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The Crystal Structure of AgCN . 2 $AgNO_3$

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AgCN . $2AgNO_3$ is monoclinic, $a=6·202$, $b=11·343$, $c=7·274$ Å, $\beta=45·55°$, $Z=2$, space group $P2_1/c$. The structure has been determined, and has been refined by least-squares analysis of three-dimensional counter data. Approximately linear chains, –Ag–CN–Ag–CN–Ag– can be identified, running parallel to [10$\bar{1}$] with Ag–CN = 2·06 Å and C–N = 1·20 Å. The NO_3 groups and the remaining Ag atoms are packed between these chains. There is no evidence for Ag_2CN complex ions.

Introduction

In the course of an attempt to prepare a small amount of silver fulminate (Britton & Dunitz, 1965), a few crystals of another silver-containing substance were obtained. There was too little for a chemical analysis, and since it was felt that any silver-containing product in this system was interesting we decided to attempt to determine its nature by X-ray analysis. After the space group and unit cell had been determined and the Ag positions located from Patterson and electron-density projections, we found a report of a partial determination of the structure of AgCN . $2AgNO_3$ (Lindqvist, 1954) which suggested strongly that this was our compound. Since Professor Lindqvist informed us that he did not intend to complete the structure determination, and since it seemed surprising that cyanide should have been formed under the oxidizing conditions of our preparation, we completed the structure determination on our crystal, which was indeed AgCN . $2AgNO_3$, and which is described below.

Experimental

The crystals used were prepared by mixing 4 drops of a silver nitrate stock solution (7 g $AgNO_3$, 12 g concentrated nitric acid, 20 g water), 3 drops of concentrated nitric acid, and a few drops of ethanol, heating the mixture until all the silver nitrate dissolved, and allowing the solution to evaporate to dryness at room temperature. One large prism, with unmistakable $2/m$ symmetry, and a few small needles were left. When one of the crystals was heated strongly in a reducing flame a residue of silver metal was observed. No other analysis was attempted.

Our crystal data are compared in Table 1 with those of Lindqvist. The cell constants were determined from precession photographs (Mo $K\alpha=0·7107$ Å). The space group was determined from precession and Weissenberg photographs.

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

	This work	Lindqvist* (1954)	This work†
a	6·202 ± 0·010 Å	6·20 Å	6·202 Å
b	11·343 ± 0·019	11·34	11·343
c	5·310 ± 0·009	5·30	7·274
β	102·05 ± 0·15°	101·95°	45·55°
Z	2	2	2
D_{calc}	4·305 g.cm^{-3}		
Vol.	365·3 Å^3		
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$

* a and c are interchanged to agree with our labelling.

† This setting was necessary in order to use the least-squares program available to us, and is the reference set for all the following tables and discussion.

The needles and the prism were different habits of the same crystal. The prism was slightly elongated along [10$\bar{1}$] with {111} prominently, {131} less prominently, and {10$\bar{1}$} barely developed, and terminated by {100}. The needles were elongated along [10$\bar{1}$].

Determination and refinement of the structure

The *hkh* reflexions were recorded from the needle-like crystal (dimensions 0·03 × 0·03 × 0·3 mm) on zero-layer

Table 2. *Final positional parameters and isotropic temperature factors*

Standard deviations (given on the line below for the significant figures only) are from a diagonal approximation and are optimistic

	Position	x	y	z	B*
Ag(1)	2(a)	0	0	0	5·02
					0·03
Ag(2)	4(e)	0·3264	0·1168	0·2980	3·47
		1	1	1	0·01
O(1)	4(e)	0·8014	0·2680	0·0549	4·28
		11	6	9	0·14
O(2)	4(e)	0·7958	0·4149	0·2487	3·90
		10	5	9	0·13
O(3)	4(e)	0·3937	0·3008	0·4562	4·14
		10	7	10	0·14
N	4(e)	0·6736	0·3257	0·2460	2·74
		10	6	9	0·13
CN	4(e)	0·6060	0·0017	0·3853	3·13
(average)		10	8	10	0·14

* From last cycle in which the atom was isotropic.

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Table 3. *Anisotropic thermal parameters* ($\times 10^4$)

Standard deviations are given in brackets.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Ag(1)	688 (3)	119 (1)	500 (2)	1 (3)	27 (1)	−939 (3)
Ag(2)	517 (1)	53 (1)	390 (1)	−44 (2)	35 (2)	−662 (1)
O(1)	796 (17)	74 (6)	483 (11)	36 (19)	−81 (16)	−1048 (16)
O(2)	704 (16)	42 (5)	533 (12)	−5 (15)	30 (12)	−1028 (16)
O(3)	471 (18)	95 (7)	457 (15)	−33 (19)	−42 (17)	−678 (20)
N	579 (18)	36 (5)	377 (12)	−19 (17)	40 (13)	−819 (17)
CN (average)	367 (14)	72 (6)	402 (13)	53 (18)	−31 (18)	−674 (13)

Weissenberg photographs (Cu *Kα* radiation), the 0*kl* reflexions from the large prism-like crystal on zero-layer precession photographs (Mo *Kα* radiation). The relative intensities were estimated visually. Patterson projections were prepared and the positions of the Ag atoms determined. From the cell volume, we had expected the cell to contain four Ag atoms together with four anions, each containing five or six atoms. However, the Patterson projections told us clearly that there were six Ag atoms (Fig. 1). In the subsequent electron-density projections, a set of nitrate groups in fourfold general positions could be identified, but the nature of the two remaining anions required for electric neutrality remained obscure.

It was at this point that Lindqvist's work was discovered; we decided to complete the structure analysis of our crystal in order to confirm the surprising suggestion that cyanide had been formed in the reaction mixture. It did not seem likely that Lindqvist had a cyanide and we had a cyanate or fulminate, but it was remotely possible and we wished to make sure. Therefore, we collected three-dimensional data with the semi-automatic linear diffractometer of Arndt & Phillips (1961), using Mo radiation with balanced filters. The previous needle-like crystal was used. Data were collected for seven layers perpendicular to [10$\bar{1}$] out to sin $\theta \sim 30°$. Measurements were made of 855 independent reflexions, of which 177 had an intensity less than twice the standard deviation of the measurement. These latter, which we have labelled unobserved reflexions in Table 5, were included in the subsequent least-squares calculations with assigned intensities equal to their standard deviations or observed values, whichever was larger. Lorentz and polarization corrections were applied, but no correction was made for absorption (linear absorption coefficient = 77·5 cm^{-1}).

A three-dimensional Fourier map with phases determined by the silver atoms revealed all of the light atoms unambiguously. The peak heights were: Ag(1), 109 e.Å^{-3}; Ag(2), 131; O(1), 11·6; O(2), 11·6; O(3), 10·6; N, 11·0; CN(average), 10·6; with the next highest peak of height 6·2 e.Å^{-3}.

