Tetrasulphur Tetraimide Complexes of Silver(I)

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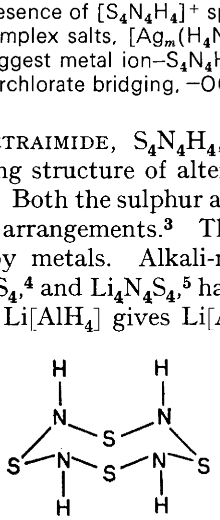
Three new tetrasulphur tetraimide complexes of silver(I), $Ag[ClO_4]\cdot S_4N_4H_4$ (1), $2Ag[ClO_4]\cdot S_4N_4H_4$ (2), and $Ag[ClO_4]\cdot 2S_4N_4H_4$ (3), have been prepared and characterised. The mass spectra of (1) and (3) show the presence of $[S_4N_4H_4]^+$ species in the fragmentation pattern. Conductimetric evidence shows that the species are complex salts, $[Ag_m(H_4N_4S_4)_n][ClO_4]_m$ (n = 1, m = 1 or 2; n = 2, m = 1), in solution. The ^1H n.m.r. spectra suggest metal ion–$S_4N_4H_4$ ring π complexation, and the i.r. spectra give evidence for the existence of bidentate perchlorate bridging, $-OCl(O_2)O-$, between the silver nuclei in the solid state.

TETRASULPHUR TETRAIMIDE, $S_4N_4H_4$, has a puckered eight-membered ring structure of alternate sulphur and nitrogen atoms.[1-3] Both the sulphur and nitrogen atoms have square-planar arrangements.[3] The hydrogen atoms can be replaced by metals. Alkali-metal derivatives, $Na_2H_2N_4S_4$, $Na_4N_4S_4$,[4] and $Li_4N_4S_4$,[5] have been prepared. The reaction with $Li[AlH_4]$ gives $Li[Al(N_4S_4)]$.[6] These compounds are believed to be ionic and are unstable. The instability is attributed to the $[S_4N_4H_{4-n}]^{n-}$ anions.



Some heavy-metal derivatives of $S_4N_4H_4$ have been made which are relatively stable. Copper(I) chloride reacts with $S_4N_4H_4$ in pyridine to give copper thionitrosylate, $[\{Cu(NS)\}_4]$.[7] Copper(II) salts give partially substituted products, $(CuCl)_2H_2N_4S_4$ or $[Cu(NO_3)]_2$-$H_2N_4S_4$. Silver(I) nitrate under similar conditions also gives silver thionitrosylate, $[\{Ag(NS)\}_4]$.[7] While mercury(I) nitrate produces $Hg_4N_4S_4$,[8a] mercury(II) acetate gives two products, $Hg_2N_4S_4$ and $Hg_5(NS)_8$, by a complex mechanism.[8b] The structures of these metal derivatives are unknown. It is however reported that the reaction of $[\{Ag(NS)\}_4]$ with ethyl iodide produces $(EtNS)_4$, suggesting a metal-to-nitrogen linkage.[7]

Very few examples are known where $S_4N_4H_4$ acts as a co-ordinating ligand to a metal ion. A molecular adduct, $2Ag[NO_3]\cdot S_4N_4H_4$ was first reported by Meuwsen,[2] but its structure is not known. More recently, 1 : 1 adducts, $TeBr_4\cdot S_4N_4H_4$,[9] $AlCl_3\cdot S_4N_4H_4$,[5] and $AlBr_3\cdot S_4N_4H_4$,[5] have been prepared. These are considered to be simple Lewis acid–base type adducts involving σ linkage through the nitrogen lone pair. The reaction with tin(IV) bromide, on the other hand, led to $SnBr_4(N_4S_4)_2$.[5] The pK_a' value † of $S_4N_4H_4$ determined in nitrobenzene solution shows it to possess very little formal basic strength,[11] raising doubt about its ability to form strong enough σ-donor bonds. On the other hand, substantial π character of the S–N bond has been recognised,[12,13] but no study has been made of the π-donor properties of the cyclic sulphur–nitrogen systems. It was therefore of interest to study the behaviour of $S_4N_4H_4$ as a ligand towards the transition metals.

