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On the Molecularity of Crystalline Cyclohexanethiolatosilver(I)

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The literature contains very little information on the structural chemistry of the compounds $(MSR)_n$, M = Cu, Ag, Tl, in crystalline or solution phases. Åkerström [1] has investigated the silver(I) alkanethiolates and cycloalkanethiolates, and found that the ligand structure influences the general solubility and the degree of association, n, in benzene and chloroform. In general n is related to the chain branching at the thiolate α-carbon atom: silver *tert*-alkanethiolates are octameric in solution, and silver *sec*-alkanethiolates are normally dodecameric in solution. Where there is less chain branching close to the sulphur atom the silver alkanethiolates have very low solubilities. It is presumed that the insoluble AgSR compounds are non-molecular in at least one dimension, but structures for the molecular oligamers have not been proposed.

Recently Hesse *et al.* [2] reported the first crystal structure for an AgSR compound, namely that of silver cyclohexanethiolate. The structure was described as being one-dimensionally non-molecular, with the infinite chain composed of a roughly tubular core of silver and sulphur atoms, surrounded by the cyclohexyl groups. However, $(AgSC_6H_{11})_n$ is evidently molecular when dissolved in benzene, as Åkerström reported an uncertain value of n = 25.

I have examined Hesse's structure of crystalline $AgSC_6H_{11}$ in terms of its molecularity and possible structures for $AgSC_6H_{11}$ and related silver alkanethiolates in solution. The conclusion I reach is that the crystal structure is more appropriately interpreted as being composed of the $(AgSC_6H_{11})_{12}$ cyclic molecules shown in Fig. 1.

In the following description Hesse's notation has been retained, that is the silver atoms in the asymmetric unit are numbered 1 to 6, the sulphur atoms lettered A to F, and a bar denotes an atom related by a centre of symmetry. Silver atoms 1 and 2 possess approximately linear twofold coordination (SA–Ag1–S$\bar{C}$ = 169, SE–Ag2–SD = 167°). Silver atoms 4 and 6 possess severely distorted trigonal planar stereochemistry of the type shown in Figure 2; distance *c* (2.75, 2.87 Å) is substantially longer than distances

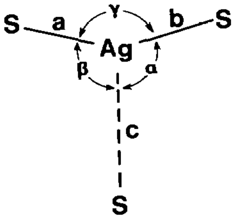

Figure 2. The stereochemistry about silver.

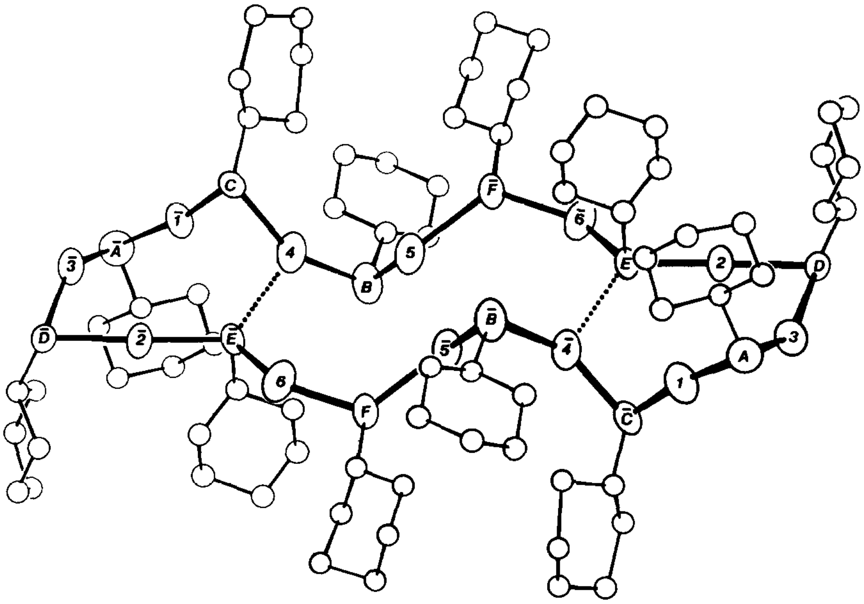

Figure 1. The $(AgSC_6H_{11})_{12}$ cycle. Silver atoms are numbered, sulphur atoms lettered. The weaker contra-cycle linkages are marked as broken lines.

