Polymorphism in Silver Thiocyanate: Preparation of a New Phase and Its Characterization by X-ray Powder Diffraction

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Abstract
A new crystalline phase of silver thiocyanate, AgSCN, has been prepared in the presence of gelatin. X-ray powder diffraction data were indexed for an orthorhombic cell with $a = 4.083(1)$, $b = 7.043(1)$, $c = 11.219(2)$ Å, $Z = 4$. The crystal structure was solved and refined in $Pmnn$ to $R_F = 0.11$ from 54 peak-height powder intensities. Strongly bonded, approximately linear AgNCS units [Ag-N = 2.00(5) Å] are joined together into a three-dimensional polymeric network by three long Ag-S bonds [2.70(2), 2 x 2.64(1) Å]. The configurations at both Ag and S are intermediate between tetrahedral and trigonal pyramidal.

Introduction
More than twenty years ago, while studying the effect of thiocyanate ions on the formation and growth of silver halide crystals, Berry & Marino (1959) of our laboratories discovered a new crystalline phase of AgSCN. They were unable to index the X-ray powder diffraction pattern, and the material was forgotten until one of us (JEM) rediscovered it during new studies of silver halides.

We call the new phase $\beta$-AgSCN and the long-established phase $\alpha$-AgSCN. The single-crystal structure (Lindqvist, 1957) and an accurate X-ray powder diffraction pattern (JCPDS, 1979) have been published for the $\alpha$ phase. We report here the preparation, the X-ray powder diffraction data, and the crystal structure of the $\beta$ phase.

Experimental

1. Preparation
Preparation of AgSCN under most conditions yields the $\alpha$ phase. However, in the presence of gelatin and at low pAg (<5) or at rapid precipitation rates, the $\beta$ phase can be formed exclusively. Despite numerous attempts, we have not been able to grow the $\beta$ phase in the absence of gelatin or as large crystals suitable for a single-crystal X-ray structure determination.

(a) Low pAg preparation. To a deionized bone-gelatin solution (1.5%, 350 ml, 313 K), silver nitrate (2 mol dm$^{-3}$, 200 ml) and sodium thiocyanate (2 mol dm$^{-3}$, ~200 ml) solutions were added simultaneously with vigorous stirring while a constant pAg of 3.0 was maintained by slight variations of the NaSCN addition rate. The solutions were added at 1 ml min$^{-1}$ for 5 min. The addition rate was then accelerated at a rate of 3.2 ml min$^{-2}$ until 0.4 mol of AgNO$_3$ had been added. The microcrystals of $\beta$-AgSCN were freed of soluble salts by centrifugation. These crystals are ca 4 x 1.2 μm in projection and have a unique ‘fish-tail’ shape (Fig. 1a).

(b) Rapid-precipitation preparation. To a bone-gelatin solution (12.5%, 19.2 l, 343 K), silver nitrate (1.15 mol dm$^{-3}$, 20.8 l, 323 K) and sodium thiocyanate (1.22 mol dm$^{-3}$, 20.0 l, 323 K) solutions were added simultaneously at 41 rain$^{-1}$ with vigorous stirring, starting the NaSCN solution 5 s before the AgNO$_3$ solution. The pAg varied between 6.4 and 7.4 during the precipitation. The resulting suspension was cooled to solidify the gelatin, cut into ‘noodles’, and washed for 1 h with chilled water to remove the sodium nitrate. The final pAg was 6-0 at 313 K. The crystals of $\beta$-AgSCN are prismatic with a coffin-like appearance and are ca 0.3 x 0.3 x 0.4 mm (Fig. 1b).

(c) Removal of gelatin. An 800 g portion of an AgSCN/gelatin suspension was warmed to 313 K, centrifuged free of nonadsorbed gelatin, and suspended in 800 ml of distilled water containing 80 mg of Takamine enzyme. The mixture was stirred (0.5 h, 313 K), centrifuged, resuspended in distilled water with the aid of sonication, centrifuged again, resuspended in distilled water (120 ml), and freeze dried to a free-flowing white powder. Although this procedure removes most of the gelatin, some gelatin fragments probably remain, which is known to happen when similar procedures are used on silver halides (Weiss, Ericson & Herz, 1967). The sample used to obtain the X-ray data was prepared by the low pAg technique and its chemical analysis gave (%): Ag, 65.4; S, 17.7; C, 8.3; N, 8.9. The theoretical values for AgSCN are (%): Ag, 65.0; S, 19.3; C, 7.2; N, 8.4; and indicate that the sample is reasonably pure.
2. DSC and IR data

The β phase is thermally unstable and upon heating converts irreversibly to the α phase. Differential scanning calorimetry data were obtained with a DuPont 990 thermal analyzer equipped with a DTA/DSC cell. Samples were nitrogen purged and heated between 5 and 20 K min⁻¹. These data show that β-AgSCN undergoes an exothermic change between 423 and 443 K, depending on the sample and the heating rate. There is no loss of weight, which shows that the samples are not hydrates.