RESULTS AND DISCUSSION

When an acetone solution of tetrasulphur tetraimide was titrated conductimetrically with an acetone solution of silver(I) perchlorate the conductance of the solution slowly increased and the conductance curve [Figure 1(*a*)] had sharp breaks at points corresponding to the $Ag[ClO_4] : S_4N_4H_4$ molar ratio of 1 : 1, 2 : 1, and 0.5 : 1. A similar mode of conductance variation was observed when a suspension of $S_4N_4H_4$ in acetonitrile was titrated with an acetonitrile solution of $Ag[ClO_4]$ [Figure 1(*b*)]. These results indicated the formation of the adducts $Ag[ClO_4]\cdot S_4N_4H_4$ (1), $2Ag[ClO_4]\cdot S_4N_4H_4$ (2), and $Ag[ClO_4]\cdot 2S_4N_4H_4$ (3) in the solutions. Based on the

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† For an explanation of pK_a', see ref. 10.

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[6] M. Goehring and G. Zirker, *Z. Naturforsch.*, 1955, **B10**, 58.

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conductimetric evidence, these adducts may be formulated as the complex salts (tetrasulphur tetraimide)-silver(I) perchlorate, $[Ag(H_4N_4S_4)][ClO_4]$, (tetrasulphur tetraimide)disilver(I) perchlorate, $[Ag_2(H_4N_4S_4)][ClO_4]_2$, and bis(tetrasulphur tetraimide)silver(I) perchlorate, $[Ag(H_4N_4S_4)_2][ClO_4]$, respectively.

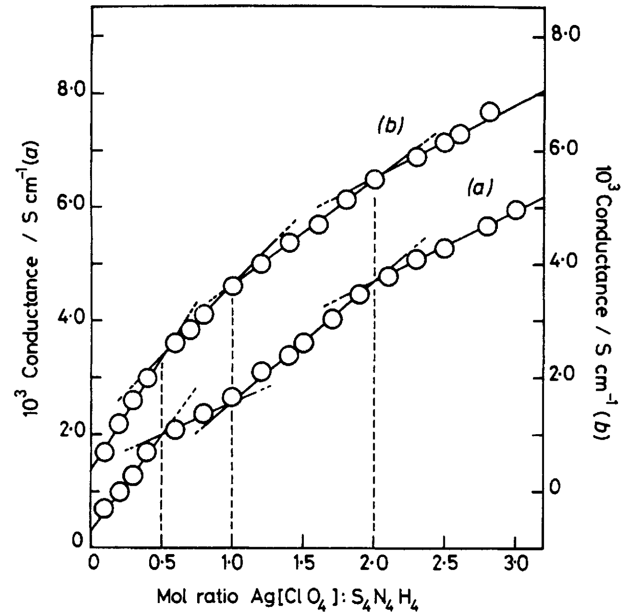

FIGURE 1 Conductimetric titration of tetrasulphur tetraimide with silver(I) perchlorate in (*a*) acetone and (*b*) acetonitrile solution

With equimolar proportions of $S_4N_4H_4$ and $Ag[ClO_4]$, complex (1) could be isolated from acetone solutions. Use of higher molar proportions of $Ag[ClO_4]$ (*i.e.* 1 : 2 or 1 : 4) gave (2). Complex (1) was also obtainable from acetonitrile, but in this medium a higher proportion of $Ag[ClO_4]$ (1 : 2) was required; the yield of (2) was poor in acetonitrile. By allowing $S_4N_4H_4$ to react with $Ag[ClO_4]$ in the molar proportion of 2 : 1, complex (3) was obtained from an acetonitrile medium. With a molar proportion of 1 : 1 in acetonitrile, (3) was also formed as the major product. The yield of (3) was not satisfactory in an acetone medium.

Complexes (1) and (2) are white powdery solids, while (3) is crystalline and is obtained as shiny flat plates. The mass spectra of complexes (1) and (3) showed the presence of the $[S_4N_4H_4]^+$ species in the fragmentation pattern. This indicates that the composition of $S_4N_4H_4$ remains unaltered on combination with the metal ion.

