Crystal and Molecular Structure of Bis(tetrasulphur tetraimide)silver(I) Perchlorate Sesquihydrate †

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The crystal structure of the title compound has been determined by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.064$ for 1 895 observed diffractometer data. The crystals are monoclinic, with $a = 11.487(5)$, $b = 14.623(6)$, $c = 11.684(5)$ Å, $\beta = 105.39(6)°$, space group $P2_1/c$, and $Z = 4$. The structure consists of $[Ag(S_4N_4H_4)_2]^+$ cations, ClO_4^- anions, and water molecules, all interconnected by an extensive network of hydrogen bonds. The cation has a sandwich structure with the S_4N_4 crowns arranged so that the sulphur atoms are nearest the cation and there are no Ag–N bonds. The silver ion is displaced sideways from a central position and the $S_4N_4H_4$ ligands are tilted, with an angle of 20.4° between the two S_4 mean planes. Notwithstanding these distortions, the two ligands can be seen to have adopted a staggered configuration with respect to the two S_4 groups. As a result of the silver-ion positioning, two sulphur atoms from each ligand are closer (2.696—2.792 Å) to the metal than the other two pairs (3.141—3.226 Å) and are arranged so as to produce a distorted tetrahedral metal co-ordination. The bonds between the four nearest sulphur atoms and the metal ion are thus considered to possess significant covalent character. As far as we are aware, this is the first example of a complex of a sulphur imide and the first proven example of donor sulphur rather than donor nitrogen in any sulphur nitride or imide adduct.

PREVIOUS work has shown that with $Ag[ClO_4]$, tetrasulphur tetraimide ($S_4N_4H_4$) forms three isolable adducts, $2S_4N_4H_4{\cdot}Ag[ClO_4]$, $S_4N_4H_4{\cdot}Ag[ClO_4]$, and $S_4N_4H_4{\cdot}2Ag[ClO_4]$.[1] Infrared spectra of the $S_4N_4H_4$ moieties in the adducts show very little change from those recorded for the free molecule. In the ^1H n.m.r. spectra of all three complexes the NH protons give only one sharp signal, which indicates that the silver ion either bonds symmetrically to the $S_4N_4H_4$ molecules or exchanges rapidly between several positions. In view of these results, the known low basic strength of the $S_4N_4H_4$ molecule,[2] the substantial π character of the S–N bonds,[3,4] and the well characterised π complexes formed between $Ag[ClO_4]$ and aromatic hydrocarbons,[5] an analogous π-type interaction between the silver ion and the $S_4N_4H_4$ ring was postulated for the present complexes.[1] Very few other examples are known where $S_4N_4H_4$ forms complexes with metal ions,[6,7] and, indeed, examples of metal complexation by ring systems containing any second-row elements are quite rare. In fact, no *X*-ray study of a sulphur imide complex has previously been reported.

Accordingly we considered it worthwhile to investigate the nature of the bonding in the present compounds by *X*-ray analysis. Of the three complexes mentioned above, only the 2 : 1 adduct gave large enough crystals (from acetonitrile–carbon tetrachloride), and although these were mostly twinned a few single specimens of moderate quality were found, and these were used for the crystallographic study.

RESULTS AND DISCUSSION

The results of the present study, presented in Tables 1—6, have confirmed the proposed formulation of this complex. The crystal structure, a projection of which down the *b* axis is given in Figure 1, comprises $[Ag(S_4N_4H_4)_2]^+$ and ClO_4^- ions and also water molecules (1.5 per mol complex), these presumably being picked up during the recrystallisation process.

