

The Crystal Structure of Silver Fulminate

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Silver fulminate occurs in two polymorphic forms. One is orthorhombic, $a = 3.864$, $b = 10.722$, $c = 5.851$ Å, $Z = 4$, space group $Cmcm$. The other is trigonal with a rhombohedral lattice, $a = 9.109$ Å, $\alpha = 115^\circ 44'$, $Z = 6$, space group $R\bar{3}$. The structures have been determined, and have been refined by full-matrix least-squares analysis of three-dimensional counter data in the first case and of film data in the second. In the orthorhombic structure infinite chains $-C-Ag-C-Ag-C-$ running in the c direction can be identified, with $Ag-C$ distance, 2.23 Å; the bond angles are 180° at Ag , and 82° at C , leading to $Ag \cdots Ag$ separations of $c/2 = 2.93$ Å. The fulminate ions are linear, with $C-N$, 1.09 Å; $N-O$, 1.25 Å.

The rhombohedral form contains cyclic hexameric units, with distances $Ag-C$, 2.16 and 2.19 Å, bond angles 163° at Ag and 81° at C , leading to $Ag \cdots Ag$ separations of only 2.82 Å, slightly shorter than in metallic silver (2.89 Å).

Introduction

Silver fulminate was recognized by Gay-Lussac (1824) to have the same composition as silver cyanate, thus providing the first example of isomerism. Despite the long history of these compounds their crystal structures have not been determined until now. In a previous article (Britton & Dunitz, 1965) we described the crystal structure of silver cyanate. We report here the crystal structures of two polymorphic forms of silver fulminate.

Singh (1959) reported a space group and unit cell for silver fulminate which would require that the fulminate groups be disordered, statistically centric. Since the reported space group and unit cell were not isomorphous with known disordered cyanates, and since, in any event, one would expect that the bonding between silver and fulminate would involve sufficient covalent character to preserve structural non-equivalence of the two ends of the fulminate ion, we doubted the correctness of Singh's result. This provided an additional incentive for our investigation.

Experimental – unit cell and space group

The silver fulminate used in these studies was prepared by dissolving 8.4 g silver nitrate in 39.5 g concentrated nitric acid diluted with 8.4 g water, and heating a mixture of 1 part of this solution with 1.2 parts of ethanol to about $60^\circ C$ until a precipitate formed. This precipitate of silver fulminate was recrystallized from $6M$ ammonia.

The crystals left after evaporation of the ammonia were a mixture of needles and multiple growths which tended to a leaf-like habit. X-ray examination showed that there were two polymorphic forms present, one form orthorhombic, the other trigonal (rhombohedral), but both forms occurred as needles and as part of the

leaf-like clusters. We could not distinguish the two forms under the microscope. We have not yet carried out studies to determine the relative stability and the conditions necessary for the formation of the two forms, but we report here the crystal structures of both. Since we do not know which form is more stable we shall not label them α and β but rather refer to them as orthorhombic and rhombohedral $AgCNO$ throughout this work.

The previously reported unit-cell dimensions and space group for the orthorhombic modification are reported in Table 1 along with our data for both modifications. The cell constant measurements were made from precession photographs ($Mo K\alpha = 0.7107$ Å).

The space group determinations were made with both precession and Weissenberg photographs. In the orthorhombic modification hkl reflexions with $h+k$ odd and $h0l$ reflexions with l odd are absent, indicating the possible space groups to be $Cmc2_1$ (C_{2v}^{12}), $C2cm$ (C_{2v}^{6}), and $Cmcm$ (D_{2h}^{12}). The last is shown to be correct by the subsequent determination of the structure. Reflexions with l odd are much weaker than those with l even, the latter being common to both our space group and Singh's. A long exposure of an hkl photograph shows, however, reflexions with $h+k$ even but none with $h+k$ odd, indicating that the unit cell is C - and not I -centred.

In the trigonal modification there were no systematic absences if the photographs were indexed on the rhombohedral unit cell (reflexions only for $-h+k+l = 3n$ if indexed on the hexagonal unit cell). The Laue symmetry is $\bar{3}$, leading to $R\bar{3}$ (C_3^2) and $R\bar{3}$ (C_3^2) as possible space groups; the latter is shown to be correct by the structure determination.

