Hydrogen-Bonded Network and Layered Supramolecular Structures Assembled from ClO_4^- Counterions with Unprecedented Monomeric $[AgL_2]^+$ and Chain Polymeric $[AgL_2]_n^{n+}$ Complex Cations (L = Thioamide or Thiourea-Like Ligands)

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Dedicated to Professor Heribert Barrera on the occasion of his 87th birthday

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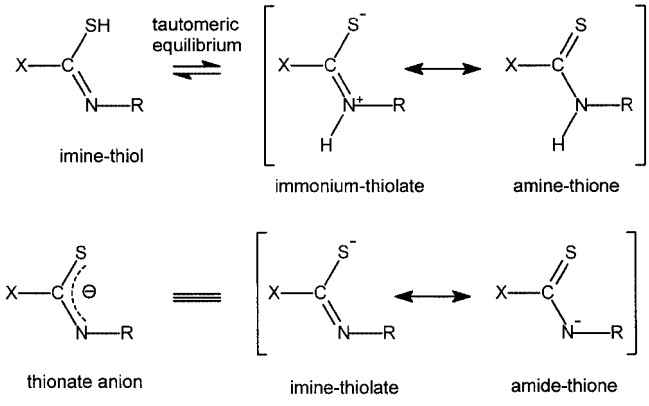
The complexes $[Ag(etu)_2]ClO_4$ (**1**) and $[\{Ag(py2tH)_2\}(ClO_4)(H_2O)_{0.5}]_n$ (**2**) have been obtained from the reactions of $AgClO_4$ with the corresponding thioamide ligands (etu = imidazolidine-2-thione; py2tH = pyridine-2-thione). Complex **1**, consisting of centrosymmetric monomeric $[Ag(etu)_2]^+$ cations and ClO_4^- counterions, constitutes the first bis[thio(mono- or di)amide] complex (M = Cu, Ag) known thus far to possess a linear MS_2 mononuclear core. Component ions behave in the crystal structure as complementary partners, with all four N–H groups of each $[Ag(etu)_2]^+$ cation and all four oxygen atoms of each ClO_4^- anion involved in N–H···O–Cl hydrogen bonding associations. This leads to the assembly of a three-dimensional supramolecular network. Complex **2**, whose previously reported structure has been redetermined with higher precision, contains *catena*-$[Ag(py2tH)_2]_n^{n+}$ polymeric cations consisting of linear chains of linked $Ag_2(\mu\text{-}S)_2$ rings, with distorted tetrahedral AgS_4 centres. Supramolecular association through N–H···O–Cl, N–H···O(water) and Cl–O···H–O–H···O–Cl hydrogen bonding, where all N–H groups and H_2O molecules and only one or two oxygen atoms of each ClO_4^- anion are involved, leads to the formation of a two-dimensional layered supramolecular structure. A correlation of some stereochemical parameters and a simple qualitative sulfur-bridge bonding model has been developed for **2** and other related thioamide complexes containing $M_2(\mu\text{-}S)_2$ rings or M–S–M′ single bridges. For these structural units, suitable ranges of tilt and twist dihedral angles have been estimated and assigned to different bonding types.

Introduction

Considerable attention is currently directed to the study of metal−thioamide coordination chemistry with both heterocyclic and thiourea-like ligands. This interest is mainly encouraged by the flexible coordination capability of the thioamide group which, as a neutral ligand, may be involved, as shown in Scheme 1, in equilibrium with its imino−thiol and amino−thione tautomers. The latter form, with sulfur as donor atom, is dominant for metal coordination, while a "zwitterionic" immonium−thiolate resonance form contributes to the delocalisation of the π-electron density and to some electron enrichment at the thione sulfur atom, which may be seen as formally close to a thiolate sulfur atom. On the other hand, thioamide ligands are easily deprotonated to give their thionate anionic form. In this case, and because of the accumulation of the actual anionic



Scheme 1. The equilibrium and structure of the thioamide group in neutral and basic solutions; likely resonance forms contributing to the electronic structure are indicated

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charge mainly at the sulfur atom, its coordination potential is not only closer to that of a thiolate group, but also further enhanced by the donor capacity of the nitrogen atom via the S-to-N backbone.

Extensive reviews and publications, mainly from Raper, focus on the study of the donor behaviour of heterocyclic thioamides and related ligands towards transition and non-transition metal ions,[1−5] silver being the least referenced within the Group 11 metals. One of the points of interest arises from the Cu^{II}-thione redox chemistry as a way of modelling the electronic and structural properties of Cu−cysteine environments in "blue" copper proteins.[2] Additional attention is directed to the employment of thioamide ligands, with the aim of reducing the toxicity associated with coinage metal thiolate complexes and their heteroleptic phosphane derivatives (M^{I} = Au, Ag), which are used as both effective antiarthritic and antitumour (Au),[6] and potential antimicrobial (Ag)[7] drugs. Current research on inorganic-organic hybrid materials containing S,N-donor ligands has led to the characterization of silver thioamide coordination polymers,[8−10] which show interesting infinite chain (1D), layered (2D), and network (3D) structures containing these ligands in a variety of coordination modes.

A bibliographic and database search covering homoleptic complexes of neutral thioamide ligands with monovalent Group 11 metals of known structure, with general formula $[M_x(L)_y]^{x+}$, has revealed an extensive and varied family of compounds, which possess many different stoichiometries ranging from M/L = 1:1 to 1:4 ratios. Although we restrict our attention here to homoleptic complexes, unexpected variations are found when comparing observed structures, and this even occurs, in some cases, for compounds of almost the same chemical formula. No 1:1 cationic complex has so far been crystallographically characterised.[11]

The adamantane-like tetrahedral cage $M_4(\mu\text{-}S)_6$, which is the most frequently encountered structural unit in polynuclear thiolates,[12,13] is also present in cationic thioamide complexes. This tetrahedral cage is known to exist, with no terminal ligands and thus with trigonal coordination of all four metal atoms, in $[Cu_4L_6]^{4+}$ species [L = tu (thiourea),[14,15] thpym2tH$_2$ (tetrahydropyrimidine-2-thione),[16] and with the accommodation of some terminal ligands and both tetrahedral and trigonal metal sites in complexes $[Cu_4(tu)_7](SO_4)_2$,[17] $[Cu_4(tu)_9](NO_3)_4$,[18] and $[\{Cu_4(tu)_6(tu)_{3/2}\}(SO_4)_2]_n$.[19] To the best of our knowledge, none of the reported $[Cu_4L_{10}]^{4+}$ complexes of thioamide ligands contains such a tetrahedral cage with all four metal centres tetrahedrally coordinated.

