Schlussbemerkung

Welche Methoden man zur genauen Schweratomparameterbestimmung heranziehen wird, hängt vom Problem ab. Im Falle von Eiweisskristallen ist, wie die Betrachtung der Korrelationsfunktionen gezeigt hat, der quasistatistische Zusammenhang der Reflexe so ausgeprägt, dass die gewichtete C'- oder C''-Funktion bereits gute Näherungswerte liefern sollte, die nachträglich noch verfeinert werden können. In niederatomigeren azentrischen Kristallen kann allerdings die $u^{\pm}$-Funktion bessere Resultate liefern. Von den Verfeinerungsmethoden scheint uns die Differenzfouriersynthese die geeignetere zu sein, da sie nicht nur die Schweratomparameter zu verbessern gestattet, sondern auch die Güte der gefundenen Struktur beurteilen lässt. Allerdings ist die Rechnung nach der Methode der kleinsten Quadrate insbesondere im dreidimensionalen Fall schneller und einfacher, so dass es sich vielleicht empfiehlt, zur Abkürzung der Rechenarbeit zuerst die beste Lösung nach der Methode der kleinsten Quadrate zu suchen und diese dann durch eine Differenzsynthese zu prüfen.

Die vorliegende Arbeit wurde anlässlich eines Gastaufenthalts am Cavendish-Laboratorium, Universität Cambridge, Cambridge, England, durchgeführt.

Ich darf auch an dieser Stelle den Herren Dr. M. F. Perutz und Dr. J. C. Kendrew bestens für die Gastfreundschaft danken. Dem Verband der Chemischen Industrie-Fonds der Chemischen Industrie danke ich für eine Reisebeihilfe.

Literaturverzeichnis

Blow, D. (1957). Doctoral Thesis, Univ. of Cambridge, Cambridge, England.

Bragg, W. L. (1958). *Acta Cryst.* **11**, 70.

Harker, D. (1956). *Acta Cryst.* **9**, 1.

Hoppe, W. (1957). *Z. Elektrochem.* **61**, 1076.

Kendrew, J. C. (1958). *Nature, Lond.* **81**, 662.

Perutz, M. F. (1956). *Acta Cryst.* **9**, 867.

Acta Cryst. (1959). **12**, 674

A Neutron-Diffraction Study of Potassium Cobalticyanide

By N. A. Curry and W. A. Runciman*

Atomic Energy Research Establishment, Harwell, Berks, England

(*Received* 4 *September* 1958 *and in revised form* 19 *January* 1959)

The methods of neutron diffraction, which permit a distinction to be made between carbon and nitrogen atoms, have been used to extend the earlier X-ray studies of $K_3Co(CN)_6$. It appears that the carbon atoms are in positions adjacent to the cobalt ions. The methods of Fourier synthesis and least squares have been used to obtain improved atomic co-ordinates and values for the Debye–Waller temperature factors. The length of the C–N bonds is 1·15 Å.

Introduction

Cyanide complexes are of considerable interest, the platinocyanides showing marked dichroism and fluorescence, and iron-group cyanides having been studied by paramagnetic-resonance techniques. The structures of some cyanides have been investigated by X-rays, but these do not distinguish whether the carbon or nitrogen atoms are next to the central metal ion. However, neutron diffraction often enables one to distinguish between atoms which are neighbours in the periodic table. (Bacon, 1955, Chapter VIII). It was felt that it would be easiest to study a cyanide for which preliminary X-ray information was available, and which did not contain any water of crystallization involving additional work in the location of hydrogen atoms. Potassium cobalticyanide, $K_3Co(CN)_6$, is suitable, having been studied using X-ray methods by Barkhatov & Zhdanov (1942) and by Barkhatov (1942). Furthermore, a consideration of the scattering amplitudes, Table 1, indicates that neutron diffraction will be suitable for the determination of carbon and nitrogen positions, since the scattering amplitudes of these atoms are considerably different, and are the largest present; whereas for X-rays the heavy metal atoms are predominant.

