molecule of tetrabenzmonazaporphin may be distorted by the presence of the nitrogen atom.

Secondly, some detail in the transforms is lost by reproduction and some geometrical distortion is introduced by non-linearities in the electronic equipment. The transforms in Figs. 2(a) and 2(c) are not as detailed as those shown by Hanson, Lipson & Taylor (1953). The lack of clarity is, however, partly caused by the difficulty of photographing the television screen; the exposure for Figs. 2(a) and 2(c) is of the order of 30 sec. and the pattern is not completely steady over this period.

Finally, the weighted reciprocal lattice is not in the same plane as the television screen and some parallax errors may result.

Work is in progress to reduce as far as possible those difficulties caused by the apparatus itself, but obviously the problem of non-planarity of the molecule is one that sets a limiting factor to the methods described. Nevertheless, the results should serve as a sound basis for refinement by standard methods.

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On the Crystal Structure of Silver Thiocyanate

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The crystal structure of AgSCN has been determined from three-dimensional X-ray data. There is still some question about the exact positions of the light atoms, but the general picture of the structure is well established. The structural unit is an endless chain with the composition AgSCN, formed by covalent bonds from a silver atom to the end sulphur of one thiocyanate group and the end nitrogen of another thiocyanate group. The chain has a zigzag shape and is bent at S (104°) as well as at Ag (165°). There is silver–sulphur interaction between the chains as they are packed together.

A thorough reinvestigation of the structure has been started.

1. Introduction

This investigation forms part of a study of the crystal chemistry of silver salts. Its aim is to elucidate the stereochemistry of the monovalent silver ion in solid compounds. The results are incomplete and a thorough reinvestigation has been started by Mr Strandberg in this Institute along lines indicated in this paper. It has, however, been thought worth while to publish the paper in the present state because of the theoretical interest of the structure.

2. Crystals

AgSCN was first precipitated as a powder in two different ways: with a slight excess of SCN⁻ and with a large excess of Ag⁺. The two precipitates gave identical powder photographs, thus showing no sign of the dimorphism existing in the case of AgI (Block &

Müller, 1931). The powder was dissolved in an aqueous ammonia solution and single crystals of AgSCN were formed by free evaporation from this solution. The identity of the crystals with the powder was confirmed by powder photographs.

A roughly prismatic needle with the dimensions $0.2 \times 0.1 \times 0.04$ mm.³ was used for the X-ray work. Rotation and Weissenberg photographs were taken around the needle axis (c axis) with Cu K radiation. Seven layer lines (0–6) were obtained.

The crystal symmetry was found to be monoclinic and the cell dimensions are

$$a = 8.74, \ b = 7.96, \ c = 12.32 \text{ Å}, \ \beta = 138.6°,$$

as determined from powder photographs taken with Cu $K\alpha$ radiation in a Guinier camera. The density of AgSCN has been determined as 3.746 g.cm.⁻³ (Huttner & Knappe, 1930). This corresponds to 7.7 formula units

AgSCN in the cell. The deviation from the whole number 8 seemed rather large considering the accuracy claimed for the density determination. A new measurement was therefore made by a pycnometric method, giving the value $3 \cdot 751$ g.cm.$^{-3}$. The fact that too low a value was obtained could be traced back to the use of benzene (dissolving AgSCN) in the determination. A new determination with carbon tetrachloride gave the value $3 \cdot 920$ g.cm.$^{-3}$, corresponding to $8 \cdot 0$ molecules in the unit cell. (I wish to thank Mr Lars Henrik Andersson for valuable aid with this determination.)

The conditions for possible reflexions were: $h+k = 2n$ for hkl; $l = 2n$ for $h0l$. The two possible space groups with these conditions fulfilled are Cc (No. 9) and $C2/c$ (No. 15). No measurable piezoelectricity could be detected, indicating the space group to be $C2/c$. (I am grateful to Mr J. Bæcklund for his aid with this investigation.)

Relative $|F|^2$ values were calculated from the estimated intensities, using Lu's (1943) curves. No effort was made to correct for the absorption. It was possible, however, to calculate that there cannot be any great discontinuous changes in the absorption, the maximum absorption being of the order of 30%.