Infrared Spectra.—The i.r. spectrum of $S_4N_4H_4$ showed all the strong bands reported earlier [5,14] for this compound (Table). Very little changes in frequency in the near-i.r. region of the spectra were observed on complex formation. The three moderately strong sharp absorptions in the 3 240—3 330 cm^{-1} region are characteristic of the NH groups and provide clear evidence that all the original N–H linkages of the parent $S_4N_4H_4$ ring survive on complex formation, *i.e.* there is no substitution of the hydrogen atoms by the metal. The NH bands, however, showed appreciable increases in intensity. The NH bending mode occurred at 1 310 cm^{-1}. The far-i.r. region of the spectra showed certain structural variations depending on the extent of complex formation. The S–N band at 840 cm^{-1} broadened (830—845 cm^{-1}) and that at 550 cm^{-1} shifted to 545 cm^{-1}. A new band appeared at 525 cm^{-1}. The band in the region of 310 cm^{-1}, which has been assigned to the N–S–N–S bending and torsion mode,[14] broadened and shifted to 290—300 cm^{-1}. The very strong and broad absorption in the 1 020—1 190 cm^{-1} region due to the free $[ClO_4]^-$ group in $Ag[ClO_4]$ split into three strong bands (1 150, 1 120, and 1 095 cm^{-1}) and that at 630 cm^{-1} into two bands (645 and 635 cm^{-1}). These indicate that the perchlorate group is also bound to the metal.[15a]

Infrared absorption bands (cm^{-1})

Assignments [14,15]	$S_4N_4H_4$	$Ag[ClO_4]$	$Ag[ClO_4]{\cdot}S_4N_4H_4$	$2Ag[ClO_4]{\cdot}S_4N_4H_4$	$Ag[ClO_4]{\cdot}2S_4N_4H_4$
NH stretching ν(NH)	3 330m		3 330s	3 330s	3 330s
	3 300m		3 300s	3 305s	3 300s
	3 240m		3 240s	3 240s	3 240s
		2 030w			
NH bending δ(NH)	1 310m		1 310m	1 310m	1 310w
	1 270w				
ClO stretching ν(ClO_4)		1 190—	1 150s	1 150s	1 155s
		1 020s	1 120s	1 120s	1 130s
			1 095s	1 090s	1 100s
ν(ClO_4)		950m	950w	950w	
SN stretching ν(SN)	840s		845—830s	845—830s	845—835s
	730w		730w	730w	
	710w		710w	710w	710vw
ClO stretching ν(ClO_4)		630s	645s	645s	650m
			635s	635s	645m
					640m
SN stretching ν(SN)	550s		545s	545s	550s
			525s	525s	530m
	470s		470s	470s	475s
	420s		420s	420s	420s
N–S–N–S bending and torsion δ(SN)	310s		300—290s	300—290s	305s

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[14] (*a*) E. R. Lippincott and M. C. Tobin, *J. Amer. Chem. Soc.*, 1951, **73**, 4990; (*b*) *J. Chem. Phys.*, 1953, **21**, 1559; (*c*) D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, 1962, **58**, 1291.

[15] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Interscience, New York, 1970, (*a*) pp. 175, 176; (*b*) p. 259.

^{1}H *N.M.R. Spectra.*—The ^{1}H n.m.r. spectrum of $S_4N_4H_4$ gave a broad signal for the imide protons at δ 6.56 p.p.m. in $(CD_3)_2CO$ solution [Figure 2(*a*)]. The broadness of the signal is attributed to the nitrogen nuclear-quadrupole relaxation effect.[16] On formation of the complexes the imide proton signal was shifted downfield to 7.64 p.p.m. for (1) [Figure 2(*b*)] and (2) and to 7.54 p.p.m. for (3). The deshielding of the NH protons is probably caused by polarisation of charge by the metal ion. The NH signals were also considerably sharpened on complex formation [Figure 2(*b*) and 2(*c*)]. This can be attributed to the consequential decrease in the field gradient at the nitrogen atoms as a result of which the quadrupolar effect of nitrogen is reduced.

