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The Crystal Structure of Succinonitrilo-disilver Nitrate, $2AgNO_3 \cdot NC(CH_2)_2CN$

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The structure of $2AgNO_3 \cdot NC(CH_2)_2CN$ has been determined by X-ray analysis. It is monoclinic; $a=5.87$, $b=17.79$, $c=4.61$ Å, $\beta=118.2°$, space group $P2_1/a$, two formula units in the cell. The structure is essentially ionic and consists of the complex cations, $[AgNC(CH_2)_2CNAg]^{2+}$ (Ag–N, 1.97 Å), and the nitrate anions. All the bond lengths are normal. The molecule of succinonitrile was found to take the trans configuration; this is in conformity with the conclusion drawn from the infrared study.

In a series of investigations of the structures of the complexes with the general formula $[Cu\{NC(CH_2)_nCN\}_2]NO_3$,[1-3] Kinoshita and one of the present authors have found that succinonitrile molecules coordinate to central metal atoms, taking a "gauche" configuration. In the case of succinonitrile silver nitrate complexes, however, Shimanouchi et al. concluded, by infrared study, that succinonitrile molecules take a trans configuration in the crystals of $2AgNO_3 \cdot NC(CH_2)_2CN$.[4] In cooperation with their study, this crystal has now been subjected to X-ray analysis in order to establish the coordination about the silver atoms and the configuration of the succinonitrile molecules.

Crystallographic Data

White needle-like crystals of $2AgNO_3 \cdot NC(CH_2)_2CN$ were kindly supplied by Prof. Shimanouchi. From oscillation and Weissenberg photographs taken using Cu$K\alpha$ radiation ($\lambda=1.542$ Å), the unit cell was found to be monoclinic and to have the

1) Y. Kinoshita, I. Matsubara and Y. Saito, This Bulletin, **32**, 741 (1959).
2) Y. Kinoshita, I. Matsubara and Y. Saito, ibid., **32**, 1216 (1959).
3) Y. Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, ibid., **32**, 1221 (1959).
4) M. Ohara, T. Fujiyama and T. Shimanouchi, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

following cell dimensions:

$$a = 5.87 \pm 0.04 \text{ Å}$$
$$b = 17.79 \pm 0.05 \text{ Å}$$
$$c = 4.61 \pm 0.03 \text{ Å}$$
and $$\beta = 118.2 \pm 0.2°.$$

On the basis of this unit cell, the needle axis of the crystals was determined to be [$\bar{2}$01]. The space group was found to be $P2_1/a$—C_{2h}^5 from systematic absences. The cell contains two formula units of $2AgNO_3 \cdot NC(CH_2)_2CN$ (density; calculated, 3.30 g./cm^3; found, 3.34 g./cm^3).

The crystals are fragile and decompose gradually on exposure to daylight as well as to X-rays. The intensity data for the *hk*0, 0*kl* and *h*0*l* reflections were recorded about each principal axis on zero-level Weissenberg films by the multiple film technique, in each case using 0.05 mm. × 0.05 mm. × 1mm. crystals. Since we are merely interested in the establishment of the coordination about the silver atom and the configuration of the ligand molecule, and not in attaining high precision in the structural parameters, no special pains have been taken with the intensity estimates; they were carried out visually and were uncorrected for absorption errors. The estimated intensities were corrected for Lorentz and polarization factors. The observed structure amplitudes were brought to an absolute scale by scaling them against the calculated values at a later stage.

The Determination of the Structure

Since there are two molecules of succinonitrile in the unit cell, their center of gravity must lie on a set of twofold special positions. Thus, the succinonitrile molecule must have a center of symmetry and must assume a trans configuration.