Table 1. *Scattering amplitudes for neutrons and X-rays* (10^{-12} cm.)

		X-rays	
Atom	Neutrons	$\sin\theta/\lambda = 0$	$\sin\theta/\lambda = 0{\cdot}5$ Å^{-1}
C	0·66	1·69	0·48
N	0·94	1·97	0·53
K	0·35	5·3	2·2
Co	0·28	7·6	3·4

---

* Now at the Department of Physics, University of Canterbury, Christchurch, New Zealand.

Barkhatov & Zhdanov (1942) found that the true symmetry of $K_3Co(CN)_6$ is monoclinic, and not orthorhombic, as earlier supposed. They found the unit cell to be

$$a = 7{\cdot}1,\ b = 10{\cdot}4,\ c = 8{\cdot}4\ \text{Å};\ \beta = 107°\ 20',$$

with two molecules per unit cell. The space group is $P2_1/c(C_{2h}^5)$ with the cobalt and some potassium ions in special positions, as follows (Barkhatov, 1942):

$$\begin{aligned} &2\,\text{Co in } 2a\ (0,0,0)(0,\tfrac{1}{2},\tfrac{1}{2}) \\ &2\,\text{K}_1 \text{ in } 2c\ (0,0,\tfrac{1}{2})(0,\tfrac{1}{2},0)\,. \end{aligned}$$

The X-ray intensities indicated that a twofold symmetry axis of the octahedral $[Co(CN)_6]^{3-}$ group is directed along the c-axis, while the fourfold symmetry axis perpendicular to this twofold axis lies roughly perpendicular to the (130) plane. The octahedra are in two groups, those in one group being mirror images of those in the other group. This is shown in Fig. 1, which is a sketch of the structure projected along the c axis. Barkhatov found the C–N distance to be about 1·2 Å, and the distance from the cobalt ion to the centre of the cyanide group to be about 2·5 Å. This information was used in a preliminary calculation of structure factors.

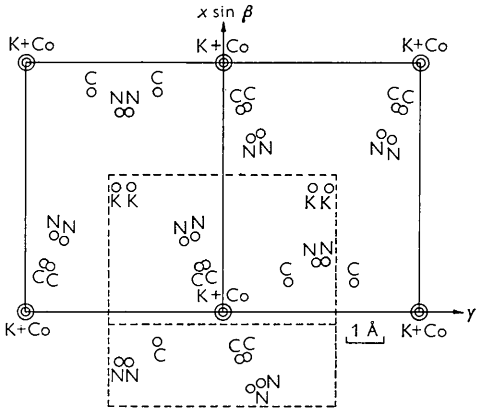

Fig. 1. The arrangement of the atoms in a projection of the structure on a plane normal to the z axis. The areas enclosed by dashed lines are those which appear in the Fourier projections of Fig. 2 and Fig. 3.

Experimental details

Crystals were readily grown from aqueous solution. The directions of the principal axes of some crystals were determined by X-ray diffraction, and we are grateful to Mr S. A. Wilson of this Establishment for carrying out this work. Most of the crystals had their largest dimension in the direction of the c-axis, and so it was decided to measure the intensities of the $[hk0]$ zone. The crystal used in the experiment had dimensions approximately $14 \times 5 \times 3$ mm., the longest dimension being in the direction of the c-axis. A series of 117 $hk0$ reflexions was measured, and the observed Bragg angles for this zone were found to be consistent with $a \sin \beta = 6{\cdot}67$ Å, whereas the unit-cell dimensions earlier quoted yield $a \sin \beta = 6{\cdot}78$ Å. The value of b was observed as 10·4 Å, as stated by Barkhatov & Zhdanov (1942). All but two of the reflexions were measured at a neutron wavelength of 1·09 Å, using a lead crystal as monochromator. With a neutron wavelength of 0·80 Å, obtained from a copper monochromator, one additional reflexion was found in each of the main series of spectra $h00$ and $0k0$. These were both small in intensity, and it was not considered worth while to search for additional reflexions at this wavelength. The minimum spacing for the reflexions measured was about 0·65 Å. The spectrometer used was the powder-type spectrometer described by Bacon, Smith & Whitehead (1950). The most intense reflexions were corrected for secondary extinction by the method of Bacon & Pease (1953).

