Tetrakis(tetrasulphur tetranitrogen dioxide)silver Hexafluoroarsenate(v) †

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A complex of silver(I) containing tetrasulphur tetranitrogen dioxide ligands has been prepared. The crystals of $[Ag(S_4N_4O_2)_4]^+[AsF_6]^-$ are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 1 142.6(6), b = 1 194.9(5), c = 1 254.8(6) pm, α = 66.44(4), β = 96.71(4), γ = 91.30(4)°, and Z = 2, final R = 0.039 for 4 968 unique diffractometer data with $F > 3\sigma(F)$. The Ag atom lies 53 pm below a square of four nitrogen atoms (mean Ag–N 256 pm). Bisdisphenoidal (triangulated dodecahedral) co-ordination of Ag is completed by two intramolecular Ag–O contacts (mean 307 pm), and intermolecular Ag–N and Ag–O interactions (both 273 pm). These intermolecular interactions give rise to a centrosymmetric cationic dimer. The $S_4N_4O_2$ ligands are approximately planar except for the SO_2 units; only nitrogen and oxygen atoms attached to S^{VI} interact with Ag, thereby causing the least disruption of delocalised bonding in the rest of the ring.

A few years ago we reported the synthesis of tetrasulphur tetranitrogen dioxide, $S_4N_4O_2$, from sulphamide and $S_3N_2Cl_2$.[1] Several papers [2–5] have been published describing the products of reactions of $S_4N_4O_2$. The X-ray crystal structure of $S_4N_4O_2$ was of low precision,[6,7] while an isomer of $S_4N_4O_2$ contained the $S_5N_5^+$ cation and the $S_3N_3O_4^-$ anion. Recently we were able to show [8] that S_3N_2O, a five-membered sulphur–nitrogen ring, forms a crystalline product $[Ag(S_3N_2O)_4]^+[AsF_6]^-$ with silver(I). We have now studied the reaction of $S_4N_4O_2$ with silver hexafluoroarsenate(v) to determine the nature of the co-ordination and its effect on the sulphur–nitrogen π-system. Co-ordination by sulphur, nitrogen, or oxygen is in principle possible.

Experimental

The general preparative and spectroscopic techniques were as described in other recent papers from this laboratory.

Tetrakis(tetrasulphur tetranitrogen dioxide)silver Hexafluoroarsenate(v).—Silver hexafluoroarsenate(v) (1.44 g, 0.0048 mol) and $S_4N_4O_2$ (2.1 g, 0.0097 mol) [1,2] were cooled to −78 °C in a pressure flask and SO_2 (20 cm^3) added. The flask was allowed to warm to room temperature, stirred for 20 h, and the solid removed by filtration. Orange crystals were obtained by slowly removing SO_2 from the filtrate (yield 98%, freezing point 152—153 °C) (Found: F, 9.5; N, 20.2. Calc. for $AgAsF_6N_{16}O_8S_{16}$: F, 9.8; N, 19.3%). A parallelopiped crystal with approximate dimensions 0.4 × 0.4 × 0.6 mm was sealed in a Lindemann glass capillary for the X-ray data collection.

X-Ray Structural Analysis.—Intensities were collected at 18 °C by a real-time profile-fitting procedure [9] on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-K_α radiation. 5 735 Reflections were measured in the range $7 < 2\theta < 55°$. After application of Lorentz, polarisation, and empirical absorption corrections (based on measurements of equivalent reflections at different azimuthal angles) the data were merged to yield 5 450 unique reflections, of which 4 968 with $F > 3\sigma(F)$ were employed for all calculations. The unit cell was determined by a least-squares fit to the optimum angles for 40 strong reflections, 2θ values being determined from ω measurements at $\pm 2\theta$.

Crystal data. $AgAsF_6N_{16}O_8S_{16}$, Triclinic, space group $P\bar{1}$, a = 1 142.6(6), b = 1 194.9(5), c = 1 254.8(6) pm, α = 66.44(4), β = 96.71(4), γ = 91.30(4)°, U = 1.559 nm^3, Z = 2, D_c = 2.475 mg m^{-3}, $F(000)$ = 1 132, Mo-K_α radiation, λ = 71.069 pm, and μ = 2.82 mm^{-1}.

