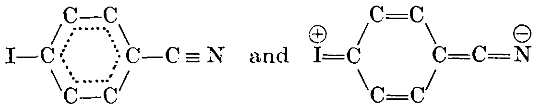
twice the estimated standard deviations, but, as discussed above, the diagonal approximation used to estimate the standard deviation in the positional parameter gives optimistic estimates. If one ignores the normal I–C distance and takes the shortest C–C distance in the ring as significantly shorter, then all of the distances between light atoms suggest that the resonance forms



are both important. The second form could contribute to the intermolecular interaction.

It is not apparent why the external bond in ICN should be so much stronger than in this molecule. Except for the N–I there are no unusually short distances between the molecules. In particular the hydrogen atoms on one chain of molecules do not appear to be interfering with the formation of N–I bonds on the next chain. One possibility for the decrease in strength is that the σ bonds in ICN are affected, that the external interaction involves a d orbital which then contributes to the I–C σ bond and causes some rehybridization of the C and N σ orbitals, and that all this rehybridization is necessary for the formation of the external bond. This would not be possible with the benzene ring in between, and the bond would be weakened.

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The Crystal Structure of Silver Cyanate

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Silver cyanate is monoclinic, $a=5\cdot473$, $b=6\cdot372$, $c=3\cdot416$ Å, $\beta=91°\ 0'$, $Z=2$, space group $P2_1/m$. The structure has been determined, and refined by full-matrix least-squares analysis of three-dimensional counter data. The silver atoms occupy positions 2(*a*) (0, 0, 0, *etc.*), the other atoms positions 2(*e*) ($x, \frac{1}{4}, z$, *etc.*) with $x_{\rm N}=0\cdot786$, $z_{\rm N}=0\cdot221$; $x_{\rm C}=0\cdot579$, $z_{\rm C}=0\cdot326$; $x_{\rm O}=0\cdot377$, $z_{\rm O}=0\cdot441$. Each silver atom has two linearly coordinated nitrogen atoms at 2·115 Å; distances within the linear cyanate group are, N–C $=1\cdot195\pm0\cdot011$, C–O $=1\cdot180\pm0\cdot011$ Å.

Introduction

Silver cyanate and silver fulminate provided the first example of isomerism (Liebig & Gay-Lussac, 1824). In spite of the simplicity of these compounds, the crystal structure of neither appears to have been established. As the first part of an investigation of the structural relationships between these compounds in the solid state, we describe here the crystal structure of silver cyanate. The structures of two polymorphic forms of silver fulminate will be reported later.

Two determinations of unit-cell dimensions and

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[†] A reinvestigation of potassium cyanate in this laboratory confirms that the crystals are tetragonal, $a=6\cdot096$, $c=7\cdot056$ Å, space group $I4/mcm$, in agreement with the early work of Hendricks & Pauling (1925).

space group of silver cyanate have been made (Capela, 1959; Waddington, 1959), but they are in discord with each other. Nevertheless, they do indicate that the crystal structure is different from that of the azide. Although the alkali cyanates are isomorphous with their respective azides,[†] such a difference might have been anticipated, since silver salts tend to be less ionic than alkali metal salts. This should lead to a difference in coordination of the two ends of the cyanate anions. However, any reasonable structure based on the space groups and unit cells reported by Waddington or Capela would require disordered arrangements of cyanate ions.

Unit cell and space group

The previously reported values and our results are summarized in Table 1. Our cell-constant measurements were made on precession photographs (Mo $K\alpha = 0{\cdot}7107$ Å); both Weissenberg and precession photographs were used to establish the space group. The hkl reflexions with k odd are much fainter than with k even, so it is easy to understand why Capela's result differs from ours. Waddington's reported cell, however, would require us to have missed some reflexions. A 24 hour precession photograph of the $hk\frac{1}{2}$ level showed no reflexions, and an oscillation photograph about the c axis showed no extra layer-lines, even though it was exposed to the background limit. Also, the body-centring would have required half the reflexions on our $h0l$ picture to be missing, and none were; they showed, rather, an almost normal decline in intensity. We reject, therefore, both of the previously reported unit cells, although we cannot suggest the cause of the discrepancy in the second case. The only systematic absences shown by our photographs were $0k0$, k odd, indicating the space group to be $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2).