Results

A preliminary calculation of structure factors was based on the information obtained from Barkhatov's work. It was assumed that the Co–C–N bond was straight, and that the carbon atom was adjacent to the cobalt ion. The values of B in the Debye factor $\exp(-B \sin^2 \theta/\lambda^2)$ for correcting the structure amplitude factors for the effect of thermal vibrations, were taken as 1·0, 1·5, 2·5 and 2·5 Å^2 respectively for cobalt, potassium, carbon and nitrogen. The signs of these calculated structure factors and the experimentally observed amplitudes were used in a preliminary Fourier synthesis showing the scattering density projected on a plane perpendicular to the c axis. This confirmed that the main features of the assumed structure were correct, but unfortunately could not distinguish unambiguously between carbon and nitrogen atoms. This was partly because the differences in peak heights which should result from the different scattering lengths of carbon and nitrogen atoms were masked by differences in the amplitudes of their thermal vibrations. Moreover, in projection there are three pairs of overlapping atoms, one pair of carbon atoms and two pairs of nitrogen atoms. The amounts by which the atoms overlap are different in the three cases, and this further obscures the simple relationship one would expect to find between scattering length and peak height.

It was decided to examine the data further by the method of least-squares. Two trial structures were assumed, one (hereafter called the α-structure) having the carbon atom of the C–N group adjacent to the cobalt ion, and the other (hereafter called the β-structure) with the nitrogen atom next to the cobalt ion. For each structure the positions of the carbon and nitrogen atoms were re-estimated from the Fourier projection, and new values of B were estimated from the heights of the peaks. Each structure was then refined by successive cycles of least-squares, and it was found that satisfactory results were obtained from the α-structure but not from the β-structure. For this and other reasons, which we give in detail later in the paper, we have concluded that the α-structure is the correct one.

As a result of the refinement of the α-structure, it was found that several of the calculated structure factors changed sign. A second Fourier synthesis was then carried out, using these altered signs. This is shown in Fig. 2, which shows the scattering density within the region bounded by the outer dashed line in Fig. 1. The distribution of scattering density within the unit cell is quite consistent with that which would be obtained from atoms placed at the positions obtained from the least-squares analysis of the α-structure. These positions are marked by crosses in the figure.

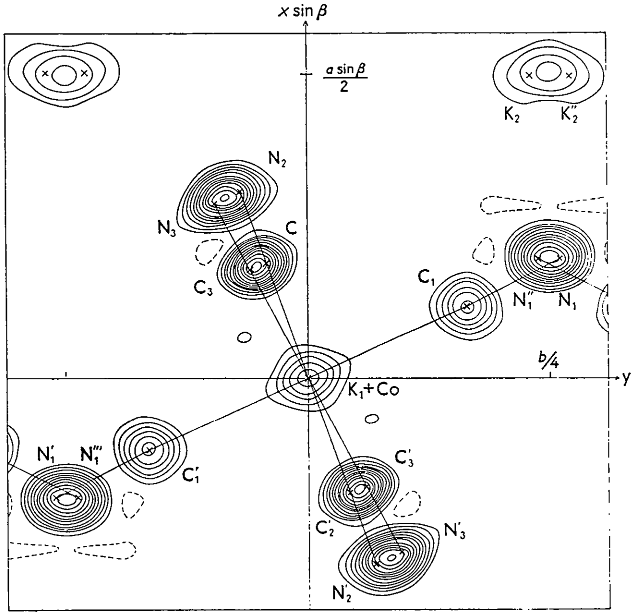

Fig. 2. Projection of the neutron scattering density on a plane normal to the z axis. Full lines are positive contours, broken lines are negative. Contours are drawn at intervals of 50 units.