Full-matrix least-squares refinement gave $R=0·148$, $r=0·055$* for all atoms isotropic; $R=0·126$, $r=0·031$

Table 4. *Amplitudes and direction angles* of the ellipsoids of vibration*

	$\langle u^2\rangle^{\frac{1}{2}}$	φ	ψ	ω
Ag(1)	0·281	38·7	19·4	75·4
	0·268	115·1	106·9	71·6
	0·211	25·1	99·2	23·8
Ag(2)	0·235	104·4	74·4	60·7
	0·215	17·2	95·3	29·6
	0·181	99·2	163·5	86·9
O(1)	0·29	121	102	77
	0·23	56	145	61
	0·17	49	58	33
O(2)	0·28	109	87	64
	0·20	27	70	33
	0·16	72	160	71
O(3)	0·27	67	135	46
	0·24	100	55	63
	0·19	157	114	124
N	0·25	118	84	73
	0·16	50	43	51
	0·13	53	133	44
CN(average)	0·24	94	116	54
	0·21	82	28	66
	0·12	9	99	46

* φ, ψ and ω are the angles between the ellipsoid axes and the positive directions of *a*, *b*, and *c*, respectively.

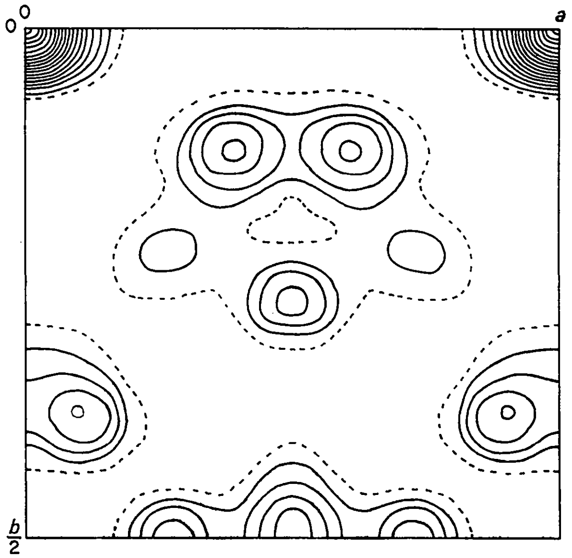

Fig. 1. Patterson projection along [10$\bar{1}$]. This corresponds to the bottom view in Fig. 2.

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* $r=\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4$ with $w=1$ for $F_o\le 39$, $w=(39/F_o)^4$ for $F_o>39$. The numerator of r is the quantity refined in the least-squares calculation.

for Ag only anisotropic; $R=0{\cdot}122$, $r=0{\cdot}029$ for all atoms anisotropic.[†]

The final positional parameters are given in Table 2 and the final anisotropic thermal parameters in Table 3. The latter have been converted to the parameters of the ellipsoids of vibration in Table 4. The observed and calculated structure factors are given in Table 5.

Discussion

The structure is shown in Fig. 2. Interatomic distances are given in Table 6 along with selected values from other compounds for comparison. The structure does not suggest any obvious reason for the existence of the mixed compound. Certainly no Ag_2CN groups are present. The molar volume, $182{\cdot}6 \pm 0{\cdot}5$Å^3 per AgCN . $2AgNO_3$ is only slightly less than the sum $184{\cdot}2$ Å^3 $= 54{\cdot}5$ Å^3 (AgCN, West, 1935) plus $2 \times 64{\cdot}8$ Å^3 ($AgNO_3$, Swanson, Gilfrich & Ugrinic, 1955).

The structure consists of infinite parallel chains –Ag–CN–Ag–CN – in the $[10\bar{1}]$ direction (the direction of elongation of the needles) with Ag atoms and NO_3 groups packed between the chains. These chains are very similar to those that have been suggested to occur in AgCN itself; the Ag–Ag distance here is 5·30 Å, in AgCN it is 5·26 Å. The chains are in an approximately hexagonal array about 6 Å apart. Except for one Ag at 2·58 Å from a CN group (with a CN–CN–Ag angle of 95°) none of the $AgNO_3$ atoms are closer than 3 Å to the Ag–CN chain. The chain is distorted slightly from linearity in the direction of the external Ag atoms.

The NO_3 group does not have the expected D_{3h} symmetry. The variation in the bond lengths, 1·202 to 1·309 Å, is greater than can be explained in terms of the standard deviation of 0·010 Å, even if allowance is made for the optimistic estimate of the diagonal ap-

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[†] To study the quality of the counter data, refinement was also carried out omitting the unobserved reflexions. At the end of this refinement all of the parameters were the same within one standard deviation (the positional parameters within one half a standard deviation) with $R=0{\cdot}102$, $r=0{\cdot}031$ for Ag anisotropic, and $R=0{\cdot}091$, $r=0{\cdot}028$ for all atoms anisotropic. Inspection showed 56 reflexions with a discrepancy of a factor of 2 or greater between F_o and F_c. Of these, 52 have $F_o \le 4\sigma(F_o)$ and the other four ($\bar{1}04$, $\bar{1}13$, $\bar{1}14$, and $\bar{1}23$) are almost certainly measuring errors. If these 56 reflexions are omitted $R=0{\cdot}079$ for all atoms anisotropic.