The cation does indeed have a sandwich structure, consistent at first sight with the proposed π-bonding model. The only contacts, between the cation and the anion are some N–H · · · O interactions which form part of an extensive hydrogen-bonded network (also incorporating the water molecules). There is thus no direct contact between the silver ion and the perchlorate oxygen atoms, in contrast to the structures of most $Ag[ClO_4]$–π-arene complexes.[5]

TABLE 1

Final non-hydrogen atomic fractional co-ordinates ($\times 10^4$) *

Atom	*x*	*y*	*z*
Ag	−52(1)	3 253(1)	2 577(1)
S(11)	1 154(2)	4 990(2)	3 984(2)
S(12)	1 172(2)	3 291(2)	5 330(2)
S(13)	2 025(2)	2 273(2)	3 542(2)
S(14)	2 027(2)	3 953(2)	2 205(2)
S(21)	−1 193(2)	4 979(2)	1 046(2)
S(22)	−1 110(2)	3 270(2)	−272(2)
S(23)	−2 103(2)	2 253(2)	1 439(2)
S(24)	−2 176(2)	3 945(2)	2 745(2)
N(11)	1 632(8)	4 381(6)	5 212(7)
N(12)	2 111(7)	2 593(6)	4 933(7)
N(13)	2 723(6)	3 050(6)	2 934(7)
N(14)	2 107(6)	4 830(6)	3 133(7)
N(21)	−1 538(8)	4 360(6)	−183(8)
N(22)	−2 099(7)	2 553(6)	52(7)
N(23)	−2 830(7)	3 021(6)	2 020(7)
N(24)	−2 208(7)	4 817(7)	1 811(8)
Cl	5 049(2)	1 169(2)	3 026(2)
O(1)	6 117(7)	921(8)	2 725(8)
O(2)	4 051(7)	1 171(7)	2 014(7)
O(3)	5 211(6)	2 054(6)	3 576(7)
O(4)	4 828(8)	577(7)	3 891(8)
W(1)	4 518(7)	3 426(7)	1 074(8)
W(2)	4 812(12)	−559(13)	372(14)

* Estimates of the standard deviations are given in parentheses, in this and other tables throughout this paper.

The structure of the cation is shown in detail in Figure 2, which also gives the atomic numbering scheme

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† More systematically, bis(cyclotetra-azathiane)silver(I) perchlorate sesquihydrate.

used. The silver ion is sandwiched between the two $S_4N_4H_4$ molecules with the sulphur atoms closest to it. Although the metal ion is equidistant (2.07 Å) from the S_4 planes of the two ligands, the sandwich structure is somewhat distorted. First, the two S_4 planes are not parallel, but inclined at an angle of 20.4° to each other. Secondly, the silver ion is not disposed symmetrically with respect to the four sulphur atoms of each ring, but has moved sideways and is closer to two of the atoms in each S_4 unit than to the other two pairs. In spite of these distortions, the two ligands are seen to adopt a *staggered* configuration with respect to the two S_4 squares. These latter two features are well demonstrated by Figure 3, which also shows the approximate C_2 symmetry of the cation. In addition, this view of the cation also helps to show why the idea of metal–ligand π bonding is not really acceptable.

TABLE 2

Fractional co-ordinates ($\times 10^3$) and isotropic temperature factors ($Å^2 \times 10^3$) for the hydrogen atoms

Atom	x	y	z	U_{iso}
H(11)	215	468	596	41
H(12)	265	239	547	32
H(13)	341	301	301	33
H(14)	288	519	331	35
H(21)	−215	457	−94	45
H(22)	−274	237	−61	40
H(23)	−361	287	198	36
H(24)	−291	507	171	34
H(1)W(1)	507	378	58	75
H(2)W(1)	473	278	77	75

