# Preparation and Crystal and Molecular Structure of a Polymeric Bis(sulphinylnitrilo)sulphur Complex of Silver(I): $[Ag_4\{S(NSO)_2\}_9][AsF_6]_4{\cdot}SO_2$ †

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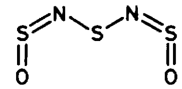
The title compound was isolated from the reaction of $AgAsF_6$ with $S(NSO)_2$ in liquid $SO_2$. It crystallises in the rhombohedral space group *R*3*c*, with $a = b = 18.249(5)$, $c = 35.95(2)$ Å, and $Z = 6$. The structure was refined to $R = 0.070$ for 1 653 unique observed diffractometer data. There are two crystallographically independent silver atoms. One lies on a three-fold axis and is octahedrally co-ordinated by the terminal oxygens of six $S(NSO)_2$ ligands; the other occupies a general position and is unsymmetrically co-ordinated by the nitrogen atoms of three $S(NSO)_2$ ligands. The ligands bridge the silver atoms to form a polymeric cationic network; the $AsF_6^-$ anions and $SO_2$ solvent molecule occupy holes in this network without themselves acting as ligands.

Bis(sulphinylnitrilo)sulphur, $S(NSO)_2$, was discovered in 1953 by Goehring and Heinke.[1] An *X*-ray diffraction study by Weiss [2] showed it to be acyclic. Several papers describe the reaction of $S(NSO)_2$ to yield heterocyclic [3,4] or acyclic [5] sulphur–nitrogen compounds, but to our knowledge no metal complexes of it have been reported.[6]



Recently we have shown that $S_3N_2O$ and $S_4N_4O_2$ form co-ordination compounds with the $Ag^+$ cation,[7,8] the co-ordination to silver being *via* nitrogen or oxygen. We have also observed a co-ordination of sulphur towards silver in the compound $[Ag(S_8)_2]AsF_6$.[9] The compound $S(NSO)_2$ can be considered as a thionylimino-derivative of sulphur(II), so co-ordination *via* sulphur should be possible.

## Experimental

The solvent and apparatus were carefully dried prior to use. The reaction was carried out under an inert nitrogen atmosphere and protected against light with aluminium foil. Silver hexafluoroarsenate (0.8 g, 2.7 mmol) and $S(NSO)_2$ (1.68 g, 10.8 mmol) were placed in a pressure flask and cooled to −78 °C. Sulphur dioxide (20 cm$^3$) was condensed into the flask. The mixture was allowed to warm to room temperature, stirred for 2 h, and filtered. During slow removal of $SO_2$ orange crystals formed, m.p. 82—84 °C (Found: F, 16.8; N, 10.3. $[Ag_4\{S(NSO)_2\}_9][AsF_6]_4{\cdot}SO_2$ requires F, 17.2; N, 9.5%). I.r. (Nujol mull): 1 200s, 1 180s, 1 170s, 720m, 700s, 390s, and 365s cm$^{-1}$.

*Crystal Data.*—$Ag_4As_4F_{24}N_{18}O_{20}S_{28}$, $M = 2\,656.9$, Rhombohedral, space group *R*3*c*, $a = b = 18.249(5)$, $c = 35.95(2)$ Å, $U = 10\,368$ Å$^3$, $Z = 6$, $D_c = 2.55$ g cm$^{-3}$, $F(000) = 7\,620$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 39.5$ cm$^{-1}$, crystal dimensions 0.50 × 0.45 × 0.23 mm.

Data collection on a Stoe-Siemens four-circle diffractometer by a profile-fitting method [10] in the range $7 < 2\theta < 50°$ afforded 2 214 reflections. After Lorentz, polarisation, and semi-empirical absorption corrections, equivalent reflections were merged to give 2 066 unique data, of which 1 653 with $F > 4\sigma(F)$ were used for all calculations, which were performed with the SHELXTL programs (written by G. M. S.).

