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Article

Structural and Infrared Spectroscopic Studies of Some Novel Mechanochemically Accessed Adducts of Silver(I) Oxoanion Salts with Thiourea

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An investigation of the silver(I) nitrate/thiourea (“tu”) system, exploiting the uniquely powerful access provided by the recently developed combination of mechanochemical synthesis coupled with vibrational spectroscopy, has resulted in the identification of solid adducts $AgNO_3$/tu (x:y) for x:y = 1:1, 1:1.5, 15:23 (= 1:1.5333), and 1:3. This contrasts with previously published claims for the existence of 1:2 and 1:4 complexes and was confirmed in the case of the 1:3 and 15:23 complexes by X-ray crystal structure determinations on samples prepared by crystallization from aqueous solution. The 1:3 sulfate and perchlorate complexes were also prepared for comparison with the corresponding nitrate compound. In the 1:3 nitrate complex, the one independent silver atom major component (0.78(1)) is closely trigonal planar AgS_3 (Ag−S 2.518(2)−2.592(1) Å, Σ(S−Ag−S) 359.7_0°); there are minor nearby components (0.11(1)) which may be regarded as four-coordinate, forming a putative one-dimensional polymer. The sulfate, obtained as its tetrahydrate, has a cation of the familiar binuclear form $[\{(tu)_2Ag(\mu\text{-}S\text{-}tu)\}_2](SO_4)\cdot 4H_2O$, while the perchlorate, previously also characterized with the binuclear cation in the anhydrate, has now been isolated as the hemihydrate, having a single-stranded polymeric cation, $[\ldots Ag(tu)_2(\mu\text{-}S\text{-}tu)\ldots]_{(\infty|\infty)}(ClO_4)\cdot 0.5H_2O$, similar to that observed in CuX/tu (1:3) (X = Cl, Br, I). The remarkable 15:23 nitrate complex (shown to be distinct from the 1:1.5 complex) may be regarded as essentially ionic $[Ag_{15}(tu)_{23}(ONO_2)]^{14+}_{(\infty|\infty)}(NO_3^-)_{14}$ (the cation incorporating one *O*-nitrate ion loosely associated) and comprising one-dimensional polymer strands made up of four-, six-, and eight-membered $Ag_{2n}S_{2n}$ rings, cross-linked by the sulfur of one of the tu ligands. The ν(CS) and ν_a(CN) bands in the infrared spectra of the complete series of adducts show a monotonic wavenumber decrease and increase, respectively, with decreasing tu content of the adduct, indicating a decrease in the C−S bond strength and a concomitant increase in the C−N bond strength with increasing Ag−S bond strength. The increase in Ag−S bond strength with decreasing tu content is also indicated by an increase in the wavenumbers of the bands assigned to ν(AgS) in the 140−200 cm^{-1} region in the far-IR. These and the structural data for the 1:3 and 15:23 complexes provide the basis for establishing a correlation between ν(AgS) and the Ag−S bond length d(AgS) for silver complexes involving the tu ligand.

Introduction

A considerable number of complexes of simple copper(I) salts, formed with thiourea (“tu”; $SC(NH_2)_2$) and its simple substituted derivatives (xtu), involving a wide variety of compositions and structures, have been reported in the past;[1] in these, the thiourea and its derivatives (x)tu behave as “soft” ligands, capable of unidentate or diverse bridging modes. Much of the interest in these compounds derives from the many and varied structures that they show and the relevance of these in areas as diverse as bioinorganic chemistry and

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10.1021/ic802312j CCC: $40.75

electrochemistry.[2−4] Complexes CuX/(x)tu (1:*n*), where X is a coordinating or noncoordinating anion (halide, nitrate, perchlorate, etc.), with a range of integral and nonintegral *n* values are known, and the complexity of the structural types ranges from mononuclear to infinite polymeric, with a number of tetranuclear complexes of diverse composition and structure being featured in the compounds reported to date.[1] In contrast to the situation for copper(I), a considerably smaller number of silver(I) complexes of thiourea and its derivatives have been reported, with mainly mononuclear or binuclear structures being observed for compounds of the form AgX/(x)tu (1:*n*), in the main with integral $n = 1, 2, 3$, and 4,[5,6] although an infinite polymeric $n = 0.5$ complex has also been reported.[7]