The structure determination is based mainly on the analysis of the *hk*0 and 0*kl* reflections, which can be carried out in quite a straightforward fashion. Because of the occurrence of the heavy silver atoms, the Patterson functions are extremely simple and can be solved without difficulty, thus yielding the approximate positions of silver atoms. The signs for all but weak reflections can be derived on the basis of the positions of the silver atoms. Fourier syntheses of the electron density projected along [001] and [100] were evaluated without the weak reflections of uncertain signs. On both projections, all the atoms appeared. The maxima of some light atoms deformed under the influence of heavy silver atoms. In the refined two-dimensional Fourier syntheses, including all the terms, all the peaks of the light atoms were found in the expected positions. The atomic parameters thus obtained were refined by performing cycles of least-squares refinement of the positional and isotropic thermal parameters of the atoms: the programme employed was devised by Iitaka. The value of the discrepancy factor was 0.15 for all *hk*0, 0*kl* and *h*0*l* reflections.

The final projection of the electron density, together with that of the structure, is shown in Fig. 1.

Table I contains the final parameters of all the atoms. The observed and calculated structure amplitudes are compared in Table II.

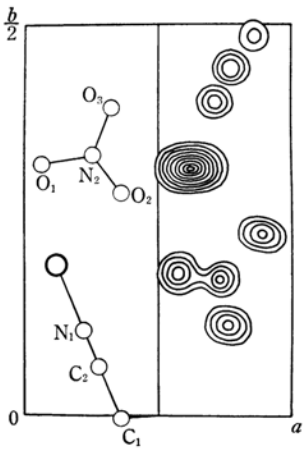


Fig. 1. The electron density and the structure projected along [001].

Table I. Final atomic coordinates and temperature factors

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Ag	0.1103	0.1921	0.1623	3.3
C1	0.354	−0.004	0.896	4.3
C2	0.274	0.061	0.660	3.2
N1	0.209	0.109	0.483	3.0
N2	0.240	0.333	0.653	3.1
O1	0.052	0.324	0.635	3.8
O2	0.312	0.395	0.646	4.3
O3	0.356	0.282	0.673	4.7

The calculations of the structure amplitudes, Fourier syntheses and least-squares refinement were carried out on the PC 2 computer of this Institute.

Description of the Structure and Discussion

The interatomic distances and bond angles are given in Table III.

The structure is essentially ionic and consists of the complex ion, $[AgNC(CH_2)_2CNAg]^{2+}$, and nitrate ions. The structure is most easily understood with the aid of Fig. 2, in which the arrangement of the complex ions and nitrate ions projected upon the crystallographic plane ($\bar{2}$01) is illustrated. The complex ion has a center of symmetry. A succinonitrile molecule takes a trans configuration; this is in conformity with the conclusion drawn from the infrared study. It is coordinated to two silver