Table 5. *Observed and calculated structure factors*

Items in order are h, k, l, F_o, F_c *indicates $F_o < 2\sigma(F_o)$

	0	2	43.6	-47.0
0	0	4	54.7	56.8
0	0	6*	5.0	7.9
0	1	1	36.1	34.6
0	1	2	45.6	45.8
0	1	3	96.8	99.2
0	1	4	36.1	-37.3
0	1	5	12.6	-10.7
0	1	6	11.6	13.5
0	2	0	76.7	73.8
0	2	1	105.5	-105.6
0	2	2	24.0	23.4
0	2	3	41.8	43.1
0	2	4	20.6	18.8
0	2	5	7.5	4.6
0	2	6	7.1	7.0
0	3	1	76.3	73.3
0	3	2	57.9	57.0
0	3	3*	4.6	-4.0
0	3	4	41.4	-39.7
0	3	5	38.7	35.1
0	3	6	18.1	15.9
0	4	0	52.1	-53.3
0	4	1	35.3	-33.7
0	4	2	164.7	157.4
0	4	3*	4.5	2.6
0	4	4	9.5	-4.4
0	4	5	10.4	-7.2
0	4	6*	4.3	1.0
0	5	1	80.9	76.6
0	5	2	38.8	-37.3
0	5	3	16.7	-14.0
0	5	4	19.3	18.5
0	5	5	38.7	37.9
0	5	6	12.1	-9.7
0	6	0	15.0	10.5
0	6	1	106.1	101.0
0	6	2	57.7	55.6
0	6	3	36.8	-32.3
0	6	4	10.8	3.5
0	6	5	11.0	3.9
0	6	6*	7.5	4.6
0	7	1	14.5	13.8
0	7	2	31.7	-32.0
0	7	3	44.5	41.5
0	7	4	40.9	36.2
0	7	5*	6.9	-2.1
0	7	6	14.8	-13.6
0	8	0	101.3	97.6
0	8	1	24.1	23.0
0	8	2	20.9	-20.6
0	8	3	17.2	-19.0
0	8	4	20.0	12.7
0	8	5*	6.2	1.1
0	8	6*	7.6	7.7
0	9	1	9.4	-6.2
0	9	2*	6.7	9.0
0	9	3	44.8	44.6
0	9	4	15.5	-15.0
0	9	5	19.7	-13.6
0	9	6*	6.1	2.4
0	10	0	55.3	55.2
0	10	1	56.8	-58.0
0	10	2	10.2	-10.0
0	10	3	23.6	26.6
0	10	4	18.2	14.4
0	10	5	9.9	-1.5
0	10	6*	7.9	1.0
0	11	1	14.8	17.3
0	11	2	25.0	24.0
0	11	3*	7.8	1.9
0	11	4	25.0	-20.2
0	12	0	19.0	-16.6
0	12	1	22.7	-20.9
0	12	2	16.6	21.8
0	12	3*	8.2	9.1
0	12	4*	8.4	.7
0	13	2*	7.8	-5.3
0	13	3	15.9	-15.8
0	14	0	19.0	-15.4
0	14	1	23.5	24.1
1	0	0	29.4	-27.5
1	0	2	182.4	216.6
-1	0	2	15.3	19.6
1	0	4	28.2	-29.7
-1	0	4	16.9	36.6
1	0	6	50.1	44.5
-1	1	0	56.7	-57.2
1	1	1	26.3	-23.1
-1	1	1	155.3	172.5
1	1	2	13.5	10.6
-1	1	2	42.0	-57.0
1	1	3	93.3	90.5
-1	1	3	5.7	-30.0
1	1	4	6.3	7.5
-1	1	4	5.4	12.2
1	1	5	29.7	28.0
-1	1	5	9.7	16.8
1	1	6	23.7	-21.9
1	1	7	8.1	-3.9
1	2	0	72.7	67.3
1	2	1	95.9	93.8
-1	2	1	29.1	28.6
1	2	2	49.6	49.3
-1	2	2	51.5	52.7
1	2	3	118.1	-118.3
-1	2	3	11.1	24.7
1	2	4	22.5	25.1
-1	2	4	17.9	23.2
1	2	5	44.2	42.6
-1	2	5	18.0	-19.8
-1	2	6	10.8	12.9
1	2	7	14.2	-9.3
1	3	0	96.5	-93.8
1	3	1	179.3	185.8
-1	3	1	12.9	-13.8
1	3	2	32.3	32.7
-1	3	2	49.8	-53.7
1	3	3	31.5	33.0
-1	3	3	40.8	55.6
1	3	4	18.7	17.6
-1	3	4	25.2	22.0
1	3	5	10.9	6.8
-1	3	5	7.5	-.6
1	3	6	18.3	-15.0
1	3	7	13.6	13.0
1	4	0	105.3	105.1
1	4	1	56.7	54.1
-1	4	1*	5.0	4.5
1	4	2	49.9	-49.5
-1	4	2	42.6	40.0
1	4	3	13.0	-15.7
-1	4	3	7.2	-2.8
1	4	4	111.3	107.6
-1	4	4	14.2	-11.4
1	4	5	17.1	14.9
-1	4	5*	4.8	-1.6
1	4	6	11.1	-7.6
1	4	7	10.2	-4.6
1	5	0	66.6	64.3
1	5	1	131.4	130.1
-1	5	1	59.4	-55.8
1	5	2	21.8	-18.3
-1	5	2	30.4	28.5
1	5	3	14.8	11.3
-1	5	3	49.9	50.7
1	5	4	9.8	-10.4
-1	5	4	17.6	-10.4
1	5	5	7.9	-.9
-1	5	5	7.5	-5.1
1	5	6*	7.2	9.1
1	5	7	15.6	16.1
1	6	0	33.7	34.0
1	6	1	91.5	-90.0
-1	6	1	7.5	-5.5
1	6	2	9.2	6.7
-1	6	2	30.9	28.1
1	6	3	68.6	65.4
-1	6	3	21.1	-17.9
1	6	4	35.2	33.9
-1	6	4	10.6	6.2
1	6	5	40.2	-38.2
-1	6	5	16.1	13.9
1	6	6*	6.3	3.5
1	6	7	10.5	6.8
1	7	0	60.7	63.7
1	7	1	32.3	30.7
-1	7	1	65.2	58.2
1	7	2	49.5	-48.2
-1	7	2	61.4	57.1
1	7	3	30.2	28.4
-1	7	3*	6.4	-1.0
1	7	4	10.2	-5.4
-1	7	4	24.4	-20.9
1	7	5	18.8	20.6
-1	7	5*	7.3	4.4
1	7	6	16.3	12.3
1	7	7*	8.1	-2.8
1	8	0	8.1	-4.0
1	8	1	19.2	-20.1
-1	8	1	14.3	-18.2
1	8	2	83.8	84.3
-1	8	2	11.4	10.1
1	8	3	30.2	30.1
1	8	4	21.1	-23.0
-1	8	4	26.9	23.7
1	8	5	14.3	-14.8
1	8	6	22.6	19.0
1	8	7*	7.4	3.8
1	9	0	20.4	-23.0
1	9	1	20.4	-20.6
-1	9	1	61.1	64.5
1	9	2	23.6	21.9
-1	9	2	21.5	-21.7
1	9	3	19.2	17.6
-1	9	3	21.7	-20.3
-1	9	4	10.9	5.4
1	9	5	14.0	15.4
1	9	6	10.7	-4.7
1	9	7	10.1	-7.9
1	10	0*	5.8	-5.5
1	10	1	31.8	33.1
-1	10	1	13.5	10.1
1	10	2	30.6	30.5
-1	10	2*	10.7	8.9
1	10	3	43.7	-42.3
-1	10	3	13.9	12.3
1	10	4*	7.5	-8.6
-1	10	4	10.3	9.0
1	10	5	22.6	19.9
1	10	6	17.9	12.7
1	10	7	11.6	-4.3
1	11	0	44.8	-47.4