Many of the diverse structural types that have been reported for copper(I)/(x)tu complexes involve the parent (unsubstituted) tu ligand together with noncoordinating nitrate and sulfate (oxo-)counterions.[1,8−13] It is therefore rather surprising that there have been no reports of structures of silver(I)/thiourea complexes involving these anions. In a recent solid-state NMR study of the silver(I) nitrate/thiourea system, it was claimed that the results demonstrated the existence of $AgNO_3$/tu (1:*n*), for $n = 1$ and 4 only.[14] This contrasts with a much earlier report of the existence of a 1:3 complex.[15] There appear to be no reports of the formation and composition of Ag_2SO_4/tu complexes, although the structure of a 1:6 ethylenethiourea complex is known.[5] We report here the results of studies of the synthesis, crystal structures, and IR spectra of the $AgNO_3$/tu, $AgClO_4$/tu, and Ag_2SO_4/tu systems, which showed unexpected and unprecedented degrees of complexity in a number of systems. These compounds have provided a good basis for a study of the relationship between the IR spectra and the composition and structures of the complexes concerned, and the results are reported herewith. We have recently shown that the method of solvent-assisted mechanochemical synthesis coupled with IR spectroscopy provides a unique and powerful window into the systematic study of the formation of metal complexes;[1,16,17] the further exploitation of this technique in the present work has been fundamental in enabling the access of new and surprising stoichiometries and forms.

Experimental Section

Preparation of Compounds. Mechanochemical Experiments. Reactants producing about 0.2−0.4 mmol of the silver complex were mixed and ground using an agate mortar and pestle of the type normally used for preparing samples for IR spectroscopy. A small amount of solvent (2−4 drops), just sufficient to allow the formation of a paste during grinding, was added and the mixture further ground for a few minutes. The solvent was removed from the resulting paste of product by allowing it to stand for a few minutes in the air, and the IR spectra of the products were recorded immediately by using the attenuated total reflectance (ATR) method. The systems studied (and the solvents used) are as follows:

$$AgNO_3{:}n\text{tu};\ n = 1, 1.5, 2, 3, 4\ \text{(water)}$$

$$AgNO_3{:}n\text{tu};\ n = 4\ \text{(methanol)}$$

$$Ag_2SO_4{:}n\text{tu};\ n = 6\ \text{(water)}$$

Solution-Based Syntheses. $AgNO_3$/tu (1:3), 1. A solution of $AgNO_3$ (0.340 g, 2 mmol) in water (5 mL) was added rapidly with stirring to a solution of thiourea (0.760 g, 10 mmol) in water (7 mL) at room temperature. An initial white precipitate dissolved upon stirring. Fine colorless crystals suitable for X-ray diffraction studies separated upon standing. The product was collected and washed with ice-cold water. Yield: 0.423 g (53.1%). Anal. calcd for $C_3H_{12}AgN_7O_3S_3$: C, 9.05; H, 3.04; N, 24.62. Found: C, 9.1; H, 2.9; N, 24.5%. The same complex was obtained from an acetonitrile/methanol solvent mixture: A solution of $AgNO_3$ (0.340 g, 2 mmol) in boiling acetonitrile (5 mL) was added rapidly with stirring to a solution of thiourea (0.760 g, 10 mmol) in boiling methanol (5 mL). An initial white cloudiness dissolved upon stirring. A fibrous mass of white solid separated upon standing. The product was collected and washed with acetonitrile/methanol (1:1 v/v). Yield: 0.318 g (39.9%). Anal. calcd for $C_3H_{12}AgN_7O_3S_3$: C, 9.05; H, 3.04; N, 24.62. Found: C, 9.3; H, 3.0; N, 24.9%. The IR spectrum of this product is identical to that of the corresponding compound obtained from aqueous solution.

$AgNO_3$/tu (1:1.5), 2, and (15:23), 3. A solution of $AgNO_3$ (0.340 g, 2 mmol) in water (10 mL) was added rapidly with stirring to a solution of thiourea (0.228 g, 3 mmol) in water (10 mL) at room temperature. A white flocculent precipitate formed as the last of the $AgNO_3$ solution was added. Heating the mixture dissolved the precipitate but caused some decomposition, resulting in the formation of a black precipitate. The warm solution was filtered twice to remove most of the black material, and the filtrate was allowed to stand and cool. After about 30 min, the whole solution had become a solid mass of interlocked colorless microcrystalline solid. This was collected and washed with water. Yield: 0.170 g (29.9%). Anal. calcd for the 1:1.5 complex $C_{1.5}H_6AgN_4O_3S_{1.5}$: C, 6.34; H, 2.13; N, 19.72. Found: C, 6.4; H, 2.4; N, 19.5%. Small colorless crystals suitable for X-ray diffraction studies formed in the filtrate upon standing in an open beaker in the fume cupboard to facilitate evaporation for 4 days, and these were collected and washed with

