Trimeric Thioformaldehyde as a Ligand: Preparation and Crystal Structure of $[Ag_2\{(CH_2S)_3\}_5][AsF_6]_2\cdot SO_2$ †

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The reaction of trimeric thioformaldehyde with $AgAsF_6$ in liquid SO_2 leads to the compound $[Ag_2\{(CH_2S)_3\}_5][AsF_6]_2\cdot SO_2$, which was characterised by *X*-ray structure determination [space group *Pbca*, with a = 16.286(3), b = 28.487(5), c = 18.118(3) Å, and Z = 8; R = 0.061 for 5 150 unique observed reflections]. The isolated cations, of the form $L_2AgLAgL_2$ (L = ligand), display irregular co-ordination geometry at silver; one silver is co-ordinated by four sulphurs from three ligands, the other by five sulphurs from three ligands.

We showed recently [1] that it is possible to prepare the complex $[Ag(S_8)_2]^+$ in which the Ag cation is 1,3-co-ordinated by each of two S_8 rings. The S–S distances change little on co-ordination. It has been reported [2] that $AgNO_3$ and thioformaldehyde form adducts of unknown composition and structure. We have investigated the reaction of $AgAsF_6$ with $(CH_2S)_3$ in order to establish whether the latter functions as a uni-, bi-, or tri-dentate ligand, and whether it retains its chair conformation.[3]

Experimental

The reaction was performed under nitrogen and protected against light with aluminium foil. Sulphur dioxide and $(CH_2S)_3$ were dried before use. Silver hexafluoroarsenate (0.52 g, 1.75 mmol) and $(CH_2S)_3$ (0.48 g, 3.48 mmol) were mixed in a pressure flask, and liquid SO_2 (20 cm³) condensed in at −80 °C. The mixture was allowed to warm up slowly to room temperature, stirring continuously. After stirring for a further 72 h, the residue was filtered off and the solution evaporated slowly to dryness, yielding 0.60 g of a crystalline product which was sensitive to daylight but surprisingly stable to moisture (Found: C, 13.7; H, 2.30; F, 16.8; S, 38.0. $C_{15}H_{30}Ag_2As_2F_{12}O_2S_{16}$ requires C, 13.4; H, 2.25; F, 16.9; S, 38.0%). I.r. (Nujol mull): 1 330s, 1 315w, 1 218m, 1 183m, 1 166m, 1 157m, 1 144s, 968w, 902s, 907w, 789w, 725s, 690s, 650m, 643m, 566w, 519s, 390s, and 313m cm^{-1}. Raman: 750w, 731s, 677s, 656s, 650(sh), 412s, 368m, 321m, 287s, 221w, and 148w cm^{-1}.

Crystal Data.—$C_{15}H_{30}Ag_2As_2F_{12}O_2S_{16}$, M = 1 348.9, Orthorhombic, space group *Pbca*, a = 16.286(3), b = 28.487(5), c = 18.118(3) Å, U = 8 406 Å³, Z = 8, D_c = 2.13 g cm^{-3}, $F(000)$ = 5 280, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 33 cm^{-1}, crystal size 0.5 × 0.4 × 0.4 mm.

8 215 Profile-fitted [4] intensities were measured in the range $7 < 2\theta < 50°$. After Lorentz, polarisation, and empirical absorption corrections, merging equivalents gave 7 372 unique reflections, 5 150 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL, written by G. M. S.). The structure was solved by direct methods, with which two Ag, two As, and twelve S atoms were located. Other non-hydrogen atoms were found in successive difference maps. Hydrogen atoms were included in the refinement using a riding model [C–H 0.96 Å, H–C–H 109.5°, U(H) = $1.2U_{iso}$(C)]. Refinement with all atoms except H and O anisotropic converged at R = 0.061, $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$ = 0.058, weighting scheme $w^{-1} = \sigma^2(F) + 0.0003\ F^2$.

Final co-ordinates are presented in Table 1, bond lengths and angles in Table 2.

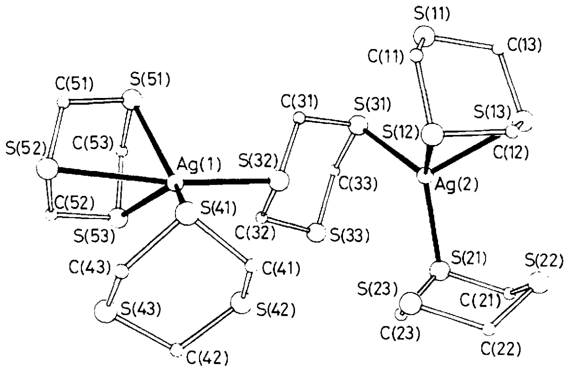

Figure. A view of the $[Ag_2\{(CH_2S)_3\}_5]^{2+}$ cation, showing the atom labelling scheme