The structure was solved with difficulty by Patterson and Fourier methods and refined with anisotropic Ag, As, and S, and isotropic N, O, and F, to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.070$,

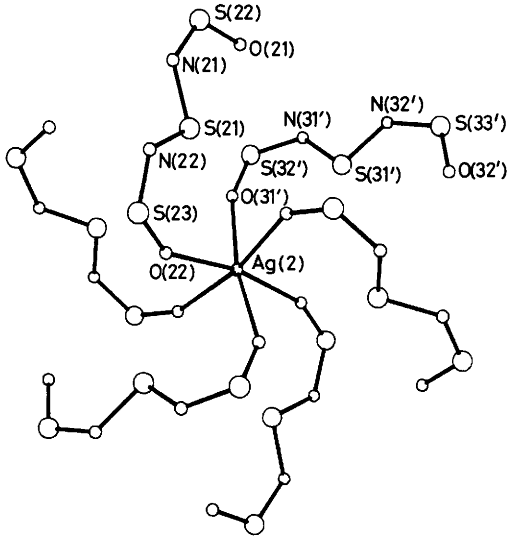


**Figure 1.** The co-ordination of Ag(2), viewed down the crystallographic three-fold axis

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† *Supplementary data available* (No. SUP 23559, 18 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Atom co-ordinates ($\times 10^4$) with standard deviations in parentheses

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Ag(1) | 6 821(1) | 6 626(1) | 5 000 |
| Ag(2) | 10 000 | 10 000 | 4 115(1) |
| S(11) | 7 430(3) | 5 559(3) | 5 573(2) |
| S(12) | 6 122(3) | 4 544(3) | 5 082(1) |
| S(13) | 8 680(4) | 7 109(3) | 5 841(2) |
| N(11) | 6 836(10) | 5 434(10) | 5 213(5) |
| N(12) | 7 949(9) | 6 601(10) | 5 580(4) |
| O(11) | 6 053(9) | 3 886(9) | 5 320(4) |
| O(12) | 8 909(10) | 6 649(9) | 6 111(4) |
| S(21) | 7 855(3) | 8 303(3) | 4 457(1) |
| S(22) | 6 150(3) | 7 601(4) | 4 290(2) |
| S(23) | 9 163(3) | 8 302(3) | 4 869(1) |
| N(21) | 6 842(9) | 7 587(9) | 4 522(4) |
| N(22) | 8 235(9) | 7 987(9) | 4 808(4) |
| O(21) | 6 436(9) | 8 303(9) | 4 018(4) |
| O(22) | 9 739(9) | 8 917(9) | 4 614(4) |
| S(31) | 5 717(4) | 7 376(4) | 5 519(2) |
| S(32) | 4 523(4) | 5 928(3) | 5 135(2) |
| S(33) | 7 362(4) | 8 480(5) | 5 744(2) |
| N(31) | 5 436(9) | 6 586(9) | 5 222(4) |
| N(32) | 6 724(10) | 7 712(9) | 5 506(4) |
| O(31) | 3 885(10) | 5 999(10) | 5 338(4) |
| O(32) | 7 031(12) | 8 897(12) | 5 969(5) |
| As(1) | 174(1) | 6 786(1) | 4 948(1) |
| F(11) | 646(13) | 7 829(9) | 5 027(7) |
| F(12) | 623(16) | 6 640(17) | 5 326(5) |
| F(13) | −221(16) | 5 761(9) | 4 859(7) |
| F(14) | 1 107(11) | 6 949(17) | 4 799(7) |
| F(15) | −76(21) | 6 958(23) | 4 524(5) |
| F(16) | −824(10) | 6 510(19) | 5 038(10) |
| As(2) | 0 | 0 | 5 844(1) |
| F(21) | −685(16) | 164(21) | 5 604(7) |
| F(22) | 160(20) | 787(15) | 6 135(6) |
| S | 3 333 | 6 667 | 4 396(4) |
| O | 2 658(24) | 6 741(24) | 9 547(12) |