TABLE II. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$
2	0	0	6.4	− 6.7	1	7	0	18.6	−17.6	4	1	0	7.4	− 8.0	0	14	1	2.8	0.4
4	0	0	15.4	−14.0	1	8	0	3.9	4.0	4	2	0	13.5	11.7	0	15	1	10.5	7.2
6	0	0	3.8	− 4.0	1	9	0	3.0	3.3	4	3	0	4.6	2.7	0	16	1	10.0	6.5
0	0	1	8.7	2.0	1	10	0	9.3	6.8	4	4	0	6.7	− 4.8	0	17	1	11.0	−11.0
0	0	2	16.1	−14.6	1	11	0	10.4	8.9	4	6	0	9.6	− 7.6	0	18	1	6.6	− 6.9
0	0	3	11.2	−11.9	1	12	0	12.8	−10.3	4	7	0	7.1	− 5.2	0	19	1	7.5	7.5
0	0	4	10.7	− 9.2	1	13	0	14.2	−14.0	4	8	0	11.5	10.1	0	1	2	35.6	−34.7
2	0	1	18.2	−18.5	1	14	0	12.6	12.4	4	9	0	3.8	5.5	0	2	2	11.6	12.2
2	0	2	18.6	−16.0	1	15	0	9.1	7.5	4	10	0	11.0	−10.9	0	3	2	9.3	9.4
2	0	3	4.9	− 4.3	1	16	0	6.7	− 4.3	4	12	0	3.8	3.9	0	4	2	2.5	− 3.3
2	0	4	4.0	4.1	1	18	0	2.5	− 2.2	4	15	0	3.3	2.1	0	5	2	4.9	6.6
2	0	5	3.4	3.7	1	19	0	4.3	− 3.3	4	16	0	5.9	− 5.4	0	6	2	5.4	− 6.6
4	0	1	9.2	− 9.2	1	20	0	5.2	4.1	4	17	0	3.0	− 2.1	0	7	2	17.0	−19.4
4	0	2	1.2	− 0.6	1	21	0	5.6	4.8	4	18	0	5.9	5.5	0	8	2	9.3	11.8
4	0	3	4.0	5.5	1	22	0	5.2	− 4.7	5	1	0	3.6	− 3.0	0	9	2	18.7	19.2
2	0	−1	47.3	48.5	2	1	0	29.2	−27.7	5	2	0	4.4	2.6	0	10	2	6.3	− 5.6
2	0	−2	25.4	21.6	2	2	0	9.7	− 8.2	5	3	0	10.5	8.6	0	11	2	8.9	− 8.7
2	0	−3	4.2	− 3.1	2	3	0	10.5	13.1	5	4	0	5.2	− 5.4	0	12	2	6.1	2.1
2	0	−4	10.2	−10.4	2	4	0	7.5	5.4	5	5	0	11.2	−11.0	0	14	2	2.1	1.1
2	0	−5	4.7	− 6.2	2	5	0	14.1	11.5	5	7	0	6.2	5.5	0	15	2	8.7	7.4
4	0	−1	8.2	−11.8	2	6	0	8.3	7.0	5	9	0	6.2	2.9	0	16	2	5.4	− 3.7
4	0	−2	18.4	19.8	2	7	0	21.3	−24.0	5	10	0	2.7	− 2.8	0	17	2	5.4	− 6.8
4	0	−3	14.2	14.7	2	8	0	5.6	− 6.1	5	11	0	4.8	− 4.7	0	18	2	3.9	3.4
4	0	−4	1.2	1.7	2	9	0	23.6	20.5	5	12	0	4.6	2.7	0	19	2	4.5	3.2
4	0	−5	5.9	− 4.3	2	11	0	9.5	−10.2	5	13	0	6.5	5.1	0	20	2	1.9	− 1.0
4	0	−6	3.8	− 4.2	2	13	0	3.5	− 2.4	5	14	0	1.6	− 1.1	0	21	2	1.9	− 1.0
6	0	−1	8.6	− 8.8	2	15	0	10.9	9.4	5	15	0	4.6	− 4.3	0	2	3	10.9	10.4
6	0	−2	4.2	− 5.1	2	17	0	10.0	−10.3	6	1	0	5.1	4.7	0	6	3	8.8	− 8.1
6	0	−3	2.4	3.5	2	18	0	3.8	− 3.8	6	2	0	4.0	3.1	0	8	3	11.6	10.2
6	0	−4	7.0	7.8	2	19	0	7.7	5.9	6	3	0	3.0	− 2.3	0	10	3	10.1	−11.6
6	0	−5	3.8	3.7	2	20	0	2.1	0.0	6	6	0	3.0	− 2.5	0	12	3	3.2	4.4
0	2	0	32.2	−35.6	3	1	0	4.1	− 6.2	6	7	0	4.8	4.2	0	14	3	5.7	3.0
0	4	0	1.2	− 1.8	3	2	0	13.3	−11.5	6	8	0	4.2	4.0	0	16	3	7.1	− 6.5
0	6	0	21.7	23.2	3	3	0	12.5	16.1	6	9	0	5.2	− 4.5	0	18	3	7.5	6.4
0	8	0	34.0	−30.2	3	4	0	17.2	20.1	6	11	0	3.0	2.3	0	1	4	10.6	10.3
0	10	0	27.5	27.4	3	5	0	8.1	− 7.9	0	1	1	13.6	−13.6	0	2	4	4.3	5.0
0	12	0	5.8	− 4.3	3	6	0	10.1	−12.6	0	2	1	8.4	− 8.9	0	3	4	2.2	− 3.3
0	14	0	9.7	− 8.4	3	7	0	9.5	7.7	0	3	1	16.0	16.6	0	6	4	6.0	− 4.7
0	16	0	12.0	11.8	3	8	0	3.2	2.3	0	4	1	12.9	12.9	0	7	4	5.9	6.2
0	18	0	8.4	− 5.3	3	9	0	2.3	− 1.8	0	5	1	6.8	5.8	0	8	4	6.9	6.2
0	20	0	5.9	4.3	3	10	0	6.1	6.6	0	6	1	11.4	12.6	0	9	4	6.2	− 7.2
0	22	0	1.9	0.5	3	11	0	5.6	− 5.4	0	7	1	17.6	−17.5	0	10	4	7.5	− 3.9
1	1	0	5.7	8.8	3	12	0	12.7	−11.0	0	8	1	8.4	−11.0	0	11	4	4.1	3.7
1	2	0	8.2	−11.3	3	13	0	6.8	7.7	0	9	1	17.1	17.5	0	14	4	4.1	1.2
1	3	0	24.4	−27.4	3	14	0	7.9	7.7	0	10	1	9.7	8.9	0	15	4	3.3	− 3.1
1	4	0	10.0	11.0	3	15	0	3.6	− 1.5	0	11	1	10.7	−12.4	0	7	5	3.8	3.6
1	5	0	20.2	20.1	3	16	0	3.9	− 3.8	0	12	1	5.0	− 3.0	0	9	5	3.7	− 3.7
1	6	0	18.9	−15.3	3	20	0	4.3	4.3	0	13	1	4.4	0.8					

