

The Crystal Structure of Silver Dicyanamide, $\text{AgN}(\text{CN})_2$

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Silver dicyanamide is trigonal with $a = 3.601(2)$, $c = 22.868(22)$ Å, $Z = 3$, space group $P3_121$ (No. 152). The crystals are twinned. Least-squares refinement of diffractometer data converged to a conventional R value of 0.058. The structure consists of infinite spiral chains $-\text{Ag}-\text{N}\equiv\text{C}-\text{N}-\text{C}\equiv\text{N}-\text{Ag}-$ running parallel to the c direction and close-packed perpendicular to it. Bond lengths and angles are $\text{Ag}-\text{N}$ 2.111(10); $\text{N}\equiv\text{C}$ 1.148(12); $\text{C}-\text{N}$ 1.291(14) Å; $\text{N}-\text{Ag}-\text{N}$ 172.9(9); $\text{Ag}-\text{N}\equiv\text{C}$ 156.3(13); $\text{N}\equiv\text{C}-\text{N}$ 170.3(19); $\text{C}-\text{N}-\text{C}$ 127.0(18)°.

In the crystalline compounds $(\text{CH}_3)_3\text{SnN}(\text{CN})_2$ and $(\text{CH}_3)_2\text{Sn}[\text{N}(\text{CN})_2]_2$ the $\text{N}(\text{CN})_2$ groups act as bidentate bridging ligands with the two cyanide N atoms being the basic sites (Chow, 1971). In the considerably more ionic $(\text{CH}_3)_2\text{TlN}(\text{CN})_2$ a single $\text{N}(\text{CN})_2$ group is coordinated to four Tl atoms, once at the central N atom, once at one cyanide N atom, and twice at the other (Chow & Britton, 1975). It is also conceivable that $\text{N}(\text{CN})_2$ could act as a tridentate ligand with each N atom being bonded to a single metal atom. Since three-coordinate Ag had been found in the structure of $\text{AgC}(\text{CN})_3$ (Konnert & Britton, 1966) we chose to look at $\text{AgN}(\text{CN})_2$ as a possible compound in which to find tridentate $\text{N}(\text{CN})_2$ and we report the structure here. The IR spectrum of $\text{AgN}(\text{CN})_2$ (Kuhn & Mecke, 1961) is similar to those of $(\text{CH}_3)_2\text{SnN}(\text{CN})_2$ and $(\text{CH}_3)_2\text{Sn}[\text{N}(\text{CN})_2]_2$ (Chow, 1971), which could be taken as an argument against the tridentate possibility. However, on the basis of the existence of the bidentate compounds we would expect the central N atom to be more weakly basic and a metal atom attached at this site might have only a slight effect on the IR spectrum of the $\text{N}(\text{CN})_2$ group.

Experimental

Silver dicyanamide was prepared from silver nitrate and sodium dicyanamide, which in turn was prepared from sodium cyanamide and cyanogen bromide, both as described by Madelung & Kern (1922). Crystals suitable for X-ray diffraction studies were obtained by recrystallization from ammonia solution. The analysis and the IR spectrum confirm that the preparation was correct. [Calculated: C 13.81; N 24.16%. Found: C 13.81; N 24.33%. Previously reported (Kuhn & Mecke, 1961): 1326, 2183, 2227, 2283 cm^{-1} . Found: 1344, 2180, 2230, 2288 cm^{-1} .]

Precession photographs showed the crystals to be

hexagonal with apparent $6/mmm$ Laue symmetry. However, the diffractometer data on the crystal used for data collection showed that hkl and kh reflexions had unequal intensities. Therefore, the Laue symmetry is only $\bar{3}m1$. Systematic extinctions ($00l$, $l \neq 3n$) indicate the space group to be $P3_121$ (No. 152) or its enantiomer $P3_221$. The former was chosen and no attempt was made later to decide between the two alternatives after it was found that twinning was present. The crystal used was cut down from a hexagonal plate to a more nearly uniform shape and was bounded by the planes or forms (at a distance from the center in mm): $\{001\}$ at 0.050; (010) and $(0\bar{1}0)$ at 0.090; (100) at 0.096; $(\bar{2}10)$ at 0.100 mm. Data were collected at room temperature with a four-circle Hilger & Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The cell dimensions, determined from the least-squares mean of eight crystallographically independent planes, are $a = 3.601(2)$ and $c = 22.868(22)$ Å. For three formula units per unit cell the calculated density is 3.308 g cm^{-3} , which is consistent with the reported value of greater than 3.24 g cm^{-3} (Huttner & Knappe, 1930); the molecular volume is 85.6 Å³.