Table 1. *Unit-cell parameters and space group*

Reference	This work	Waddington (1959)	Capela* (1959)
a (Å)	$5{\cdot}473 \pm 0{\cdot}009$	$5{\cdot}48$	$5{\cdot}53 \pm 0{\cdot}05$
b (Å)	$6{\cdot}372 \pm 0{\cdot}011$	$6{\cdot}37$	$3{\cdot}18 \pm 0{\cdot}03$
c (Å)	$3{\cdot}416 \pm 0{\cdot}006$	$6{\cdot}82$	$3{\cdot}42 \pm 0{\cdot}05$
β	$91^\circ\ 0' \pm 5'$	—	$91^\circ\ 7'$
Space group	$P2_1/m$	$Imcb$	$P2/m$
Z	2	4	1
Volume	$119{\cdot}1$ Å^3		
D_c	$4{\cdot}27$ g.cm^{-3}		

* We have converted the values reported by Capela from kX to Å.

The crystals used were prepared by Dr R. Gut by dissolving 1·7 g silver nitrate and 200 g urea in 500 ml of water and allowing this to stand in darkness for two months. The product was a mixture of well developed crystals and an almost colloidal sludge, which was removed by decantation. The crystals were of two habits. The more abundant were elongated along [010] with {001} prominently and {101} slightly less prominently developed, and terminated by {120}. The less abundant were thick needles elongated along [001] with prominent {120} and terminated by {001} and {101}. Both habits indicated the holohedral symmetry of the crystal. Cleavage occurred readily along (101).

Crystals of both habits were twinned in about 90% of the samples examined. Often the twinning was apparent in an optical examination of the crystal, either through a diffuse boundary between the twins in the first habit, or through reentrant angles in the second habit. There were no clearly defined boundary planes, but rather irregular and uneven boundaries. X-ray examination showed that the two twins shared a common (100) plane.

Determination of the structure

Inspection of the preliminary X-ray photographs revealed that reflexions with $k=2n$ were nearly uniformly intense, apart from normal decline, whereas reflexions with $k=2n+1$ were weak and variable. This, combined with the apparent holohedry of the crystals, suggested that the space group is $P2_1/m$ with Ag at $0, 0, 0$; $0, \frac{1}{2}, 0$; and cyanate groups at $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$. Multiple film Mo $K\alpha$ Weissenberg photographs of the $h0l$ and $hk0$ layers were taken, and the intensities measured by comparison with a series of timed exposures. In the (010) electron-density projection calculated with all signs positive, every atom was resolved and identifiable; the peak heights were 183 ($=2\times 91$), 8, 6, and 10 e.Å^{-2} for Ag, N, C and O respectively. The N, C and O atoms were linear, with N nearest to Ag. A difference map based on the Ag contributions alone confirmed the light atom positions and indicated that the Ag was strongly anisotropic. The R index was 0·143 with all atoms isotropic and 0·077 when the anisotropic motion of the Ag was allowed for.

An apparent difficulty arose in connection with the $hk0$ data when it was observed that corresponding $h10$, $h30$ and $h50$ reflexions had quite different intensities, contrary to expectation based on the special positions of all the atoms. It was at first thought that this indicated that the space group was not $P2_1/m$ but $P2_1$. However, electron-density projections in the lower space group led to exactly the same structure as before.

At this point, it was realized that the special reflexion condition: hkl, $k=2n$, for atoms at $0, 0, 0$ and $0, \frac{1}{2}, 0$ is valid only for isotropic atoms. In this crystal the Ag anisotropy is so large that, in many cases, the calculated structure factors for the reflexions with k odd are dominated by the Ag contributions.

These calculations were done on the IBM 1620 computer of this laboratory with programs prepared by M. Dobler, H. C. Mez, P. Strickler and H. P. Weber.