3. Atomic positions

The general position of space group $C2/c$ is

$$8(f): \pm(x, y, z), \ \pm(\tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z), \ \pm(x, \bar{y}, \tfrac{1}{2}+z),$$
$$\pm(\tfrac{1}{2}-x, \tfrac{1}{2}-y, \bar{z}) \, .$$

The parameters x_{Ag}, y_{Ag}, z_{Ag} and x_S, y_S, z_S of the eight silver and sulphur atoms in the unit cell could be derived from a study of the three-dimensional Patterson function, which was calculated on the Hägg–Laurent (1946) machine. The following parameters were obtained:

$$8 \text{ Ag in } 8(f): x_{Ag} = 0 \cdot 05, \ y_{Ag} = 0 \cdot 10, \ z_{Ag} = 0 \cdot 41;$$
$$8 \text{ S } \text{ in } 8(f): x_S = 0 \cdot 23, \ y_S = 0 \cdot 22, \ z_S = 0 \cdot 68.$$

Considering only the region $x=0-\tfrac{1}{2}$, $y=0-\tfrac{1}{4}$, $z=0-1$ because of the symmetry of the space group, the corresponding maxima in $P(x, y, z)$ are:

Ag–Ag	(0·10, 0·20, 0·82)	21	22
	(0·10, 0·00, 0·32)	43	44
	(0·00, 0·20, 0·50)	49	44
Ag–S	(0·18, 0·12, 0·27)	14	15
	(0·28, 0·12, 0·59)	15	15
	(0·32, 0·18, 0·23)	15	15
	(0·22, 0·18, 0·91)	13	15

The relative magnitudes of the maxima are given in the third column compared with the weights (fourth column) calculated from the space-group symmetry and the atomic numbers of silver and sulphur. The agreement is satisfactory.

The signs of the F values were calculated, using the silver and sulphur positions. A three-dimensional electron-density calculation was performed. The silver atoms appeared with a relative magnitude 1400 compared with 500 for the sulphur atoms, giving a ratio $2 \cdot 8$ in agreement with the ratio $2 \cdot 94$ between the atomic numbers. No other maximum exceeded the magnitude 150. The parameters arrived at were:

$$x_{Ag} = 0 \cdot 048, \ y_{Ag} = 0 \cdot 105, \ z_{Ag} = 0 \cdot 404;$$
$$x_S = 0 \cdot 211, \ y_S = 0 \cdot 217, \ z_S = 0 \cdot 700.$$

The next step in the structure determination was to try to obtain an idea about the positions of the carbon and nitrogen atoms giving the orientation of the thiocyanate group. In the three-dimensional electron-density distribution there were, however, more than two other pronounced maxima. A difference electron-density projection along the c axis was then attempted, based on the structure factors calculated from the silver and sulphur contributions. This excluded the maxima due to series-termination errors and left the following positions:

$$x_N = 0 \cdot 349, \ y_N = 0 \cdot 067, \ z_N = 0 \cdot 047;$$
$$x_C = 0 \cdot 465, \ y_C = 0 \cdot 186, \ z_C = 0 \cdot 089.$$

The F_c values for all observed reflexions were calculated for the positions assumed above, using an empirical temperature factor $\exp\{-2 \cdot 5 \,(\sin \theta/\lambda)^2\}$ (which partly includes absorption effects). The reliability index was $0 \cdot 127$.

4. Refinement and assessment of accuracies

A three-dimensional back-shift correction was made with the F_c values but the refined positions of the light atoms (N and C) did not seem to correspond to a real improvement of the structure. (The shifts in Ag and S were very small.) The reliability index increased to $0 \cdot 133$, and a detailed study showed that the increased error was mainly due to the shift in the light atoms. The following sources of error, which may cause this effect, have to be considered:

1. Absorption effects which can be eliminated only by use of a cylindrical or spherical crystal for which the effect can be calculated.
2. Errors in the atomic form factors of silver and sulphur.
3. Anisotropic temperature factors.
4. The threshold value of the intensities is too large.
5. The reflexion statistics in l is unsatisfactory owing to the rotation around the long c axis.

Some of these errors might have been at least partly eliminated in this investigation by more elaborate technique. A complete reinvestigation has, however, been thought worth while in view of the indications it may give of the possibilities of determining light

atoms accurately in the presence of dominating heavy atoms. The detailed experimental data will in due course be published, together with the results of that investigation.

In the following discussions the original atomic parameters obtained from the three-dimensional electron-density function were used.

The standard deviations in the atomic coordinates were calculated using Cruickshank's (1949) method. The following results were obtained:

Ag: $\sigma(x) = 0\cdot004,$ $\sigma(y) = 0\cdot004,$ $\sigma(z) = 0\cdot006$ Å;

S: $\sigma(x) = 0\cdot009,$ $\sigma(y) = 0\cdot009,$ $\sigma(z) = 0\cdot017$ Å;

C: $\sigma(x) = 0\cdot024,$ $\sigma(y) = 0\cdot017,$ $\sigma(z) = 0\cdot041$ Å;

N: $\sigma(x) = 0\cdot027,$ $\sigma(y) = 0\cdot026,\cdot$ $\sigma(z) = 0\cdot075$ Å.

