6\,K_2 & \text{in} & b: & \pm(0,0,z)\ z\approx\tfrac{1}{3}\\
9\,Au & \text{in} & d: & (\tfrac{1}{2},0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\\
18\,C & \text{in} & f: & \pm(x,y,z;\ \bar{y},x-y,z;\ y-x,\bar{x},z)\\
 & & & \text{with } x=y=0{\cdot}355,\ z=0{\cdot}425
\end{array}$$

and

$$\begin{array}{llll}
18\,N & \text{in} & f: & \\
 & & & \text{with } x=y=0{\cdot}281,\ z=0{\cdot}386.
\end{array}$$

Because the only basis for assigning the space group $R3$ was the pseudo-morphology of the twinned crystals, and because the slight rotation of the linear complex ion which was postulated in order to destroy the center of symmetry of the silver compound *does not* destroy the center of symmetry of the structure in $R\overline{3}$, we believe that $R\overline{3}$ is the correct space group.

The parameters of the trial structure were deduced by assigning a Au–C distance of 2·24 Å and a C–N distance of 1·15 Å to an assumed linear complex ion tilted 28° from the c axis. Qualitative examination of the structure factors showed that this trial structure was essentially correct. For example, the heavy atom contribution for the $hh{\cdot}l$ reflections with h odd and l even is $9f_K-3f_{Au}$ resulting in a weak reflection, and for h and l even the contribution is $9f_K+9f_{Au}$ giving a strong reflection.

The trial parameters were used as initial values in a least-squares refinement on an IBM 704 computer. The form factors used for potassium, gold, and carbon and nitrogen were those of Berghuis *et al.* (1955), Henry (1954) and McWeeney (1951), respectively. Isotropic temperature factors were assigned to each crystallographically different atom. A separate scale factor was used for each value of l because intensities had been measured for only the c axis mounting, and interlayer scaling was therefore impossible. All reflections were weighted equally. The final R factor was 10·5%. The observed and calculated structure factors are given in Table 1 and the final parameters are in Table 2. The maximum deviation of the 18 scale factors from their mean was 10·5% and their mean deviation was 3·4%.

A three-dimensional Fourier was computed in the regions of the various atoms. The carbon and nitrogen atoms were not resolved from the diffraction ripples surrounding the gold atom. However, a three-dimensional Fourier with the gold contribution subtracted from the observed structure factors did show resolved

Table 1. *Observed and calculated structure factors for* $KAu(CN)_2$.