atoms belonging to two adjacent unit cells and with a Ag–N distance of 1.97 Å. The complex ion, $[AgCN(CH_2)_2CNAg]^{2+}$, may be compared with $[AgCNAg]^+$, the existence of which has been fairly well established in cyanide solutions containing an excess of silver ions.[5-7]

The observed C–N distance of 1.12 Å is close to the value expected for the triple C–N bond length. The Ag–N–C–C bond is nearly linear. These features are similar to those found in the crystals of $[Cu\{NC(CH_2)_2CN\}_2]NO_3$. In the case of the

5) S. Glasstone, *J. Chem. Soc.*, **1930**, 1237.

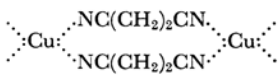
6) K. Hellwig, *Z. anorg. Chem.*, **25**, 157 (1900).

7) T. Erdey-Gruz, *Z. Physk. Chem.*, **172**, 157 (1935).

Table III. Interatomic distances and bond angles

Ag···Ag	9.69 Å		
Ag—N1	1.97	∠AgN1C1	179°
N1—C2	1.12	∠N1C2C1	178
C2—C1	1.50	∠N1C1C1′	105
C1—C1′	1.52	∠O1N2O2	120
N2—O1	1.10	∠O2N2O3	123
N2—O2	1.19	∠O1N2O3	117
N2—O3	1.11		

latter, however, there exist polymeric chains of the composition,



and a succinonitrile molecule in the complex takes a gauche configuration with respect to the central C–C bond.

As is shown in Fig. 2, the complex ions and the nitrate ions are arranged approximately in one layer parallel to the ($\bar{2}01$) plane. In each layer nitrate ions are arranged with their planes nearly perpendicular to it.

A silver atom at the end of the complex ion is surrounded by four oxygen atoms of the nitrate ions, with interatomic distances ranging from 2.49 Å to 3.36 Å. Two of them belong to the nitrate ions in the same layer as the silver atom, while the others belong to those in the adjacent layers. All the interatomic distances are in good agreement with those obtained for other crystals.

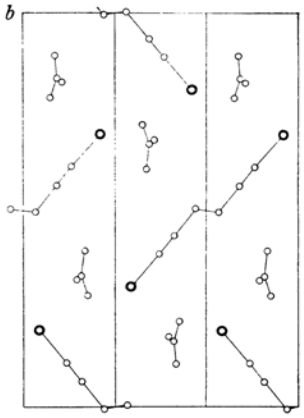


Fig. 2. The arrangement of the complex ions and nitrate ions projected on the plane ($\bar{2}01$).

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