An alternative structure to the tetrahedral $M_4(\mu\text{-}S)_6$ cage has been found in the complex $[Cu_4(mpym2tH)_6](BF_4)_4$ (mpym2tH = 1-methylpyrimidine-2-thione).[20] It consists of an $M_4(\mu\text{-}S)_4$ eight-membered ring with a rhomboidal planar array of metal atoms. In this case, two S-terminal, two μ_2-S bridging and two μ_3-S,N bridging ligands give rise to CuS_3 and CuS_2N trigonal-planar environments. A silver complex of the same stoichiometry, $[\{Ag_4(py2tH)_6\}(NO_3)_4]_n$ (py2tH = pyridine-2-thione), shows a third structural pattern consisting of a double chain polymeric framework, where silver atoms are linked in a tetrahedral fashion by two μ_2-S and two remarkable μ_4-S bridging ligands.[21]

The structural diversity already noted for some $[M_4L_6]^{4+}$ cations also extends to $[M_4L_9]^{4+}$ species. As cited above, a *tetrahedro*-$[M_4(\mu\text{-}SR)_6]$ cage is present in $[Cu_4(tu)_9]^{4+}$,[18] whereas a *quadro*-$[M_4(\mu\text{-}SR)_4]$ ring containing a planar M_4 arrangement has been established in the complex $[Cu_4(etu)_9](NO_3)_4\cdot 6H_2O$ [etu = imidazolidine-2-thione (ethylenethiourea)],[1,22] where four μ_2-S bridging, four S-terminal and one central μ_4-S bridging ligand account for the tetrahedral geometry of each metal atom. A third structure for this stoichiometry has been encountered in the infinite polymer $[\{Cu_4(tu)_9\}(NO_3)_4]_n$,[23] consisting of chains of linked *quadro*-$[M_4(\mu\text{-}SR)_6(SR)_2(SR)_{2/2}]$ rings, with a planar arrangement of the four metal atoms and tetrahedral MS_4 environments.

The reported structures of the cationic complexes with the general formula $[ML_2]_n^{n+}$ include monomeric (the only cationic thioamide complexes known for Au^{I}) and cyclic tetrameric discrete species, and infinite chain polymers (we return later to some details of these structures).

Two discrete and two polymeric structures have been described for cationic thioamide complexes of stoichiometry M/L = 2:5, none of which contains a *tetrahedro*-$[M_4(\mu\text{-}SR)_6]$ cage. Two trigonal-planar CuS_3 units share a unique μ_2-S bridging ligand in the dinuclear complex $[Cu_2(mimtH_2)_5]SO_4$ (mimtH$_2$ = 1-methylimidazoline-2-thione).[24] A planar core of four tetrahedrally coordinated metal atoms, which is encompassed by four S-terminal and six μ_2-S bridging ligands, *quadro*-$[(MSR)_4(\mu\text{-}SR)_6]$, constitutes the structural unit adopted by the discrete tetranuclear compound $[Cu_4(bzimtH_2)_{10}](ClO_4)_4$ (bzimtH$_2$ = benzimidazoline-2-thione).[25] Making allowances for the different thioamide ligands and counter-anions present in this complex and in the previously cited $[\{Cu_4(tu)_9\}(NO_3)_4]_n$,[23] detachment of one of the terminal ligands from the discrete structure gives rise to the repeat unit *quadro*-$[M_4(\mu\text{-}SR)_6(SR)_3]$ that generates the polymeric framework of the latter.

While the structure of the infinite polymer $[\{Cu_2(tu)_5\}SO_4]_n$ is formed by cationic chains of alternating trigonal-planar MS_3 and tetrahedral MS_4 sites,[26] that of the polymeric compound $[\{Cu_4(tu)_{10}\}(SiF_6)_2]_n$[27] is somewhat more complicated. It consists of infinite chains of alternating $[(MSR)_3(\mu\text{-}SR)_3]$ six-membered rings and μ_2-S bridging ligands, which are in turn cross-linked via $[\{M(SR)_2\}_2(\mu\text{-}SR)_2]$ four-membered rings to give a three-dimensional polymer with all the metals in tetrahedral MS_4 sites.

Cationic thioamide complexes of stoichiometry corresponding to the general formula $[ML_3]_n^{n+}$ are the most numerous for Cu and Ag, with crystallographically demonstrated nuclearities *n* of 1, 2, and (in only one case) 4. While monomers, as in $[Ag(mimtH_2)_3](NO_3)$, show a trigonal planar MS_3 coordination,[28−31] dimeric cations, as in $[Ag_2(dmtu)_6](ClO_4)_2$ (dmtu = *N*,*N*′-dimethylthiourea), contain $[\{M(SR)_2\}_2(\mu\text{-}SR)_2]$ four-membered rings with tetrahedral MS_4 sites.[32−36] These latter sites are also present in

the complex $[Cu_4(tu)_{12}](SO_4)_2$,[37] which contains a *quadro*-$[\{Cu(SR)_2\}_4(\mu\text{-}SR)_4]$ cationic eight-membered ring. Finally, the structural pattern richest in thioamide ligands possesses a stoichiometry M/L = 1:4 and corresponds, as in $[Ag(mpy2tH)_4]BF_4$ (mpy2tH = 1-methylpyridine-2-thione), to monomeric complexes with an MS_4 (M = Cu, Ag) tetrahedral coordination environment.[38−40]

As evidenced by the stoichiometry-structure relationships outlined above, an extensive range of stereochemical arrangements is available for $[M_xL_n]^{x+}$ thioamide complexes. These, however, are significantly less explored for silver than for the other two coinage metals.

With the aim of obtaining further structural data, particularly for cationic thio(mono- or di)amide complexes, as well as examining their relationship to previous structures, we have carried out the synthesis and crystal structure determination of the compounds $[Ag(etu)_2]ClO_4$ (**1**) and $[\{Ag(py2tH)_2\}(ClO_4)(H_2O)_{0.5}]_n$ (**2**). Complex **1**, containing mononuclear $[M(thioamide)_2]^+$ cations with a linear MS_2 coordination, represents the first reported Ag complex displaying this structural pattern. Although not yet encountered for Cu, this pattern corresponds to the only structural type established thus far for related Au complexes. The structure of complex **2** was previously reported with a misprinted space group and only a brief discussion;[21] the redetermination reported here, from low-temperature data, is of considerably greater precision (standard uncertainties reduced by a factor of 3 or more) and permits more detailed analysis.

Results and Discussion

Spectroscopic Properties

In agreement with the increasing participation of the immonium-thiolate resonance form (Scheme 1) to the electronic structure of a thioamide complex on S-coordination, the IR bands possessing significant contribution from ν(CS) or ν_{as}(N−C−N) vibrations (at 510, 1500 cm^{-1} in etu as free ligand) shift to lower[41] and higher[42] frequencies (495, 1522 cm^{-1}), respectively, in the spectrum of complex **1**; ν(SH), which appears as a weak band near 2500 cm^{-1} in free py2tH, is absent in the IR spectrum of complex **2**. This fact, together with the positive shift of the ring breathing mode[43] of py2tH itself (984 cm^{-1}) to 995 cm^{-1} in the same complex, is also in accordance with S-coordination. As expected from the role of the perchlorate as counter-anion, no significant splitting of its IR-active bands, associated with $\nu(T_2)$ (centred at 1090 cm^{-1}) and $\delta(T_2)$ (626 cm^{-1}) vibrational modes, is observed in the spectra of the two complexes.

S-coordination causes small downfield shifts relative to the free ligand in the ^1H NMR spectra, the largest [$\Delta\delta$ = 1.0 (**1**), 0.7 (**2**) ppm] occurring for the N−H protons.[44] The chemical shifts of these [8.90 (**1**), 14.10 (**2**) ppm], as well as their positive coordination shifts, reflect, as in the IR spectra, the relevant contribution of the immonium-thiolate resonance form in both complexes. ^{13}C NMR spectra are more sensitive to S-donation, the carbon atom of the thione group being the most affected, with high-field coordination shifts[45,46] of δ = −5.2 and −10.2 ppm, respectively, for complexes **1** and **2**.