1	11	1	14.9	15.1
1	11	2	22.2	21.9
-1	11	2	35.9	-34.7
1	11	3	15.9	19.4
-1	11	3	11.6	1.5
-1	11	4	17.8	13.2
1	11	5*	8.1	-3.3
1	12	0	22.1	20.7
1	12	1	19.0	16.6
-1	12	1*	8.7	4.2
1	12	2	16.6	-20.7
-1	12	2*	8.8	11.8
1	12	3	17.8	-17.7
-1	12	3	13.2	.5
1	12	4	22.3	26.4
1	12	5	12.6	8.2
1	13	0*	10.4	10.7
1	13	1	27.0	28.8
-1	13	1	20.1	-21.1
1	13	2	12.1	-6.2
-1	13	2*	7.8	5.4
1	13	4*	7.2	-.0
1	14	0*	10.9	13.6
1	14	1	17.8	-15.4
-1	14	1*	8.2	-.2
1	14	2	16.1	-15.2
2	0	0	38.4	-38.2
2	0	2	111.6	108.6
-2	0	2	85.6	81.2
2	0	4	82.5	82.7
-2	0	4	12.3	-16.7
2	0	6	20.6	-19.6
2	0	8	23.3	19.7
2	1	0	88.5	82.2
2	1	1	144.4	149.8
-2	1	1	8.5	5.5
2	1	2	49.2	-46.1
-2	1	2	8.3	6.8
2	1	3	40.6	-37.6
-2	1	3	19.0	19.4
2	1	4	67.0	66.3
-2	1	4	5.4	5.0
2	1	5	66.0	64.3
2	1	6	11.9	-5.4
2	1	7	10.4	9.9
2	1	8	11.7	-4.6
2	2	0	54.6	54.8
2	2	1	28.9	26.5
-2	2	1	53.5	50.5
2	2	2	96.6	94.5
-2	2	2	22.8	23.7
2	2	3	60.3	57.4
-2	2	3	37.7	-34.3
2	2	4	52.7	48.2
-2	2	4	7.3	3.0
2	2	5	61.7	-60.7
2	2	6	13.4	10.4
2	2	7	29.6	28.2
2	2	8	10.8	6.2
2	3	0	65.1	63.8
2	3	1	38.9	-38.2
-2	3	1	64.7	62.3
2	3	2	142.0	-144.0
-2	3	2	20.6	21.4
2	3	3	131.9	128.0
-2	3	3	7.8	10.0
2	3	4	55.2	51.7
-2	3	4*	4.2	1.8
2	3	5*	6.9	9.0
2	3	6	20.2	-18.5
2	3	7	17.4	16.2
2	3	8*	5.8	-1.4
2	4	0	105.7	98.4
2	4	1	10.9	-8.6
-2	4	1	12.2	13.5
2	4	2	50.6	49.7
-2	4	2	38.7	-38.1
2	4	3*	7.6	4.2
-2	4	3	8.6	-5.3
-2	4	4	27.6	24.6
2	4	5	10.0	-10.7
2	4	6	48.5	48.4
2	4	7	9.5	5.3
2	4	8	10.9	-7.7
2	5	0	24.8	-22.9
2	5	1	35.4	-34.3
-2	5	1	68.6	65.2
2	5	2	54.4	51.6
-2	5	2	9.2	-2.4
2	5	3	92.9	93.9
-2	5	3	18.6	14.2
2	5	4	18.5	-17.1
-2	5	4	7.8	-5.0
2	5	5*	6.4	-5.5
2	5	6	8.1	1.6
2	5	7	8.5	6.8
2	5	8*	8.5	3.1
2	6	0	50.5	49.9
2	6	1	23.0	-23.9
-2	6	1	53.6	-52.0
2	6	2	41.8	40.5
-2	6	2	8.3	1.9
2	6	3	25.3	-24.8
-2	6	3	30.6	26.7
2	6	4	11.6	14.3
-2	6	4	12.5	10.3
2	6	5	33.4	35.2
2	6	6	15.9	13.7
2	6	7	28.2	-21.8
2	6	8*	7.8	-1.5
2	7	0	61.9	-60.2
2	7	1	57.9	56.0
2	7	2	82.9	81.8
-2	7	2	21.5	-20.2
2	7	3	10.5	-9.1
-2	7	3	8.1	4.9
2	7	4	56.0	-56.9
-2	7	4	9.0	-2.3
2	7	5	33.3	33.7
2	7	6	15.8	13.0
2	7	7	11.4	9.5
2	8	0	16.1	-12.2
-2	8	1*	7.5	-10.3
2	8	2	25.3	25.2
-2	8	2	31.6	32.3
2	8	3	13.6	-9.7
-2	8	3	9.5	9.4
2	8	4	53.3	54.2
2	8	5	15.5	12.3
2	8	6	15.2	-16.5
2	9	0	6.3	7.0
2	9	1	65.3	66.2
2	9	2	23.7	-20.3
-2	9	2*	7.6	.1
2	9	3	31.6	-32.9
-2	9	3*	7.8	7.8
2	9	4	13.2	9.3
2	9	5	28.6	28.2
2	9	6	9.9	-1.8
2	10	1	15.0	18.4
-2	10	1	32.1	31.8
2	10	2	20.7	18.5
-2	10	2	16.5	18.1
2	10	3*	9.2	1.5
-2	10	3	24.9	-18.5
2	10	4	14.6	14.8
2	10	5	19.0	-20.8
2	10	6*	8.7	-7.0
2	11	0	32.3	33.9
2	11	1	11.0	-2.3
-2	11	1*	7.8	6.2
2	11	2	42.9	-43.6
-2	11	2	14.9	8.1
2	11	3	15.2	13.8
-2	11	3	10.9	6.6
2	11	4	30.3	28.7
2	11	5*	7.5	7.2
2	12	0	16.1	18.5
2	12	1*	6.6	6.4
-2	12	1*	7.6	7.7
2	12	2	12.6	14.9
-2	12	2	17.5	-13.0
2	12	3	14.5	9.0
2	12	4	10.9	-11.6
2	13	0*	7.9	-3.2
2	13	1	30.5	-26.7
-2	13	1	16.4	19.9
2	13	2*	11.8	4.6
2	13	3	30.5	34.2
2	14	0*	7.4	11.2
2	14	1	9.1	-12.1
3	0	0	110.0	108.5
3	0	2	60.4	-59.0
-3	0	2	21.9	-12.3
3	0	4	91.6	92.6
3	0	6	34.4	36.4
3	0	8	10.8	-.3
3	1	0	10.7	-8.0
3	1	1	50.4	45.2
-3	1	1	7.8	-1.9
3	1	2	35.9	32.1
-3	1	2	21.8	19.8
3	1	3	123.2	121.5
-3	1	3	21.6	19.1
3	1	4	52.5	-53.2
3	1	5	9.1	-9.3
3	1	6	48.6	45.4
3	1	7	37.0	35.2
3	1	8	13.5	-8.4
3	1	9*	5.7	-.2
3	2	0	41.6	36.6
3	2	1	100.2	-95.8
-3	2	1	45.0	-43.2
3	2	2	51.3	46.8
-3	2	2	17.6	13.7
3	2	3	73.6	70.8
-3	2	3	9.5	10.6
3	2	4	33.0	32.3
3	2	5	16.3	-13.4
3	2	6	32.6	29.7
3	2	7	16.4	-15.3
3	2	8	6.7	5.3
3	2	9	15.1	11.1
3	3	0	14.6	9.0
3	3	1	39.2	37.2
-3	3	1	31.1	26.8
3	3	2	49.8	50.0
-3	3	2	15.0	12.0
3	3	3*	6.6	3.8
-3	3	3	9.0	-5.7
3	3	4	85.7	-79.3
3	3	5	65.5	64.4
3	3	6	36.0	36.3
3	3	7	12.7	-7.7
3	3	8	22.1	-16.7
3	3	9	11.1	7.4
3	4	0	40.4	-37.8
3	4	1	21.2	-24.2
-3	4	1	22.2	-19.2