Determination and refinement of the orthorhombic structure

Inspection of the preliminary X-ray photographs showed that reflexions with $l = 2n$ are strong, with nearly

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Table 1. Unit-cell parameters and space groups

	Orthorhombic		Trigonal	
	Singh (1959)	This work	Rhombohedral	Hexagonal
	$a(\text{Å})$	3.88	3.864 ± 0.006	9.109 ± 0.015
$b(\text{Å})$	11.20	10.722 ± 0.018	—	—
$c(\text{Å})$	6.04	5.851 ± 0.010	—	5.726 ± 0.010
α	—	—	$115^\circ 44'$	—
Space group	<i>Ibam</i>	<i>Cmcm</i>	$R\bar{3}$	18
Z	4	4	6	18
Volume (Å^3)	262.5	242.4	393.3	—
Vol./Z (Å^3)	65.6	60.6	65.6	—
D_{calc} (g. cm^{-3})	3.792*	4.107	3.796	—
D_{obs}	3.938	—	—	—

* Recalculated.

uniform intensity apart from normal decline, whereas reflexions with $l=2n+1$ are of weak and variable intensity. This suggested strongly that the Ag atoms occupy the special positions 4(*a*) of *Cmcm*, *viz.* 0,0,0; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The CNO groups would then lie either in the special positions 4(*b*): $x,y,\frac{1}{4}$, etc., of *C2cm* or 4(*c*): $0,y,\frac{1}{4}$, etc., of *Cmcm*.

Three-dimensional data were collected with the semi-automatic linear diffractometer designed by Arndt & Phillips (1961), using Mo radiation with balanced filters. A flat needle 0.032 mm (b direction) by 0.10 mm (a direction) by 0.85 mm (c direction) was used for the measurements. Intensity data were collected for the layers $hk0-hk6$ out to $\sin \theta \sim 30^\circ$, and converted to structure amplitudes after application of the usual Lorentz and polarization corrections. No absorption corrections were made (linear absorption coefficient = 77 cm^{-1}). Under the experimental conditions (scintillation counter, 12 seconds per intensity measurement cycle), 127 independent reflexions were observed for which the measured value of the intensity was larger than the standard deviation of the measurement. An additional 19 reflexions were included with intensities assigned equal to the standard deviation of the measurements. When entire groups of reflexions (*e.g.* the entire $hk5$ layer) were too weak to measure, they were omitted from the data list. The quality of the data is seriously affected by the tendency of the crystal to warp on exposure to X-rays. This seems to be a general property of these crystals; in a small crystal the warping was noticeable after even a one hour exposure.

In order to determine the light atom positions the (001) electron density projection was calculated from the $hk0$ data with all signs positive. This showed clearly that all the atoms, with peak heights 157 ($= 2 \times 79$), 9, 11 and 12 e.Å^{-2} for Ag, C, N and O respectively, lie on the lines $x=0$, $x=\frac{1}{2}$. The space group is thus *Cmcm*.

It was obvious from inspection of the counter data or of the precession photographs that anisotropic thermal motion would have to be allowed for. Full-matrix least-squares refinement gave $R=0.317$, $r=0.360$ * for

* $r = \Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w|F_c|^4$. $w=1$ for $F_0 \leq 24$; $w = 2(4/F_0)^4$ for $F_0 > 24$. The numerator of r is the quantity minimized in the least-squares calculation.

all atoms isotropic; $R=0.151$, $r=0.077$ for Ag only anisotropic; $R=0.134$, $r=0.063$ for all atoms anisotropic. The final positional parameters are given in Table 2, together with the isotropic temperature factors. In view of the poor quality of the data we do not believe that the anisotropic thermal parameters for the light

Table 2. Final parameters for orthorhombic AgCNO*

	x	y	z	$B(\text{Å}^2)\dagger$
Ag	0	0	0	6.08 ± 0.10
O	0	0.3753 ± 0.0017	$\frac{1}{4}$	5.72 ± 0.48
N	0	0.2584 ± 0.0025	$\frac{1}{4}$	4.88 ± 0.51
C	0	0.1564 ± 0.0015	$\frac{1}{4}$	6.88 ± 0.84

* The standard deviations are estimated by diagonal approximation and are optimistic.