Refinement of the structure

Three-dimensional data were collected with the semi-automatic linear diffractometer designed by Arndt & Phillips (1961), molybdenum radiation with balanced filters being used. An irregular crystal, 0·15 to 0·30 mm in diameter, was used; this was the better of the two untwinned crystals that had been found by X-ray examination of twelve apparently single crystals. Data were collected for the layers *h*0*l*–*h*6*l* out to sin $\theta \sim 30°$. Measurements were made for 304 independent reflexions, of which 30 had an intensity less than the standard deviation of the measurement. These 'unobserved' reflexions were included in the subsequent least-squares calculations with assigned intensities equal to their corresponding standard deviations. The linear absorption coefficient was 80 cm^{-1}, but no absorption corrections were made. Lorentz and polarization corrections were applied. Least-squares refinement was carried out in three stages starting from the positions determined in the preceding analysis. In order to assess the relative importance of the anisotropy we first refined with all atoms isotropic, then with only Ag anisotropic, and finally with all atoms anisotropic. In all these calculations the scattering curves for the neutral atoms were used. The progress of the refinement is shown in Table 2.

Table 2. *Stages of the refinement*

Refinement parameter	Fourier results	All atoms isotropic	Ag only an-isotropic	All atoms an-isotropic
r(*hkl*)*	0·809	0·224	0·024	0·019
R(*hkl*)†	0·220	0·212	0·072	0·067
R(*h*0*l*)	0·184	0·169	0·069	0·068
R(*h*1*l*)	0·415	0·329	0·199	0·162
R(*h*2*l*)	0·192	0·160	0·056	0·054
R(*h*3*l*)	0·591	0·563	0·180	0·170
R(*h*4*l*)	0·166	0·190	0·047	0·043
R(*h*5*l*)	0·692	0·706	0·211	0·191
R(*h*6*l*)	0·166	0·228	0·037	0·031
R(*hkl*) (*k* even)	0·181	0·177	0·057	0·054
R(*hkl*) (*k* odd)	0·540	0·499	0·193	0·172
N–C distance	1·179	1·176	1·217	1·195 Å
C–O distance	1·124	1·171	1·163	1·180 Å

* $r=\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w|F_c|^4$.

This is the function being minimized in the least squares calculations.

† $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

The introduction of anisotropy leads to a striking improvement. Also striking is the difference between the residuals for *k* even, which depend primarily on Ag in a fixed position, and those for *k* odd, which depend on the light atoms with variable positions and on the Ag anisotropy. The larger residuals in the odd layers arise in part from the diffractometer arrangement of counting for a fixed time rather than measuring the time for a fixed count.

Table 3. *Final positional parameters*

	x	*y*	*z*
Ag	0	0	0
N	0·7865 ± 0·0009	¼	0·2211 ± 0·0015
C	0·5792 ± 0·0012	¼	0·3259 ± 0·0017
O	0·3772 ± 0·0007	¼	0·4415 ± 0·0015

The final positional parameters are shown in Table 3 and the final thermal parameters in Table 4. The observed and calculated structure factors are listed in Table 5.

The least-squares calculations were carried out on the CDC 1604 Computer at the Numerical Analysis Center of the University of Minnesota, with programs prepared at Princeton University under the direction of Prof. R. Jacobson.

Discussion

The crystal structure of silver cyanate is shown in Fig. 1. The important interatomic distances in the crystal are listed in Table 6, together with some pertinent values in other structures.

The overall structure can be regarded as roughly corresponding to a tetragonal distortion of the caesium chloride arrangement. Within this broad picture, however, many of the details fit rather well with the idea that the Ag–N bonds are strongly covalent. The Ag atoms are linearly bonded to two nitrogen atoms so as to form infinite chains –Ag–N–Ag–N–Ag– running parallel to the *b* axis. The Ag–N distance (Table 6) is nearly as short as in silver cyanide, and the Ag–N–C angle is 128·2° (compare with 128·1° for the H–N–C angle in hydrogen isocyanate and with 125 ± 5° for the CH_3–N–C angle in methyl isocyanate (Sutton, 1958)). It is interesting to note that in crystalline hydrogen isocyanate, HNCO (von Dohlen & Carpenter, 1955), hydrogen bonds appear to be formed to adjacent nitrogen, rather than oxygen,