The column headings are h, k, l, F_o and F_c

h	k	l	F_o	F_c
1	1	0	183	-143
1	4	0	63	-55
1	7	0	0	-12
2	2	0	494	502
2	5	0	0	-21
3	0	0	63	8
3	3	0	0	-26
4	1	0	63	-54
4	4	0	174	193
5	2	0	0	-21
6	0	0	275	267
7	1	0	0	-12
0	2	1	554	-620
0	5	1	75	81
1	0	1	246	232
1	3	1	198	160
1	6	1	67	63
2	1	1	226	153
2	4	1	272	-273
3	-1	1	218	189
3	2	1	112	106
3	5	1	39	48
4	-3	1	197	133
4	0	1	395	-380
4	3	1	73	70
5	-2	1	116	100
5	1	1	101	81
6	-4	1	273	-260
6	-1	1	99	85
6	2	1	179	-147
7	-6	1	70	58
7	-3	1	73	66
7	0	1	34	47
8	-5	1	39	47
8	-2	1	129	-147
0	1	2	236	-222
0	4	2	386	376
0	7	2	39	-49
1	2	2	206	-141
1	5	2	89	-79
2	0	2	544	614
2	3	2	119	-102
2	6	2	126	148
3	-2	2	225	-183
3	1	2	197	-163
3	4	2	73	-72
4	-1	2	193	-123
4	2	2	288	277
5	-3	2	115	-101
5	0	2	80	-82
5	3	2	39	-48
6	-5	2	91	-80
6	-2	2	284	260
6	1	2	65	-64
7	-4	2	70	-65
7	-1	2	65	-56
8	-6	2	125	145
8	-3	2	34	-48
0	3	3	297	278
0	6	3	141	-164
1	1	3	329	414
1	4	3	192	177
1	7	3	58	72
2	-1	3	291	199
2	2	3	363	-384
2	5	3	106	103
3	0	3	305	277
3	3	3	179	159
4	-2	3	340	-312
4	1	3	194	178
4	4	3	98	-124
5	-4	3	188	158
5	-1	3	192	159
5	2	3	105	104
6	-3	3	177	146
6	0	3	150	-165
7	-5	3	103	110
7	-2	3	103	110
7	1	3	61	73
8	-7	3	58	73
8	-4	3	94	-120
8	-1	3	64	73
0	2	4	455	528
0	5	4	129	-111
1	0	4	239	-221
1	3	4	172	-158
1	6	4	61	-68
2	1	4	224	-167
2	4	4	266	262
3	-1	4	227	-197
3	2	4	163	-126
3	5	4	54	-58
4	-3	4	164	-122
4	0	4	384	364
4	3	4	69	-78
5	-2	4	161	-131
5	1	4	98	-91
6	-4	4	267	249
6	-1	4	98	-87
6	2	4	110	138
7	-6	4	61	-61
7	-3	4	67	-72
7	0	4	43	-57
8	-5	4	54	-58
8	-2	4	112	133
0	1	5	227	220
0	4	5	355	-355
0	7	5	46	58
1	2	5	215	167
1	5	5	96	88
2	0	5	457	-496
2	3	5	167	135
2	6	5	102	-135
3	-2	5	218	198
3	1	5	167	152
3	4	5	68	77
4	-1	5	163	124
4	2	5	263	-258
5	-3	5	162	133
5	0	5	142	117
5	3	5	60	60
6	-5	5	96	89
6	-2	5	254	-246
6	1	5	50	66
7	-4	5	68	73
7	-1	5	50	61
8	-6	5	102	-132
8	-3	5	60	59
0	3	6	131	-89
0	6	6	244	248
1	1	6	70	11
1	4	6	39	-26
1	7	6	0	-9
2	-1	6	83	-84
2	2	6	494	464
2	5	6	28	-31
3	0	6	132	-88
3	3	6	48	-39
4	-2	6	476	507
4	1	6	44	-27
4	4	6	180	191
5	-4	6	48	-50
5	-1	6	39	-50
5	2	6	28	-30
6	-3	6	39	-35
6	0	6	249	248
7	-5	6	28	-23
7	-2	6	20	-24
7	1	6	0	-10
8	-7	6	0	-13
8	-4	6	179	185
8	-1	6	0	-13
0	2	7	470	-521
0	5	7	105	87
1	0	7	194	155
1	3	7	124	97
1	6	7	45	44
2	1	7	172	134
2	4	7	284	-264
3	-1	7	163	122
3	2	7	122	96
3	5	7	35	41
4	-3	7	130	105
4	0	7	352	-365
4	3	7	73	55
5	-2	7	121	98
5	1	7	67	62
6	-4	7	282	-269
6	-1	7	64	61
6	2	7	137	-145
7	-6	7	45	46
7	-3	7	70	56
7	0	7	40	43
8	-5	7	28	41
8	-2	7	179	-145
0	1	8	161	-137
0	4	8	370	365
0	7	8	27	-39
1	2	8	156	-130
1	5	8	60	-58
2	0	8	486	519
2	3	8	103	-87
2	6	8	125	143
3	-2	8	140	-102
3	1	8	103	-78
3	4	8	51	-48
4	-1	8	116	-104
4	2	8	280	258