† Taken from the last cycle in which the atoms were treated as isotropic.

Table 3. Observed and calculated structure factors for orthorhombic silver fulminate

H K L OBS				H K L OBS				H K L OBS							
h	k	l	obs	h	k	l	obs	h	k	l	obs				
2	0	2	116.3	140.6	1	3	6*	2.4	6.2	2	8	3	6.7	2.7	
3	2	2	119.3	130.9	1	5	0	121.7	111.1	2	8	4	15.6	15.1	
3	2	3*	2.4	-0.3	1	5	1	9.4	6.3	2	8	6*	2.4	2.3	
0	2	4	35.3	35.7	1	5	2	77.7	65.8	2	10	2	29.5	27.5	
0	2	6*	2.4	9.1	1	5	3	2.8	-1.9	2	10	2	24.3	26.0	
0	4	0	118.1	124.3	1	5	4	32.6	29.3	2	10	3	5.7	-2.1	
0	4	1	7.5	6.3	1	5	6	4.5	5.6	2	10	4	9.9	8.4	
0	4	2	95.4	106.6	1	7	0	86.3	78.7	2	10	6	6.0	2.4	
0	4	3*	2.4	.5	1	7	1	13.0	9.0	2	12	2	23.6	23.0	
0	4	4	39.9	32.5	1	7	2	59.0	55.7	2	12	2	10.4	14.9	
0	4	6	8.1	8.1	1	7	3	5.3	-3.0	2	12	4	7.5	6.5	
0	6	0	153.4	105.5	1	7	4	28.8	21.7	3	1	0	35.5	33.2	
0	6	1*	3.7	-5.9	1	7	6	7.0	5.4	3	1	1	-11.7	-11.7	
0	6	2	69.6	76.6	1	9	0	82.6	43.7	3	1	2	21.3	27.2	
0	6	3	6.2	5.6	1	9	1	11.6	-9.6	3	1	3	6.7	5.4	
0	6	4	34.5	27.1	1	9	2	47.3	48.0	3	1	4	10.1	9.2	
0	6	6	8.4	6.9	1	9	3	7.4	5.8	3	3	0	35.7	32.6	
0	8	0	97.0	90.7	1	9	4	17.6	14.3	3	3	2	18.0	22.5	
0	8	1*	3.7	-8.3	1	9	6	3.9	4.5	3	3	3	4.3	-6	
0	8	2	39.4	45.4	1	11	0	47.0	41.5	3	3	4	11.8	10.6	
0	8	3	6.5	4.2	1	11	2	15.8	26.2	3	5	0	32.9	29.7	
0	8	4	32.0	26.2	1	11	3	5.4	.1	3	5	2	16.1	18.0	
0	8	6	7.4	4.2	1	11	4	15.8	17.4	3	5	3*	2.4	.2	
0	10	0	49.6	44.5	1	13	0	75.0	32.4	3	5	4	9.0	8.9	
0	10	1	81.0	74.8	1	13	2	14.9	16.1	3	7	0	26.0	24.2	
0	10	2	38.0	45.0	1	13	4	7.4	9.3	3	7	2	13.6	15.8	
0	10	3*	2.4	-3.2	2	0	0	129.8	115.5	3	7	3	4.0	-1.8	
0	10	4	14.5	15.2	2	0	2	36.0	37.6	3	7	4	10.4	6.8	
0	10	6	4.9	4.1	2	0	4	27.3	28.0	3	9	0	13.7	12.0	
0	12	0	35.3	39.1	2	0	6	3.2	3.6	3	9	2	14.4	16.0	
0	12	1	5.5	3.2	2	2	0	71.9	63.7	3	9	3	3.7	2.5	
0	12	2	22.4	26.8	2	2	1	5.5	5.8	3	9	4*	2.4	4.3	
0	12	3	6.4	.5	2	2	2	65.3	63.8	3	11	0	14.1	13.7	
0	12	4	12.7	11.2	2	2	3*	4.4	-3.5	3	11	2	5.4	8.2	
0	12	6	5.5	7.1	2	2	6*	2.4	5.2	3	11	4	5.9	4.0	
0	14	0	27.2	25.6	2	4	0	68.1	61.6	4	0	0	19.4	19.4	
0	14	2	14.9	18.0	2	4	1*	3.7	2.8	4	0	2*	3.7	4.1	
0	14	4	8.3	7.8	2	4	2	50.9	51.4	4	0	4*	2.4	5.6	
1	1	0	150.9	137.1	2	4	3	4.4	.3	4	2	0	8.3	7.7	
1	1	1	55.7	-44.4	2	4	6	6.5	4.5	4	2	2	9.6	11.6	
1	1	2	108.5	106.1	2	6	0	60.4	53.5	4	2	4	6.7	2.6	
1	1	3	10.8	15.7	2	6	1*	3.7	-2.3	4	4	0	11.8	10.8	
1	1	4	27.5	31.4	2	6	2*	36.8	40.7	4	4	2	5.0	7.6	
1	1	6	2.9	8.2	2	6	3	6.7	2.7	4	4	4	4.2	3.6	
1	1	3	0	146.9	131.0	2	6	4	16.6	14.6	4	6	0	8.9	8.4
1	1	3	1*	3.7	.2	2	6	6	2.4	-4.0	4	6	2	7.2	7.7
1	1	3	2	161.3	82.8	2	8	0	58.6	49.3	4	6	4	5.2	2.3
1	1	3	3*	2.4	9.1	2	8	1	7.9	-5.4	4	8	0	9.8	9.9
1	1	3	4	43.4	34.9	2	8	2	21.8	24.1					