Structures of the Complexes

Homoleptic complexes of general formula $[ML_2]X$, where M = Cu^I or Ag^I, X^- is an uncoordinated anion, and L is a neutral thio(mono- or di)amide ligand, are not very numerous. To the best of our knowledge, seven complexes have so far been crystallographically characterised. Six of them are $[M(dmtu)_2]X$ (M = Cu, X = NO_3^-;[47] M = Ag, X = ClO_4^- [36]), $[Cu(quinoline\text{-}2\text{-}thione)_2]X$ (X = ClO_4^-, $PO_2F_2^-$),[48] and $[Ag(py2tH)_2]X$ (X = BF_4^-, ClO_4^-),[21] all consisting of linear-chain $[M(\mu\text{-}S)_2]_\infty$ polymeric cations formed by distorted MS_4 tetrahedra, which are linked by sharing opposite edges. The structures of the last two compounds have appeared recently, ostensibly as anhydrous and isomorphous in space group *P*1, though the corresponding entries (with refcodes MOGNAF and MOGNEB) in the Cambridge Structural Database (CSD, version 5.24, November 2002)[49] actually show them to be hydrates and in space group $P\bar{1}$. As only a brief description of the cationic chains was given by the previous authors, with no information on other aspects of the structures, and as our results for the perchlorate are more precise, from low-temperature data, further details of the crystal structure will be given here for complex **2**. The remaining previously reported compound of M/L = 1:2 stoichiometry, $[Ag(1\text{-}azacycloheptane\text{-}2\text{-}thionato)_2]_4(NO_3)_4$, has a totally different structure consisting of discrete $[(AgSR)_4(\mu\text{-}SR)_4]$ cationic rings with trigonal AgS_3 sites.[50]

By contrast, corresponding complexes with Au^I are more numerous and all of those known have mononuclear structures with strictly or essentially linear AuS_2 coordination. Reported $[AuL_2]X$ complexes include those with L = etu, X = $[AuI_2]^-$ [51] or Cl^-;[52] L = tu, X = Br^- [53] or ClO_4^-;[54] L = py2tH, X = ClO_4^-;[55] L = dmtu or detu, X = ClO_4^-.[56] The $[Au(etu)_2]^+$ cation in $[Au(etu)_2]Cl\cdot H_2O$ is somewhat more distorted, with an S−Au−S angle of 167.1°, owing to the *cis* configuration of the heterocyclic rings of the two ligands. This is favoured by the formation of hydrogen bonds that involve the O atom of water and two N−H groups belonging to different ligands.[52]

Despite the fact that $Ag(tu)_2Cl$ is not genuinely homoleptic, its polymeric structure may be referred to here for comparison.[57] It contains both nearly trigonal-planar AgS_3 and flattened tetrahedral $AgS_3\cdots Cl$ environments. The corresponding complex $Cu(tu)_2Cl$[58] adopts a similar structure.

Complex 1

This consists of ClO_4^- anions and mononuclear $[Ag(etu)_2]^+$ cations. The cation (Figure 1) lies on a crystallographic inversion centre, and thus the coordination of Ag is strictly linear (Table 1). The anion lies on a two-fold rotation axis and is disordered over two orientations. Interac-

tions among the ions appear to be of normal electrostatic and van der Waals character, together with hydrogen bonding as described below, with no significant influence on metal coordination. This is supported by the fact that the shortest Ag···Ag separation, 3.513 Å, is more than twice the van der Waals radius (3.44 Å), and the closest inter-cation Ag···S contact, 3.275 Å, is markedly greater than the sum of the corresponding covalent radii (2.55 Å) and only slightly less than the sum of the van der Waals radii (3.50 Å).[59] This is the first homoleptic silver complex of thio-(mono- or di)amide ligands with a silver/sulfur stoichiometry of 1:2 for which a monomeric cation has been crystallographically established. The closest previous approach to this is in the structure of [Ag(*N*-(diethylaminothiocarbonyl)benzamidine-*S*)$_2$]NO_3, where a secondary Ag···S interaction between two adjacent molecules (3.034 Å) induces a significant bending at the primary S−Ag−S centre (159.4°).[60]

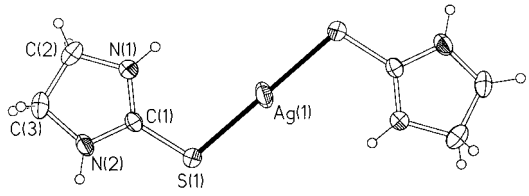

Figure 1. The structure of the cation in complex **1**, with 50% probability displacement ellipsoids and the labelling of the crystallographically independent atoms

Table 1. Selected bond lengths [Å] and angles [°] for **1**

Ag(1)−S(1)	2.4058(8)	Ag(1)−S(1A)	2.4058(8)
S(1)−Ag(1)−S(1A)[a]	180	Ag(1)−S(1)−C(1)	105.80(10)

[a] Symmetry operation for equivalent atoms: A: 1 − *x*, 1 − *y*, 1 − *z* (inversion centre).

The etu ligand is approximately planar and forms a twist dihedral angle (see later for a definition and discussion of twist and tilt dihedral angles with respect to the coordination of bridging ligands) of 11.4° with the central C−S−Ag−S−C segment, so that the whole cation does not deviate greatly from planarity. This near-planarity, together with the 105.8° bond angle at S(1), suggests that coordination of the ligand to Ag^I is essentially through a sulfur lone pair in an in-plane sp^2 hybrid orbital. The cations are arranged in planes corresponding to the (202) lattice planes of the crystal structure, as shown in Figure 2, with the anions lying between these planes. The main deviation of the ligand from planarity is a small distortion towards an envelope conformation, with C(3) as the flap; this can also be seen in Figure 2.

A three-dimensional framework of N−H···O−Cl hydrogen bonding, involving both the amine N−H groups of each ligand and all four perchlorate oxygen atoms, reinforces the ionic interactions and gives rise to a supramolecular assembly of complex cations and ClO_4^- anions, shown in Figure 3 (where only one disorder component of each anion is included). Despite the two-fold disorder of

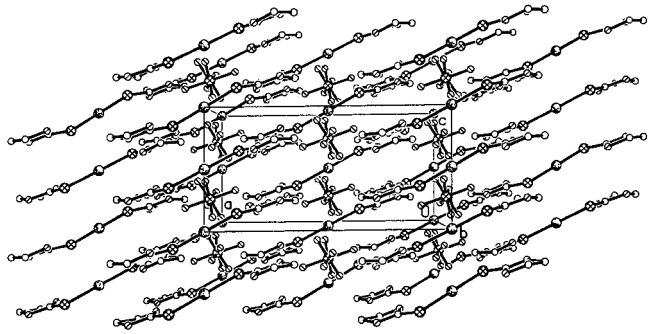

Figure 2. The crystal structure of complex **1**, viewed along the *b* axis, showing the parallel stacking of cation sheets with anions between them; H atoms are omitted