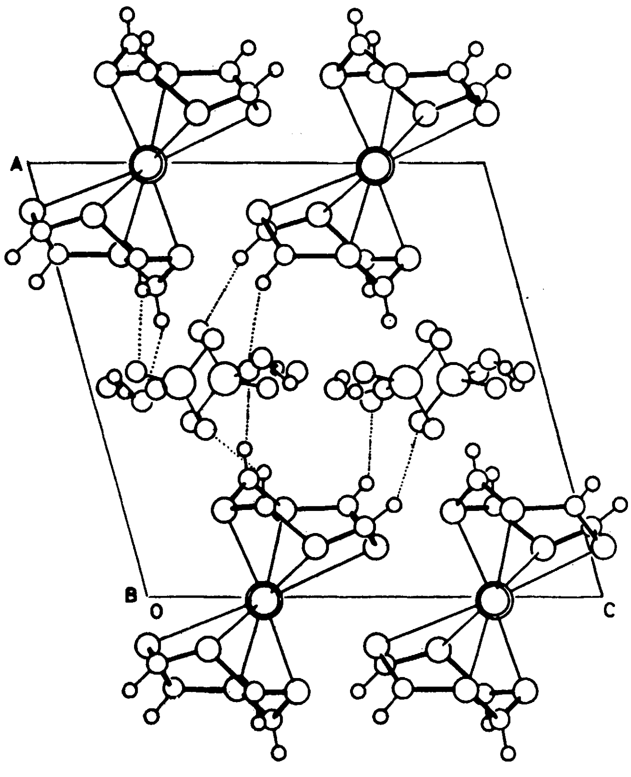


FIGURE 1 The crystal structure projected along *b*, showing a unique set only of the hydrogen bonds (dotted lines)

The off-centre positioning of the silver ion does not in itself preclude the possibility of π bonding since it could be inferred that the interaction might be between the metal and one S–N bond or perhaps one S–N–S unit. However, close examination of Figure 2 shows that those portions of the ligands closest to the metal,

TABLE 3

Interatomic distances (Å) and angles (°) in $[Ag(S_4N_4H_4)_2]^+$

(*a*) Co-ordination geometry about the Ag atom

Ag–S(11)	3.141(3)	S(12)–Ag–S(11)	55.7(1)
Ag–S(12)	3.150(3)	S(13)–Ag–S(11)	89.6(1)
Ag–S(13)	2.755(3)	S(13)–Ag–S(12)	59.2(1)
Ag–S(14)	2.738(3)	S(14)–Ag–S(11)	59.9(1)
Ag–S(21)	3.170(3)	S(14)–Ag–S(12)	89.1(4)
Ag–S(22)	3.226(3)	S(14)–Ag–S(13)	64.0(1)
Ag–S(23)	2.792(3)		
Ag–S(24)	2.696(2)	S(22)–Ag–S(21)	54.9(1)
		S(23)–Ag–S(21)	88.7(1)
Ag · · · N(11)	3.575	S(23)–Ag–S(22)	58.2(1)
Ag · · · N(12)	3.324	S(24)–Ag–S(21)	59.7(1)
Ag · · · N(13)	3.117	S(24)–Ag–S(22)	88.4(1)
Ag · · · N(14)	3.322	S(24)–Ag–S(23)	64.2(1)
Ag · · · N(21)	3.608		
Ag · · · N(22)	3.405	S(23)–Ag–S(13)	116.9(1)
Ag · · · N(23)	3.102	S(23)–Ag–S(14)	141.4(1)
Ag · · · N(24)	3.315	S(24)–Ag–S(13)	150.2(1)
		S(24)–Ag–S(14)	135.7(1)

(*b*) Ag–S–N angles

Ag–S(11)–N(11)	91.0(3)	Ag–S(21)–N(21)	91.3(3)
Ag–S(11)–N(14)	81.0(3)	Ag–S(21)–N(24)	80.0(3)
Ag–S(12)–N(11)	89.9(3)	Ag–S(22)–N(21)	88.9(3)
Ag–S(12)–N(12)	81.3(3)	Ag–S(22)–N(22)	81.6(3)
Ag–S(13)–N(12)	94.2(3)	Ag–S(23)–N(22)	96.0(3)
Ag–S(13)–N(13)	86.1(3)	Ag–S(23)–N(23)	84.4(3)
Ag–S(14)–N(13)	86.7(3)	Ag–S(24)–N(23)	87.3(3)
Ag–S(14)–N(14)	94.8(3)	Ag–S(24)–N(24)	95.9(3)