* Indicates unobserved reflexion.

atoms are significant, although they partially correct for systematic errors in the data, and therefore, presumably, lead to improved positional parameters. The thermal parameters for the Ag atom are significant, however, and indicate that the principal axes of the ellipsoid of vibration coincide within 2° with the crystal axes (coincidence with the *a* axis only is required by the space group symmetry) with root-mean-square amplitudes of vibration of 0.31, 0.19 and 0.34 Å along *a*, *b*, and *c* respectively. The observed and calculated structure factors are given in Table 3.

Determination and refinement of the rhombohedral structure

Multiple film Weissenberg photographs of the layers *hk0*–*hk4* (hexagonal indices), as well as three sets of precession photographs for correlation purposes, were taken with Mo $K\alpha$ radiation. The crystal used was a needle, elongated along *c*, 0.03–0.04 mm in diameter, and 1.1 mm long. Intensities were estimated by visual comparison with a series of timed exposures and converted to structure amplitudes after applying the usual Lorentz and polarization corrections. No correction for absorption was made (the linear absorption coefficient is 72 cm⁻¹). The data comprise 321 independent reflexions of measurable intensity, plus 99 reflexions in the same region of reciprocal space with intensities too low to be measured. These unobserved reflexions were included in the least-squares calculations with intensities equal to half the minimum observable intensity. The quality of the data is rather poor, primarily because the crystals warped under exposure to X-rays, so that the spot shape changed from layer to layer.

The silver atom position was found from the Patterson projection down the *c* axis of the hexagonal cell, together with a consideration of selected upper layer reflexions. The corresponding Fourier synthesis confirmed the silver position and showed also the partially resolved fulminate group. A three-dimensional Fourier map showed all the expected peaks plus several roughly equal in height to the light atom peaks but misshapen and impossibly located. A second Fourier map and a difference Fourier map confirmed the opinion that these latter peaks were caused by series termination errors arising from the limited data in the *c* direction. The light atom peaks could not be identified without ambiguity. The data in Table 4 summarize the information that led to our choice. After we rule out the possibility CON on chemical grounds, the consensus of the data favours CNO rather than ONC (taking the atoms in order from the Ag atom). This is also chemically more reasonable.