The large $\sigma(z)$ values are due to the unfavourable reflexion statistics in l. The values for carbon and nitrogen are certainly only crude approximations.

5. Description and discussion of the structure

The unit of the structure is an endless chain
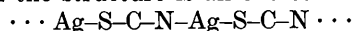
$$\cdots \text{Ag–S–C–N–Ag–S–C–N} \cdots$$

of composition AgSCN (one of the chains in Fig. 3). The bond distances within such a chain are

$$\text{Ag–S} = 2\cdot428\pm0\cdot011 \text{ Å}, \quad \text{Ag–N} = 2\cdot223\pm0\cdot028 \text{ Å},$$
$$\text{C–N} = 1\cdot186\pm0\cdot068 \text{ Å}, \quad \text{C–S} = 1\cdot636\pm0\cdot029 \text{ Å}.$$

The accuracy does not permit an assessment of bond orders to the C–S and C–N bonds. The calculated covalent bond distances for Ag–S and Ag–N are 2·4–2·5 Å and 2·1 Å (found in AgCN by Braekken (1929) and West (1935)). The ionic radius of Ag^+ is not well known but the sums of Ag^+ radius and the van der Waals radii of S and N would fall within the limits 2·90–3·05 Å and 2·55–2·70 Å, respectively. The idea of an endless chain joined by covalent bonds as the unit of the structure is thus fairly well established, even if the agreement for the Ag–N bond is not perfect.

The main problem of this structure is the question of the linearity along S–Ag–N–C–S. It has been claimed by Scouloudi (1953) that the SCN groups in $Hg(SCN)_4^{2-}$ are bent at the carbon atom with an angle of 163° 12′. Such a deviation from linearity is found in this structure too, as shown in projection along the b axis in Fig. 1. It is possible, however, to draw a
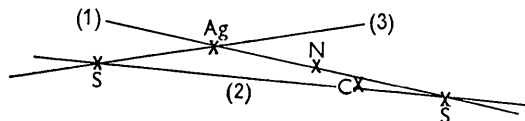

Fig. 1. The atomic positions of the chain unit in the projection along the b axis.

straight line (1) from Ag to S to which the perpendicular distance from the nitrogen and carbon atoms are

smaller than twice the standard deviation of the atomic positions. No significant deviation from linearity has thus been found along S–C–N–Ag.

The possibility of a linear bonding all along S–C–N–Ag–S can be tested by inspection of the atomic positions S–Ag–S (Fig. 1). A straight line (2) through the sulphur atoms passes in this case at a distance of no less than about $25\sigma_S$ from the silver atom, and the deviation from linearity is thus conclusively established. A line (3) through Ag and the neighbouring S passes at a shortest distance of $6\sigma_N$ from the nitrogen atom, which further confirms that the deviation from linearity is obtained at the silver atom.

It can thus be concluded that the chain AgSCN is not linear all along S–C–N–Ag–S, that the part S–C–N–Ag is linear within the limits of experimental error, and that the deviation from linearity probably occurs mainly at the silver atom. (The last conclusion can only be wrong if the calculated standard deviation σ_N is much too small.)

The bond angle at the sulphur atom has been determined from the Ag–S and Ag–Ag distances, assuming linearity along S–C–N–Ag. The value 103·79° is close to the tetrahedral angle value, and supports the idea that the electronic configuration of the SCN^- ion in AgSCN can be described as

$$\overset{\diagdown}{:}S–C\equiv N– .$$

The alternative

$$.\overset{\diagdown}{S}=C=\overset{\diagup}{N}.$$
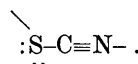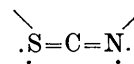
would require angles of 125·5° at nitrogen as well as sulphur and can be ruled out. This structure can be compared with the straight-chained AgCN:

$$-Ag–C\equiv N–Ag– .$$

The nature of the Ag–N and Ag–S bonds may, however, be more complicated than a mere sp hybridization, because a contribution from the d electrons of the silver atoms is not excluded.

Such caution in the conclusions about the nature of the chemical bond is particularly well motivated, considering the bond angle at the silver atom. Assuming linearity along S–C–N–Ag, this can be calculated from the silver and sulphur positions. The angle found is 164·50°. The same deviation from linearity has in fact been observed earlier by Harker (1936) in prostite and pyrargyrite, where the S–Ag–S angle is 165°. Other examples of non-linearity of the sp hybridization atoms with d electron shells is found in $Hg(SCN)Cl$ (174°) and in $NH_4Hg(SCN)_3$ (155°) (Zhdanov & Zvonkova, 1953). This configuration thus seems to be easily distorted.

