

A Redetermination of the Silver Fulminate Structure*

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Abstract. AgCNO, orthorhombic, *Cmcm*, $a = 3.880$ (2), $b = 10.752$ (5), $c = 5.804$ (2) Å, $Z = 4$, $D_c = 4.111$ (6) Mg m⁻³, $\mu(\text{Mo } K\alpha) = 7.74$ mm⁻¹. Single-crystal diffractometer data have been collected to $\sin \theta/\lambda = 0.705$ Å⁻¹; the structure has been refined to $R = 0.021$ for 206 observed independent reflections.

Introduction. Crystals were prepared following the procedure of Singh (1959). A crystal $0.054 \times 0.054 \times 1.66$ mm was selected for data collection.

Lattice constants and intensities were determined with a Syntex *P2*₁ automatic diffractometer. Graphite-monochromated Mo *K* α radiation with variable scan rate and range were employed. A collimator of 3 mm diameter was used to insure that the crystal was totally bathed in the beam. A complete sphere of diffractometer intensity information was obtained to $\sin \theta/\lambda = 0.705$ Å⁻¹, including 1137 reflections. After averaging of equivalent reflections, 220 independent reflections remained, of which 206 had an intensity $\geq 3\sigma_i$ and were classified as observed. The average difference in intensity for groups of observed equivalent reflections was 2.92%; therefore, no absorption correction was deemed necessary or applied.

The positions of all atoms were apparent from the Patterson synthesis and agreed qualitatively with those reported by Britton & Dunitz (1965). They were further confirmed by difference Fourier synthesis. A correction for secondary extinction was made and refined, but was found to be insignificantly small. Anisotropic temperature factors were refined on all atoms. All calculations, including full-matrix least-squares refinement, were carried out with the XRAY 76 system of crystallographic programs (Stewart, 1976). Scattering factors for Ag, C, N, O were those of Cromer & Mann (1968), with an anomalous-dispersion correction for Ag. Figures were drawn with the program ORTEP (Johnson, 1965). The final wR was

0.021 with $w = 2.5/(0.03F^2 + \sigma_{F^2})^2$; a weighting analysis confirmed the suitability of this function. §

Discussion. The present work confirms the structure of silver fulminate reported by Britton & Dunitz (1965), but is more accurate. While the bond angles (Table 1) do not differ substantially from those in the earlier study, the standard deviations in the bond lengths are improved in our study by a factor of 4. Moreover, while in the earlier study anisotropic temperature factors were determined only for Ag, this has now been done for all atoms, as mentioned above.

§ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33895 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Bond lengths (Å) and angles (°) for silver fulminate

Bond lengths	This work	Britton & Dunitz (1965)
	Ag–C	2.183 (5)
Ag–O	2.766 (2)	2.78 (2)
C–N	1.159 (8)	1.14 (3)
N–O	1.251 (6)	1.22 (3)
Ag–Ag	2.902 (1)	2.926 (5)
Bond angles	This work	Britton & Dunitz (1965)
	Ag–C–Ag	83.3 (2)
Ag–C–N	138.4 (1)	–
C–N–O	180.0*	180.0*
C–Ag–C	180.0*	180.0*

* By space-group symmetry.

Table 2. Atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Ag	0	0	0
O	0	0.3758 (4)	0.25
N	0	0.2595 (4)	0.25
C	0	0.1517 (6)	0.25

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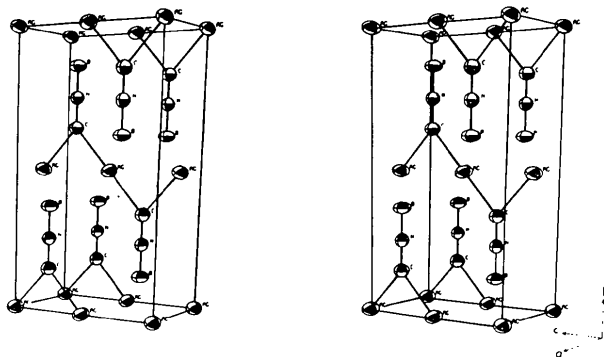


Fig. 1. Stereoscopic view of the silver fulminate crystal. The thermal ellipsoids are the 50% probability surfaces.

Our observations of anisotropic thermal motion of the Ag atoms along the c axis (Table 2) differ substantially from those reported earlier (Britton & Dunitz, 1965); the present study shows a r.m.s. amplitude of $0.168(1)$ Å along the axis, whereas an anisotropic thermal motion of 0.34 Å had been reported before. The anisotropic motion of $0.168(1)$ Å found in the present study supports the 'three-center

bond' Ag—C—Ag (Fig. 1) suggested by Britton & Dunitz (1965) to a much greater extent than their own value of 0.34 Å.

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Structure of the Potassium Molybdate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

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Abstract. $(C_{12}H_{24}O_6)_2 \cdot K_2MoO_4 \cdot 5H_2O$, triclinic, $P1$, $a = 12.089(2)$, $b = 10.547(2)$, $c = 8.472(2)$ Å, $\alpha = 113.14(2)$, $\beta = 77.88(2)$, $\gamma = 100.39(2)^\circ$, $U = 965.34(8)$ Å³, $Z = 1$, $D_m = 1.50$, $D_x = 1.47$ Mg m⁻³, $\mu = 0.625$ mm⁻¹ (for Mo $K\alpha$). One potassium ion is coordinated to an 18-crown-6 molecule and two water molecules. The other potassium ion is coordinated to another 18-crown-6 molecule, one water molecule and the molybdate anion. Both potassium ions are displaced from the mean oxygen planes of the corresponding 18-crown-6 molecules by 0.92 and 0.78 Å respectively.

Introduction. Crystals of polymolybdate and polytungstate salts often contain many waters of crystallization. The crystals, especially those with zeolitic

water molecules, are not stable during X-ray work because of the release of water molecules. By the use of a crown complex ion as a counter cation, it can be anticipated that (1) crown complexes of polymolybdate salts will be able to be crystallized in organic solvents, (2) a variety of crown compounds will make a series of counter cations of different sizes, (3) different cations in a certain crown compound will make a variety of counter cations of different charges. Therefore, the preparation of polymolybdate salts with crown compounds may provide crystals of better quality for X-ray work and may also enlarge the field of polymolybdate chemistry. In this study, we have prepared the 18-crown-6 complex of K_2MoO_4 , which is considered to be one of the precursors of polymolybdate salts (Tytko & Glemser, 1976).