Intensity data were collected for 1317 reflections comprising one-half the sphere of reciprocal space out to $\theta = 26^\circ$. A moving-crystal moving-detector scan was used with 120 0.01° steps in θ and ω ; 1 s step times were used with 60 s background counts at each end of the scan. The intensities of two check reflections were measured every 40 reflections; there was a 7% decrease in intensity with time plus an increase when the X-ray tube had to be replaced; the data were put on a common scale by reference to the check reflections. Lorentz, polarization, and absorption corrections were made ($\mu = 55 \text{ cm}^{-1}$). Inspection of the data showed that the apparent $6/mmm$ symmetry found in the photographs occurred because the crystals were twinned. In the crystal used for data collection the smaller of

the twin pair was estimated to have 39–41% of the volume of the crystal. Equivalent reflections were combined and the intensities for an untwinned crystal were estimated by the method previously reported (Britton, 1972). The crystals were very often perfectly regular, transparent, hexagonal plates. This meant that they could be viewed easily along the hexagonal axis but not in other directions. The crystals always appeared completely homogeneous when viewed along the hexagonal axis under the polarizing microscope, which suggests that they were twinned across (001). This would leave

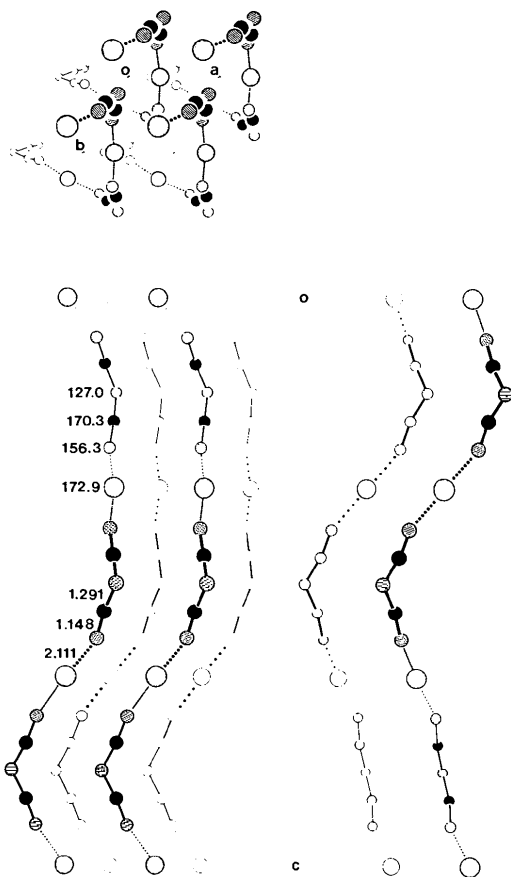


Fig. 1. The crystal structure of $\text{AgN}(\text{CN})_2$. Top: view along *c*. Bottom left: view perpendicular to the *ac* plane. Bottom right: view along *a*. Bond angles are given in degrees; interatomic distances are given in Å.

$hk0$ (five reflections) and hhl (48 reflections) with intensities unaffected by the twinning and 194 reflections (97 pairs) whose intensities had to be resolved. No reflections were omitted from the subsequent calculations but negative intensities were converted to zero F values.

Solution and refinement

The Ag atom positions were found from a Patterson map and the light-atom positions estimated from packing considerations and confirmed on a Fourier map. After the trial structure was obtained, full-matrix least-squares refinement was carried out (program *UMLSTSQ* by L. W. Finger). The structure factors for those reflections obscured by the twinning were re-estimated according to $|F_o|^2 = (|F_o|^2 + |F_o^*|^2)|F_c|^2 / (|F_c|^2 + |F_c^*|^2)$ where $F = F(hkl)$ and $F^* = F(khl)$, i.e. F and F^* are the structure factors for a twin-related pair of reflections. With anisotropic thermal parameters for all atoms the refinement converged to $R = 0.058$, $r = 0.0054$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$. The numerator of r was the function minimized. The weights used are given by $w = w_1 w_2$; $w_1 = 1$ for reflections that had been overlapped by the twinning; $w_1 = 4$ for reflections that had not been overlapped by the twinning; $w_2 = (23.9/F_o)^4$ for $F_o > 23.9$; $w_2 = 1.0$ for $F_o \leq 23.9$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962); the real part of the anomalous correction for Ag was included, the imaginary part was omitted owing to the uncertainty caused by the twinning. The final parameters are given in Table 1.*

Results

The structure is shown in Fig. 1. The $\text{N}(\text{CN})_2$ groups are bonded to the Ag atoms at the ends only and each Ag is bonded in an approximately linear fashion to

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32090 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