The structure was refined by the method of least squares. Since the programs available to us could not handle higher symmetry than orthorhombic, the structure was treated as triclinic, space group $P\bar{1}$, with three independent AgCNO units in the asymmetric crystal unit. The list of nominally independent reflexions was

Table 4. Data for the identification of C, N, and O in rhombohedral silver fulminate

Datum	Units	Ag	C	N	O
Electron density at atom position in projection	e.Å ⁻²	78	9.0	7.5	12.1
Electron density at atom position in 3-D Fourier map based on Ag only	e.Å ⁻³	89	5.1	8.0	6.0
Electron density at atom position in 3-D Fourier map based on all atoms	e.Å ⁻³	95	7.7	11.8	8.9
Number of electrons in equal large volumes in 3-D based on final structure	e	—	8.3	9.7	8.9
Number of electrons within region where electron density is 4.0 e.Å ⁻³	e	—	4.9	6.5	5.8

increased appropriately. The three sets of atoms maintained their complete equivalence throughout all the cycles of refinement.* Refinement with all atoms treated as isotropic led to $r=0.067$, $R=0.160$, and with only Ag anisotropic to $r=0.065$, $R=0.151$. Refinement with all atoms anisotropic was abandoned when it indicated complex vibration amplitudes (that is, negative components for at least one axis of the ellipsoid of vibration) for the carbon atoms. This fault is undoubtedly due to the poor quality of the intensity data. The final parameters are shown in Table 5, and a comparison of the observed and calculated structure factors is given in Table 6. Both tables refer to the rhombohedral coordinate system.

Table 5. Final parameters for rhombohedral AgCNO*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)†
Ag	0.0635	0.1493	-0.2017	2.85
	±0.0002	±0.0002	±0.0002	±0.02
O	0.8521	0.7081	0.3578	6.40
	±0.0025	±0.0024	±0.0024	±0.49
N	0.6398	0.5060	0.2106	1.92
	±0.0017	±0.0017	±0.0017	±0.20
C	0.4349	0.3285	0.0701	1.56
	±0.0020	±0.0020	±0.0020	±0.33

* Referred to the rhombohedral coordinate system. The standard deviations are estimated by diagonal approximation and are optimistic.

† Taken from the last cycle in which the atoms were treated as isotropic.

Discussion

The structures of the orthorhombic and rhombohedral forms of silver fulminate are shown in Figs. 1 and 2,

* The weighting factors in the refinement were $w=1$ for $F_o \leq 65$, and $w=(65/F_o)^4$ for $F_o > 65$.

Table 6. Observed and calculated structure factors for rhombohedral silver fulminate

Table with columns: H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC, H, K, L, OBS, CALC. It lists observed and calculated structure factors for various hkl reflections.

* Indicates unobserved reflexion.

respectively. Important interatomic distances in the two compounds, as well as comparable values from other compounds, are listed in Table 7.

The standard deviations for our results are based on a diagonal matrix approximation and are somewhat optimistic. Two sets of values are listed for the distances in the orthorhombic structure. One set is based on the refinement with all atoms treated as anisotropic, the other on the refinement with only Ag treated as anisotropic. The comparison suggests that the estimated standard deviations should be increased by perhaps 50 per cent.

From Fig. 1 it is apparent that the orthorhombic structure is built from layers of fulminate groups at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, separated by layers of Ag atoms at $y = 0$ and $y = \frac{1}{2}$. The arrangement of fulminate groups within the layers corresponds approximately to a hexagonal packing of rods, with contact distances 3.505 and 3.864 Å, the shorter being between antiparallel fulminate groups, the longer between parallel ones. Interleaved between these approximately hexagonal layers are Ag layers based on a primitive rectangular net with translations 3.864 Å and 2.926 Å, the latter distance being only slightly longer than the 2.89 Å Ag-Ag separation in metallic silver. These two kinds of net are arranged so that one end of each fulminate group, the C end, has two Ag neighbours at 2.23 Å, while the O end has four Ag neighbours at 2.77 Å. This kind of structure has no analogy in any known AB structure; it cannot be explained in terms of purely ionic interactions but only if covalent bonding is taken into account.