5	-3	8	99	-89
5	0	8	90	-78
5	3	8	33	-37
6	-5	8	60	-56
6	-2	8	281	270
6	1	8	27	-38
7	-4	8	47	-53
7	-1	8	27	-44
8	-6	8	125	145
8	-3	8	27	-38
0	3	9	192	186
0	6	9	156	-160
1	1	9	264	266
1	4	9	167	156
2	-1	9	285	292
2	2	9	297	-292
2	5	9	100	97
3	0	9	199	187
3	3	9	108	113
4	-2	9	297	-296
4	1	9	169	156
4	4	9	88	-109
5	-4	9	166	148
5	-1	9	168	147
5	2	9	98	97
6	-3	9	113	123
6	0	9	156	-160
7	-5	9	97	99
7	-2	9	97	99
8	-4	9	88	-116
0	2	10	395	437
0	5	10	110	-90
1	0	10	234	-206
1	3	10	157	-125
1	6	10	61	-61
2	1	10	200	-176
2	4	10	216	211
3	-1	10	187	-157
3	2	10	132	-119
3	5	10	49	-56
4	-3	10	170	-151
4	0	10	305	301
4	3	10	71	-71
5	-2	10	127	-114
5	1	10	86	-83
6	-4	10	216	220
6	-1	10	90	-88
6	2	10	94	113
7	-6	10	61	-67
7	-3	10	71	-76
7	0	10	45	-56
8	-5	10	49	-56
8	-2	10	94	118
0	1	11	277	222
0	4	11	268	-277
0	7	11	48	58
1	2	11	202	183
1	5	11	90	89
2	0	11	393	-414
2	3	11	135	119
3	-2	11	189	167
3	1	11	171	140
3	4	11	76	77
4	-1	11	181	160
4	2	11	199	-195
5	-3	11	126	116
5	0	11	60	99
5	3	11	51	58
6	-5	11	95	92
6	-2	11	201	-203
6	1	11	65	67
7	-4	11	72	80
7	-1	11	62	71
8	-3	11	51	58
0	3	12	94	-72
0	6	12	199	207
1	1	12	109	-78
1	4	12	58	-48
2	-1	12	100	-84
2	2	12	397	399
2	5	12	0	-19
3	0	12	96	-72
3	3	12	55	-40
4	-2	12	380	389
4	1	12	58	-47
4	4	12	138	152
5	-4	12	47	-37
5	-1	12	47	-37
5	2	12	0	-19
6	-3	12	67	-45
6	0	12	202	202
7	-5	12	0	-22
7	-2	12	0	-22
8	-4	12	147	157
0	2	13	482	-450
0	5	13	45	50
1	0	13	138	126
1	3	13	91	86
1	6	13	29	36
2	1	13	121	103
2	4	13	194	-218
3	-1	13	108	98
3	2	13	71	63
4	-3	13	102	91
4	0	13	282	-305
4	3	13	38	40
5	-2	13	67	65
5	1	13	51	52
6	-4	13	196	-221
6	-1	13	53	50
7	-6	13	34	37
7	-3	13	34	42
0	1	14	116	-94
0	4	14	296	308
1	2	14	104	-74
1	5	14	49	-39
2	0	14	434	448
2	3	14	55	-48
3	-2	14	95	-80
3	1	14	80	-71
3	4	14	26	-31
4	-1	14	94	-63
4	2	14	230	224
5	-3	14	52	-49
5	0	14	32	-37
6	-5	14	49	-38
6	-2	14	228	221
6	1	14	26	-20
7	-4	14	32	-29
7	-1	14	18	-26
0	3	15	159	144
0	6	15	116	-130
1	1	15	168	177
1	4	15	129	104
2	-1	15	200	196
2	2	15	248	-244
2	5	15	53	72
3	0	15	159	144
3	3	15	99	98
4	-2	15	257	-257
4	1	15	104	104
5	-1	15	109	118
5	2	15	53	72
6	-3	15	104	92
6	0	15	146	-131
7	-5	15	50	68
7	-2	15	50	68
0	2	16	375	379
0	5	16	68	-78
1	0	16	161	-157
1	3	16	125	-121
1	6	16	52	-56
2	1	16	142	-172
2	4	16	165	171
3	-1	16	140	-137
3	2	16	87	-92
4	-3	16	126	-103
4	0	16	235	229
4	3	16	60	-64
5	-2	16	84	-92
5	1	16	68	-71
6	-4	16	162	162
6	-1	16	63	-70
7	-6	16	48	-52
7	-3	16	58	-60
0	1	17	166	173
0	4	17	203	-200
1	2	17	150	140
1	5	17	75	81
2	0	17	294	-281
2	3	17	100	106
3	-2	17	147	150
3	1	17	137	131
3	4	17	68	72
4	-4	17	206	-200
4	-1	17	139	116
4	2	17	150	-149
5	-3	17	101	108
5	0	17	79	93
6	-5	17	79	79
6	-2	17	123	-143
7	-4	17	66	69