It is hoped that the reinvestigation of the structure will give more accurate values of bond distances so as to permit a more penetrating discussion of the nature of the chemical bonds in the AgSCN chain.
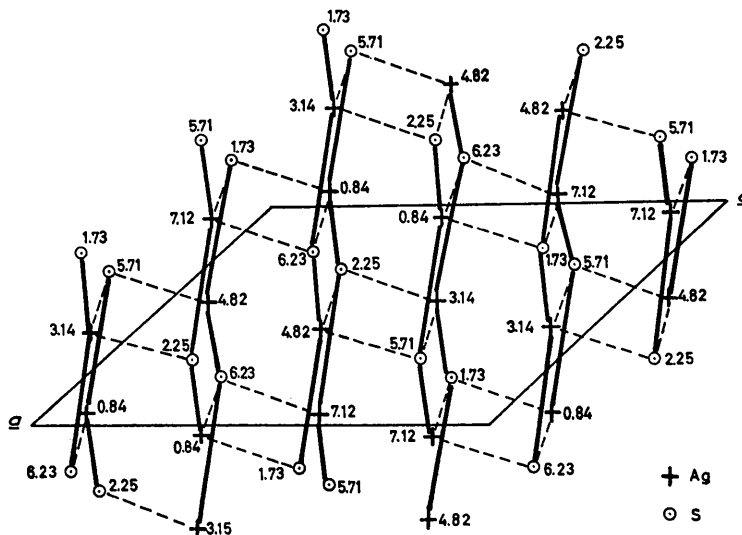
Fig. 2. The arrangement of the chains in the cell. Carbon and nitrogen atoms are omitted and the thiocyanate groups are indicated as long lines between silver and sulphur atoms. Dashed lines show ionic interaction. The figures give the heights in Ångström units.

The packing of the chains is outlined in Fig. 2, where carbon and nitrogen atoms are omitted. The dashed lines indicate Ag–S interaction between the chains. These distances of $2 \cdot 997 \pm 0 \cdot 011$ and $2 \cdot 886 \pm 0 \cdot 012$ Å are significantly different from the short Ag–S bond distance and are in agreement with an Ag^+–S distance of $2 \cdot 9$–$3 \cdot 1$ Å. This interaction between the chains is strong enough to prevent typical cleavage along the chain direction.

It is easy to see in Fig. 2 that the chain directions are almost perpendicular to the c axis. The idealized packing in one such layer of chains is shown in Fig. 3, viewed in the direction of the c axis, with approximate van der Waals radii drawn around the atomic positions.
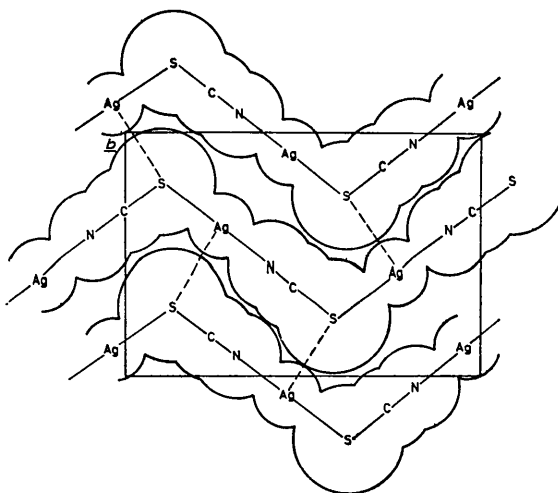
The introduction to this paper stated that our main interest in this structure was to study the stereochemistry of silver. From this point of view the most interesting results are the following: A silver atom is bound to one nitrogen and one sulphur atom by covalent bonds. This excludes such formulae as $Ag[Ag(SCN)_2]$ or $Ag[Ag(NCS)_2]$. The covalent co-ordination number two was expected, but the non-linearity of this coordination is a very interesting feature of the structure. An obvious extension of this investigation will be to study, for example, $NH_4SCN.AgSCN$ to find out whether such non-linear coordination exists in the assumed ions $Ag(SCN)_2^-$ or $Ag(NCS)_2^-$ of this compound.

Finally I wish to thank Prof. G. Hägg for all facilities put at my disposal.

Fig. 3. The packing of adjacent chains viewed along the c axis. Dashed lines show ionic interaction.

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