Table 5 (*cont.*)

3	4	2	105.4	104.5
-3	4	2	33.9	33.6
3	4	3	34.7	34.0
-3	4	3*	4.8	3.9
3	4	4	12.6	-8.9
3	4	5	18.0	-15.8
3	4	6	18.6	18.8
3	4	7*	7.2	2.9
3	4	8	19.8	22.5
3	4	9	11.4	-.8
3	5	0	12.7	-10.9
3	5	1	46.8	48.9
-3	5	1	29.3	27.8
3	5	2	16.7	-15.2
-3	5	2	11.6	-10.6
3	5	3	14.0	13.0
-3	5	3	15.9	-9.7
3	5	4	31.8	34.2
3	5	5	75.7	78.8
3	5	6	19.4	-18.9
3	5	7	10.9	-11.2
3	5	8	9.4	6.3
3	5	9	13.3	7.7
3	6	0	21.0	15.2
3	6	1	60.1	60.8
-3	6	1	37.8	36.4
3	6	2	36.8	36.6
-3	6	2	9.0	14.4
3	6	3	62.2	-60.6
-3	6	3	14.5	-7.6
3	6	4	31.6	32.5
3	6	5	9.8	7.4
3	6	6*	6.9	10.8
3	6	7	11.8	8.1
3	6	8	13.1	11.1
3	6	9*	10.7	-8.5
3	7	1	9.1	11.5
-3	7	1*	7.9	-2.0
3	7	2	35.4	-34.2
-3	7	2	14.4	-13.3
3	7	3	44.4	43.8
3	7	4	47.4	46.6
3	7	5	11.4	-10.2
3	7	6	37.3	-37.8
3	7	7	16.6	14.4
3	7	8	15.4	11.4
3	8	0	47.9	48.2
3	8	1	28.9	27.5
-3	8	1	16.2	15.9
3	8	2	37.7	-38.7
-3	8	2	11.4	-6.4
3	8	3	24.6	-23.0
3	8	4	32.3	30.2
3	8	5	14.3	12.5
3	8	6	17.2	17.0
3	8	7*	7.1	-.7
3	9	0	10.2	9.8
3	9	1*	7.2	7.9
-3	9	1	10.3	-4.6
3	9	2*	8.4	3.3
-3	9	2	11.7	7.2
3	9	3	55.3	57.7
3	9	4	12.6	-9.6
3	9	5	18.3	-21.5
3	9	7	22.0	21.6
3	10	0	21.3	24.9
3	10	1	33.3	-36.5
-3	10	1	20.3	-21.3
3	10	2*	6.2	-3.9
3	10	3	28.4	26.8
3	10	4	17.3	19.5
3	10	5*	8.0	-10.2
3	10	6*	10.7	8.7
3	10	7	12.1	-8.2
3	11	0	8.1	2.5
3	11	1*	7.3	6.8
-3	11	1	14.6	6.0
3	11	2	18.4	14.6
3	11	3*	7.4	1.8
3	11	4	29.3	-31.0
3	11	5	15.8	13.9
3	11	6	19.1	19.3
3	12	0	16.0	-15.0
3	12	1*	10.9	-16.5
3	12	2	26.7	26.5
3	12	3	14.8	11.0
3	12	4*	6.1	-7.3
3	13	1*	10.3	10.6
3	13	3	15.6	-13.9
3	13	4*	6.4	1.2
4	0	0*	6.9	-5.8
4	0	2	82.2	84.7
-4	0	2	9.7	-.5
4	0	4	50.3	-48.5
4	0	6	66.2	65.1
4	0	8*	6.4	-2.5
4	0	10	10.2	2.2
4	1	0	29.3	-27.1
4	1	1*	7.8	-7.5
-4	1	1	36.9	33.4
4	1	2	22.2	19.3
-4	1	2	13.3	-12.4
4	1	3	44.1	43.0
4	1	4	11.9	-8.7
4	1	5	50.8	48.7
4	1	6	23.0	-26.4
4	1	7*	7.3	-1.3
4	1	8	21.8	18.4
4	1	9	22.8	20.6
4	1	10*	7.8	-6.4
4	2	0	16.8	12.8
4	2	1	37.6	37.1
4	2	2	50.1	48.3
-4	2	2*	6.2	4.2
4	2	3	77.5	-77.6
4	2	4	58.1	57.5
4	2	5	61.2	61.8
4	2	6	33.9	35.4
4	2	7	28.7	-26.8
4	2	8	15.0	10.7
4	2	9*	6.9	-.3
4	2	10*	9.7	2.5
4	3	0	32.9	-32.7
4	3	1	60.7	60.7
-4	3	1	11.8	-4.8
4	3	2	43.8	43.5
-4	3	2	19.0	-14.7
4	3	3	12.3	9.9
4	3	4	11.1	-5.1
4	3	5	22.6	23.2
4	3	6	17.3	-17.1
4	3	7	32.0	31.7
4	3	8	19.6	14.3
4	3	9*	7.0	-.7
4	3	10	12.8	-7.4
4	4	0	24.1	21.9
4	4	1	9.2	9.1
-4	4	1	9.4	5.8
4	4	2	25.9	-25.8
-4	4	2	9.4	8.2
4	4	3	21.2	-20.5
4	4	4	97.7	96.9
4	4	5	22.4	19.8
4	4	6	18.2	-23.0
4	4	7*	7.7	-7.1
4	4	8	13.7	14.1
4	4	9	11.1	3.4
4	4	10*	7.5	5.0
4	5	0	16.7	13.8
4	5	1	40.5	40.6
-4	5	1	12.8	-11.5
4	5	2	16.1	-17.7
-4	5	2*	6.3	6.3
4	5	3	14.5	10.4
4	5	4	14.3	-9.9
4	5	6	17.8	19.5
4	5	7	42.9	44.4
4	5	10*	7.6	5.2
4	6	0	13.5	10.4
4	6	1	20.6	-22.7
-4	6	1*	6.0	-1.8
4	6	2	11.9	9.9
-4	6	2*	6.1	1.6
4	6	3	56.2	55.6
4	6	4	44.3	44.3
4	6	5	51.8	-53.0
4	6	6	17.2	12.9
4	6	7*	10.7	15.4
4	7	0	32.2	30.9
4	7	1*	6.9	-2.6
-4	7	1	20.1	18.4
4	7	2	31.2	-30.6
4	7	3	31.3	30.3
4	7	4	11.7	5.4
4	7	5	15.4	13.7
4	7	6	12.4	8.5
4	7	7*	7.1	3.3
4	8	0	7.9	-.4
4	8	1	19.2	-16.2
-4	8	1*	6.7	-2.6
4	8	2	48.6	47.4
4	8	3	20.3	19.2
4	8	4	25.6	-22.3
4	8	5	22.2	-20.7
4	8	6	33.2	33.2
4	9	0	12.2	-8.8
4	9	1*	9.4	-12.2
-4	9	1	19.7	19.4
4	9	2*	6.3	5.9
4	9	3	18.7	16.8
4	9	4	14.3	1.2
4	9	5	27.5	24.5
4	9	6*	7.5	-6.1
4	10	0	9.9	-5.0
4	10	1	17.1	15.0
4	10	1*	9.5	-1.0
4	10	2	18.7	21.1
4	10	3	29.7	-27.8
4	10	4	13.4	-4.8
4	10	5	28.0	27.2
4	11	0	14.8	-16.3
4	11	1*	8.5	10.9
4	11	2	15.4	15.7
4	11	3*	9.2	-1.6
4	11	4	11.6	-2.4
4	12	2	10.2	-9.6
4	12	3	20.9	-16.7
4	13	2	9.3	-5.4
5	0	0	10.2	-1.7