In addition to distinct X-ray powder diffraction patterns, the α and β phases can be distinguished by the CN stretching frequency in the infrared spectra. During our studies, a CN absorption band at 2140 cm⁻¹ has been correlated with α-AgSCN; a band at 2133 cm⁻¹ arises from β-AgSCN.*

*The infrared spectra, the calculated structure factors, and additional stereoscopic figures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36808 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3. X-ray measurements

The X-ray powder diffraction data (Table 1) were obtained at 296 K with a Siemens type F diffrac-

![Fig. 1. Electron micrographs of β-AgSCN prepared (a) at low pAg and (b) by rapid precipitation.](image-url)
Table 2. Crystal data for β-AgSCN

|                | Pmnn (No. 58) | Primitive orthorhombic unit cell using Visser’s (1969) computer technique and program. Cell constants were accepted the entire X-ray beam at all angles and its graphite monochromator. The sample area intercepted the entire X-ray beam at all angles and its thickness (0.7 nm) made absorption corrections unnecessary. From an electron micrograph, the sample comprised very fine crystals, 4 μm long by 1 μm in cross section, which allowed a smooth sample surface to be formed. We tried to minimize preferred orientation by not smearing or pressing hard on the sample. It subsequently became apparent, however, by comparison with X-ray diffractograms from samples with smaller, more spherical particles, that some preferred orientation was present and that intensities from planes with l large relative to h and k were systematically decreased. No correction was made for this effect.

Intensities represent relative peak heights from the diffractograms. The angular positions were calibrated with Si as an internal standard (a = 5.4301 Å); we estimate the measurement error in 2θ to be 0.02°. Distinct diffraction maxima extended well beyond the limit (67° 2θ) of Table 1. Many of the peaks for which 2θ values could be obtained were shoulders of other peaks. Selected scans with V-filtered Cr Kα radiation resolved several of these and also the intense reflection at 2θ = 26.52°, which was important for resolving the assignment of crystal system.

4. Unit-cell determination

Observed reflections were indexed on the basis of a primitive orthorhombic unit cell using Visser’s (1969) computer technique and program. Cell constants were refined by least squares (Appleman & Evans, 1973) in which weights of 1.0, 0.1, and 0.01 were assigned, respectively, to isolated peaks, the major peak of a doublet, and shoulders; 32 reflections were used. Cell constants and other crystal data are listed in Table 2.

The presence of the four reflections 011, 012, 101, and 130 is sufficient to eliminate 49 of the 59 possible orthorhombic space groups. The apparent systematic absences (h0l, h + l odd and hh0, h + k odd) lead to either P2nn (No. 34) or Pmnn (No. 58) as the probable space group. The structure solution indicated that Pmnn is correct. For this group, the figures of merit are M_{20} = 37 (de Wolff, 1968) and F_{30} = 44 (0.018, 38) (Smith & Snyder, 1979).

In the early stages of the analysis, a hexagonal cell with a = 8.144(1) and c = 11.217(2) Å was considered. However, several shoulders could not be accommodated by this cell and it was rejected. The hexagonal cell arises because b ≈ \sqrt{3a} for the orthorhombic cell. Diffractograms recorded with a relatively compressed 2θ scale do not show the shoulders and hence appear to be from the hexagonal cell.

5. Crystal structure determination

The structure was solved and refined using the computer programs of the Enraf-Nonius Structure Determination Package (1980), including the plotting program ORTEP II (Johnson, 1971). Neutral-atom scattering factors and corrections for anomalous scattering by all atoms were obtained from International Tables for X-ray Crystallography (1974). Refinement was by unit-weighted full-matrix least squares which minimized \( \sum (F_o - K |F_i|)^2 \).