We have also made a Fourier synthesis of the quantity $(F_o - F_c)$, where F_o is the observed structure factor amplitude, and F_c is the structure factor calculated from the parameters obtained in the α-structure in the final cycle of least squares. This synthesis is shown in Fig. 3. The portion of the unit cell shown in this figure is the upper rectangle bounded by a dashed line in Fig. 1. Contours are drawn at intervals of 25 units, compared with intervals of 50 units for the F_o synthesis. The figure shows that there is only one region in the unit cell where the scattering density is greater than 50 units, and this is not close to any of the atoms. Only one feature of this figure appears to be due to an error in the assumptions made in calculating F_c, namely the two positive peaks on either side of the potassium and cobalt atoms which are superimposed at the origin. These peaks may be due to anisotropic vibration of either or both of these atoms, the preferred direction of vibration lying in projection along the bond Co–C$_1$. However we have not attempted a detailed analysis of anisotropic vibrations.

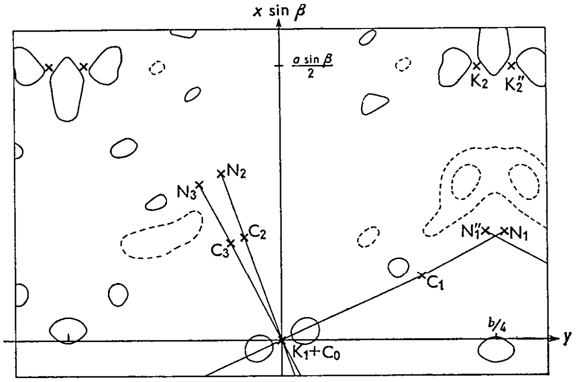

Fig. 3. The Fourier projection on a plane normal to the z axis obtained by synthesis of $F_o - F_c$. Contours are drawn at intervals of 25 units.

The co-ordinates, and the values of B which we have assigned to the atoms in the structure, are listed in Table 2. They are the values obtained from the least-squares analysis of the α-structure, and in the case

Table 2. *Atomic parameters and temperature factors*

	x/a		y/b		z/c*		$B(10^{-16}$ cm.$^2)$	
Atom	Least squares	Fourier	Least squares	Fourier	Set 1	Set 2	Least squares	Fourier
Co	(0)		(0)		(0)		1·8	1·5
K$_1$	(0)		(0)		(0·500)			
K$_2$	0·499	—	0·230	—	—	—	1·8	—
C$_1$	0·118	0·118	0·165	0·165	0·014	0·044	1·3	1·2
C$_2$	0·189	—	−0·043	—	0·206	−0·113	1·5	—
C$_3$	0·179	—	−0·059	—	−0·114	0·203	1·1	—
N$_1$	0·199	—	0·261	—	0·024	0·075	2·3	—
N$_2$	0·306	—	−0·070	—	0·331	−0·179	2·1	—
N$_3$	0·286	—	−0·096	—	−0·184	0·326	1·9	—

* By geometrical calculation as described in the text.

of four parameters, a value obtained directly from the Fourier synthesis is also listed. In these four cases there is good agreement between the parameters obtained by the two methods. Because of overlapping, the remaining parameters cannot be obtained directly from the Fourier synthesis.