5	0	2	33.7	31.7
5	0	4	54.3	54.4
5	0	6	29.6	-28.7
5	0	8	40.8	40.8
5	0	10*	9.0	-4.8
5	1	0	12.8	10.9
5	1	1	37.5	34.0
-5	1	1*	5.7	-2.6
5	1	2	29.7	-26.8
5	1	3	14.3	-13.5
5	1	4	31.6	31.7
5	1	5	64.7	66.6
5	1	6	15.7	-13.1
5	1	7	13.0	11.4
5	1	10*	8.3	7.1
5	2	0	9.4	7.6
5	2	1	19.0	16.4
-5	2	1	17.5	13.1
5	2	2	11.8	10.1
5	2	3	10.0	9.9
5	2	4	25.8	26.7
5	2	5	34.2	-31.8
5	2	6	19.1	15.6
5	2	7	36.3	37.7
5	2	8	27.1	25.1
5	2	9	15.1	-16.7
5	2	10	12.4	5.5
5	3	0	18.8	14.1
5	3	1	15.9	-12.3
-5	3	1	9.5	6.1
5	3	2	33.7	-35.2
5	3	3	57.3	56.3
5	3	4	39.3	42.6
5	3	5	11.1	3.7
5	3	6	20.7	-19.2
5	3	7	24.1	25.4
5	3	8*	7.1	-1.7
5	3	9*	8.8	8.3
5	4	0	24.4	24.5
5	4	1*	7.3	2.3
-5	4	1*	6.1	2.6
5	4	2	13.9	14.7
5	4	3*	6.2	-9.8
5	4	4*	4.9	-6.0
5	4	5	14.3	-8.2
5	4	6	53.2	54.3
5	4	8	16.2	-14.5
5	4	9*	7.5	-2.4
5	4	10	12.2	11.7
5	5	0	9.5	-5.9
5	5	1	12.1	-13.8
-5	5	1*	6.4	9.2
5	5	2	14.9	14.4
5	5	3	54.1	55.5
5	5	4	23.4	-24.1
5	5	7	13.9	15.7
5	6	0*	6.6	7.0
5	6	1	14.8	-10.8
5	6	2	17.1	17.9
5	6	5	31.4	31.9
5	6	6	29.7	30.9
5	6	7	20.2	-25.4
5	6	8*	8.3	1.0
5	7	0	11.6	-13.6
5	7	1	15.7	12.0
5	7	2	31.9	33.2
5	7	3	11.6	-3.5
5	7	4	30.3	-32.2
5	7	5	28.4	30.6
5	7	6	19.7	20.8
5	7	7	14.7	6.5
5	7	8*	8.5	-2.5
5	8	0	9.1	-5.9
5	8	1	9.7	-3.6
5	8	2*	7.8	12.7
5	8	3	10.2	-4.4
5	8	4	21.0	21.7
5	8	6	17.0	-16.6
5	8	7	12.6	-9.3
5	9	1	20.2	18.6
5	9	2*	10.6	-10.0
5	9	3	15.8	-16.3
5	9	4*	7.6	6.9
5	9	5	23.5	30.5
5	9	6*	10.5	-9.0
5	10	2*	7.8	-3.6
5	10	3*	7.0	2.6
5	10	4	14.2	14.8
5	10	5	19.0	-15.8
5	10	6	13.1	-6.7
5	11	4	23.0	23.5
5	11	5*	9.1	3.9
6	0	0	18.6	14.2
6	0	2	22.7	-19.6
6	0	4	51.2	51.4
6	0	6	27.3	24.4
6	0	8*	7.4	4.5
6	0	10	20.1	13.6
6	1	0*	6.4	1.9
6	1	1	12.7	6.5
6	1	2	10.2	2.9
6	1	3	31.2	31.7
6	1	4	24.2	-24.0
6	1	5	17.0	-17.8
6	1	6	19.6	18.7
6	1	7	44.4	42.6
6	1	8	15.3	-17.2
6	1	9*	7.7	1.2
6	1	10	12.5	1.3
6	2	0*	7.8	3.5
6	2	1	19.0	-18.3
6	2	3	22.4	20.9
6	2	4	13.2	14.3
6	2	5*	9.2	-10.4
6	2	6	22.3	21.3
6	2	7	17.2	-13.3
6	2	8	10.0	7.2
6	2	10	13.6	7.1
6	3	0*	9.0	2.7
6	3	1	10.8	7.5
6	3	2*	7.3	6.5
6	3	3*	7.4	3.3
6	3	4	13.7	-18.9
6	3	5	30.6	32.0
6	3	6	28.8	28.9
6	3	7	9.3	-6.1
6	3	10*	10.9	3.4
6	4	0	13.0	-9.2
6	4	1*	6.9	-3.0
6	4	2	30.2	27.9
6	4	4*	6.9	-3.2
6	4	5*	9.5	-2.9
6	4	6	23.0	24.6
6	4	10	14.3	-7.2
6	5	0	6.3	-1.6
6	5	1	10.9	7.9
6	5	2*	7.1	-2.3
6	5	3*	10.5	-7.8
6	5	4	15.4	12.4
6	5	5	37.7	41.7
6	5	6	25.8	-22.5
6	6	1	20.4	12.6
6	6	3	21.5	-23.6
6	6	4*	9.9	10.4
6	6	5*	7.4	9.1
6	7	1*	6.7	7.9
6	7	2*	8.9	-6.9
6	7	3*	9.5	10.9
6	7	4	15.2	16.9
6	7	5*	6.9	-.9
6	8	1*	8.5	5.6
6	8	2	15.9	-11.2
6	8	3*	11.6	-5.5
6	8	4	17.1	20.3
6	8	5*	7.8	3.5
6	9	2*	8.8	1.5
6	9	3	19.8	16.0
6	9	5	20.4	-19.3
6	10	3	17.1	14.1
6	10	4*	7.5	9.3
6	11	5*	7.8	5.0
7	0	2	21.4	16.7
7	0	4	16.2	-17.0
7	0	6	32.4	36.6
7	0	8*	7.1	-4.1
7	1	1	10.8	-5.0
7	1	2*	8.0	6.9
7	1	3	13.9	10.2
7	1	5*	7.4	13.8
7	1	6	18.0	-10.5
7	1	7	10.9	4.9
7	1	8	22.3	14.3
7	1	9	20.9	18.6
7	2	2	10.4	8.4
7	2	3	14.8	-14.4
7	2	4*	8.1	7.7
7	2	5	20.8	22.1
7	2	6*	8.3	10.7
7	2	7	14.8	-16.3
7	2	8	13.9	7.0
7	3	2	12.9	5.0
7	3	3*	6.6	-1.9
7	3	4*	9.5	-3.5
7	3	5	13.2	15.6
7	3	6*	7.7	-11.6
7	3	7	23.7	24.3
7	3	8	16.2	15.9
7	4	2*	8.3	-3.8
7	4	4	27.6	29.6
7	4	5*	7.7	3.0
7	4	6*	7.8	-15.7
7	4	7*	9.5	-2.3
7	5	6*	8.7	6.3
7	5	7	22.5	24.3
7	6	6*	9.6	-3.6
8	0	4	17.0	6.1
8	0	6	11.6	-.8
8	1	4*	8.1	7.5
8	1	5*	12.1	17.4
8	1	6*	11.1	-2.9
8	1	7	11.2	-1.5
8	2	4*	7.3	2.4
8	2	5*	9.7	-10.3
8	2	6*	8.3	6.1
8	2	7	19.6	19.0
8	3	4*	7.3	8.1
8	3	5*	9.1	-3.9
8	3	7*	10.0	8.9
8	4	6	17.0	19.8
8	4	7*	7.7	2.0
8	5	5*	8.5	-2.7
8	5	6*	7.7	4.3
8	5	7*	10.3	7.4
8	6	7	13.1	-12.3