The structure was solved by Patterson and Fourier methods. Least-squares refinement with all atoms anisotropic, complex neutral-atom scattering factors, and the weighting scheme $w = [\sigma^2(F) + 0.000\,53\ F^2]^{-1}$ converged to $R' = \Sigma w^{\frac{1}{2}}|\Delta| / \Sigma w^{\frac{1}{2}}|F_o| = 0.043$, $R = 0.039$. A final difference map showed no peaks higher than 0.0009 e nm^{-3}; the largest difference peaks were in the AsF_6^- region. Atomic parameters are given in Table 1 and bond distances and angles in Table 2. The structure of the $[Ag(S_4N_4O_2)_4]^+$ cation is shown in the Figure. Calculations were performed using the SHELXTL program system (written by G. M. S.).

Results and Discussion

The Ag atom lies 53 pm below the plane of four nitrogen atoms (deviations from coplanarity ±6 pm). The cation exhibits approximately two-fold symmetry, with two *trans* Ag–N distances [250.8(3), 253.4(3) pm] slightly shorter than the other two [259.7(5), 259.0(5) pm]. The two ligands with the longer Ag–N distances also exhibit weak intramolecular Ag–O interactions [314.3(4), 300.5(4) pm], involving an O ··· O distance of 329.7(7) pm. The other two SO_2 groups are further from each other and from the Ag atom [Ag–O 332.4(5), 334.2(5); O ··· O 628.3(8) pm], leaving a co-ordination 'hole' beneath the Ag, which is occupied by two atoms of another cation [Ag–N(14′) 272.7(4), Ag–O(11′) 273.4(4) pm].‡ This

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† Tetrakis(1,1-dioxo-1λ^6,3,5,7,2,4,6,8-tetrathiatetra-azocine-N^2)silver hexafluoroarsenate(v).

Supplementary data available (No. SUP 23468, 35 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ The primed atoms are related to the unprimed ones by the transformation $-x$, $1 - y$, $1 - z$.

Table 1. Atomic parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	1 752(1)	3 733(1)	6 295(1)	N(11)	2 053(3)	5 339(3)	4 325(3)
As	8 054(1)	6 301(1)	8 794(1)	N(12)	3 543(3)	6 192(4)	2 684(4)
S(11)	1 198(1)	6 549(1)	3 785(1)	N(13)	1 661(4)	7 277(3)	1 046(3)
S(12)	3 298(1)	5 279(1)	3 914(1)	N(14)	306(3)	6 347(3)	2 777(3)
S(13)	3 053(1)	7 143(1)	1 425(1)	N(21)	2 232(3)	2 223(3)	5 376(4)
S(14)	448(1)	6 882(1)	1 445(1)	N(22)	1 441(3)	378(3)	4 797(3)
S(21)	3 597(1)	1 722(1)	5 782(1)	N(23)	3 560(3)	313(3)	3 985(3)
S(22)	1 185(1)	1 467(1)	5 114(1)	N(24)	4 149(3)	2 203(3)	4 548(3)
S(24)	4 336(1)	1 420(1)	3 852(1)	N(31)	2 094(3)	5 322(3)	7 216(3)
S(23)	2 354(1)	−326(1)	4 408(1)	N(32)	1 224(3)	7 291(3)	7 430(4)
S(32)	1 017(1)	6 108(1)	7 218(1)	N(33)	3 340(4)	7 476(4)	8 594(4)
S(31)	3 411(1)	5 848(1)	6 992(1)	N(34)	4 063(3)	5 497(3)	8 302(3)
S(34)	4 194(1)	6 369(1)	8 950(1)	N(41)	2 487(3)	2 175(3)	8 321(3)
S(33)	2 093(1)	8 068(1)	7 915(1)	N(42)	4 395(3)	1 587(3)	9 937(3)
S(41)	1 935(1)	816(1)	8 762(1)	N(43)	3 015(4)	73(3)	11 535(3)
S(42)	3 750(1)	2 467(1)	8 760(1)	N(44)	1 206(3)	774(3)	9 808(3)
S(43)	4 290(1)	485(1)	11 171(1)	O(11)	477(3)	6 450(3)	4 673(3)
S(44)	1 674(1)	208(1)	11 138(1)	O(12)	1 862(3)	7 620(3)	3 296(3)
F(1)	8 001(4)	4 956(3)	9 970(3)	O(21)	4 131(3)	2 402(4)	6 403(4)
F(2)	9 451(3)	6 510(5)	9 222(3)	O(22)	3 641(3)	419(3)	6 335(3)
F(3)	8 095(3)	7 616(3)	7 581(3)	O(31)	3 944(3)	5 094(3)	6 530(3)
F(4)	6 650(3)	6 069(5)	8 353(4)	O(32)	3 349(3)	7 143(3)	6 351(3)
F(5)	8 507(4)	5 547(4)	8 018(4)	O(41)	1 078(3)	838(3)	7 834(3)
F(6)	7 564(5)	7 064(4)	9 519(5)	O(42)	2 856(3)	−98(3)	9 195(3)