Our results do not yield values for the third co-ordinate z directly, as we have measured only the $(hk0)$ reflexions. However, values of z for the carbon and nitrogen atoms may be obtained by assuming that the cyanide groups surround the cobalt ions in regular octahedra. It is found that the values of z can be chosen so as to make the octahedron of carbon atoms a very close approximation to a regular octahedron, with the three Co–C distances differing from one another by less than 0·01 Å, and the angles between the three bonds differing from right angles by less than 1°. The departures from regularity of the octahedron formed by the nitrogen atoms are roughly twice the corresponding values in the case of the carbon atoms. However, the values of z obtained by this method are not unambiguous. Two sets of values may be obtained, yielding two distinct octahedra. The relationship between the two is that each may be obtained from the other by reflexion across the plane through the origin perpendicular to the c axis. The two alternative sets of values for z are listed in Table 2. The bond lengths which we deduce from our data are listed in Table 3. The values obtained for the bond lengths do not depend upon which set of z-values is chosen.

Table 3. *Bond lengths*

Co–C		C–N	
Co–C_1	1·89 Å	C_1–N_1	1·14 Å
Co–C_2	1·89	C_2–N_2	1·15
Co–C_3	1·89	C_3–N_3	1·15
Mean	1·89	Mean	1·15

The standard deviation of the co-ordinates of carbon atom C_1, which does not overlap with other atoms in projection, is estimated by the method of Cruickshank (1949) to be 0·009 Å. The accuracy of the co-ordinates of the atoms which overlap in projection will obviously be less than this.

Discussion

The main interest in this substance lies in the attempt to distinguish between the α and β structures. We base our conclusion that the α-structure is the correct one upon the following evidence.

1. The least-squares refinement of the α-structure proceeded satisfactorily. In six cycles the value of the reliability index $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ fell from 27·5 % to 12·4 % and in the final cycle the changes were small, the maximum changes being 0·0003 in a positional parameter (fractional co-ordinates) and 0·5 in a Debye factor. The reliability index for the β-structure fell in two cycles from 31·7 % to 22·9 %. This in itself would be satisfactory, but after the second cycle values of the Debye factor ranging from 0·5 to 6·7 had to be assigned to the carbon and nitrogen atoms. We considered these values so improbable that we did not refine this structure beyond two cycles.
2. The least-squares refinement of the α-structure yielded results which are wholly consistent with the Fourier projection shown in Fig. 2. The results for the β-structure yield inconsistencies in the positions of the overlapping atoms C_2, C_3, N_2, N_3.
3. In the Fourier 'difference' synthesis, the absence of large peaks (positive or negative) near to atomic positions suggests that the α-structure cannot be substantially wrong.
4. We have made a detailed study of the shape of the atom at (0·118, 0·165) which is the only carbon or nitrogen atom that does not overlap in projection. We calculate from its peak height in the Fourier projection that this atom could be either carbon with $B = 1·2$ or nitrogen with $B = 2·7$. We have calculated the shapes to be expected in the two cases, using the expression given in equation (3a) of the paper by Bacon & Pease (1953). The shapes obtained are shown in Fig. 4, together with a set of points giving the observed shape taken from the results of our Fourier synthesis. It will be seen that the observed shape is much closer to the shape calculated on the assumption that this atom is carbon with $B = 1·2$. This is additional evidence that the α-structure is the correct one.

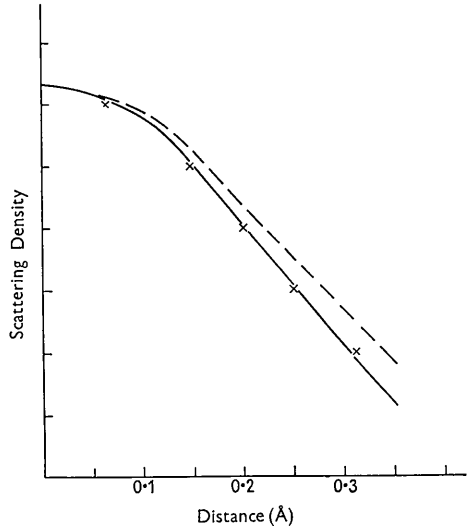

Fig. 4. The diffraction pattern of the atom at (0·118, 0·165). The full line shows the pattern expected from a carbon atom. The dashed line shows the pattern expected from a nitrogen atom. The crosses indicate points on the observed pattern. The divisions along the ordinate axis correspond to the contours in Fig. 2.