Table 4. *Final thermal parameters*

The standard deviations are 0·0001–0·0004 for the Ag parameters, and 0·0010–0·0042 for the light atom parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}	*B**
Ag	0·0239	0·0197	0·1051	0·0084	−0·0194	0·0270	4·04 Å^2
N	0·0228	0·0117	0·0677	0	0	0·0273	2·59
C	0·0230	0·0140	0·0569	0	0	0·0000	2·67
O	0·0113	0·0325	0·0766	0	0	0·0152	3·28

* From last cycle in which the particular atom was isotropic.

Table 5. *Observed and calculated structure factors*

HH	KK	LL	F(OBS)	F(CALC)
0	0	1	59.3	60.7
0	0	2	42.7	39.6
0	0	3	20.7	19.6
0	0	4	8.5	8.6
0	1	1	21.5	-18.8
0	1	2	7.7	6.9
0	1	3	2.3	1.0
0	2	1	68.6	70.9
0	2	2	41.2	39.1
0	2	3	18.0	18.0
0	2	4	5.7	6.8
0	3	1	16.3	14.8
0	3	2	1.4*	.1
0	3	3	3.6	2.4
0	4	1	35.3	34.4
0	4	2	24.7	23.0
0	4	3	13.7	13.3
0	5	1	3.3	-3.3
0	5	2	5.2	5.5
0	5	3	2.4	3.6
0	6	1	23.4	23.0
0	6	2	16.5	16.6
0	6	3	8.0	8.0
1	0	0	52.5	69.9
1	0	1	73.8	87.0
-1	0	1	71.7	73.0
1	0	2	39.7	38.7
-1	0	2	41.6	37.2
1	0	3	13.4	12.9
-1	0	3	24.1	23.6
1	0	4	8.2	8.0
-1	0	4	8.5	8.6
1	1	0	5.9	5.5
1	1	1	13.5	13.3
-1	1	1	1.1*	1.0
1	1	2	12.8	-11.9
-1	1	2	4.5	4.5
1	1	3	3.3	3.2
-1	1	3	2.6	2.6
1	2	0	66.2	81.8
1	2	1	40.3	41.5
-1	2	1	62.1	59.0
1	2	2	34.0	32.5
-1	2	2	44.2	41.3
1	2	3	20.4	20.1
-1	2	3	18.1	16.6
1	2	4	5.8	5.4
-1	2	4	8.0	8.0
1	3	0	5.6	-5.4
1	3	1	5.9	-5.6
-1	3	1	4.8	4.4
1	3	2	12.4	11.7
-1	3	2	3.5	2.6
1	3	3	1.8*	.4
-1	3	3	1.8*	2.3
1	4	0	36.5	38.0
1	4	1	42.6	44.2
-1	4	1	42.1	37.9
1	4	2	24.0	23.3
-1	4	2	25.8	23.8
1	4	3	8.4	8.5
-1	4	3	15.3	15.2
1	5	0	1.2	1.4
1	5	1	4.5	4.7
-1	5	1	4.5	4.2
1	5	2	2.1	-2.6
-1	5	2	5.3	5.8
1	5	3	2.4	3.1
-1	5	3	3.3	4.2
1	6	0	24.4	25.7
1	6	1	15.0	15.6
-1	6	1	22.9	22.3
1	6	2	12.9	13.1
-1	6	2	16.6	16.0
1	6	3	8.9	9.4
-1	6	3	7.9	8.3
2	0	0	58.2	66.7
2	0	1	51.3	54.4
-2	0	1	59.4	56.4
2	0	2	35.4	33.1