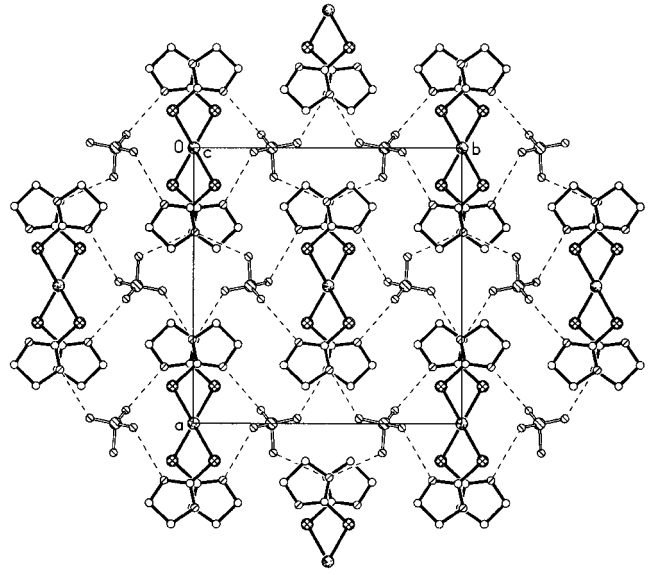

Figure 3. The crystal structure of complex **1**, viewed along the *c* axis, showing NH···O hydrogen bonding interactions; only one disorder component is included for each anion; H atoms are omitted for clarity

the anions, the hydrogen bonding interactions appear to be significant; details of their geometry are given in Table 2. Comparable N···O distances are found in similar Ag^I com-

Table 2. Geometry of hydrogen bonds [Å, °] in the structures of **1** and **2** (symmetry operation for equivalent atoms: B: 1 − *x*, *y*, 1/2 − *z*; C: 1/2 + *x*, 1/2 + *y*, *z*; D: 3/2 − *x*, 1/2 + *y*, 1/2 − *z*; E: 1 − *x*, 1 − *y*, 1 − *z*; F: *x*, 1 + *y*, *z*; G 1 + *x*, *y*, *z*)

D−H...A	D−H	H···A	D···A	D−H···A
Compound **1**				
N(1)−H(1)...O(1)	0.88	2.16	2.950(11)	149
N(1)−H(1)...O(3B)	0.88	2.29	3.109(10)	154
N(2)−H(2)...O(2C)	0.88	2.26	2.998(6)	141
N(2)−H(2)...O(4D)	0.88	2.38	2.904(7)	118
Compound **2**				
N(1)−H(1)...O(22)	0.88	2.03	2.893(4)	165
N(2)−H(2)...O(31E)	0.88	2.01	2.867(3)	165
N(3)−H(3)...O(31)	0.88	2.09	2.946(4)	165
N(4)−H(4)...O(14)	0.88	2.02	2.895(5)	170
O(31)−H(31a)...O(13F)	0.82(3)	2.00(3)	2.805(4)	164(4)
O(31)−H(31b)...O(22G)	0.82(3)	2.30(3)	3.036(4)	149(4)

plexes of thiourea and thioamide ligands recorded in the CSD.

Complex 2

The complex $[\{Ag(py2tH)_2\}(ClO_4)\cdot 0.5(H_2O)]_n$ contains polymeric $[Ag(py2tH)_2]_n^{n+}$ cations, discrete ClO_4^- anions, and uncoordinated water molecules. All three chemically distinct components are linked together by a network of hydrogen bonds, in addition to the ionic interactions involving the polymeric cations and the anions.

All the py2tH ligands employ only sulfur atoms for coordination to Ag^I, each ligand bridging a pair of metal atoms in distorted AgS_4 tetrahedral environments, to give linear polymeric chains of linked $Ag_2(\mu\text{-}S)_2$ rings, which run parallel to the crystallographic *b* axis. Figure 4 shows the three crystallographically independent Ag_2S_2 rings, and Figure 5 the resultant chain polymer. The two outer rings in Figure 4 are crystallographically centrosymmetric, and hence are strictly planar, with the ligands in *anti* configurations. The central ring, by contrast, is not planar but folded, with its ligands in the *syn-exo* configuration; the two AgS_2 planes define a dihedral (hinge) angle of 152° about the S···S diagonal. Planar *anti* and folded *syn* Ag_2S_2 rings thus alternate along the chain. Ag−S bond lengths span the range

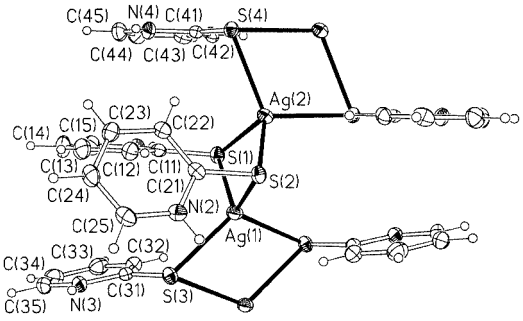

Figure 4. The asymmetric unit of the polymeric cation chain of complex **2**, together with additional Ag^I ions and ligands to complete the bonding environment of this unit; the crystallographically independent atoms are labelled, and displacement ellipsoids are drawn at the 50% probability level

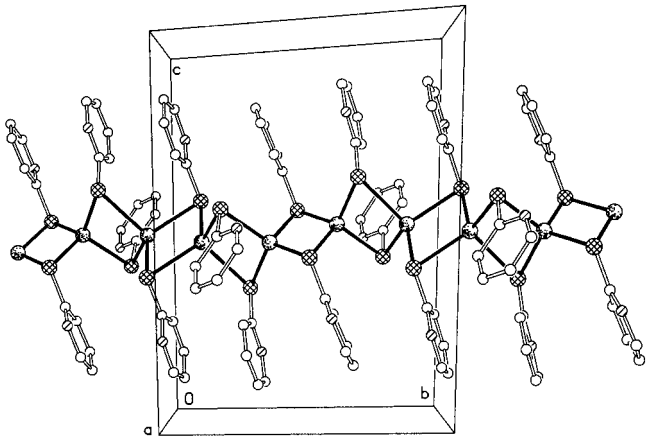

Figure 5. A section of the polymeric cation chain of complex **2**; H atoms are omitted

Table 3. Selected bond lengths [Å] and angles [°] for **2** (symmetry operations for equivalent atoms: H: $-x$, $1-y$, $1-z$; I: $-x$, $-y$, $1-z$)

Ag(1)−S(1)	2.5491(7)	Ag(1)−S(2)	2.6122(7)
Ag(1)−S(3)	2.5724(7)	Ag(1)−S(3H)	2.6900(7)
Ag(2)−S(1)	2.7770(7)	Ag(2)−S(2)	2.5901(7)
Ag(2)−S(4)	2.5873(7)	Ag(2)−S(4I)	2.6322(7)
S(1)−Ag(1)−S(2)	115.40(2)	S(1)−Ag(1)−S(3)	120.29(2)
S(1)−Ag(1)−S(3H)	89.62(2)	S(2)−Ag(1)−S(3)	100.80(2)
S(2)−Ag(1)−S(3H)	115.20(2)	S(3)−Ag(1)−S(3H)	116.542(17)
S(1)−Ag(2)−S(2)	108.71(2)	S(1)−Ag(2)−S(4)	103.94(2)
S(1)−Ag(2)−S(4I)	104.60(2)	S(2)−Ag(2)−S(4)	119.39(2)
S(2)−Ag(2)−S(4I)	108.48(2)	S(4)−Ag(2)−S(4I)	110.658(18)
Ag(1)−S(1)−Ag(2)	64.735(17)	Ag(1)−S(2)−Ag(2)	66.641(16)
Ag(1)−S(3)−Ag(1H)	63.458(17)	Ag(2)−S(4)−Ag(2I)	69.342(18)