Table 2. *Parameters from the least-squares refinement of* $KAu(CN)_2$

Atom	x	y	z	$B\times10^{16}$ cm.^{2}
K_1	0	0	0	2·11 ± 0·37
K_2	0	0	0·3441 ± 0·0007	1·87 ± 0·24
Au	½	0	½	2·96 ± 0·04
C	0·403 ± 0·009	0·406 ± 0·009	0·424 ± 0·003	5·56 ± 1·40
N	0·337 ± 0·009	0·348 ± 0·009	0·383 ± 0·003	7·62 ± 1·60

carbon and nitrogen peaks at $x_c=0{\cdot}410$, $y_c=0{\cdot}418$, $z_{\rm C}=0{\cdot}430$, $x_{\rm N}=0{\cdot}336$, $y_{\rm N}=0{\cdot}363$ and $z_{\rm N}=0{\cdot}393$ in reasonable agreement with the least-squares results. A composite of three-dimensional sections through the atoms is shown in Fig. 1. The asymmetry of these peaks is caused by the limited nature of the data, i.e. $l\leq 17$ and no reflections of the type $00l$.

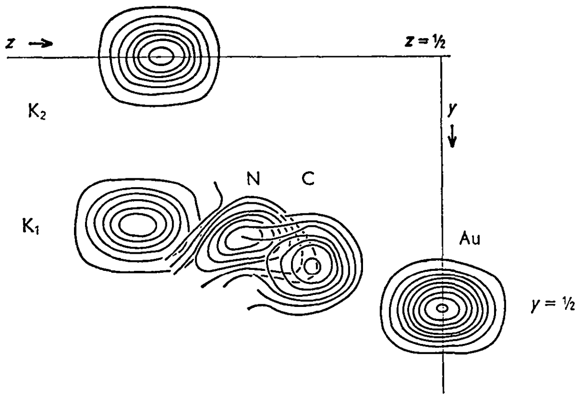

Fig. 1. Composite of electron-density sections through the atoms of $KAu(CN)_2$. The gold atom contours are from the F_o Fourier. The other contours are from the Fourier with the gold atom removed. The initial contour about K_1, K_2, and Au is at $\varrho=0$ electrons/Å^3 and is at $\varrho=0{\cdot}5$ about C and N. The contour interval for C and N is 0·5 electrons, 5 electrons for K, and K_2 and 20 electrons for Au.

Accuracy of the structure

The standard deviations given in Table 2 have been computed from the usual formula

$$\sigma(\xi_i)=\left[\frac{\Sigma(\Delta F)^2}{(m-s)\Sigma\left(\dfrac{\partial F}{\partial \xi_i}\right)^2}\right]^{\frac{1}{2}}$$

where m is the number of observations and s is the number of parameters. Unfortunately, because of the large temperature factors of carbon and nitrogen their positions are subject to a larger error than anticipated. The interatomic distances (Table 3) are all quite reasonable, and the C–N distance of 1·17 Å, although subject to a large standard deviation, nevertheless is found to be very close to that observed in other cyanide compounds.

Discussion of the structure

The structure of $KAu(CN)_2$ is essentially the same as that of $KAg(CN)_2$ and is made up of layers of potassium ions alternating with layers of complex ions, each pair of layers being shifted $\frac{1}{3}$ the length of the long diagonal of the cell base. This shift of the layers gives rise to a rhombohedral primitive cell. In the silver compound the shift is $\frac{1}{2}$ the length of the diagonal, and thus the cell is hexagonal. A drawing of a portion of the unit cell is given in Fig. 2. Bonding between layers is such as to result in little if any cleavage parallel to the layers. However, bonding within layers is weak, and complex ions can be 'peeled' from the sides with relative ease. This gives a qualitative explanation for the failure to grind spheres. It is of interest to note that attempts to grind spheres of $KAg(CN)_2$ also yielded prolate spheroids.

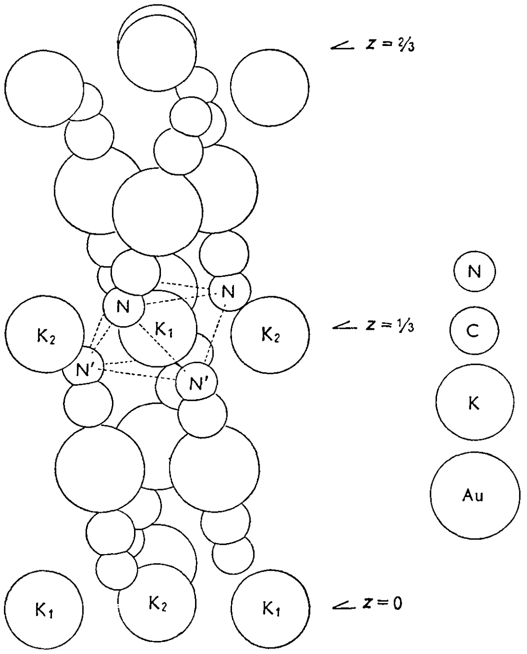

Fig. 2. A drawing of a portion of the unit cell of $KAu(CN)_2$.