-2	0	2	46.5	42.8
2	0	3	18.5	17.9
-2	0	3	21.9	20.8
2	0	4	4.4	2.9
-2	0	4	10.2	10.2
2	1	0	7.6	7.5
2	1	1	2.0	-1.9
-2	1	1	13.0	11.2
2	1	2	7.4	6.5
-2	1	2	2.2	1.4
2	1	3	4.3	-3.4
-2	1	3	3.8	2.9
2	2	0	56.8	62.3
2	2	1	46.7	47.5
-2	2	1	59.5	56.7
2	2	2	25.6	26.0
-2	2	2	35.1	32.1
2	2	3	10.2	10.3
-2	2	3	17.8	17.8
2	2	4	6.6	7.7
-2	2	4	7.0	6.9
2	3	0	7.2	-7.2
2	3	1	1.2*	1.0
-2	3	1	1.2*	-.6
2	3	2	2.8	-2.5
-2	3	2	4.9	5.0
2	3	3	4.7	4.6
-2	3	3	2.0	2.5
2	4	0	36.8	36.3
2	4	1	28.8	30.2
-2	4	1	36.4	32.9
2	4	2	21.4	20.9
-2	4	2	27.6	26.0
2	4	3	11.6	11.6
-2	4	3	15.1	14.8
2	5	0	1.3	-.7
2	5	1	1.1*	.6
-2	5	1	7.2	7.1
2	5	2	3.8	4.0
-2	5	2	5.4	5.7
2	5	3	1.8*	-.6
-2	5	3	4.1	4.7
2	6	0	23.9	22.2
2	6	1	17.2	18.3
-2	6	1	21.5	21.0
2	6	2	9.9	10.1
-2	6	2	14.8	14.5
2	6	3	5.3	4.9
-2	6	3	7.7	8.1
3	0	0	53.4	55.0
3	0	1	35.4	35.6
-3	0	1	55.3	46.9
3	0	2	26.6	26.8
-3	0	2	42.6	39.2
3	0	3	11.4	10.6
-3	0	3	18.8	18.8
3	0	4	5.5	6.0
3	1	0	7.0	-6.8
3	1	1	2.9	3.0
-3	1	1	2.1	1.7
3	1	2	1.8	.7
-3	1	2	6.6	5.8
3	1	3	2.7	1.2
-3	1	3	4.3	-4.1
3	2	0	44.5	45.3
3	2	1	40.0	40.9
-3	2	1	48.0	44.8
3	2	2	20.2	19.6
-3	2	2	27.4	25.6
3	2	3	10.4	10.8
-3	2	3	17.1	16.9
3	2	4	3.5*	2.5
-3	2	4	10.4	10.5
3	3	0	3.2	.4
3	3	1	2.4	-2.6
-3	3	1	4.9	4.4
3	3	2	1.6*	.3
-3	3	2	2.8	2.5
3	3	3	1.8*	.0
-3	3	3	8.2	8.2
3	4	0	32.3	31.3
3	4	1	22.2	22.5
-3	4	1	30.8	28.9
3	4	2	16.1	16.2
-3	4	2	27.7	25.6
3	4	3	7.4	7.4
-3	4	3	12.3	13.0
3	5	0	3.9	-4.4
3	5	1	1.7	.4
-3	5	1	6.1	6.2
3	5	2	1.5*	1.1
-3	5	2	6.9	6.6
3	5	3	3.2	1.7
-3	5	3	1.8*	1.1
3	6	0	18.4	18.6
3	6	1	15.0	15.5
-3	6	1	19.3	18.1
3	6	2	9.0	9.1
-3	6	2	11.6	11.4
3	6	3	4.4	4.6
-3	6	3	9.0	8.8
4	0	0	36.9	34.5
4	0	1	30.4	30.8
-4	0	1	48.7	48.0
4	0	2	17.0	16.0
-4	0	2	24.2	23.3
4	0	3	9.7	9.0
-4	0	3	14.7	14.4
4	0	4	3.0	3.0
4	1	0	6.4	-6.3
4	1	1	1.6*	.8
-4	1	1	2.5	2.1
4	1	2	2.4	-.2
-4	1	2	5.6	-4.6