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Table 1. Crystal/Refinement Data, AgX/tu (x:y)($\cdot n$H$_2$O)

	compound X/x:y(:n)			
	1(NO$_3$)/1:3	**3** (NO$_3$)/15:23	**5** (SO$_4$)/1:6:4	**6** (ClO$_4$)/2:6:1
formula	$C_3H_{12}AgN_7O_3S_3$	$C_{23}H_{92}Ag_{15}N_{61}O_{45}S_{23}$	$C_6H_{32}Ag_2N_{12}O_8S_7$	$C_6H_{26}Ag_2Cl_2N_{12}O_9S_6$
M_r (Da)	398.3	4299	840.6	889.4
cryst syst	tetragonal	monoclinic	tetragonal	orthorhombic
space group	$I4_122$ (No. 98)	$P2_1$ (No. 4)	$P4/n$ (No. 85)	$Pna2_1$ (No. 33)
a (Å)	14.2104(2)	13.2388(2)	21.3314(2)	26.3181(3)
b (Å)		24.6552(3)		13.1235(1)
c (Å)	24.5695(8)	19.1194(2)	6.2920(1)	8.3189(1)
β (deg)		107.293(2)		
V (Å^3)	4961	5959	2863	2873
D_{calcd} (g cm^{-3})	2.13_3	2.40_0	1.95_0	2.05_6
Z	16	2	4	4
μ_{Mo} (mm^{-1})	2.14	2.91	1.93	2.04
specimen (mm^3)	0.29 × 0.08 × 0.06	0.29 × 0.16 × 0.11	0.16 × 0.10 × 0.045	0.22 × 0.14 × 0.055
$T_{min/max}$	0.72	0.87	0.95	0.63
$2\theta_{max}$ (deg)	65	65	62	65
N_t	35931	77302	33760	34651
N (R_{int})	4487 (0.051)	37946 (0.027)	4783 (0.040)	8253 (0.048)
N_o ($I > 2\sigma(I)$)	3581	30348	3542	6686
$R1$	0.046	0.029	0.034	0.029
$wR2$ (a(,b))	0.105 (0.042,14.8)	0.050 (0.020)	0.086 (0.048)	0.069 (0.038)
$\|\Delta\rho_{max}\|$ (e Å^{-3})	0.80	1.16	2.1	1.17
x_{abs}	−0.01(4)	0.305(7)	n/a	0.08(6)

ice-cold water. Yield: 0.159 g (28.0%). Anal. calcd for the 15:23 complex $C_{23}H_{92}Ag_{15}N_{61}O_{45}S_{23}$: C, 6.43; H, 2.16; N, 19.88. Found: C, 6.6; H, 2.2; N, 20.1%.

AgNO$_3$/tu (1:1), 4. A solution of thiourea (0.152 g, 2 mmol) in water (5 mL) was added rapidly with stirring to a solution of AgNO$_3$ (0.340 g, 2 mmol) in water (5 mL) at room temperature. A white precipitate formed, which started to turn gray after about 1 min. This was collected and washed with water and required overnight drying. The particles of product had fused together to form a thin cake on the filter. Yield: 0.455 g (92.5%). The compound turned black upon further standing and was unsuitable for microanalysis. The product from the same reaction carried out in a 1:1 acetonitrile/methanol solvent mixture was more stable and gave the same IR spectrum as the initial product from the aqueous solution reaction. Yield: 0.492 g (100%). Anal. calcd for $CH_4AgN_3O_3S$: C, 4.88; H, 1.64; N, 17.08. Found: C, 5.1; H, 1.9; N, 16.5%.

[Ag$_2$(tu)$_6$](SO$_4$)·4H$_2$O, 5. Water (5 mL) was added to a mixture of Ag$_2$SO$_4$ (0.31 g, 1 mmol) and thiourea (0.61 g, 8 mmol), and the mixture was heated. Most of the solids dissolved to give a clear solution. A small amount of undissolved solid melted upon further heating to give a clear oil. Futher oil separated, and colorless crystals suitable for X-ray diffraction studies formed upon cooling. These were collected and washed with ice-cold water. Yield: 0.83 g (98.3%). Anal. calcd for $C_6H_{32}Ag_2N_{12}O_8S_7$: C, 8.57; H, 3.84; N, 20.00. Found: C, 8.6; H, 4.0; N, 19.7%.

[Ag$_2$(tu)$_6$](ClO$_4$)$_2$·H$_2$O, 6. A solution of AgClO$_4$ (0.79 g, 3.8 mmol) in water (2.5 mL) was added to a solution of thiourea (0.87 g, 11.4 mmol) in water (7 mL). No product separated from the resulting clear solution upon standing in an open beaker overnight, so it was seeded with a small amount of solid obtained by evaporating all of the water from a 0.5 mL sample of the solution at 70 °C for 3 h. Colorless crystals of the product suitable for X-ray diffraction studies separated slowly from the solution upon standing and were collected and washed with ice-cold water. Yield: 0.43 g (25.0%). Anal. calcd for $C_6H_{26}Ag_2Cl_2N_{12}O_9S_6$: C, 8.10; H, 2.95; N, 18.90. Found: C, 8.3; H, 2.8; N, 19.1%.