2.5491(7)−2.7770(7) Å (Table 3), the sum of the corresponding covalent radii being about 2.55 Å.[59] The nonplanar ring contains the least and the most symmetrical bridges, with the difference in Ag−S bond lengths being approximately 0.23 Å for S(1) and only 0.02 Å for S(2), while it is 0.12 Å for S(3) and 0.04 Å for S(4). Other structural parameters characteristic of these Ag_2S_2 rings are the Ag···Ag distances ranging from 2.769 to 2.969 Å (less than twice the covalent radius, 3.06 Å[59]) and the markedly acute Ag−S−Ag angles, between 63.5 and 69.3°.

Distortion of the two crystallographically independent AgS_4 centres from a regular tetrahedron is clearly reflected in the S−Ag−S angles [Table 2; a range of 30.7° for Ag(1) and 15.5° for Ag(2)], and in the dihedral angles formed by the two AgS_2 half-ring planes at each Ag atom [74.5° for Ag(1) and 86.9° for Ag(2); these would be 90° for a regular tetrahedron]. These figures show that the tetrahedral coordination is substantially less regular for Ag(1). The surrounding sheaths of pyridine rings prevent secondary covalent interactions between Ag and S atoms of different chains. However, the N−H amine groups of these rings, together with the ClO_4^- anions and the uncoordinated water molecules, provide a hydrogen-bonding pathway linking neighbouring cationic chains, causing these to assemble into a two-dimensional sheet supramolecular structure, as shown in Figure 6, where parts of two chains are included, together with the anions and water molecules lying between them. Contacts between hydrogen-bonded sheets involve only ligand C−H groups and perchlorate oxygen atoms, which do not take part in the interactions within the sheets.

Details of the hydrogen bonds are given in Table 2. Each water molecule (there is one for every two Ag^I centres and two anions) acts as a donor in two hydrogen bonds to perchlorate oxygen atoms, and as an acceptor of two hydrogen bonds from amine groups. Thus, two of the four crystallographically independent amine groups form hydrogen bonds to water molecules, while the other two form hydrogen bonds to perchlorate anions. There are two crystallographically distinct anions; for one of them, two oxygen atoms act as hydrogen-bond acceptors (O13 from water, O14 from amine), while the other has just one oxygen atom (O22) accepting two hydrogen bonds, one from water and

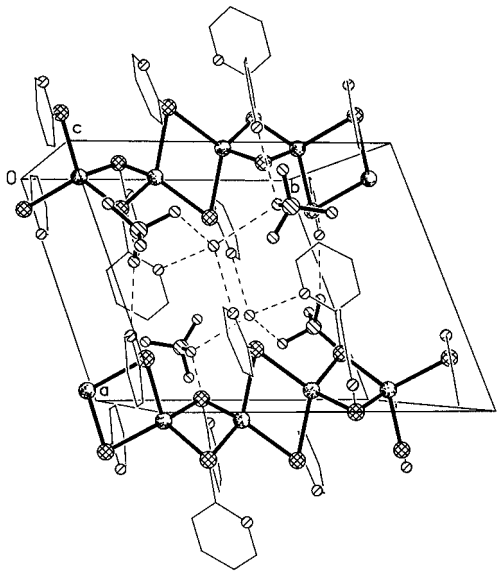

Figure 6. The crystal structure of complex **2**, showing hydrogen bonding interactions as dashed lines; H atoms are omitted for clarity

the other from an amine group. There is no disorder in the structure, and the hydrogen bonds are somewhat stronger (shorter and more linear) than those in the structure of complex **1** discussed above.

Stereochemistry and Sulfur-Bridge Bonding

The bonding of the ligands to Ag^I in the polymeric complex **2** is clearly not as simple as the single lone-pair donation from the sulfur sp^2 orbital to the metal atom for the terminal ligands in **1**. Examination of some details of the varied orientation of the bridging ligands may be informative in order to rationalise the stereochemistry and metal−ligand bonding for the Ag_2S_2 rings of the polymeric cation in **2**, in terms of electron donation by a combination of suitable molecular orbitals of the ligands. These include one or both of the two non-bonding sulfur sp^2 in-plane hybrid orbitals and the thioamide pπ-molecular orbital of the heterocycle; this orbital is perpendicular to the others and is concentrated in the C−S portion of the ligand molecule, with a major contribution of the sulfur atom.[61] These bridging ligand molecular orbitals (HOMOs), each accommodating one electron pair, are able to interact with two

Table 4. Some angular parameters and proposed sulfur-bridge bonding for **2** and other related thioamide complexes containing $M_2(\mu_2\text{-}S)_2$ rings or M−S−M′ single bridges

Bridging sulfur atom	Tilt angle[a]	Twist angles[b]	Δ_{tw}[c]	M–S–M' bond angle	M–S–M bonding mode[d]	Ref.
[{Ag(py2tH)$_2$}(ClO$_4$)(H$_2$O)$_{0.5}$]$_n$ (**2**)						
S(1) (ring 1)	79.2	(−31.1, 36.1)	67.2	64.7	sp^2 (C)	this work
S(2) (ring 1)	84.6	(21.5, 88.8)	67.3	66.6	sp^2 + C=S pπ (B)	
S(3) (ring 2)	82.4	(−32.1, 34.0)	66.1	63.5	sp^2 (C)	
S(4) (ring 3)	85.5	(−1.7, 70.0)	71.7	69.3	sp^2 + C=S pπ (B)	
[{Ag(*N*,*N*'-dimethylthiourea)$_2$}(ClO$_4$)]$_n$						
S(1) (ring1)	83.0	(18.5, 94.5)	76.0	74.9	sp^2 + C=S pπ (B)	[36]
S(2) (ring 2)	73.7	(18.0, 98.0)	80.0	76.6	sp^2 + C=S pπ (B)	
(μ_4-S) in [{Ag$_4$(py2tH)$_6$}(NO$_3$)$_4$]$_n$						
S(2)[e]	88.6	(−36.9, 41.9)	78.8	72.3	sp^2 (C)	[21]
Cu$_2$(μ_2-S)$_2$ rings in [Cu$_2$(py2tH)$_6$]X$_2$ (X = Cl; X = Cl, Br; X = *p*-MeC$_6$H$_4$SO$_3$)						
(X = Cl) S	80.6	(6.5, 84.5)	78.0	74.3	sp^2 + C=S pπ (B)	[33]
(X = Cl) S	79.9	(7.0, 85.0)	78.0	74.6	sp^2 + C=S pπ (B)	[62]
(X = Br) S	82.0	(6.5, 83.5)	77.0	73.8	sp^2 + C=S pπ (B)	[62]
(X = *p*-MeC$_6$H$_4$SO$_3$) S	86.1	(−37.0, 38.0)	75.0	69.6	sp^2 (C)	[35]
[{Cu(quinoline-2-thione)$_2$}(PO$_2$F$_2$)]$_n$						
S(1) (chain 1)	90[f]	(−45.0, 45.0)	90.0	84.0	sp^2 + C=S pπ (B)	[48]
S(2) (chain 2)	90[f]	(−44.0, 44.0)	88.0	84.0	sp^2 + C=S pπ (B)	
Cu$_2$(μ_2-S)$_2$ rings in [*cyclo*-{(μ_2-L)$_6$(CuL)$_4$}](ClO$_4$)$_4$·14 H$_2$O [L = benzimidazoline-2-thione]						
S(3)	88.3	(−28.5, 44.5)	73.0	69.1	sp^2 (C)	[25]
S(4)	86.0	(−17.5, 54.5)	72.0	66.8	sp^2 + C=S pπ (B)	
M–S–M' bridges in [MCl(tu)$_2$]$_n$ (M = Ag, Cu)						
(M = Ag) S(2)	76.2	(−42.1, 58.8)	79.1	77.3	C=S pπ (D)	[57]
(M = Ag) S(3)	26	(7.5, 167.0)	159.5[g]	133.5	sp^2 + sp^2 (A)	
(M = Cu) S(2)	69.8	(−39.3, 54.6)	86.1	82.5	C=S pπ (D)	[58]
(M = Cu) S(3)	14.8	(0.6, 169.6)	169.0[g]	138.1	sp^2 + sp^2 (A)	
Cu–S–Cu bridge in [Cu$_2$Cl$_2$(etu)$_3$(μ-etu)]						
S(2)	12.6	(−4.8, 167.0)	171.8[g]	137.3	sp^2 + sp^2 (A)	[63]