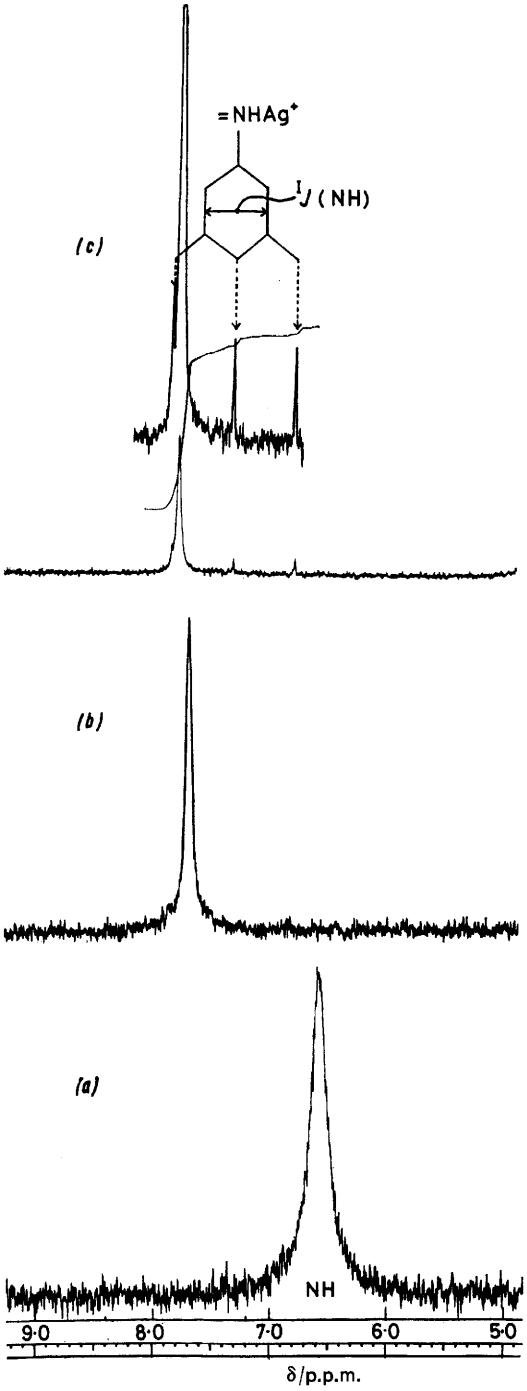

FIGURE 2 100-MHz ^{1}H n.m.r. spectra of (*a*) $S_4N_4H_4$, (*b*) $Ag[ClO_4]{\cdot}S_4N_4H_4$ (1), and (*c*) $S_4N_4H_4$ with excess of $Ag[ClO_4]$. All the spectra were recorded in $(CD_3)_2CO$ solution at *ca.* 30 °C

Bonding.—Two alternative possibilities exist for the mode of linkage of $S_4N_4H_4$ to the silver ions: (*i*) σ donation through either the nitrogen or sulphur lone pairs; and (*ii*) metal–ring π interaction. The σ linkage of a metal ion to a nitrogen atom of the $S_4N_4H_4$ ring should result in the particular NH proton being non-equivalent to the remaining imide protons. However, the occurrence of a single sharp signal in the n.m.r. spectra of all the three complexes indicates that all the four protons are equivalent. This may suggest a symmetric central location of the Ag^+ ion, or that the ion may be in rapid exchange with the four nitrogen atoms. The n.m.r. spectrum of $S_4N_4H_4$ in $(CD_3)_2CO$ saturated with $Ag[ClO_4]$ (in excess) showed, in addition to a singlet, a sharp triplet at 7.26 p.p.m. with ^1J(NH) 53 Hz [see Figure 2(*c*)], indicating formation of the quaternary ion =$NHAg^+$. The appearance of such a triplet is also comparable with the n.m.r. spectrum of the $[NH_4]^+$ ion [^1J(NH) 51.5 Hz].[16] The proportion of the quaternised ion =$NHAg^+$ to the neutral imide group =NH was however found to be <15% from measurement of the peak areas [Figure 2(*c*)]. This demonstrates that an overwhelming proportion of the $S_4N_4H_4$ molecules is not linked to Ag^+ through the nitrogen atoms, even though the metal ion is present in the solution in high concentration.

Several workers [12,13] observed π character in the S–N bonds of $S_{8-n}(NH)_n$ ring systems. Full or partial involvement of the nitrogen lone-pair electrons in the S–N d_π–p_π bonding diminishes the Lewis-base activity of the nitrogen atoms. The $S_4N_4H_4$ molecule has in fact been found to possess a very low overall basicity (pK_a' −5.8, measured in nitrobenzene;[11] *cf.* pK_a' 7.0 for NMe_2H,[10] 7.6 for $N_4P_4Et_8$ [17]), which is not compatible with strong σ bonding through the nitrogen lone pairs. The drift of electrons towards sulphur however may activate the sulphur lone pairs for external donation. On the other hand, delocalisation of π electrons would distribute the charge over the whole ring and the π charge cloud can be easily polarised by the silver ion. As a result the π electrons might act centrally on the metal ion.