(*c*) Geometry of the $S_4N_4H_4$ ligands

S(11)–N(11)	1.654(9)	S(21)–N(21)	1.655(10)
S(11)–N(14)	1.679(8)	S(21)–N(24)	1.663(8)
S(12)–N(11)	1.696(9)	S(22)–N(21)	1.680(9)
S(12)–N(12)	1.639(9)	S(22)–N(22)	1.662(9)
S(13)–N(12)	1.669(9)	S(23)–N(22)	1.680(9)
S(13)–N(13)	1.656(8)	S(23)–N(23)	1.649(9)
S(14)–N(13)	1.658(8)	S(24)–N(23)	1.664(9)
S(14)–N(14)	1.665(9)	S(24)–N(24)	1.673(9)
N(11)–H(11)	1.01	N(21)–H(21)	1.02
N(12)–H(12)	0.81	N(22)–H(22)	0.96
N(13)–H(13)	0.77	N(23)–H(23)	0.91
N(14)–H(14)	1.00	N(24)–H(24)	0.87
S(11) · · · S(12)	2.938(4)	S(21) · · · S(22)	2.951(4)
S(11) · · · S(14)	2.955(4)	S(21) · · · S(24)	2.948(4)
S(12) · · · S(13)	2.937(4)	S(22) · · · S(23)	2.953(4)
S(13) · · · S(14)	2.912(4)	S(23) · · · S(24)	2.919(4)
N(11) · · · N(12)	2.709	N(21) · · · N(22)	2.751
N(11) · · · N(14)	2.708	N(21) · · · N(24)	2.724
N(12) · · · N(13)	2.696	N(22) · · · N(23)	2.736
N(13) · · · N(14)	2.723	N(23) · · · N(24)	2.750
N(14)–S(11)–N(11)	108.7(4)	N(24)–S(21)–N(21)	110.4(5)
N(12)–S(12)–N(11)	108.6(5)	N(22)–S(22)–N(21)	110.8(5)
N(13)–S(13)–N(12)	108.4(4)	N(23)–S(23)–N(22)	110.5(5)
N(14)–S(14)–N(13)	110.1(4)	N(24)–S(24)–N(23)	111.0(5)
S(12)–N(11)–S(11)	122.5(5)	S(22)–N(21)–S(21)	124.5(5)
S(13)–N(12)–S(12)	125.2(5)	S(23)–N(22)–S(22)	124.2(5)
S(14)–N(13)–S(13)	123.0(4)	S(24)–N(23)–S(23)	123.5(5)
S(14)–N(14)–S(11)	124.2(5)	S(24)–N(23)–S(21)	124.2(5)
H(11)–N(11)–S(11)	121.8	H(21)–N(21)–S(21)	122.8
H(11)–N(11)–S(12)	109.4	H(21)–N(21)–S(22)	112.1
H(12)–N(12)–S(12)	115.2	H(22)–N(22)–S(22)	115.4
H(12)–N(12)–S(13)	119.6	H(22)–N(22)–S(23)	120.1
H(13)–N(13)–S(13)	119.7	H(23)–N(23)–S(23)	114.5
H(13)–N(13)–S(14)	117.2	H(23)–N(23)–S(24)	121.8
H(14)–N(14)–S(11)	119.1	H(24)–N(24)–S(21)	128.5
H(14)–N(14)–S(14)	115.3	H(24)–N(24)–S(24)	106.2

TABLE 4

Least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Deviations (Å × 10^3) of relevant atoms are given in square brackets

Plane (1): S(11), S(12), S(13), S(14)

$$9.6452x + 2.5717y + 3.1849z = 3.6700$$

[S(11) −4, S(12) 4, S(13) −4, S(14) 4, N(11) 691, N(12) 604, N(13) 675, N(14) 602, Ag −2 063]

Plane (2): S(21), S(22), S(23), S(24)

$$9.2749x - 2.5427y + 3.8471z = -1.9677$$

[S(21) −2, S(22) 2, S(23) −2, S(24) 2, N(21) −638, N(22) −608, N(23) −648, N(24) −609, Ag 2 084]

Angle between normals to planes (1) and (2) = 20.4°

Torsion angles (°)