[a] Dihedral angle of each independent planar thioamide ligand with respect to its M_2S_2 planar lozenge or its M−S−M′ unit. [b] Pair of dihedral angles of each independent ligand about its respective M−S−C and M′−S−C planes, (α_1, α_2), where $\alpha_2 > \alpha_1$. [c] For bonding modes A, B and C, $\Delta_{tw} = \alpha_2 - \alpha_1$; for mode D, $\Delta_{tw} = 180 - (\alpha_2 + |\alpha_1|)$. [d] Sulfur-localised molecular orbitals, each with one electron pair, mainly contributing to the bridge bonding. [e] S2 lies on a mirror plane, so that the two Ag−S2−Ag′ and Ag−S2−Ag′ equivalent moieties constituting the quadruple bridge correspond to a pair of bonding systems of type C. [f] Crystallographically imposed value. [g] For this bonding mode A, there is no relationship between Δ_{tw} and the M−S−M′ bond angle.

vacant tetrahedral sp^3 or other hybrid orbitals, one for each silver atom of the Ag−S−Ag bridge. Considerations of this kind, aimed at proposing an M−S bonding model from an analysis of the stereochemistry, have previously been performed for dinuclear[1,32] and some polymeric[22,23,27,55,56] sulfur-bridged complexes of thioamide or thiourea ligands. All these earlier examples, however, contain both bridging and terminal ligands, which is not the case here.

Two structural parameters may be used to describe the orientation of each of the four independent planar bridging ligands in the complex cation of **2**. These are: (a) the "tilt" angle of each ligand S−C bond with respect to its Ag−S−Ag′ planar unit, and (b) the pair of "twist" dihedral angles of each ligand plane relative to its respective Ag−S−C and Ag′−S−C planes (Figure 7). Values of these parameters have been calculated for **2** and for related complexes (in this case from the corresponding crystallographic data in the CSD), and they are listed in Table 4.

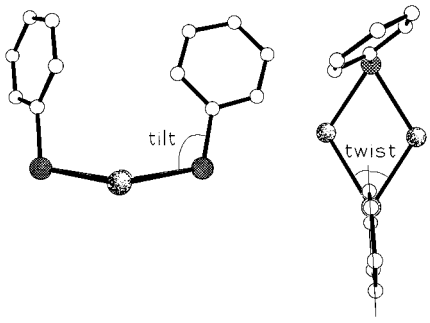

Figure 7. Two views of an M_2S_2 ring with bridging ligands, illustrating the tilt and twist angles characterising the stereochemistry of the ligand arrangement

As defined above, a "tilt" angle close to 0° would imply that the ligand plane and the Ag_2S moiety tend to be coplanar, so that the two S−Ag bonds are formed primarily from the two sulfur sp^2 orbitals with their two electron pairs. This corresponds to an Ag−S−Ag three-centre, four-electron bonding system (type **A**), with ideal "twist" angles of 0° and 180° and an Ag−S−Ag bond angle of 120°; here the line defined by the two N atoms (in thiourea ligands) or its corresponding N···C vector (in thiomonoamides) would be essentially parallel to the Ag···Ag line. Some examples of this arrangement[57,58,63] are included in Table 4, which also shows that all four ligands in complex **2** have tilt angles between 79 and 85° and pairs of "twist" angles markedly different from 0 or 180°. Thus, each of these ligands is almost normal to the Ag_2S unit to which it is attached, making the simultaneous involvement of both sulfur sp^2 orbitals and electron pairs in the formation of Ag−S−Ag bridges unlikely.

On the other hand, a "twist" angle close to 0° would indicate that one of the two silver atoms of a given Ag−S−Ag′ bridge lies nearly in the ligand plane, allowing conventional electron donation from one sulfur sp^2 orbital to an orbital of the Ag atom. In order to complete the bonding scheme for the Ag−S−Ag′ bridge, taking into account that the planar bridging ligands are approximately normal to the Ag−S−Ag′ fragment (Table 4), optimal overlap of an orbital on the Ag′ atom would be obtained by using the thioamide (C=S) pπ-MO, which is perpendicular to the sp^2 orbital. In this case, the Ag−S−Ag′ three-centre, four-electron bridge bonding system (type **B**) would be related to a pair of ideal "twist" angles of 0° and 90° for the atoms Ag and Ag′, respectively (difference, $\Delta_{tw} = 90°$), provided the corresponding "tilt" angle is close to 90°. While this optimal bonding model presumes an ideal value of about 90° for the Ag−S−Ag′ bond angle, this is actually significantly lower in most M_2S_2 rings formed with thioamide ligands (in the range 67−80°, with a few reaching 90°; below 70° in our case).[1,64]

The results in Table 4 show that, for complex **2**, only ligands 2 and 4 [i.e. those containing S(2) and S(4)] approach the above ideal conditions, as can be seen by comparison of Figures 4 and 7. Whereas one of the two twist angles of these ligands closely matches the value of 90° [S(2)] or 0° [S(4)], the second twist in each of the two pairs departs by about 20° from the ideal value. However, the differences between the two twist angles within the pairs, $\Delta_{tw} = 67.3°$ [S(2)] and 71.7° [S(4)], are very close to the respective values of the Ag−S−Ag′ bond angles (66.6, 69.3°), both being far from 90° in contrast to the bonding model initially assumed. These features suggest that maximal overlap of either one sulfur sp^2 or (C=S) pπ-MO orbital on the bridging thioamide ligand is not accomplished in the Ag(1)−S(2)−Ag(2) unit nor in the ring containing ligand 4, so that the proposed bonding mode needs some modification to allow for the actual value of Δ_{tw}. This parameter corresponds, in fact, to the dihedral angle defined by the Ag−S−C and Ag′−S−C planes about the common S−C line, and is always slightly larger than the corresponding Ag−S−Ag′ in-plane angle. Exact coincidence of these two angles would only be attained if the S−C internuclear vector were normal to the Ag−S−Ag′ plane, the difference between the two values increasing as the inclination of the S−C vector decreases.