Results and Discussion

The Raman spectrum (for example the disappearance of the band at 400 cm^{-1}) clearly indicated that complex formation had taken place, but the crystal-structure determination was necessary to establish the nature of the co-ordination. The structure consists of isolated $[Ag_2\{(CH_2S)_3\}_5]^{2+}$ cations, $[AsF_6]^-$ anions, and solvent SO_2 molecules. The structure of the cation is shown in the Figure; the co-ordination geometry of the two Ag atoms and the Ag–S distances are somewhat irregular, but Ag(2) may be considered to be co-ordinated tetrahedrally by four sulphurs from three ligands, whereas Ag(1) is co-ordinated by five sulphurs from three ligands. The Ag–S distances are in the same range as those

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† μ-(1,3,5-Trithiane-S^1S^3)-bis[bis(1,3,5-trithiane)silver(I)] bis[hexafluoroarsenate(V)]-sulphur dioxide (1/1).

Supplementary data available (No. SUP 23558, 48 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[Ag_2\{(CH_2S)_3\}_5][AsF_6]_2\cdot SO_2$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ag(1)	5 243(1)	5 478(1)	2 207(1)	C(33)	2 956(5)	4 030(3)	1 379(5)
Ag(2)	4 637(1)	3 383(1)	2 130(1)	C(41)	6 062(5)	4 938(3)	3 612(5)
S(11)	5 854(1)	3 367(1)	621(1)	C(42)	5 027(6)	5 546(3)	4 330(5)
S(12)	6 372(2)	3 483(1)	2 204(1)	C(43)	6 416(5)	5 885(3)	3 664(5)
S(13)	5 501(1)	2 610(1)	1 767(2)	C(51)	5 256(5)	6 350(3)	989(4)
S(21)	3 704(1)	3 260(1)	3 222(1)	C(52)	4 313(6)	6 537(3)	2 217(4)
S(22)	5 072(1)	2 638(1)	3 832(1)	C(53)	3 743(5)	5 951(3)	1 146(5)
S(23)	5 158(2)	3 699(1)	4 001(1)	As(1)	7 108(1)	7 597(1)	−899(1)
S(31)	3 972(1)	3 841(1)	1 076(1)	F(11)	7 547(8)	7 354(5)	−202(8)
S(32)	4 616(1)	4 620(1)	2 054(1)	F(12)	6 630(10)	7 898(4)	−1 498(9)
S(33)	2 884(1)	4 252(1)	2 302(1)	F(13)	6 249(5)	7 373(4)	−567(6)
S(41)	6 529(1)	5 389(1)	3 051(1)	F(14)	7 047(6)	8 064(3)	−340(6)
S(42)	4 987(1)	5 017(1)	3 785(1)	F(15)	7 974(6)	7 807(4)	−1 218(6)
S(43)	5 385(1)	6 060(1)	3 868(1)	F(16)	7 107(7)	7 172(3)	−1 489(6)
S(51)	4 743(1)	5 809(1)	789(1)	As(2)	7 759(1)	4 959(1)	5 640(1)
S(52)	5 371(2)	6 479(1)	1 945(1)	F(21)	7 028(5)	4 656(3)	5 187(5)
S(53)	3 713(1)	6 013(1)	2 134(1)	F(22)	8 470(6)	5 224(3)	6 109(8)
C(11)	6 620(6)	3 550(3)	1 239(5)	F(23)	7 196(6)	5 446(3)	5 633(7)
C(12)	6 373(5)	2 860(3)	2 231(6)	F(24)	7 337(8)	4 745(4)	6 398(5)
C(13)	5 808(6)	2 763(3)	841(5)	F(25)	8 316(4)	4 463(2)	5 606(5)
C(21)	3 985(6)	2 727(3)	3 687(5)	F(26)	8 095(9)	5 092(4)	4 823(7)
C(22)	5 285(6)	3 128(3)	4 422(5)	S	7 680(2)	6 489(1)	847(3)
C(23)	4 072(6)	3 681(3)	3 881(5)	O(1)	8 463(8)	6 459(4)	801(7)
C(31)	4 516(5)	4 388(2)	1 125(4)	O(2)	7 390(9)	6 767(5)	1 377(8)
C(32)	3 541(4)	4 760(2)	2 223(5)				

Table 2. Bond lengths (Å) and angles (°)