**Table 2.** Bond lengths and short non-bonded distances (Å); see Table 3 for symmetry operators

| | | | |
|---|---|---|---|
| Ag(1) · · · S(11) | 3.382(8) | Ag(1) · · · S(12) | 3.363(7) |
| Ag(1)–N(11) | 2.321(21) | Ag(1)–N(12) | 2.948(18) |
| Ag(1) · · · S(21) | 3.310(6) | Ag(1)–N(21) | 2.441(19) |
| Ag(1)–N(22) | 2.626(13) | Ag(1)–N(31) | 2.616(20) |
| Ag(1)–N(32) | 2.760(19) | Ag(1)–O(12$^{\mathrm{I}}$) | 2.903(18) |
| Ag(2)–O(22) | 2.530(15) | Ag(2)–O(31$^{\mathrm{II}}$) | 2.504(20) |
| N(11)–S(11) | 1.629(20) | N(11)–S(12) | 1.562(15) |
| N(12)–S(11) | 1.647(17) | N(12)–S(13) | 1.510(16) |
| O(11)–S(12) | 1.428(19) | O(12)–S(13) | 1.474(22) |
| N(21)–S(21) | 1.663(15) | N(21)–S(22) | 1.523(20) |
| N(22)–S(21) | 1.674(19) | N(22)–S(23) | 1.508(18) |
| O(21)–S(22) | 1.485(18) | O(22)–S(23) | 1.423(15) |
| N(31)–S(31) | 1.656(19) | N(31)–S(32) | 1.522(15) |
| N(32)–S(31) | 1.621(19) | N(32)–S(33) | 1.554(16) |
| O(31)–S(32) | 1.435(23) | O(32)–S(33) | 1.437(28) |

$R = 0.070$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0008 F^2$. The $AsF_6^-$ groups exhibited considerable thermal motion and it was necessary to restrain all As–F bonds to be approximately equal; their mean refined to 1.669(11) Å. The $SO_2$ solvent molecule lies with its S on a crystallographic three-fold axis and is therefore three-fold disordered. The polar axis direction was established in a separate refinement, in which a factor multiplying all $\Delta f''$ values refined to 1.4(2).[11] The strongest peaks in a final difference map are about 1 e Å$^{-3}$, and all lie in the vicinity of the $AsF_6^-$ groups.

**Table 3.** Bond angles (°) (bonds >2.7 Å at silver being omitted)

| | |
|---|---|
| N(11)–Ag(1)–N(21) | 154.5(7) |
| N(21)–Ag(1)–N(22) | 58.7(6) |
| N(21)–Ag(1)–N(31) | 84.4(7) |
| O(22)–Ag(2)–O(31$^{\mathrm{II}}$) | 94.4(7) |
| O(22$^{\mathrm{IV}}$)–Ag(2)–O(31$^{\mathrm{II}}$) | 168.6(6) |
| O(31$^{\mathrm{II}}$)–Ag(2)–O(31$^{\mathrm{V}}$) | 83.7(6) |
| N(11)–S(11)–N(12) | 97.7(10) |
| N(12)–S(13)–O(12) | 118.2(10) |
| Ag(1)–N(11)–S(12) | 118.7(12) |
| S(11)–N(12)–S(13) | 122.8(14) |
| N(21)–S(22)–O(21) | 116.1(9) |
| Ag(1)–N(21)–S(21) | 106.0(10) |
| S(21)–N(21)–S(22) | 121.0(11) |
| Ag(1)–N(22)–S(23) | 135.1(11) |
| Ag(2)–O(22)–S(23) | 148.1(12) |
| N(32)–S(33)–O(32) | 117.7(12) |
| Ag(1)–N(31)–S(32) | 128.3(11) |
| S(31)–N(32)–S(33) | 121.4(14) |
| N(11)–Ag(1)–N(22) | 120.4(7) |
| N(11)–Ag(1)–N(31) | 109.7(7) |
| N(22)–Ag(1)–N(31) | 125.9(7) |
| O(22$^{\mathrm{III}}$)–Ag(2)–O(31$^{\mathrm{II}}$) | 107.3(7) |
| O(22)–Ag(2)–O(22$^{\mathrm{III}}$) | 75.4(5) |
| N(11)–S(12)–O(11) | 111.8(11) |
| Ag(1)–N(11)–S(11) | 116.7(9) |
| S(11)–N(11)–S(12) | 122.4(13) |
| N(21)–S(21)–N(22) | 95.6(9) |
| N(22)–S(23)–O(22) | 116.9(11) |
| Ag(1)–N(21)–S(22) | 133.0(8) |
| Ag(1)–N(22)–S(21) | 98.2(7) |
| S(21)–N(22)–S(23) | 123.9(10) |
| N(31)–S(31)–N(32) | 96.3(10) |
| Ag(1)–N(31)–S(31) | 107.3(8) |
| S(31)–N(31)–S(32) | 124.1(14) |
| N(31)–S(32)–O(31) | 116.2(11) |