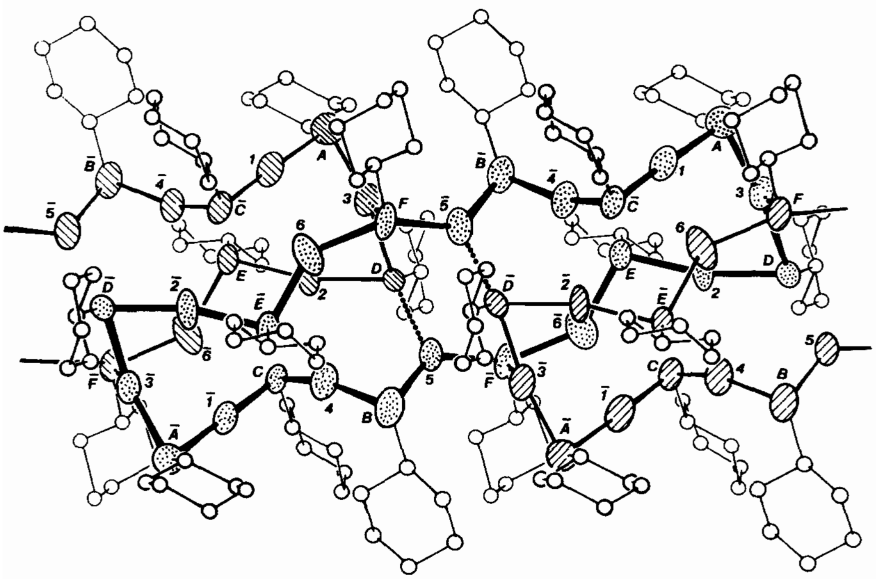

Figure 3. The association of $(AgSC_6H_{11})_{12}$ cycles in the crystal. The inter-cycle contacts are marked as broken lines.

a and *b* (2.40, 2.43, 2.44, 2.50 Å) and the angles γ (154, 141°) are much larger than the angles α and β (99, 107, 90, 127°). The two remaining silver atoms, 3 and 5, also possess the distorted trigonal planar stereochemistry of Figure 2; for Ag3 this is revealed in both the distance (a, $b < c$) and angle (α, $\beta < \gamma$ = 146°) criteria, while for Ag5 it is apparent only in the angle criterion, α, $\beta < \gamma$ = 135°. Therefore for each silver atom it is possible to identify unambiguously a pair of coordinated sulphur atoms which, to varying degrees, approach linear coordination. These bonds are SA–Ag1–S$\bar{C}$, S$\bar{D}$–Ag2–SE, SA–Ag3–SD, SB–Ag4–SC, SB–Ag5–S$\bar{F}$, S$\bar{E}$–Ag6–SF. Together with an equivalent set generated by a centre of symmetry they constitute the $(AgSC_6H_{11})_{12}$ cycles shown in Figure 1.

These intra-cycle bonds are also, with one minor exception, the shortest Ag–S distances in the crystal, while the longer Ag–S distances constitute inter-cycle contacts and one contra-cycle linkage, Ag4–S$\bar{E}$ = 2.75 Å, shown as a broken line in Fig. 1. The minor exception is the intra-cycle distance Ag5–S$\bar{F}$ = 2.60 Å, which is slightly greater than the inter-cycle distance Ag5–SD = 2.58 Å. The average intra-cycle Ag–S distance is 2.45 Å, while the average of the contra-cycle and inter-cycle Ag–S distances is 2.71 Å.

In the crystal the $(AgSC_6H_{11})_{12}$ cycles are overlapped along the *c* direction, as shown in Fig. 3. The association of the cycles is strengthened by the two significant types of inter-cycle contact, Ag3–SF = 2.64 Å and Ag5–SD = 2.58 Å, which are marked as broken lines on Figure 3.

Recognition of the molecularity of crystalline $(AgSC_6H_{11})_{12}$ leads to a straightforward explanation for the solubility and the dodecameric nature of silver secondary alkanethiolates in solution. The structure of crystalline $(AgSC_6H_{11})_{12}$ also suggests that $(AgSR)_8$ and $(AgSR)_{12}$ compounds in solution possess cyclic structures with two-coordinate silver, rather than possible cluster structures similar to those of $[Ag_5(SPh)_7]^{2-}$ [3] and $[Ag_{12}(SPh)_{16}]^{4-}$ [4].

Further hypotheses on solution structure are encouraged by these observations. Although it is unlikely that a single conformation predominates for an $(AgSR)_n$ cycle in solution, I note that a "chaise longue" conformation like that of crystalline $(AgSC_6H_{11})_{12}$ could be stabilised by contra-cycle linkages such as those between Ag4 and S$\bar{E}$. It also appears that inter-cycle linkages may occur in solution. Åkerström's value of n ~ 25 for $(AgSC_6H_{11})_n$ in benzene is easily interpreted in terms of dimerisation of $(AgSC_6H_{11})_{12}$ cycles, possibly by linkages such as Ag3–SF and Ag5–5D in crystalline $(AgSC_6H_{11})_{12}$.

Finally, it is evident that the preferred coordination number for silver(I) with alkanethiolate ligands only is less than three, and that the electrophilicity of Ag^+ is virtually satisfied by two doubly-bridging alkanethiolate ligands.

Acknowledgment

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References

1 S. Akerström, *Arkiv. Kemi, 24,* 505 (1965).
2 S. Hong, A. Olin and R. Hesse, *Acta Chem. Scand., A29,* 583 (1975).
3 I. G. Dance, *Chem. Commun., 103* (1976), and paper in preparation (1977).
4 I. G. Dance, to be published (1977).