The peak-height intensities were corrected for Lorentz-polarization, monochromator, and multiplicity effects to yield a set of 54 nonzero uniquely indexed relative structure factors, including 9 reflections between 67 and 89° 2θ not listed in Table 1.

The initial structure solution was in P2nn. A Patterson map revealed the position of the Ag atom, for which isotropic least-squares refinement gave R_{f} = 0.29. The subsequent electron density map contained many peaks, all at x = 0 and 1/2, but could not be interpreted. To include all of the important observed amplitudes in the Fourier calculations, the data set was expanded to 76 reflections by apportioning the observed intensities of the multiple reflections according to the calculated structure factors. The electron density map obtained from the expanded data set contained fewer peaks; two were interpreted as S and C. Refinement in P2nn with the original 54 reflections gave R_{f} = 0.19, but the x parameters of S and C oscillated around x = 0. In Pmnn, with the atoms constrained to the mirror at x = 0, the parameters converged to give R_{f} = 0.19. Refinement with anisotropic thermal parameters for Ag further reduced R_{f} to 0.16.

From the C–S and C–Ag distances and the low temperature factor for C, we postulated that the refined C atom was actually located at the mean position of C and N. This position was split into two positions to give reasonable distances and angles. Refinement of the four atoms (16 parameters, 54 reflections) converged to a reasonable structure with R_{f} = 0.11. The final atomic parameters are listed in Table 3. The use of peak height rather than integrated intensities and the probable presence of preferred orientation are reflected in the relatively large values of the temperature factors obtained. Calculated peak-height intensities (Smith & Holomany, 1978) are included in Table 1. The rather poor agreement for
Table 3. Least-squares parameters for $\beta$-AgSCN

| Equivalent positions of $Pmn\bar{n}$ (No. 58) are $z(x,y,z)$, $\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$. |
|---|---|---|---|
| $x$  | $y$  | $z$  | $B$  |
| Ag  | 0.1718(20) | 0.1434(14) | $* $ |
| S   | 0.525(7)  | 0.239(5)  | 6.8(13)  |
| C   | 0.656(18) | 0.106(11) | 3.1(32)  |
| N   | 0.758(15) | 0.029(11) | 6.1(37)  |

*Anisotropic: $T = \exp - \left[0.169(14)h^2 + 0.024(3)k^2 + 0.018(2)l^2 + 0.01 l(5)k(f) \right]$.  

002 and 012 arise from the preferred orientation apparently present in the sample.

### Discussion

Bond lengths and angles are given in Table 4. The uncertainties in these quantities are very large and allow only a qualitative discussion of the bonding. The structure, shown stereoscopically in Fig. 2, comprises approximately linear AgNCS units linked together into a three-dimensional polymeric network. Both Ag and S are tetracoordinate with the configuration around each being intermediate between tetrahedral and trigonal pyramidal. For Ag, the atoms Si, Sii, and Niii form a base [\( \Sigma \text{angles} = 352(1) \text{°} \)] with Ag located 0.38(2) Å above the base. For S, the base i

![Fig. 2. Stereoscopic view of a portion of the structure of $\beta$-AgSCN tilted 15° from (010). The c axis is horizontal, left to right, and a is vertical, bottom to top, but tilted 15° into the figure. The filled circles represent silver atoms. All atoms lie in the mirror planes of $Pmn\bar{n}$.

Fig. 3. (a) (10\(\bar{1}\)) projection of $\beta$-AgSCN. (b) (102) projection of $\alpha$-AgSCN. The drawings have the same scale and silver atoms are represented by filled circles.

![Fig. 3](image)

Table 4. Bond lengths (Å) and angles (°) for $\beta$-AgSCN

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-S</td>
<td>2.707(18)</td>
</tr>
<tr>
<td>Ag-N</td>
<td>1.75(5)</td>
</tr>
<tr>
<td>S-C</td>
<td>1.74(5)</td>
</tr>
<tr>
<td>C-N</td>
<td>1.14(5)</td>
</tr>
<tr>
<td>Ag-S-C</td>
<td>105(2)</td>
</tr>
<tr>
<td>Ag-N-C</td>
<td>105(2)</td>
</tr>
<tr>
<td>N-C-S</td>
<td>105(2)</td>
</tr>
</tbody>
</table>

Symmetry code:
(a) $-\frac{1}{2} + x, -\frac{1}{2} + y, \frac{1}{2} - z$  
(b) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$  
(c) $x, 1 - y, z$

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### References