In order to identify a better correlation of a given pair of twist angles (α_1, α_2 with $\alpha_2 > \alpha_1$ and $\Delta_{tw} = \alpha_2 - \alpha_1$) with the bonding mode **B**, we consider angles within the limits $-45 \le \alpha_1 \le 45$ and $45 \le \alpha_2 \le 135°$. These, with associated tilt angles close to 90°, would correspond to the full set of possible orientations of the bridging thioamide ligands, given by (α_1, $\alpha_1 + \Delta_{tw}$), to which both sulfur sp^2 and (C=S) pπ-MO orbitals would contribute. Among all these geometries, optimal overlap with one of the two Ag orbitals would be achieved through the sp^2 orbital in the (0, Δ_{tw}) ideal case ($\alpha_1 = 0$), but through the (C=S) pπ orbital for the (90 − Δ_{tw}, 90) ideal pair ($\alpha_2 = 90°$). Conversely, poor overlap would be expected for orientations close to those defined by the extreme values of the given ranges, (−45, 45) and (45, 135). A combination of the steric requirements of the bridging ligands, hydrogen-bonding effects and crystal packing requirements affects to some extent the ideal geometry based on electronic factors alone, and gives rise to the large variations observed in the structural parameters α_i and Δ_{tw} (see Table 4). This bonding model **B**, which allows

us to rationalise the stereochemistry of the ligands 2 and 4 in complex **2**, has been proposed to be involved in most of the $M_2(\mu\text{-}S)_2$ (M = Ag, Cu) rings in reported thio(mono- or di)amide complexes.[1,57]

Although all four ligands in complex **2** show tilt angles close to 90°, ligands 1 and 3 behave differently from the case of ligands 2 and 4 considered above, in that their respective twist angles have opposite signs and very close absolute values (Table 4). As can be seen in Figures 4 and 7, this means that the planes corresponding to ligands 1 and 3 are not only almost normal to their respective Ag−S−Ag′ units, but virtual bisectors of these. With this geometry, the only orbital that a thioamide ligand can contribute to bridge bonding is one sulfur non-bonding sp^2 orbital with its electron pair. In either of these ligands, this orbital with two orbitals of a pair of Ag atoms would lead to delocalised three-centre, two-electron, electron-deficient bonding systems (type **C**) at the S(1) and S(3) bridges, as was previously proposed for the Cu_2S_2 rings present in the $[Cu_4(tu)_9]_n(NO_3)_{4n}$ polymer.[23] This assessment is supported by the short metal−metal distances and accompanying sharp bridge angles [Ag(1)···Ag(1A) 2.769 Å, Ag(1)−S(3)−Ag(1A) 63.46°; and Ag(1)···Ag(2) 2.858 Å, Ag(1)−S(1)−Ag(2) 64.74°], while corresponding values for bridges at S(2) and S(4), assumed to be three-centre, four-electron conventional bonding systems, are larger [Ag(1)···Ag(2) 2.858 Å, Ag(1)−S(2)−Ag(2) 66.64°; and Ag(2)···Ag(2B) 2.969 Å, Ag(2)−S(4)−Ag(2B) 69.34°]. Therefore, a pair of twist angles (−α, α), where $\Delta_{tw} = 2\alpha$, would correspond to the above ideal orientation in which a thioamide plane is exactly bisecting the M−S−M′ angle, the bridge bonding being probably related to an electron-deficient system to which sulfur supplies only two electrons from one of its two sp^2 orbitals. However, other geometry-determining factors such as crystal packing, hydrogen bonding or steric demands of the ligands, can cause the thioamide plane to deviate somewhat from the bisector of the M−S−M′ plane while preserving the close perpendicularity between these planes. This results in general orientations for this bonding mode, which are more accurately denoted by pairs of different twist angles ($-\alpha_1$, α_2), with suitable α_i values in the approximate range $25° < |\alpha_i| < 45°$ and where $\Delta_{tw} = \alpha_2 + |\alpha_1| < 80°$. This latter condition ensures a relatively sharp bridge angle and concomitant short metal−metal distance, both characteristic features of this bonding mode **C**.

Although not present in complex **2**, it is worth mentioning here another ideal orientation in which a thioamide plane, also tending to be orthogonal to its M−S−M′ unit, would not lie in the bisector plane of the latter but perpendicular to it. Here, the N···N line (in thiourea ligands) or its corresponding N···C vector (in thiomonoamides) would be parallel to the M···M′ line. In this geometry, the (C=S) pπ-MO orbital, with the sulfur atom as the major contributor, would extend nearly along the bisector of the M−S−M′ angle, thus allowing the interaction of this ligand-based orbital, accommodating one electron pair, with two empty orbitals of the metal atoms. This would also give rise to a delocalised three-centre, two-electron, electron-deficient bridge bonding system (type **D**). Whereas (−α, α) is a general notation for twist angles that would hold for the two ideal orientations attributable to electron-deficient bridge bonding, the relation $\Delta_{tw} = 180 - 2\alpha$ applies only to the present situation. As reported for $M(tu)_2Cl$ (M = Cu, Ag),[55,56] to the best of our knowledge the only known complexes for which sulfur-bridge bonding has been explained according to model **D**, the overall effect of both stereochemical constraints and electronic factors leads to a deviation of the thiourea plane, and thus of the N···N line, by about 8° from the direction of the M···M′ line, the tilt angle being reasonably close to 90°. For electron-deficient sulfur-bridged bonding with only two electrons supplied by the thioamide (C=S) pπ-MO (type **D**), probable general orientations would be given, though on the basis of only those two complexes, by pairs of twist angles ($-\alpha_1$, α_2), with $\Delta_{tw} = 180 - (\alpha_2 + |\alpha_1|)$ and suitable α_i values both falling within the approximate range $40 \leq |\alpha_i| < 65°$. This should result in a relatively short metal−metal distance.

Assignment of one of the four sulfur-bridge bonding modes here described for thioamide complexes can, therefore, be made quite confidently from the observed stereochemistry, provided the values corresponding to the defined tilt and twist angles lie in the ranges given above. According to these criteria, some selected complexes containing M−S−M′ angular bridges have been included in Table 4, with an indication of the bonding mode thereby deduced. Thus, the four crystallographically independent Ag−S−Ag′ bridges in complex **2**, all with a tilt angle in the range 79.2−85.5° and with different pairs of twist angles for S(2) and S(4) versus S(1) and S(3), are associated with four-electron sp^2 + C=S (mode **B**) and two-electron sp^2 electron-deficient (mode **C**) sulfur-bridging bonding modes, respectively. Although some correlation might be expected between the sulfur-bridge bonding mode (as evidenced by the tilt and twist angles) and Ag−S distances, no simple pattern is found in complex **2**. In particular, mode **C** does not give more symmetrical Ag−S−Ag′ bridges than mode **B**, despite the approximately equal contributions of S orbitals to the two corresponding Ag−S bonds. Clearly, the situation is more complex, with Ag−S distances also depending on the coordination geometry at the soft Ag centre, which is somewhat distorted tetrahedral for Ag(2) and highly distorted for Ag(1), with one S−Ag−S angle as small as 89.62(2)°.