Ag(1)–S(32)	2.664(3)	C(23)–S(23)	1.783(11)	Ag(1)–S(41)	2.606(3)	C(31)–S(31)	1.793(8)
Ag(1)–S(51)	2.856(3)	C(31)–S(32)	1.815(9)	Ag(1)–S(52)	2.898(4)	C(32)–S(32)	1.820(8)
Ag(1)–S(53)	2.924(3)	C(32)–S(33)	1.804(8)	Ag(2)–S(12)	2.844(4)	C(33)–S(31)	1.823(9)
Ag(2)–S(13)	2.694(3)	C(33)–S(33)	1.793(10)	Ag(2)–S(21)	2.519(3)	C(41)–S(41)	1.805(10)
Ag(2)–S(31)	2.555(3)	C(41)–S(42)	1.794(10)	C(11)–S(11)	1.756(11)	C(42)–S(42)	1.804(9)
C(11)–S(12)	1.804(11)	C(42)–S(43)	1.784(9)	C(12)–S(12)	1.774(11)	C(43)–S(41)	1.807(10)
C(12)–S(13)	1.796(10)	C(43)–S(43)	1.791(10)	C(13)–S(11)	1.768(10)	C(51)–S(51)	1.791(10)
C(13)–S(13)	1.803(11)	C(51)–S(52)	1.781(10)	C(21)–S(21)	1.796(10)	C(52)–S(52)	1.799(10)
C(21)–S(22)	1.807(10)	C(52)–S(53)	1.790(9)	C(22)–S(22)	1.792(10)	C(53)–S(51)	1.800(10)
C(22)–S(23)	1.807(10)	C(53)–S(53)	1.798(10)	C(23)–S(21)	1.795(10)		

S(32)–Ag(1)–S(41)	106.2(2)	Ag(1)–S(32)–C(32)	98.7(3)	S(32)–Ag(1)–S(51)	95.7(2)	C(31)–S(32)–C(32)	98.6(5)
S(41)–Ag(1)–S(51)	142.1(2)	C(32)–S(33)–C(33)	99.8(5)	S(32)–Ag(1)–S(52)	156.0(2)	Ag(1)–S(41)–C(41)	93.5(4)
S(41)–Ag(1)–S(52)	97.7(2)	Ag(1)–S(41)–C(43)	101.7(4)	S(51)–Ag(1)–S(52)	63.2(2)	C(41)–S(41)–C(43)	99.7(5)
S(32)–Ag(1)–S(53)	98.4(2)	C(41)–S(42)–C(42)	99.5(5)	S(41)–Ag(1)–S(53)	139.7(2)	C(42)–S(43)–C(43)	100.0(5)
S(51)–Ag(1)–S(53)	62.9(2)	Ag(1)–S(51)–C(51)	88.2(4)	S(52)–Ag(1)–S(53)	62.7(2)	Ag(1)–S(51)–C(53)	90.5(4)
S(12)–Ag(2)–S(13)	64.8(2)	C(51)–S(51)–C(53)	98.9(5)	S(12)–Ag(2)–S(21)	125.2(2)	Ag(1)–S(52)–C(51)	87.0(4)
S(13)–Ag(2)–S(21)	113.2(2)	Ag(1)–S(52)–C(52)	88.6(4)	S(12)–Ag(2)–S(31)	113.9(2)	C(51)–S(52)–C(52)	100.6(5)
S(13)–Ag(2)–S(31)	117.1(2)	Ag(1)–S(53)–C(52)	88.0(4)	S(21)–Ag(2)–S(31)	113.7(2)	Ag(1)–S(53)–C(53)	88.3(4)
C(11)–S(11)–C(13)	100.1(6)	C(52)–S(53)–C(53)	98.6(5)	Ag(2)–S(12)–C(11)	100.8(4)	S(11)–C(11)–S(12)	115.3(6)
Ag(2)–S(12)–C(12)	84.4(4)	S(12)–C(12)–S(13)	112.5(6)	C(11)–S(12)–C(12)	97.6(6)	S(11)–C(13)–S(13)	117.1(6)
Ag(2)–S(13)–C(12)	88.6(4)	S(21)–C(21)–S(22)	115.9(6)	Ag(2)–S(13)–C(13)	100.1(4)	S(22)–C(22)–S(23)	115.3(6)
C(12)–S(13)–C(13)	97.0(6)	S(21)–C(23)–S(23)	115.5(6)	Ag(2)–S(21)–C(21)	109.4(4)	S(31)–C(31)–S(32)	114.0(5)
Ag(2)–S(21)–C(23)	103.2(4)	S(32)–C(32)–S(33)	114.1(5)	C(21)–S(21)–C(23)	99.7(5)	S(31)–C(33)–S(33)	116.4(5)
C(21)–S(22)–C(22)	99.6(5)	S(41)–C(41)–S(42)	114.8(5)	C(22)–S(23)–C(23)	98.0(5)	S(42)–C(42)–S(43)	116.1(6)
Ag(2)–S(31)–C(31)	101.4(4)	S(41)–C(43)–S(43)	116.1(6)	Ag(2)–S(31)–C(33)	108.1(4)	S(51)–C(51)–S(52)	115.1(6)
C(31)–S(31)–C(33)	100.2(5)	S(52)–C(52)–S(53)	115.1(5)	Ag(1)–S(32)–C(31)	117.8(3)	S(51)–C(53)–S(53)	113.9(6)

observed in $[Ag(S_8)_2]^+$.[1] The five independent $(CH_2S)_3$ ligands adopt the chair conformation observed [3] in the free ligand, with little distortion from the idealised 3*m* (C_{3v}) geometry, although the C–S bond lengths involving co-ordinated sulphur tend to be slightly longer than the others.

Acknowledgements

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