Table 6. *Interatomic distances and angles*

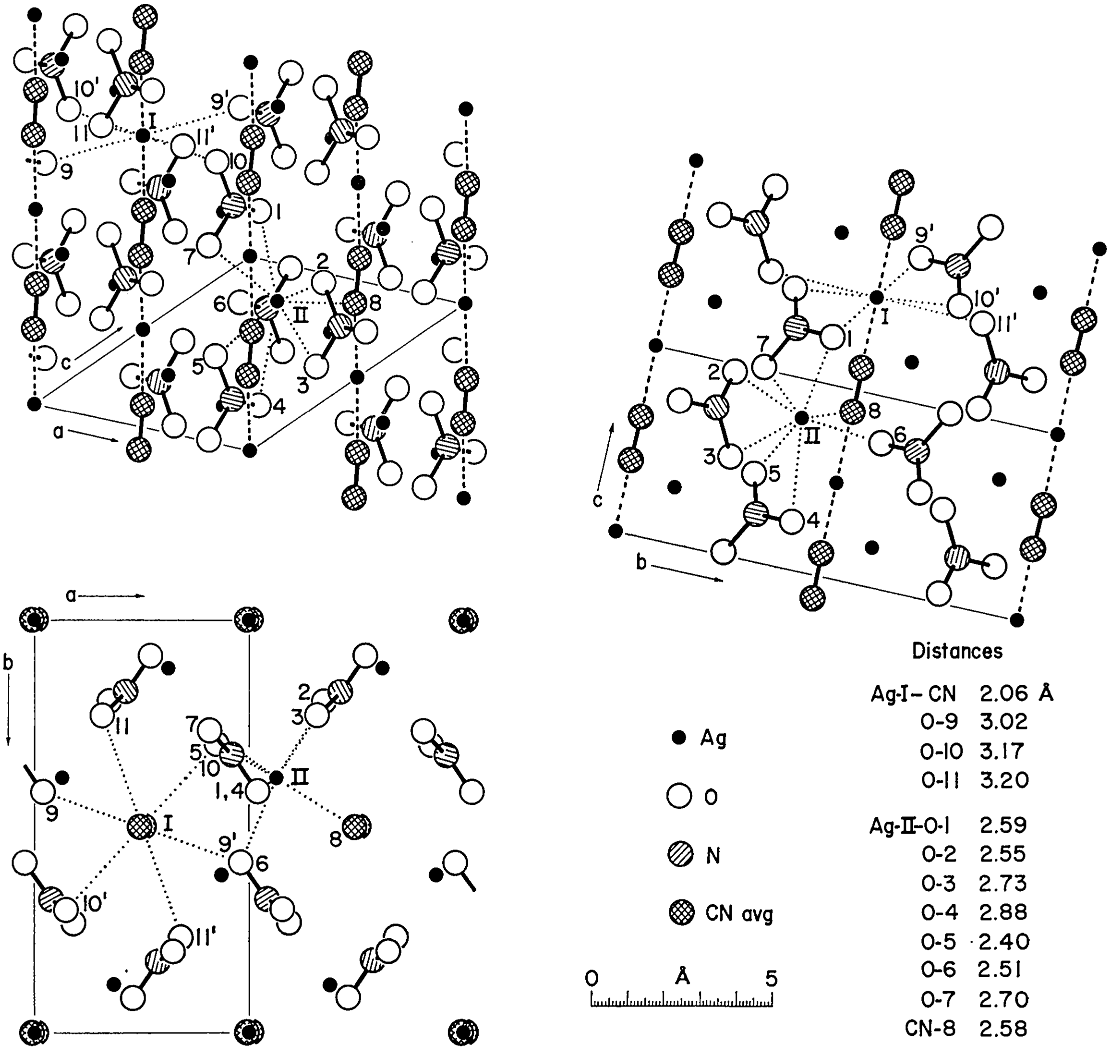
Distance or angles	Compound	Value	Reference
C–N	AgCN . 2AgNO$_3$	1·201 ± 0·015 Å	(*a*)
C–N	X–CN (average)	1·158 ± 0·002	(*b*)
Ag–CN	AgCN . 2AgNO$_3$	2·058 ± 0·008	(*a*)
Ag–C–N	AgCN . 2AgNO$_3$	173·0°	(*a*)
N–O(1)	AgCN . 2AgNO$_3$	1·202 ± 0·010 Å	(*a*)
N–O(2)		1·272 ± 0·010	(*a*)
N–O(3)		1·309 ± 0·010	(*a*)
N–O	Single bond (average)	1·36 ± 0·02	(*b*)
N–O	X–NO$_2$ (average)	1·24 ± 0·01	(*b*)
N–O	CH$_3$ON–O	1·22 ± 0·02	(*b*)
O(2)–N–O(3)	AgCN . 2AgNO$_3$	118·1 ± 0·6°	(*a*)
O(3)–N–O(1)		119·6 ± 0·6	(*a*)
O(1)–N–O(3)		122·2 ± 0·6	(*a*)
Ag–O	Ag$_2$C$_2$O$_4$	2·17 Å	(*b*)
Ag–O	AgClO$_4$. 3 dioxane	2·46	(*c*)