From this point of view it is more convenient to take as the structural units not the layers of fulminate groups and silver atoms but rather the infinite coplanar chains formed by the sequence of Ag-C bonds (2.23 Å), linear at Ag, zigzag at C (Ag-C-Ag angle, 82.2°) and running in the c direction. In silver cyanate (Britton & Dunitz, 1965) somewhat similar chains are formed by the sequence of Ag-N bonds (2.12 Å) in the b direction, but here the two Ag atoms bonded to each N atom are not quite coplanar with the corresponding cyanate group and the angle Ag-N-Ag is 98° . In spite of the shorter Ag-N distance, the larger Ag-N-Ag angle leads to a Ag...Ag separation (3.19 Å) that is 0.25 Å greater than in the fulminate. Whereas in silver cyanate the principal bonding features seem compatible with approximate sp^2 hybridization of the terminal N atom (I), this description does not apply so well in the fulminate. The shorter C-N and Ag...Ag distances, and the Ag-C-Ag angle, all suggest a description in terms of a three-centre Ag-C-Ag bond, involving an sp orbital on C, and sp orbitals on the Ag atoms pointing more nearly towards each other (II). Only the anisotropic thermal motion of the Ag atoms (r.m.s. amplitudes of

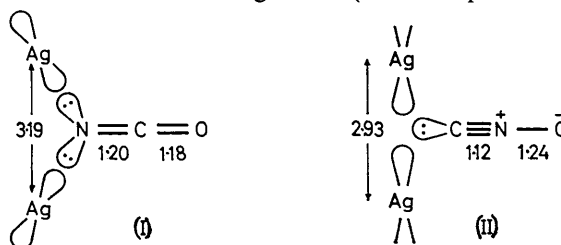


Table 7. *Interatomic distances*

Atoms	Distances (Å)	Compound	Reference
Ag-C	2.23 ± 0.02	Orthorhombic AgCNO	(a)
	(2.19 ± 0.02)*		(a)
	2.16 ± 0.03 } 2.19 ± 0.03 }	Rhombohedral AgCNO	(a)
	2.05	AgCN (assumed CN = 1.16)	(b)
	2.13	KAg(CN) ₂	(c)
Ag-O	2.77 ± 0.02	Orthorhombic AgCNO	(a)
	(2.78 ± 0.02)*		(a)
	2.45 ± 0.03	Rhombohedral AgCNO	(a)
	2.46	AgClO ₄ · 3C ₄ H ₈ O ₂	(d)
	2.42 } 2.47 }	AgNO ₂	(e)
	3.00 ± 0.01	AgNCO	(g)
C-N	1.09 ± 0.03	Orthorhombic AgCNO	(a)
	(1.14 ± 0.03)*		(a)
	1.12 ± 0.03	Rhombohedral AgCNO	(a)
	1.207	HNCO	(f)
	1.20 ± 0.01	AgNCO	(g)
N-O	1.25 ± 0.03	Orthorhombic AgCNO	(a)
	(1.22 ± 0.03)*		(a)
	1.20 ± 0.03	Rhombohedral AgCNO	(a)

(a) This work.

(b) Natta & Vecchia (1933).

(c) Hoard (1933).

(d) Prosen & Trueblood (1956).

(e) Long & Marsh (1962).

(f) Sutton (1958).

(g) Britton & Dunitz (1965).

* The values in parentheses are the results of the least-squares refinement with Ag only treated as anisotropic.

vibration 0.31, 0.19 and 0.34 Å along *a*, *b* and *c* respectively) is not satisfactorily accounted for by this bonding picture and is clearly related to the layer structure of the crystal, the vibration amplitudes being considerably greater within the plane of the Ag layers than perpendicular to them.

The rhombohedral structure is also of a new type, quite unrelated to any known AB structure. The structural units (Fig. 2) consist of cyclic hexamers. Although the crystallographic symmetry of the rings is only $\bar{3}$ (S_6) the actual symmetry approximates quite closely to $\bar{3}m$ (D_{3d}) with the 6 Ag atoms lying nearly, but not quite, in a plane. The primary bonds are similar to those involved in the chains of the orthorhombic structure; the two independent Ag-C distances are 2.16 and 2.19 Å (*cf.* 2.23 Å), the C-Ag-C angle is 163° (*cf.* 180°) and the Ag-C-Ag angle is 81° (*cf.* 82°). The biggest difference, and certainly the best established one, is in the Ag-Ag distance, which is here only 2.83 Å (*cf.* 2.93 Å), even shorter than the atomic separation in metallic silver (2.89 Å). Our description of the primary bonding in terms of three-center Ag-C-Ag bonds is thus at least as valid for the rhombohedral as for the orthorhombic structure.