Table 2. Bond distances (pm) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Ag-N(11)	250.8(3)	Ag-N(21)	259.7(5)	S(24)-N(23)	154.0(4)	S(24)-N(24)	154.6(5)
Ag-N(31)	259.0(5)	Ag-N(41)	253.4(3)	S(23)-N(22)	158.8(5)	S(23)-N(23)	160.0(4)
As-F(1)	169.8(3)	As-F(2)	166.9(4)	S(32)-N(31)	156.5(4)	S(32)-N(32)	154.9(5)
As-F(3)	170.0(3)	As-F(4)	168.9(4)	S(31)-N(31)	163.0(4)	S(31)-N(34)	161.6(4)
As-F(5)	169.3(5)	As-F(6)	166.8(7)	S(31)-O(31)	142.9(4)	S(31)-O(32)	143.0(3)
S(11)-N(11)	162.2(3)	S(11)-N(14)	162.1(4)	S(34)-N(33)	154.4(4)	S(34)-N(34)	155.3(5)
S(11)-O(11)	142.8(4)	S(11)-O(12)	142.4(3)	S(33)-N(32)	157.7(5)	S(33)-N(33)	159.3(4)
S(12)-N(11)	158.1(4)	S(12)-N(12)	154.6(4)	S(41)-N(41)	162.9(3)	S(41)-N(44)	161.8(4)
S(13)-N(12)	157.7(4)	S(13)-N(13)	159.9(4)	S(41)-O(41)	142.3(4)	S(41)-O(42)	142.9(3)
S(14)-N(13)	152.9(4)	S(14)-N(14)	156.0(4)	S(42)-N(41)	156.6(4)	S(42)-N(42)	154.0(3)
S(21)-N(21)	163.2(4)	S(21)-N(24)	162.1(4)	S(43)-N(42)	159.7(3)	S(43)-N(43)	158.7(4)
S(21)-O(21)	141.8(5)	S(21)-O(22)	142.8(3)	S(44)-N(43)	154.7(4)	S(44)-N(44)	156.0(4)
S(22)-N(21)	156.6(4)	S(22)-N(22)	154.7(5)				