It is known that silver(I) complexes of ligands containing second- or third-row elements (P, S, As, or Se) as donor atoms are more stable than those containing the analogous first-row elements (N or O).[18,19] Their relative

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[19] L. D. Pettit, A. Royston, and R. J. Whewell, *J. Chem. Soc.* (*A*), 1968, 2009; L. D. Pettit, C. Sherrington, and R. J. Whewell, *ibid.*, p. 2204; L. D. Pettit and A. Royston, *ibid.*, 1969, 1570.

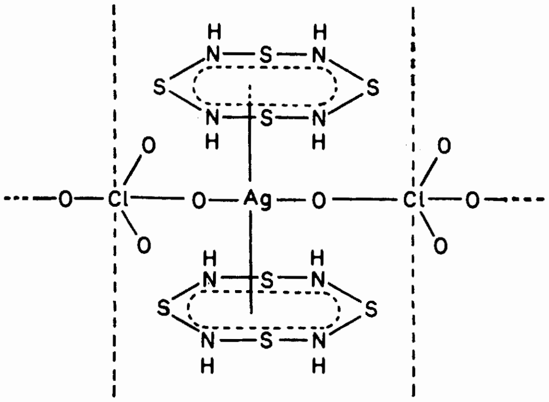
stabilities have been variously attributed to (*i*) back co-ordination from filled metal-ion *d* orbitals to empty ligand *d* orbitals [18] and (*ii*) the high polarisability of the second- and third-row donor atoms and the polarising power of the silver ion.[19] A polarised metal–sulphur bond in the present cases will almost certainly affect the electron density of the S–N bonds and tend to create asymmetry in the charge distibution of the $(SNH)_4$ ring. It is observed, however that, although the extent of polarisation of the ring varies from the mono-complex, $[AgL]^+$ (1), to the bis complex, $[AgL_2]^+$ (3) ($L = S_4N_4H_4$), as reflected by the small difference in their n.m.r. chemical shifts (see above), their overall charge symmetry is maintained. It is also interesting to note that in the i.r. spectra no marked shift of the NH frequency bands occurs on complex formation, only the NH band intensities increasing, while the SN vibration frequencies undergo small changes. These observations are suggestive of π-type interaction [15b,20] rather than σ bonding with the metal ion.

Examples of metal π complexation with ring systems bearing second-row elements however are rare. On the other hand, several examples of π complexes between aromatic moieties and silver(I) perchlorate are well established.[21–25] The crystal structure of $Ag[ClO_4]\cdot C_6H_6$ showed [22] that each silver ion is π-bonded to two benzene rings in such a way that the structure consists of $-C_6H_6-Ag-C_6H_6-Ag-$ chains and perchlorate ions. As has been pointed out here, the equivalent nature of all the imide protons in the n.m.r. spectra suggests a symmetric location of the Ag^+ ion in the $Ag^+-S_4N_4H_4$ complexes. It is possible therefore that the π interaction in these complexes may be more central than is observed in the silver–arene complexes.[22,24] The occurrence of three strong bands in the 1 150, 1 120, and 1 095 cm^{-1} region for all the complexes (1)—(3) is in accord with the existence of bidentate bridging perchlorate groups as established in other cases.[15a,26] There is, however, no evidence to support this in solution.

The solid structures of these complexes appear to be relatively more complicated than those in solution. By analogy with silver–arene complexes, the structure of $Ag[ClO_4]\cdot 2S_4N_4H_4$ (3) in the solid state may be represented by one π-donor bond from each of the two $S_4N_4H_4$ rings to one silver ion and $-OCl(O_2)O-$ bridges linking two such silver nuclei as outlined below. The structure of $Ag[ClO_4]\cdot S_4N_4H_4$ (1) may consist of $-(SNH)_4-Ag-(SNH)_4-Ag-(SNH)_4-Ag-$ chains with the perchlorate ions acting as links between the chains. The structure of $2Ag[ClO_4]\cdot S_4N_4H_4$ (2) is difficult to visualise in this context. If two Ag^+ ions are attached to only one $(SNH)_4$ ring from the two sides of the nodal plane, such a structure appears to be inherently unstable. Complex (2) is of course noticeably less stable, and violently detonates, than either (1) or (3).