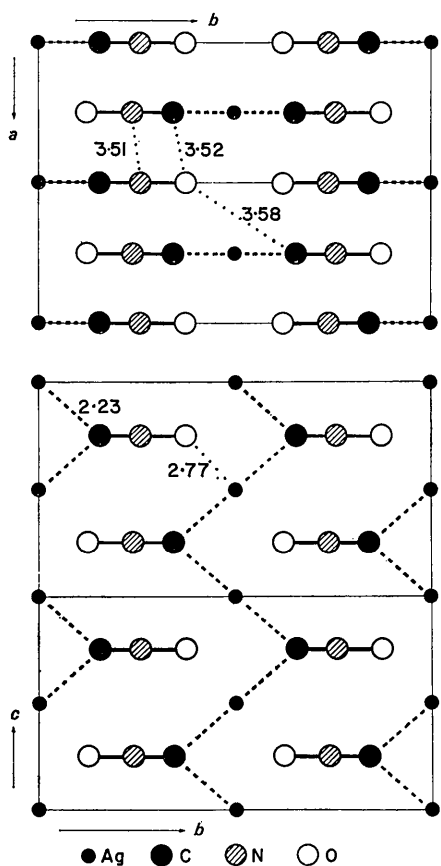


Fig. 1. Orthorhombic silver fulminate. Top; view along *c* axis. Bottom: view along *a* axis. Distances are given in Å. All Ag-C distances are shown as dashed lines.

The main difference between the two kinds of polymeric unit, planar zigzag chains and cyclic hexamers, is seen to be a conformational one. Whereas the torsion angle around successive C-Ag-C directions is 180° in the chains (anti-planar), this angle is 98° in the cyclic hexamers*. There are also a number of smaller differences, of somewhat dubious significance. In contrast to the orthorhombic structure, the fulminate groups are not quite linear (C-N-O = 172°), nor are they quite coplanar with their bonded pairs of Ag atoms (Ag-C-N, 135° and 142°; sum of angles at C = 358°), but it is uncertain how far these slight deviations are real and how far they may be caused by secondary interactions between atoms in different hexameric units. The main interactions of this kind occur between O atoms of one unit and Ag atoms of others (see Fig. 2). The shortest Ag...O distance is 2.45 Å, much shorter than the corresponding distances of 2.77 Å in the orthorhombic form and quite comparable to Ag...O

* For a ring of $\bar{3}m$ (D_{3d}) symmetry the torsion angle τ is given by

$$2 \sin^2 \tau/2 = (1 + 2 \cos \theta)/(1 + \cos \theta)$$

where θ is the bond angle (here 81°).