Conclusion

Two silver cationic complexes with perchlorate as the counterion and neutral thio(mono- or di)amide ligands have been prepared and structurally characterised. The centrosymmetric monomeric $[Ag(etu)_2]^+$ complex species in **1** contains a linear MS_2 mononuclear core, unprecedented for bis(thioamide) complexes (M = Cu, Ag). These cations and ClO_4^- counterions assemble as complementary partners involving all available hydrogen bond donor (4 N−H of each

cation) and acceptor (4 O of each ClO_4^-) sites in a three-dimensional supramolecular network. Despite having the same stoichiometry, a sulfur-bridged polymeric cation with tetrahedral AgS_4 centres is obtained instead in **2**. There are in this case fewer available hydrogen bond donor (4 N−H + 2 water O−H) than potential acceptor [8 O (ClO_4^-) + 2 O (H_2O)] sites, and so the two crystallographically distinct ClO_4^- counterions act as two connectors (through one or two oxygen atoms, respectively). A two-dimensional layered supramolecular structure assembled through N−H···O−Cl, N−H···O(water) and Cl−O···H−O−H···O−Cl hydrogen bonding results, with no significant connections of this type between sheets. Stereochemical parameters (tilt and twist dihedral angles) for **2** indicate two different sulfur-bridge bonding modes, one conventional four-electron and the other electron-deficient two-electron.

Experimental Section

General Remarks: Reagent-grade solvents were used with no further purification. Ethylenethiourea (Fluka) and pyridine-2-thione (Aldrich) were used as received, while silver(I) perchlorate (Alfa) was recrystallized from acetonitrile. Microanalyses (C, N, H, S) were performed with a Carlo-Erba CHN EA-1108 analyser at the Servei d'Anàlisi Química de la UAB. Infrared spectra (4000−400 cm^{-1}) were recorded from KBr pellets with Perkin-Elmer FT-1710 and FT-2000 spectrometers, and ^1H and ^{13}C NMR spectra from [D_6]DMSO solutions with a Bruker AC-250 spectrometer operating at 250 MHz for ^1H NMR nuclei.

[Ag(etu)$_2$](ClO$_4$) (1): A solution of $AgClO_4$ (0.409 g, 4.0 mmol) in 60 mL of a mixture of methanol/water (2:1, v/v) was added dropwise with stirring to a methanol solution (10 mL) of the ligand (0.414 g, 2.0 mmol). After stirring for 2 h, the volume of the solution was reduced to about 30 mL by passing a slow stream of N_2 through it, and then cooled to 0°C. A precipitate separated, which was filtered, washed with 5 mL of cold ethanol and then with 10 mL of diethyl ether, and dried in vacuo. Colourless crystals of the product, suitable for X-ray diffraction, were isolated by slow concentration of an acetonitrile solution of the complex at room temperature. Total yield 60%. This compound is soluble in methanol, acetonitrile, acetone and DMSO. $C_6H_{12}AgN_4S_2{\cdot}ClO_4$ (438.7): calcd. C 11.64, H 1.95, N 9.05, S 10.36; found C 11.68, H 2.15, N 8.78, S 10.27. IR (KBr): $\tilde{\nu}$ = 3350−3270, 2890, 1522, 1355, 1319, 1280, 1200, 1087, 990, 920, 670, 626, 560, 495 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 8.90, 3.67 ppm. ^{13}C NMR ([D_6]DMSO): δ = 178.4, 44.9 ppm.

[{Ag(py2tH)$_2$}(ClO$_4$)(H$_2$O)$_{0.5}$]$_n$ (2): A solution of 0.311 g (1.5 mmol) of $AgClO_4$ in 10 mL of ethanol was added dropwise with stirring to an ethanol solution (15 mL) of the ligand (0.334 g, 3.0 mmol). A yellow precipitate formed immediately. After stirring for 1 h, the resulting mixture was kept in an ice bath for 15 min, and then filtered. The yellow solid was washed with 15 mL of diethyl ether and dried in vacuo. Yield 80%. Light yellow crystals of the product were isolated by slow vapour diffusion of diethyl ether into a concentrated acetonitrile solution of the complex at room temperature. This compound is soluble in acetonitrile, acetone and DMSO. $C_{10}H_{10}AgN_2S_2{\cdot}ClO_4{\cdot}0.5H_2O$ (411.6): calcd. C 27.38, H 2.52, N 6.38, S 14.62; found C 27.54, H 2.69, N 6.40, S 14.36. IR (KBr): $\tilde{\nu}$ = 3160, 3100, 3075, 3020, 2908, 1605, 1570, 1500, 1440, 1366, 1257, 1132, 1090, 995, 747, 726, 627, 484, 444 cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 14.10, 8.10, 7.69, 7.19 ppm. ^{13}C NMR ([D_6]DMSO): δ = 167.6, 141.1, 141.0, 131.9, 118.4 ppm.

X-ray Crystallographic Study: Crystals of both complexes were examined with a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), at 173 or 160 K. Almost a whole sphere of data was collected in each case,

Table 5. Crystal data

	1	**2**
Empirical formula	$C_6H_{12}AgN_4S_2^+{\cdot}ClO_4^-$	$C_{10}H_{10}AgN_2S_2^+{\cdot}ClO_4^-{\cdot}0.5H_2O$
Formula mass	411.6	438.7
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$
a [Å]	13.964(3)	9.8871(5)
b [Å]	13.564(3)	10.9878(6)
c [Å]	7.0256(15)	14.8197(8)
α [°]	90	82.816(2)
β [°]	90.642(6)	73.570(2)
γ [°]	90	72.209(2)
V [Å^3]	1330.6(5)	1469.07(14)
Z	4	4
d [g cm^{-3}]	2.055	1.983
μ [mm^{-1}]	2.04	1.85
T [K]	173	160
Crystal size [mm]	0.30 × 0.11 × 0.11	0.60 × 0.21 × 0.16
θ range [°]	2.1−28.6	2.0−28.7
Reflections measured	3972	11929
Unique data, R_{int}	1567, 0.027	6660, 0.024
Transmission factors	0.58−0.81	0.40−0.76
Refined parameters	103	376
R (F; $F^2 > 2\sigma$)	0.032 (1315 data)	0.030 (6023 data)
R_w (F^2; all data)	0.088	0.082
Max./min. electron density [e Å^{-3}]	+0.92/−0.69	+1.10/−1.25

using narrow-slice ω scans;[65] semi-empirical absorption corrections were based on repeated and symmetry-equivalent data.[66] The structures were solved by heavy-atom or automatic direct methods, and refined by full-matrix least-squares methods on all unique F^2 values, with anisotropic displacement parameters for all non-H atoms. H atoms bonded to C and N were placed in idealised positions and constrained with a riding model; those of the water molecule in **2** were found in difference maps and were freely refined, with the O−H bond lengths restrained to be similar. Largest features in final difference maps were close to heavy atoms and disordered groups. Details are given in Table 5. CCDC-220964 and -220965 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc. cam. ac. uk].

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