Table 4. *Observed and calculated structure factors*

h,k	F_o	F(i)	F(iii)	h,k	F_o	F(i)	F(iii)	h,k	F_o	F(i)	F(iii)
0 2	31	28	40	3 7	22	20	23	6 8	16	13	11
0 4	25	24	24	3 8	<4	4	10	6 9	19	19	19
0 6	74	75	55	3 9	25	27	26	6 10	20	24	22
0 8	33	27	34	3 10	62	67	66	6 11	<5	2	9
0 10	42	41	42	3 11	<5	11	9	6 12	<5	5	2
0 12	38	37	41	3 12	22	20	19	6 13	13	12	20
0 14	<5	4	2	3 13	<5	8	7	7 0	20	19	19
0 16	<5	4	4	3 14	16	21	24	7 1	18	20	18
0 18	21	24	8	3 15	<5	4	10	7 2	39	36	38
1 0	27	30	49	4 0	27	29	15	7 3	59	56	55
1 1	4	0	0	4 1	46	38	22	7 4	44	39	40
1 2	15	10	20	4 2	13	9	10	7 5	24	19	17
1 3	126	136	123	4 3	19	13	25	7 6	<4	5	3
1 4	20	14	8	4 4	28	25	28	7 7	39	42	38
1 5	65	58	75	4 5	12	11	2	7 8	<4	13	18
1 6	42	37	38	4 6	44	41	40	7 9	10	9	15
1 7	19	18	22	4 7	69	68	68	7 10	25	27	33
1 8	<4	2	7	4 8	33	29	29	7 11	24	24	19
1 9	51	48	43	4 9	21	21	20	7 12	19	20	18
1 10	22	19	19	4 10	24	25	24	8 0	33	37	40
1 11	<5	2	2	4 11	<5	9	15	8 1	28	29	31
1 12	<5	9	8	4 12	<5	2	8	8 2	35	31	25
1 13	28	28	23	4 13	28	30	29	8 3	24	20	20
1 14	<5	6	6	4 14	<5	4	1	8 4	11	10	8
1 15	<5	5	7	4 15	21	19	13	8 5	18	15	18
2 0	65	95	83	5 0	8	8	0	8 6	53	51	52
2 1	54	50	42	5 1	12	8	8	8 7	14	13	20
2 2	38	30	40	5 2	10	6	19	8 8	26	26	22
2 3	20	13	27	5 3	13	11	14	8 9	<5	9	12
2 4	21	14	10	5 4	73	67	64	8 10	22	23	22
2 5	25	19	42	5 5	34	31	32	8 11	11	11	10
2 6	73	80	70	5 6	<4	7	5	9 0	9	14	16
2 7	32	30	27	5 7	14	13	13	9 1	11	10	5
2 8	37	34	37	5 8	24	19	21	9 2	15	16	13
2 9	10	12	11	5 9	<4	4	4	9 3	54	50	55
2 10	32	24	25	5 10	34	31	32	9 4	<4	3	11
2 11	21	24	24	5 11	<5	5	6	9 5	21	17	11
2 12	<5	4	9	5 12	30	29	22	9 6	37	36	32
2 13	34	36	32	5 13	19	23	21	9 7	24	23	19
2 14	<5	12	12	5 14	<5	6	12	9 8	11	10	7
2 15	15	17	12	6 0	53	60	61	10 0	48	57	64
3 0	38	40	65	6 1	22	21	16	10 1	19	20	15
3 1	33	25	31	6 2	25	25	26	10 2	8	7	3
3 2	53	46	25	6 3	5	4	1	10 3	27	24	20
3 3	73	71	61	6 4	41	35	35	10 4	17	11	13
3 4	54	48	40	6 5	34	31	30	10 5	7	7	2
3 5	4	3	3	6 6	29	26	25	10 6	21	19	34
3 6	6	2	5	6 7	67	62	61	11 0	18	20	15

All structure factors are expressed as multiples of 10^{-13} cm. F(i) and F(iii) are calculated from sets of parameters (i) and (iii) as described in the text.