4	1	3	2.5	1.0
-4	1	3	4.5	4.5
4	2	0	37.8	38.0
4	2	1	26.9	26.4
-4	2	1	26.7	24.6
4	2	2	16.7	17.2
-4	2	2	30.1	28.6
4	2	3	7.0	7.0
-4	2	3	15.8	16.5
-4	2	4	7.1	6.5
4	3	0	1.7	1.0
4	3	1	1.7	-1.8
-4	3	1	4.9	4.6
4	3	2	2.0	.2
-4	3	2	10.1	9.8
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4	4	2	10.7	10.8
-4	4	2	16.4	16.3
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-4	4	3	9.8	10.1
4	5	0	6.3	-6.0
4	5	1	1.6*	-.6
-4	5	1	3.9	4.6
4	5	2	1.7*	.4
-4	5	2	1.9*	1.8
4	5	3	2.9	.8
-4	5	3	4.4	5.7
4	6	0	15.8	15.2
4	6	1	12.1	12.2
-4	6	1	11.9	11.4
4	6	2	7.0	7.3
-4	6	2	13.8	13.5
5	0	0	35.5	34.3
5	0	1	21.5	20.9
-5	0	1	22.6	22.0
5	0	2	10.6	10.4
-5	0	2	22.1	22.3
5	0	3	6.5	6.3
-5	0	3	11.7	12.4
5	1	0	3.5	3.4
5	1	1	5.8	-6.3
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5	1	2	2.0	1.4
-5	1	2	3.8	3.2
5	1	3	2.5*	.1
-5	1	3	2.0*	1.6
5	2	0	20.6	18.9
5	2	1	19.2	18.8
-5	2	1	30.8	29.9
5	2	2	12.8	13.0
-5	2	2	19.2	19.2
-5	2	3	12.3	13.0
5	3	0	6.2	-6.1
5	3	1	3.8	3.4
-5	3	1	5.6	5.7
5	3	2	1.8*	-1.1
-5	3	2	2.8	2.8
-5	3	3	2.9*	2.8
5	4	0	23.0	22.2
5	4	1	15.3	14.1
-5	4	1	15.6	15.3
5	4	2	6.0	6.8
-5	4	2	14.5	15.1
-5	4	3	9.1	9.4
5	5	0	1.8*	-.8
5	5	1	4.2	-4.2
-5	5	1	3.4	3.0
5	5	2	2.2	.3
5	6	0	9.2	8.8
5	6	1	8.4	8.1
-5	6	1	14.4	13.8
6	0	0	17.8	17.1
6	0	1	17.6	15.1
-6	0	1	19.9	20.0
6	0	2	10.7	10.4
-6	0	2	14.6	14.7
-6	0	3	11.4	12.2
6	1	0	1.8*	-2.3
6	1	1	3.5	3.3
6	1	2	2.8	-2.6
-6	1	2	3.5	3.4
-6	1	3	1.9*	.9
6	2	0	20.0	19.0
6	2	1	11.9	12.0
-6	2	1	17.8	17.9
6	2	2	6.1	5.7
-6	2	2	14.9	16.1
6	3	0	2.4	-1.5
6	3	1	3.0	-4.0
-6	3	1	3.9	4.1
6	3	2	3.3	1.8
-6	3	2	3.1	1.9
6	4	0	11.7	11.6
6	4	1	11.1	10.5
-6	4	1	13.8	13.8
6	4	2	7.5	7.1
-6	4	2	10.5	10.9
7	0	0	12.3	11.2
7	0	1	9.6	10.0
-7	0	1	13.5	14.0
7	1	0	2.0*	.5
7	1	1	2.6*	-.9
-7	1	1	2.0*	3.2
7	2	0	13.0	12.9
7	2	1	5.5	7.9
-7	2	1	12.7	12.3