Symmetry operators: I $-\frac{1}{3} + x, \frac{1}{3} + x - y, -\frac{1}{6} + z$; II $\frac{5}{3} - y, \frac{4}{3} - x, -\frac{1}{6} + z$; III $2 - y, 1 + x - y, z$; IV $1 + y - x, 2 - x, z$; V $\frac{2}{3} + x, \frac{4}{3} + x - y, -\frac{1}{6} + z$.

Final co-ordinates, bond lengths, and angles are given in Tables 1—3.

## Results and Discussion

One of the two crystallographically independent Ag atoms [Ag(2), shown in Figure 1] lies on a three-fold axis, and is octahedrally co-ordinated by the terminal oxygen atoms of six ligands, with Ag–O 2.504(20) and 2.530(15) Å. In contrast Ag(1) (Figure 2) is co-ordinated unsymmetrically by the six N atoms of three ligands, with a further single oxygen [O(12)] at 2.903(18) Å. There are also three relatively short Ag(1) · · · S interactions (see Table 2). Since two of the nitrogens [N(11) and N(21)] are significantly closer than the other atoms (indicated by full bonds in Figure 2) the co-ordination of Ag(1) may also be described as distorted linear two-fold. The $S(NSO)_2$ ligands are all planar within 0.12 Å. If the weak O(12) · · · Ag(1) interaction is included, then each ligand is co-ordinated to silver atoms by two N and one of its two O atoms, although there is no regular pattern to the silver–ligand distances involved. The $S^{IV}$–N bonds [mean 1.530(23) Å] are appreciably shorter than the $S^{II}$–N bonds [mean 1.649(21) Å], indicating fairly localised double and single bonds. Two of the three $S(NSO)_2$ ligands attached to Ag(1) also bond, *via* terminal oxygens, to Ag(2), producing a polymeric cationic network. The $AsF_6^-$ anions and $SO_2$ solvent molecule occupy holes in this network, without themselves acting as ligands.

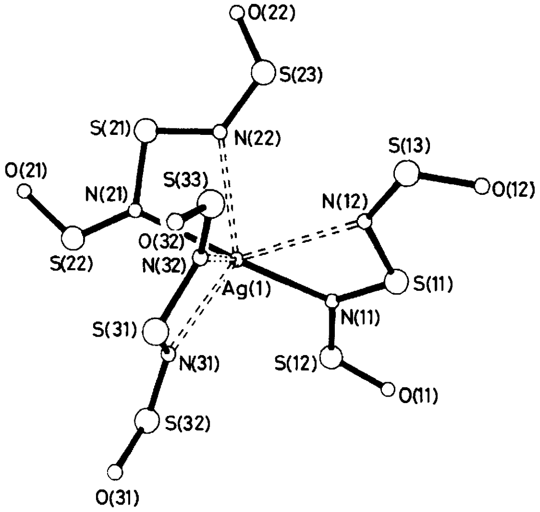

**Figure 2.** The co-ordination of Ag(1). An additional weak Ag ⋯ O interaction of 2.903 Å is omitted for clarity

## Acknowledgements

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