Table 3. *Interatomic distances and angles in* $KAu(CN)_2$

K_1–N (6)	2·79 ± 0·14 Å	∠ Au–C–N	172·8 ± 7·5°
K_2–N (3)	2·70 ± 0·14	∠ c axis–Au–N	20·4 ± 2·9
K_2–N′(3)	2·83 ± 0·14	∠ c axis–Au–C	19·5 ± 4·4
Au–C	2·12 ± 0·14		
C–N	1·17 ± 0·20		

The interatomic distances and angles are given in Table 3. The angle between the complex ion and the c axis is smaller than that found by Hoard in $KAg(CN)_2$ and is also smaller than the one Jones (1954) found in his infrared study of $KAu(CN)_2$. Our results are subject to fairly large error. Jones (1954, 1958) did not consider certain possible systematic errors so that his estimate of an error of 1·8° is perhaps small.

Our results, therefore, differ from Jones' by only a possibly significant amount. The smaller tilt that we find has the virtue of making the K–N distances more nearly equal than those found by Hoard. Hoard observed a particularly short K–N distance of 2·58 Å. Our results do not answer the question of whether the complex ion is rotated out of the plane of the a and c axes. Because of its significance in assigning the proper space group to $KAg(CN)_2$, an answer to this question was really the main object of our work. The criteria for the ion to lie in the plane is that $x_C=y_C$ and $x_N=y_N$. The parameters for nitrogen differ by a little more than one standard deviation, but this is not a significant difference.

The habit of the twinned crystals indicates that the composition plane, which is perpendicular to the c axis, is a mirror for the twinned individuals insofar as the forms observed are concerned. The two operations which would produce this condition are rotations of 180° about the zone axes [00·1] and $[1\bar{1}\cdot0]$. In the point group $\bar{3}$, rotation about [00·1] would result in a mirror with regard to all forms $(hk\cdot l)$, while rotation about $[1\bar{1}\cdot0]$ would result in a mirror for forms of the type $(h0\cdot l)$, $(0k\cdot l)$, and $\{hh\cdot l\}$ but not generally for $\{hk\cdot l\}$. Because the only forms observed are {10·1} and {01·2}, the morphology yields no information as to the choice of twin operations.

In examining the structure with regard to the two rotational operations above, it is further necessary to consider the location of the composition plane. It may be placed at the height $z=0$ so that the potassium ions are in or near the composition plane, or it may be placed at the height $z=\frac{1}{2}$ so that the gold atoms lie in the composition plane. Rotation about [00·1] with the composition plane at $z=0$ changes the near octahedral configuration of nitrogen about potassium to one where the nitrogens lie at the corners of a distorted trigonal prism with the potassium at its center. Placing the composition plane at $z=\frac{1}{2}$ results in a non-linear complex at the twin boundary. Rotation about $[1\bar{1}\cdot0]$ with the composition plane at $z=0$ results in a slight distortion of the configuration of nitrogens about potassium but it remains essentially octahedral. The gold atoms now lie at a distance $c/3$ across the twin boundary and, since some of the potassiums are slightly displaced from $z=0$, not all the atoms at or near the composition plane are properly oriented for either member of the twin. Placing the twin plane at $z=\frac{1}{2}$ does not alter the nitrogen–potassium configuration at all, and does not affect the complex if it is assumed to lie in the a–c plane.

The configuration of a single crystal may be regarded as representing a minimum free energy state for the particles involved (Buerger, 1945). This condition is influenced primarily by the first sphere of coordination or nearest neighbors of an atom, subsequent spheres of coordination having less and less influence. For twinning to occur, it must be possible to change the orientation of part of the structure with but a slight deviation from the minimum free energy condition. The last twinning operations discussed, rotation about $[1\bar{1}\cdot0]$ with the composition plane at $z=\frac{1}{2}$, satisfies this requirement. There is no change in the nitrogen–potassium configuration, no distortion of the complex ion, and the complex ions and potassium ions at and adjacent to the composition plane are in proper position for either orientation.

No such twinning can occur in the analogous silver compound in which, being hexagonal, the only permissible operations result in identity. Furthermore, it is noted that the non-centrosymmetric habit of some crystals of $KAg(CN)_2$ observed by Staritzky cannot be explained as a result of twinning, and, hence, the space group $P31c$ is probably correct. A small but real rotation of the silver dicyanide complex from the a–c plane is probably present, and this condition in the structure would further hamper the possibility of twinning.

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