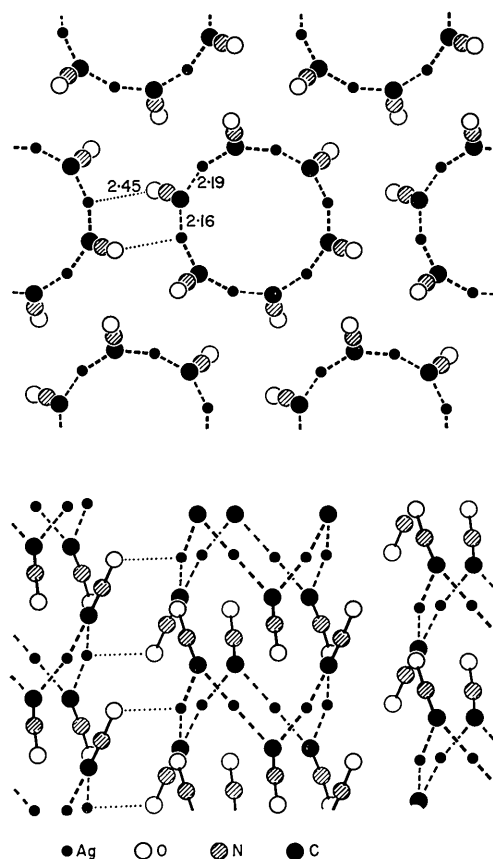


Fig. 2. Rhombohedral silver fulminate. Top; view down hexagonal *c* axis. Bottom: side view of the central line of hexamer units shown in the top view. Distances are given in Å. All Ag-C distances are shown as dashed lines.

distances in AgNO_2 and $\text{AgClO}_4 \cdot 3$ dioxane (see Table 7), structures in which ionic bonding must be fairly important. Although the apparent bending of the fulminate groups must be regarded as rather uncertain – the temperature factor for the O atom is much larger than for the C and N atoms – it is interesting that it appears to occur *towards* the neighbouring Ag atom at 2.45 Å distance, thus suggesting some bonding interaction between the residual negative charge on O and the residual positive charge on Ag. The next shortest $\text{Ag} \cdots \text{O}$ distances are 2.89 Å and 2.92 Å and must correspond to much weaker interactions.

Silver fulminate is held in poor regard as a detonator, as is shown by the following quotation (Rinkenbach, 1951): *Unlike mercuric fulminate, silver fulminate as ordinarily produced consists of fine amorphous aggregates instead of crystals. While normally it is slightly less sensitive to impact and more sensitive to heat than mercury fulminate, it has been found that under certain conditions of temperature some small clusters of crystals are formed that are much more sensitive than the amorphous aggregates. This explains the general conclusion that silver fulminate is dangerously sensitive.*

We did not find the amorphous form mentioned, but we did find these two polymorphs, both formed near room temperature in the same sample. They have quite different molecular volumes (see Table 1) as well as structures, and it seems likely that the difference in sensitivity depends on the presence or absence of the second form. Since these are both crystalline modifications with presumably a well-defined transition temperature, it should be possible to avoid the formation

of the unstable form by careful control of the temperature in the manufacturing process.

This work was performed during the tenure of a fellowship for which D.B. would like to thank the National Science Foundation. The preliminary calculations for both structures were carried out on the IBM 1620 computer of this laboratory, using programs prepared by M. Dobler, H.C. Mez, P. Strickler, and H. P. Weber. The least-squares calculations were carried out on the CDC 1604 computer at the Numerical Analysis Center of the University of Minnesota, using programs prepared at Princeton University under the direction of Professor R. Jacobson. This part of the work was performed by Mr E. O. Schlemper, and supported by a grant from the National Science Foundation. We thank them all for their help.

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The Crystal Structure of ScB_2C_2

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A compound of synthetic composition ScB_2C_2 was prepared, and its crystal structure was established by X-ray diffraction procedures. The presence of graphite lines in powder patterns of this material as well as small variations in lattice constants from preparations on the boron-poor side of ScB_2C_2 indicates some amount of compositional variation. Crystals are orthorhombic with space group $Pb21m$. Lattice constants for the particular crystal used are $a = 5.175 \pm 0.005$, $b = 10.075 \pm 0.007$, $c = 3.440 \pm 0.005$ Å. A novel feature of the structure is the incorporation of boron and carbon into nets of aromatic-like five- and seven-membered rings. The scandium atoms lie between the seven-membered rings of adjacent layers. In addition to these 14 light atoms, each Sc is surrounded by 5 other Sc atoms at distances which are nearly the same as in metallic scandium.

Introduction

In a recent investigation of the ternary compounds formed between rare earth elements (M) and boron and carbon, Smith (1964) has reported the occurrence

of a stable, high-melting compound, MB_2C_2 , for nearly all of the lanthanides studied. X-ray diffraction studies clearly indicated that this phase is identical with the one previously thought to be either a pure boride or a boride stabilized by carbon. A notable feature of the structure proposed by Smith (1964; see also Smith & Giles, 1965) is the incorporation of boron and carbon into nets of fused four- and eight-

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