(*b*) Angles

N(11)-Ag-N(21)	84.1(1)	N(11)-Ag-N(31)	90.3(1)	N(34)-S(31)-O(31)	106.7(2)	N(31)-S(31)-O(32)	110.2(2)
N(21)-Ag-N(31)	159.1(1)	N(11)-Ag-N(41)	153.0(1)	N(34)-S(31)-O(32)	110.7(2)	O(31)-S(31)-O(32)	119.6(2)
N(21)-Ag-N(41)	90.7(1)	N(31)-Ag-N(41)	85.2(1)	N(33)-S(34)-N(34)	120.9(2)	N(32)-S(33)-N(33)	118.7(2)
F(1)-As-F(2)	92.3(2)	F(1)-As-F(3)	177.7(2)	N(41)-S(41)-N(44)	102.9(2)	N(41)-S(41)-O(41)	105.8(2)
F(2)-As-F(3)	88.8(2)	F(1)-As-F(4)	87.4(2)	N(44)-S(41)-O(41)	106.1(2)	N(41)-S(41)-O(42)	110.4(2)
F(2)-As-F(4)	179.0(3)	F(3)-As-F(4)	91.4(2)	N(44)-S(41)-O(42)	110.8(2)	O(41)-S(41)-O(42)	119.4(2)
F(1)-As-F(5)	90.1(2)	F(2)-As-F(5)	90.7(3)	N(41)-S(42)-N(42)	120.3(2)	N(42)-S(43)-N(43)	118.5(2)
F(3)-As-F(5)	87.9(2)	F(4)-As-F(5)	88.3(3)	N(43)-S(44)-N(44)	120.2(2)	Ag-N(11)-S(11)	118.5(2)
F(1)-As-F(6)	91.0(2)	F(2)-As-F(6)	91.1(3)	Ag-N(11)-S(12)	114.9(2)	S(11)-N(11)-S(12)	123.6(2)
F(3)-As-F(6)	90.9(2)	F(4)-As-F(6)	89.9(3)	S(12)-N(12)-S(13)	149.0(3)	S(13)-N(13)-S(14)	145.6(2)
F(5)-As-F(6)	177.8(2)	N(11)-S(11)-N(14)	104.1(2)	S(11)-N(14)-S(14)	125.7(2)	Ag-N(21)-S(21)	110.8(2)
N(11)-S(11)-O(11)	106.0(2)	N(14)-S(11)-O(11)	104.7(2)	Ag-N(21)-S(22)	116.7(2)	S(21)-N(21)-S(22)	124.6(3)
N(11)-S(11)-O(12)	110.7(2)	N(14)-S(11)-O(12)	110.9(2)	S(22)-N(22)-S(23)	147.9(3)	S(24)-N(23)-S(23)	144.8(3)
O(11)-S(11)-O(12)	119.2(2)	N(11)-S(12)-N(12)	118.7(2)	S(21)-N(24)-S(24)	125.1(2)	Ag-N(31)-S(32)	118.8(2)
N(12)-S(13)-N(13)	119.0(2)	N(13)-S(14)-N(14)	119.6(2)	Ag-N(31)-S(31)	107.5(2)	S(32)-N(31)-S(31)	123.9(2)
N(21)-S(21)-N(24)	102.4(2)	N(21)-S(21)-O(21)	106.2(3)	S(32)-N(32)-S(33)	147.9(3)	S(34)-N(33)-S(33)	145.0(3)
N(24)-S(21)-O(21)	106.3(2)	N(21)-S(21)-O(22)	110.3(2)	S(31)-N(34)-S(34)	125.1(2)	Ag-N(41)-S(41)	118.6(2)
N(24)-S(21)-O(22)	111.2(2)	O(21)-S(21)-O(22)	119.2(2)	Ag-N(41)-S(42)	111.9(2)	S(41)-N(41)-S(42)	124.5(2)
N(21)-S(22)-N(22)	119.6(2)	N(23)-S(24)-N(24)	120.1(2)	S(42)-N(42)-S(43)	147.0(3)	S(43)-N(43)-S(44)	146.1(2)
N(22)-S(23)-N(23)	119.1(2)	N(31)-S(32)-N(32)	120.0(2)	S(41)-N(44)-S(44)	125.3(2)		
N(31)-S(31)-N(34)	103.0(2)	N(31)-S(31)-O(31)	105.3(2)				

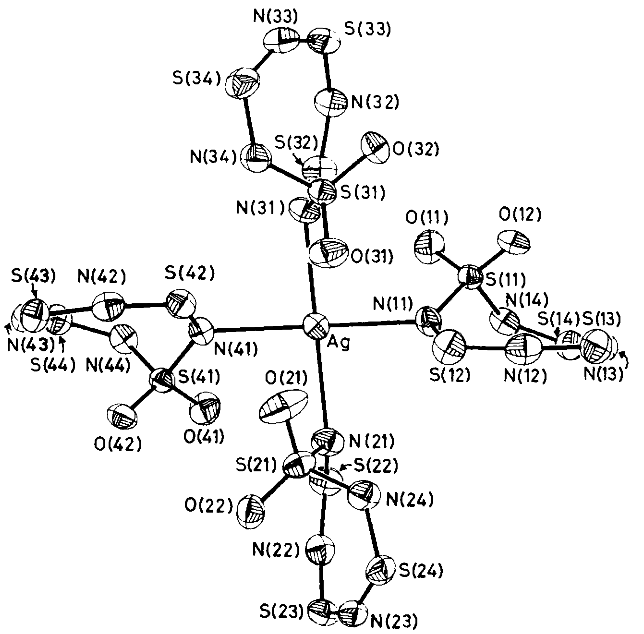

Figure. The structure of the $[Ag(S_4N_4O_2)_4]^+$ cation showing 50% thermal ellipsoids and the atomic numbering scheme

gives rise to dimeric cations in which the two monomer units are related by a crystallographic centre of symmetry. The overall co-ordination of Ag may be described as bis-disphenoidal (triangulated dodecahedral).

The four $S_4N_4O_2$ ligands adopt similar conformations; in each case the ring is within 20 pm coplanar, except for the S atom of the SO_2 group, which lies 113(1) pm out of the plane of the other seven ring atoms. The maximum spread of equivalent S–N bond lengths in the four ligands is only 2 pm, with the longest bonds involving the SO_2 sulphurs. The similarity of the S–N bond lengths in the planar S_4N_3 units indicates significant electron delocalisation; all the atoms which co-ordinate to Ag are attached to the S^{VI} atoms, thereby causing the least disruption of this delocalisation.

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