For the Lewis-acid adducts $AlCl_3\cdot S_4N_4H_4$ and $AlBr_3\cdot S_4N_4H_4$, Banister and Younger [5] suggested σ bonding *via* donor nitrogen atoms. No n.m.r. data for these compounds are available. Their i.r. spectra, however, show some significant differences when compared with those of the silver complexes (1)—(3), suggesting structural differences between the two cases.

It may therefore be concluded that structurally the $S_4N_4H_4$ complexes of silver are more similar to silver–arene complexes [21–25] than the Lewis-acid adducts.[5] Compared with the silver–arene complexes, the present complexes are more stable. Reinforcement of a metal–ligand bond by back donation from a filled metal *d* orbital is usually accompanied by an upfield shift of the n.m.r. signal compared with that of the free ligand.[20] On this basis, very little back donation is considered to be present in silver–olefin complexes.[20] The net shift of the imide proton signal downfield in the present cases suggests that the effect of polarisation of the charge cloud of the $S_4N_4H_4$ ring by the silver ion contributes predominantly towards the stability of these complexes. This lends independent support to the observations of Pettit and his co-workers [19] in respect of the stability of silver complexes of ligands containing highly polarisable donor atoms.



Structure of $Ag[ClO_4]\cdot 2S_4N_4H_4$; the ring conformation is assumed to be planar for simplicity

EXPERIMENTAL

Tetrasulphur tetraimide was prepared by reduction of S_4N_4 with methanolic tin(II) chloride.[27] Silver(I) perchlorate was obtained from B. D. H. Solvents used were of high quality and were dried and distilled before use. ' Conductivity ' acetone was of the order of purity described earlier [28]

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and had a conductance of 2.0×10^{-8} S cm^{-1} at 25 °C. Acetonitrile for conductance measurements was purified by distilling over phosphorus pentaoxide and was redistilled twice before use. It had a conductance of 5.4×10^{-8} S cm^{-1} at 25 °C.

A precision Philips type G4249/10 (D3563) conductivity bridge was used for conductance measurements. The cell was of the dipping-electrode type, fitted with ground joints and a side arm for passing nitrogen, and the electrodes were of smooth platinum (cell constant, 0.4 cm^{-1}). The i.r. spectra were recorded on a Perkin–Elmer model 457 grating infrared spectrometer within the range 250—4 000 cm^{-1} in the solid state in KBr pellets, and also as Nujol mulls in some cases. The ^{1}H n.m.r. spectra were obtained on a Varian HA-100D spectrometer in $(CD_3)_2CO$ solutions at a probe temperature of *ca.* 30 °C. Mass spectra were recorded on an A.E.I. MS30 double-beam mass spectrometer.

Preparations.—(*Tetrasulphur tetraimide*)*silver*(I) *perchlorate*, (1). To a solution of tetrasulphur tetraimide (0.188 g, 1 mmol) in acetone (20 cm^3) was added slowly an acetone solution (10 cm^3) of silver(I) perchlorate (0.207 g, 1 mmol). By saturating the clear solution with carbon tetrachloride or light petroleum, a white solid was separated and identified as the complex $Ag[ClO_4]\cdot S_4N_4H_4$ (1) (0.24 g, 60%), m.p. 110 °C (decomp.) (Found: H, 1.2; Ag, 26.8; N, 14.5. $H_4AgClN_4O_4S_4$ requires H, 1.0; Ag, 27.3; N, 14.15%).

(*Tetrasulphur tetraimide*)*disilver*(I) *perchlorate*, (2). Tetrasulphur tetraimide (0.188 g, 1 mmol) in acetone solution (20 cm^3) and $Ag[ClO_4]$ (0.415 g, 2 mmol), also in acetone solution (10 cm^3), reacted as before to give the complex $2Ag[ClO_4]\cdot S_4N_4H_4$ (2) as a white solid (0.3 g, 50%), m.p. 120 °C (decomp.) (Found: Ag, 35.2; N, 10.0. $H_4Ag_2Cl_2N_4S_4O_8$ requires Ag, 35.8; N, 9.3%). Tetrasulphur tetraimide (0.09 g, 0.5 mmol) and $Ag[ClO_4]$ (0.415 g, 2 mmol) reacted in the molar ratio 1 : 4 in acetone giving complex (2) (0.12 g, 40%), m.p. 120 °C (decomp.) (Found: Ag, 36.0%). Complex (2) detonates violently on heating to 120 °C.