A B C D	
N(14)–S(11)–N(11)–S(12)	−90.8
N(11)–S(11)–N(14)–S(14)	84.1
N(12)–S(12)–N(11)–S(11)	90.7
N(11)–S(12)–N(12)–S(13)	−85.6
N(13)–S(13)–N(12)–S(12)	85.8
N(12)–S(13)–N(13)–S(14)	−90.0
N(14)–S(14)–N(13)–S(13)	90.8
N(13)–S(14)–N(14)–S(11)	−83.8
N(24)–S(21)–N(21)–S(22)	−86.9
N(21)–S(21)–N(24)–S(24)	83.6
N(22)–S(22)–N(21)–S(21)	87.5
N(21)–S(22)–N(22)–S(23)	−83.6
N(23)–S(23)–N(22)–S(22)	84.0
N(22)–S(23)–N(23)–S(24)	−87.7
N(24)–S(24)–N(23)–S(23)	88.4
N(23)–S(24)–N(24)–S(21)	−84.6

The sign of the angle A–B–C–D is positive when a clockwise rotation about B–C is required to bring A–B–C into coincidence with B–C–D, viewed along B–C.

S(13)–N(13)–S(14) and S(23)–N(23)–S(24), have quite the wrong orientation for a π-type interaction.

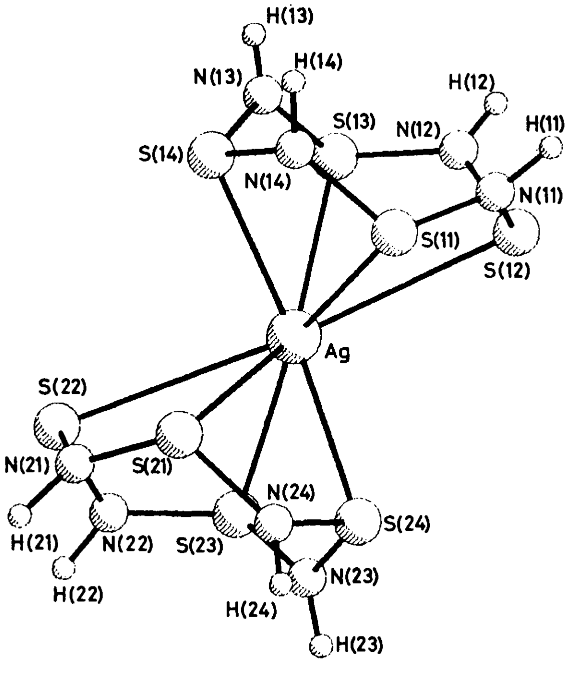


FIGURE 2 Structure of $[Ag(S_4N_4H_4)_2]^+$ showing the atom-numbering system

TABLE 5

Geometry of the ClO_4^- and H_2O molecules (distances in Å, angles in °)

Cl–O(1)	1.410(8)	O(2)–Cl–O(1)	111.0(5)
Cl–O(2)	1.411(7)	O(3)–Cl–O(1)	109.0(5)
Cl–O(3)	1.434(9)	O(3)–Cl–O(2)	110.7(5)
Cl–O(4)	1.404(8)	O(4)–Cl–O(1)	110.9(6)
		O(4)–Cl–O(2)	110.0(5)
		O(4)–Cl–O(3)	105.1(6)
W(1)–H(1)	1.09		
W(1)–H(2)	1.06		
H(1)–W(1)–H(2)	91.5		

If we discard the π-bonding model we must turn our attention to other modes of bonding. An electrostatic model is an obvious possibility, but in this case we might expect a symmetrical structure, with the silver ion equidistant from each of the eight sulphur atoms. An alternative approach is to consider a covalent model, or a covalent modification of the electrostatic model, particularly as the Ag^+ ion is considered to be quite strongly polarising. With this model a distorted structure is necessary, since four-fold co-ordination will be the practical limit, in view of the non-availability of *d* orbitals on silver. Re-examination of the cation structure, particularly the view given in Figure 3, lends much support to this model. As mentioned previously, two