Table 1. *Positional and thermal parameters*

Anisotropic temperature factors are of the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$. Estimated standard deviations for the final significant figures are given in parentheses. The positional parameters are multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	-3432 (12)	<i>x</i>	0	3.61 (8)	B_{11}	2.84 (3)	3.02 (12)	-0.16 (5)	$-B_{13}$
N(0)	7559 (70)	<i>x</i>	$\frac{1}{2}$	2.3 (6)	B_{11}	2.7 (4)	-0.1 (7)	0.3 (4)	$-B_{13}$
N(1)	5227 (45)	4354 (34)	4038 (4)	3.9 (6)	3.5 (4)	3.4 (3)	2.3 (5)	-0.5 (5)	-0.3 (3)
C(1)	6325 (47)	5591 (36)	4505 (3)	2.1 (8)	3.0 (7)	1.8 (3)	1.0 (8)	-0.3 (6)	0.3 (3)

Table 2. Average bond distances (Å) and angles (°) in the $N(CN)_2^-$ group

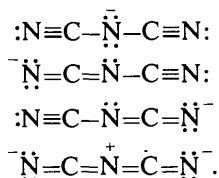
Counter ion	N—C	C≡N	C—N—C	N—C≡N	Reference
Ag ⁺	1.29 (1)	1.15 (1)	127 (2)	170 (2)	a
(CH ₃) ₃ Sn ⁺	1.26 (2)	1.12 (1)	130 (1)	173 (1)	b
(CH ₃) ₂ Sn ²⁺	1.29 (1)	1.13 (1)	124 (1)	172 (1)	b
(CH ₃) ₂ Tl ⁺	1.28 (4)	1.18 (5)	120 (3)	172 (4)	c

References: (a) This work. (b) Chow (1971). (c) Chow & Britton (1975).

two N atoms. The resultant infinite linear chains Ag—NCNCN—Ag—NCNCN— form spirals about the 3₁ axes in the crystal. Adjacent chains are closest-packed at a distance of 3.601 Å (= *a*). The tilt of the chains makes the distances of close approach 3.24, 3.26, and 3.34 Å for C···N(0), 3.35 Å for C···N(1), and 3.42 Å for N(0)···N(1) contacts. Short N(1)···Ag distances are discussed in the next paragraph.

The Ag—N(1) bond distance of 2.111(10) Å is the same as that in AgNCO, 2.115(8) Å (Britton & Dunitz, 1965), and shorter than the average found in AgC(CN)₃, 2.16 Å, three-coordinate Ag (Konnert & Britton, 1966), or in AgC(CN)₂NO, 2.23 Å, four-coordinate Ag (Chow & Britton, 1974). In addition to the two N(1) atoms at 2.111 Å each Ag atom is surrounded by four more N(1) atoms from N(CN)₂ groups in adjacent chains, two at a distance of 2.91 Å and two at a distance of 3.08 Å. The six N(1) atoms are in approximately octahedral directions from the Ag with the N—Ag—N angles ranging from 74 to 110° for *cis* N atoms and from 173 to 176° for *trans* N atoms.

The distances and angles in the N(CN)₂⁻ group are compared in Table 2 with those found in earlier structures. The results are in good agreement and can be summarized as follows. The central N—C bond distance is that of a carbon—nitrogen double bond. The terminal C—N bond distance is that of a carbon—nitrogen triple bond. The C—N—C angle is significantly greater than 120°. The N—C—N bond angle deviates significantly from linear. There are four resonance structures that can be drawn for this ion:



The first of these does not help to account for the geometric features and must be relatively unimportant, a conclusion that is supported by the observation that only in the dimethylthallium compound does the central N atom interact with a metal atom, while the terminal N atom invariably does. The second and third resonance structures are the dominant ones but the C—N—C angle tells us that the fourth resonance structure must make a significant contribution. The impor-

ance of the fourth structure also accounts, more or less, for the bond distances; the situation here is analogous to that in nitrous oxide where the N—N distance is approximately that of a triple bond and the N—O distance is approximately that of a double bond (Pauling, 1960). The bending of the N—C—N angle away from linearity cannot be explained by any resonance effect. The predominant factor in the bending is that the cyanide groups bend away from each other in the plane of the molecule. There are other examples of this kind of distortion, e.g. S(CN)₂ and CH₂(CN)₂ (Britton, 1967, pp. 112–114). Hirshfeld (1964) has pointed out that this is a widespread phenomenon, not limited to cyanides, and has suggested that it arises from repulsions between non-bonded atoms.

As can be seen in the lower right of Fig. 1, the N(CN)₂⁻ group and the Ag—NCNCN—Ag portion of the chain are not planar. If all atoms in the N(CN)₂⁻ group are given equal weight, the N(1) atoms deviate by 0.036 Å and the C atoms by 0.069 Å from the least-squares plane. The Ag atoms closest to the N(1) are 0.53 Å from this plane. These distortions presumably are a consequence of the spiral packing.

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