* indicates unobserved reflexion

Table 6. *Comparison of bond lengths*

Bond	Length	Compound	Reference
Ag–N	2·115 ± 0·008 Å	AgNCO	This work
	2·561 ± 0·008	AgN_3	Dewing & Hughes (1962)
	2·05*	AgCN	Natta & Vecchia (1933)
Ag–O	2·996 ± 0·008	AgNCO	This work
	2·46	$AgClO_4 . 3\,C_4H_8O_2'$	Prosen & Trueblood (1956)
	2·05	Ag_2O	Sutton (1958)
N–C	1·195 ± 0·011	AgNCO	This work
	1·207 ± 0·010	HNCO	Sutton (1958)
	1·19 ± 0·03	CH_3NCO	Sutton (1958)
C–O	1·180 ± 0·011	AgNCO	This work
	1·171 ± 0·010	HNCO	Sutton (1958)
	1·18 ± 0·03	CH_3NCO	Sutton (1958)

* This value is based on the unit-cell constant and an assumed C–N distance of 1·15 Å.

atoms, so that similar chains ··· H–N ··· H–N ··· H– also occur in this structure. The difference is that, whereas the silver atoms lie midway between two nitrogen atoms, the hydrogen atoms are probably displaced from the midway position.

The N–C and C–O distances are the same, within experimental error, as these distances in covalent isocyanates. The two Ag atoms bonded to each nitrogen atom do not lie far from coplanarity with the corresponding cyanate group (Ag–N–Ag, 97·7°; sum of angles at nitrogen = 354°). All these features are compatible with approximate sp^2 hybridization of the nitrogen atom. The cyanate group is linear within experimental error (the angle N–C–O = 178·2°).

Fig. 2 shows the relative amplitudes of vibration of the atoms. The anisotropies are clearly related to packing arrangement and bond directions. The vibration of the Ag atom is larger and nearly uniform in the plane perpendicular to the N–Ag–N line, and smaller parallel to this line. The vibration of the light atoms in the plane perpendicular to the axis of the cyanate group is greater than the vibration parallel to this axis; the amplitudes increase in the order N, C, O, nicely reflecting that N is bonded to Ag and, therefore, held in place, while the other end of the ion is held only by ionic and packing forces.

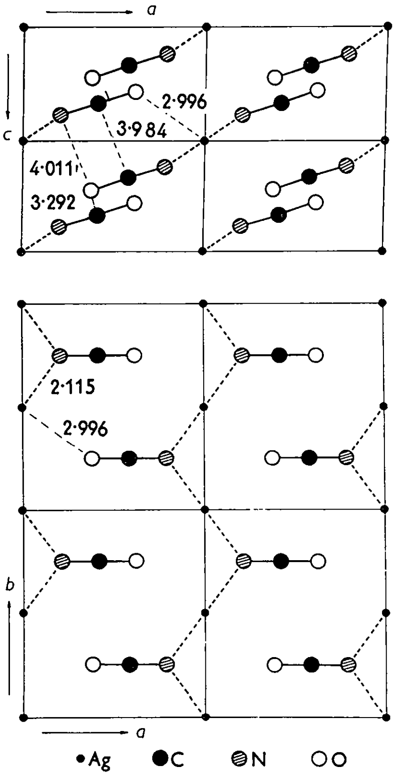

Fig. 1. The crystal structure of AgNCO, with interatomic distances (Å).

A comment on nomenclature seems appropriate. This compound has been variously named silver cyanate and silver isocyanate, with a strong preference, based on historical precedent, for the former. According to its crystal structure, it is silver isocyanate, but there seems little point in attempting to change the common usage.

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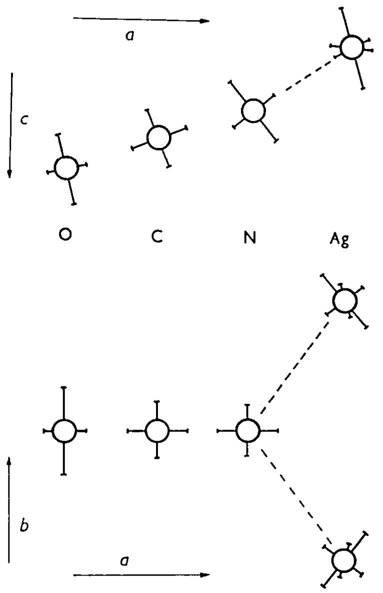

Fig. 2. Anisotropic thermal motion in AgNCO. The atoms in the figure have the same orientation as in Fig. 1. The lengths of the lines correspond to *twice* the root mean square amplitudes of vibration for the principal axes of the ellipsoids of vibration.

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