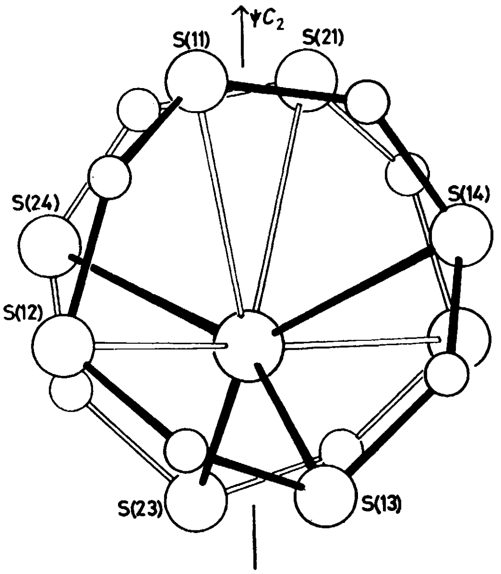


FIGURE 3 View of the $[Ag(S_4N_4H_4)_2]^+$ ion showing the approximate staggered configuration of the two S_4 squares and pseudo-two-fold axis. The hydrogen atoms are not shown

TABLE 6

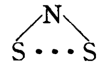
Possible hydrogen-bonded distances (Å)

D H A	DA	DH	HA
N(11)–H(11) · · · O(2^{III})	3.119	1.01	2.53
N(12)–H(12) · · · W(1^{III})	3.112	0.81	2.40
N(13)–H(13) · · · O(3^{I})	3.117	0.77	2.44
N(14)–H(14) · · · O(1^{VII})	2.967	1.00	2.16
N(21)–H(21) · · · O(1^{VI})	3.147	1.02	2.30
N(22)–H(22) · · · O(3^{VI})	3.166	0.96	2.44
N(23)–H(23) · · · W(1^{II})	3.010	0.91	2.28
N(24)–H(24) · · · O(4^{IV})	3.107	0.87	2.25
W(1)–H(1) · · · O(4^{V})	3.040	1.09	2.14

Symmetry code: I, x, y, z; II $-1 + x, y, z$; III $x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $-x, \frac{1}{2} + y, \frac{1}{2} - z$; V $x, \frac{1}{2} - y, -\frac{1}{2} + z$; VI $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; VII $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

sulphur atoms from each ring are closer to the metal than the other two. These short distances, which lie in the range 2.696—2.792 Å (and which are at least 0.35 Å shorter than those in the longer range, 3.141—3.226 Å), are only *ca.* 0.15—0.35 Å greater than the sum of covalent radii for Ag(1) and S(2.56).[8] Furthermore, the four sulphur atoms concerned are arranged so as to give a distorted tetrahedral co-ordination. In terms of orbital overlap, the situation is quite favourable. In the S_4N_4 ring, the N–S–N angles are all close to tetrahedral, and so we can picture the sulphur atoms as being sp^3 hybridised. Each sulphur atom will then have two lone pairs which will occupy ' axial ' and ' equatorial ' sites with respect to the S_4N_4 ring. The axial lone pairs on the relevant sulphur atoms can then be used for σ bonding with the metal sp^3 orbitals.

One condition arising out of the suggested mode of bonding is that, in solution, the structure is required to be fluxional, in order to explain the equivalence of all NH protons. This is not at all difficult to envisage for the cation structure found, requiring only a rotation of each ligand for the silver ion to bridge consecutive sides of the S_4 square.

Also in relation to the proposed metal–ligand bonding, it is interesting to examine the geometry of the two ligands. These are essentially equivalent, and show few changes from that of the free ligand.[7] The S–N bond lengths and S–N–S and N–S–N angles are, bearing in mind the lower precision of the present structure, essentially equal to the corresponding values in the free ligand. The S–N–S–N dihedral angles around the rings show slightly more variation in the complex (83.8—90.8°) than in the free ligand (86.2—87.6°). Also, the transannular S • • • S contacts for the two pairs of sulphur atoms bonded to the metal are slightly smaller (2.912, 2.919 Å) than other  $\overset{N}{S \cdots S}$ distances (2.937—2.955 Å).

As mentioned earlier, the components of the crystal structure are held together by an extensive network of hydrogen bonds as shown in Figure 1. The more significant H-bonded contacts are listed in Table 6. Three of the perchlorate oxygen atoms are involved in hydrogen bonding and these serve to damp down the disorder usually found for ClO_4^- groups. One of the water molecules [W(1)] takes part in hydrogen bonding but the other, W(2), which is disordered over two sites across a centre of symmetry, shows no close contacts and appears to be mechanically trapped in the lattice.