Bis(*tetrasulphur tetraimide*)*silver*(I) *perchlorate*, (3). A suspension of $S_4N_4H_4$ (0.188 g, 1 mmol) in acetonitrile (20 cm^3) reacted with $Ag[ClO_4]$ (0.103 g, 0.5 mmol) dissolved in acetonitrile (10 cm^3) to give a clear solution. The complex $Ag[ClO_4]\cdot 2S_4N_4H_4$, (3) (0.2 g, 68%), m.p. 165 °C (decomp.), crystallised from acetonitrile–carbon tetrachloride as shiny flat plates (Found: H, 1.4; Ag, 18.3; Cl, 5.6; N, 19.3. $H_8AgClN_8O_4S_8$ requires H, 1.3; Ag, 18.5; Cl, 6.0; N, 19.2%).

Reactions of Tetrasulphur Tetraimide with Silver(I) *Perchlorate.*—*In the molar ratio* 2 : 1 *in acetone*. Tetrasulphur tetraimide (0.09 g, 0.5 mmol) and $Ag[ClO_4]$ (0.05 g, 0.25 mmol) when allowed to react in acetone medium and on crystallising the products from acetone–carbon tetrachloride gave complex (1) as the major product (0.08 g, 84%), m.p. 110 °C (decomp.) (Found: H, 0.9; N, 13.6. $H_4AgClN_4O_4S_4$ requires H, 1.0; N, 14.15%).

In acetonitrile: (*i*) *in equimolar ratio*. Tetrasulphur tetraimide (0.09 g, 0.5 mmol) and $Ag[ClO_4]$ (0.103 g, 0.5 mmol) reacted in acetonitrile medium, and the products on crystallisation from acetonitrile–carbon tetrachloride gave complex (3) (0.035 g, 25%), m.p. 165 °C (decomp.) (Found: H, 1.8; Cl, 5.6; N, 19.6. $H_8AgClN_8O_4S_8$ requires H, 1.3; Cl, 6.0; N, 19.2%).

(*ii*) *In the molar ratio* 1 : 2. A suspension of $S_4N_4H_4$ (0.09 g, 0.5 mmol) reacted with $Ag[ClO_4]$ (0.207 g, 1 mmol) in acetonitrile solution. Fractional crystallisation from acetonitrile–carbon tetrachloride gave (1) as the major product (0.05 g, 25%), m.p. 110 °C (decomp.) (Found: H, 1.4; N, 14.7. $H_4AgClN_4O_4S_4$ requires H, 1.0; N, 14.15%). The products from an identical reaction when allowed to crystallise from acetonitrile gave complex (2) (0.1 g, 33%), m.p. 120 °C (decomp.).

Conductimetric Titrations.—A freshly prepared solution of $S_4N_4H_4$ (0.025 mol dm^{-3}, 10 cm^3) in acetone was titrated conductimetrically with an acetone solution of $Ag[ClO_4]$ (0.25 mol dm^{-3}). The conductance of the solution increased gradually and the conductance curve showed sharp breaks at points corresponding to the $Ag[ClO_4] : S_4N_4H_4$ molar ratios of 0.5 : 1, 1 : 1, and 2 : 1 [Figure 1(*a*)]. For titrations in acetonitrile, tetrasulphur tetraimide (0.047 g, 0.25 mmol) suspended in this medium (10 cm^3) was titrated with an acetonitrile solution of $Ag[ClO_4]$ (0.25 mol dm^{-3}) and gave similar results to those above. The suspension gradually went into solution as the reaction proceeded and the conductance of the solution slowly increased. The conductance curve showed breaks at points corresponding to $Ag[ClO_4] : S_4N_4H_4$ molar ratios of 0.5 : 1, 1 : 1, and 2 : 1 as before [Figure 1(*b*)].

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