5. We have calculated three sets of structure factors for comparison. The parameters used were (i) those obtained from the final cycle of least-squares refinement of the α-structure, as shown in Table 2. (ii) a set of parameters obtained from (i) by interchanging carbon and nitrogen, leaving the Debye factor associated with a given *position* unaltered; (iii) parameters obtained from (ii) by adjusting the Debye factors to compensate for the changes in scattering length. The reliability indices for the three sets are 12·4%, 30·5% and 20·5% respectively. The structure factors for the α-structure (set (i)) and the more favourable variant of the β-structure (set (iii)) are listed in Table 4. It should be noted that not only does the α-structure yield the best reliability index, but several of the biggest discrepancies with the β-structure occur for low angle reflexions, for which changes in the Debye factors cannot compensate for changes in the basic structure. The (060), (100), (300), (320) and (410) reflexions are particularly noteworthy in this respect.
6. It is interesting to note that for the α-structure, the thermal vibrations of the cyanide groups increase as the distance from the central cobalt ion increases. Thus the mean Debye factors are 1·3 for the 'inner' carbon atoms, and 2·1 for the 'outer' nitrogen atoms. For the β-structure, to preserve the same peak heights, we have to assume that the 'inner' nitrogen atoms have a mean Debye factor of 2·8, and the 'outer' carbon atoms have a mean Debye factor of only 0·8. Thus in this structure the inner atoms have moderately large thermal vibrations and the outer atoms are relatively stationary. The arrangement for the α-structure seems the more plausible of the two.

These six results taken together suggest very strongly that the α-structure is the correct one, and we conclude therefore that in this compound the carbon atoms are adjacent to the cobalt ion.

The other point of interest in this structure is the C–N distance. The value of 1·15 Å which we find is not unlike that found in other molecules. For instance, using electron diffraction, Brockway (1936) and Pauling, Springall & Palmer (1939) have found a C–N distance of 1·16±0·02 Å in methyl cyanide. Similar values for the C–N distance are found in complex cyanides. For example Monfort (1942) using X-rays, finds a C–N distance of 1·16 Å in potassium sodium platinocyanide.

From our results for the α-structure, we deduce that the Co–C–N bonds are collinear in the case of the cyanide groups labelled 2 and 3, but in the case of the bond Co–C_1–N_1 we find that N_1 lies 0·08 Å from the line Co–C_1 produced. This departure from collinearity is not dependent upon the values calculated for the z co-ordinates, but may be deduced qualitatively from the observed x and y co-ordinates. However, in view of the overlapping of the atoms N_1, N_1'' it may not be significant.

We wish to thank Dr G. E. Bacon for much helpful advice and for the use of the neutron spectrometer. We are also grateful to Mr A. R. Curtis and the Atomic Energy Research Establishment Computing Section for carrying out much of the computation.

References

Bacon, G. E. (1955). 'Neutron Diffraction'. Oxford: Clarendon Press.

Bacon, G. E. & Pease, R. S. (1953). *Proc. Roy. Soc.* A, **220**, 397.

Bacon, G. E., Smith, J. A. G. & Whitehead, C. D. (1950). *J. Sci. Instrum.* **27**, 330.

Barkhatov, V. (1942). *Acta Physicochimica U.R.S.S.* **16**, 123.

Barkhatov, V. & Zhdanov, H. (1942). *Acta Physicochimica U.R.S.S.* **16**, 43.

Brockway, L. O. (1936). *J. Amer. Chem. Soc.* **58**, 2516.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Monfort, F. (1942). *Bull. Soc. Roy. Sci. Liège*, **11**, 567.

Pauling, L., Springall, H. D. & Palmer, K. J. (1939). *J. Amer. Chem. Soc.* **61**, 927.