EXPERIMENTAL

Crystals used for *X*-ray work were sealed inside Lindemann capillaries. Unit-cell parameters were initially determined from oscillation and Weissenberg photographs and later refined using setting angles for 15 high-angle reflections automatically centred on an Enraf–Nonius CAD4 diffractometer.

Crystal Data.—$2S_4N_4H_4 \cdot Ag[ClO_4] \cdot 1.5H_2O$, $M = 610.9$, Monoclinic, $a = 11.684(5)$, $b = 14.623(6)$, $c = 11.487(5)$ Å, $\beta = 105.39(5)°$, $U = 1\,892.2$ Å^3, $D_m = 2.13$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.14$ g cm^{-3}, $F(000) = 1\,212$, μ(Mo-K_α) = 19.5 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å, space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences $0k0$ for k odd and $h0l$ for l odd.

Intensity data were recorded on the CAD4 diffractometer with graphite-monochromatised Mo-K_α radiation, an ω–2θ scan technique [scan width = $0.8 + 0.2\tan\theta$] and a crystal measuring 0.30 × 0.25 × 0.20 mm. All hkl and $\bar{h}kl$ reflections up to $\theta = 25°$ were measured. Each reflection was given a fast prescan (20.116 6° min^{-1}) and those with a nett count >5 were rescanned slowly to yield a total count of 3 000 subject to a maximum time of 60 s. Two standard reflections monitored after every 50 reflections showed a *ca.* 30% decrease in the intensity of the diffracted beam during data collection. All intensities were corrected for Lorentz and polarisation factors and brought to a common relative scale by allowing for crystal deterioration and variable measuring time. No corrections were made for absorption or extinction. Out of a total of 3 017 unique intensities, 1 909 were deemed observed [$F_o > 3\sigma(F_o)$] and used in the structure analysis and refinement.

The position of the Ag atom was determined from a Patterson map. The S and N atoms of the two independent $S_4N_4H_4$ rings and the Cl and O atoms of the ClO_4 ion were obtained from successive electron-density synthesis. Isotropic full-matrix least-squares refinement of these atoms ($R = 0.16$) was followed by a difference synthesis which contained two extra peaks with heights *ca.* 5 and 3 e Å^{-3}. The first peak was *ca.* 3.0 Å away from a perchlorate O atom while the second had its centrosymmetric counterpart as the only nearest neighbour at *ca.* 2.0 Å. These peaks were assumed to be O atoms of H_2O molecules and included in the refinement with fixed occupancies of 1.0 [W(1)] and 0.5 [W(2)]. Isotropic refinement of all the non-hydrogen atoms ($R = 0.14$) was followed by anisotropic refinement ($R = 0.068$). The H atoms of the two $S_4N_4H_4$ groups and one H_2O [W(1)] molecule were obtained from difference maps but an attempt to refine them did not succeed. Accordingly these atoms were assigned $U_{iso.}$ values equal to those of their parent atoms prior to anisotropic refinement and included in structure-factor calculations. No account was taken of the H atoms belonging to the disordered H_2O [W(2)] molecule. Further refinement of the parameters of the non-hydrogen atoms converged at $R = 0.062$ and $R' = 0.068$. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.000\,3\,F_o^2]$, which gave mean $\Sigma w\Delta^2$ almost independent of sin θ or $(F_o/F_{max.})^{\frac{1}{2}}$.

Final fractional co-ordinates for the non-hydrogen atoms are given in Table 1, hydrogen-atom parameters in Table 2. Anisotropic thermal parameters for the non-hydrogen atoms and lists of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22689 (14 pp.).* The interatomic distances and angles, and calculations of dihedral angles and least-squares planes, are given in Tables 3—5, while the dimensions of the possible hydrogen bonds are in Table 6. Neutral atom scattering factors were taken from refs. 9 (H) and 10 (N, O, S, and Ag) with those for the heavier elements being modified for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 11. All calculations were performed on the Queen Mary College ICL 1904S and the University of London CDC 7600 computers using SHELX-76 [12] (structure determination

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

and refinement), XANADU [13] (least-squares planes), and PLUTO [14] (diagrams).

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