(*a*) This work. (*b*) Sutton (1958). (*c*) Prosen & Trueblood (1956).

proximation to the error matrix. Similarly the angles 118·1 to 122·2° are further from 120° than would be expected. It is clear, however, that the environments of the three oxygen atoms are different. In Fig. 3 the N–O distance is plotted against the shortest Ag–O distance for each of the O atoms. The N–O distances vary in a regular way with the corresponding shortest Ag–O distances; if one takes the Ag–O distance from silver oxalate (2·17 Å) as corresponding to the strongest possible Ag–O bond and the CH_3O–N distance from methyl nitrite or methyl nitrate (1·36 Å) as corresponding to the weakest possible (*i.e.* single) N–O bond, this point also fits on the curve. Thus we can say that the observed deviation of the nitrate ion from D_{3h} symmetry is due to the formation of reasonably strong Ag–O bonds to two of the three O atoms.

The environments of the two types of Ag atom are shown in Fig. 2. The Ag in the Ag–CN chain does not have any O neighbour nearer than 3 Å so that the coordination number is clearly two, linear covalent bonds being formed to the adjacent CN groups. The other type of Ag atom has eight neighbours at distances less than 3 Å, seven O atoms and 1 CN. However, the distances and directions show no particular regularity, and we would conclude that this Ag atom is in a more or less ionic environment, a more symmetric arrangement being precluded by the restraints imposed on the packing by the Ag–CN chains.

The surprising feature of the thermal parameters is the large temperature factor for the Ag atom in the Ag–CN chain. For this atom *B* is larger than for any other atom in the structure, even for the disordered CN groups. The principal axes of the ellipsoid of vibration for this atom are roughly along the chain ($\langle \bar{u}^2 \rangle^{\frac{1}{2}} =$ 0·27 Å), parallel to the *b* axis (0·28 Å), and perpendicular to the chain and the *b* axis (0·21 Å). It is interesting that the amplitude in the chain direction is so large. This probably corresponds to a small random displace-



Distances

Ag-I–CN	2.06 Å
O-9	3.02
O-10	3.17
O-11	3.20
Ag-II-O-1	2.59
O-2	2.55
O-3	2.73
O-4	2.88
O-5	2.40
O-6	2.51
O-7	2.70
CN-8	2.58

Fig. 2. The structure of AgCN . $2AgNO_3$. All of the short Ag–CN distances are indicated by heavy dashed lines. The near neighbours of each type Ag are shown by light dashed lines. The numbers of the atoms in the legend refer to this figure only, and are not the same as in the tables.

ment of the Ag atom from the centre of symmetry depending on the orientation of the neighbouring CN groups.

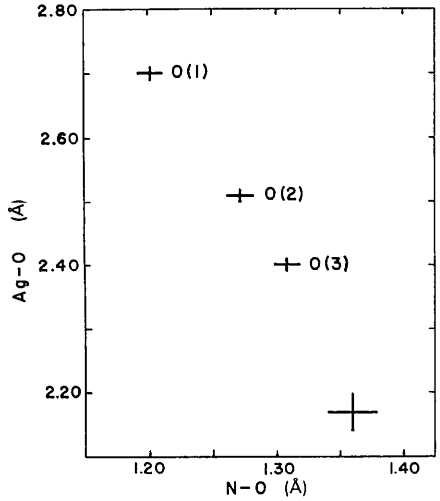


Fig. 3. N–O bond lengths *versus* Ag–O distances. The points are labelled with the numbers from Table 2. The unlabelled point corresponds to an N–O single bond and a Ag–O single bond, from CH_3ONO and $Ag_2C_2O_4$ respectively.

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The Crystal Structure of α-Methyl D-Galactoside 6-Bromohydrin

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The crystal structure of α-methyl D-galactoside 6-bromohydrin has been determined by the heavy-atom method, at 125 °K. The bromine atom coordinates were derived from Harker sections. Three-dimensional structure factors and least-squares refinement of 1203 reflexions with anisotropic temperature factors gave a final residual $R=0{\cdot}108$. All bonds, including the C(1)–O(1) bond, were found to be of normal length. The positions of the hydrogen atoms were found from the final 3-D Fourier synthesis. The hydrogen bonding system, which gives good agreement with the infrared spectroscopic data, consists of spiral linkages about the screw axes parallel to the b axis.

Experimental

α-Methyl D-galactoside 6-bromohydrin was prepared by Valentin (1952); unit-cell and density measurements were made by Cox, Goodwin & Wagstaff (1935). The unit-cell dimensions were re-measured at 125 °K by the extrapolation to $\theta=90°$ of high order reflexions on zero layer Weissenberg photographs, calibrated with aluminum wire powder lines. The a and c axes of Cox *et al.* were interchanged for convenience. The unit cell is orthorhombic with systematic absences of $h00$ for h odd and $0k0$ for k odd. The space group is $P2_12_12$ and the cell dimensions are:

$a=11{\cdot}142\pm0{\cdot}005$ Å	*cf.* Cox, *et al.*	11·23 Å
$b=\ 7{\cdot}815\pm0{\cdot}003$	at room temperature	7·81
$c=10{\cdot}612\pm0{\cdot}010$		10·58

The value of the density observed, 1·86 g.cm^{-3}, gave a cell weight of 1035 and hence $Z=4{\cdot}03$ ($C_7H_{13}BrO_5=257$).

The material was recrystallized from water, on a greased microscope slide, and a crystal with dimensions

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