Warning! *Perchlorate salts are potentially explosive and should be handled with care!*

Infrared Spectroscopy. IR spectra were recorded on dry powders using a Perkin-Elmer Spectrum 100 FT-IR spectrometer equipped with a Universal ATR sampling accessory. Far-IR spectra were recorded on powders suspended in polythene disks using a Perkin-Elmer Spectrum 400 FT-IR spectrometer.

Table 2. Selected Geometries, AgNO$_3$/tu (1:3), **1**[a]

atoms	parameter	atoms	parameter
Distances (Å)			
Ag(1)−S(1)	2.547(2)	Ag(2)−S(1)	2.356(6)
Ag(1)−S(2)	2.518(2)	Ag(2)−S(2)	2.723(6)
Ag(1)−S(3)	2.592(1)	Ag(2)−S(3)	2.872(14)
Ag(1)···Ag(1^{i})	3.203(1)	Ag(2)···S(2^{ii})	2.96(1)
Ag(1)···Ag(3^{i})	2.654(2)	Ag(3)−S(1)	2.495(8)
Ag(1)···Ag(1^{ii})	3.249(1)	Ag(3)−S(2)	2.874(13)
Ag(1)···Ag(2^{ii})	2.61(1)	Ag(3)−S(3)	2.563(8)
Ag(2)···Ag(3)	1.24(2)	Ag(3)···S(3^{i})	2.67(1)
Ag(1)···Ag(2)	0.75(1)	Ag(1)···S(3^{i})	3.152(1)
Ag(2)···Ag(2^{ii})	1.99(2)	Ag(1)···S(2^{ii})	3.533(2)
Angles (degrees)			
S(1)−Ag(1)−S(2)	124.59(5)	S(2)−Ag(1)−S(3)	102.97(6)
S(1)−Ag(1)−S(3)	132.14(7)	Σ	359.7_0
S(1)−Ag(2)−S(2)	123.8(2)	S(1)−Ag(3)−S(2)	113.1(5)
S(1)−Ag(2)−S(3)	127.6(6)	S(1)−Ag(3)−S(3)	136.4(3)
S(1)−Ag(2)−S(2^{ii})	102.1(4)	S(1)−Ag(3)−S(3^{i})	98.9(4)
S(2)−Ag(2)−S(3)	91.2(4)	S(2)−Ag(3)−S(3)	94.5(4)
S(2)−Ag(2)−S(2^{ii})	128.2(5)	S(2)−Ag(3)−S(3^{i})	95.9(2)
S(3)−Ag(2)−S(2^{ii})	76.5(1)	S(3)−Ag(3)−S(3^{i})	111.6(5)

[a] Ag lies 0.080(2), 2.466(2), 2.078(4), and 2.388(4) Å out of the S$_3$ and three SCN$_2$ ligand planes, respectively; the dihedral angles of the latter to the S$_3$ plane are 75.5(1), 65.2(1), and 65.4(1)°. Coordinate transformations i and ii are x, $1/2 - y$, $1/4 - z$ and $1 - y$, $1 - x$, $\bar{z}$.

Structure Determinations. Full spheres of CCD area-detector diffractometer data were measured (monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; ω-scans; T = ca. 110 K), yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after "empirical"/multiscan absorption correction, full matrix least-squares refinement refining anisotropic displacement parameter forms for the non-hydrogen atoms, and hydrogen atom treatment following a riding model. Neutral atom complex scattering factors were employed within the context of the SHELXL 97 program;[18] reflection weights were $[\sigma^2(F_o^2) + (aP)^2 (+ bP)]^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$). Pertinent results are given below and in Tables 1−5 and Figures 1−4, the latter showing 50% probability amplitude displacement envelopes

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Table 3. Selected Geometries, Ag_2SO_4/tu/H_2O (1:6:4), **5**[a]

atoms	parameter	atoms	parameter
Distances (Å)			
Ag−S(1)	2.5857(7)	Ag−S(3)	2.7363(7)
Ag−S(2)	2.5148(7)	Ag−S(3^{i})	2.5204(7)
Ag···Ag^{i}	3.2854(4)	S(3)···S(3^{i})	4.1091(9)
Angles (degrees)			
S(1)−Ag−S(2)	109.54(2)	S(2)−Ag−S(3)	100.81(2)
S(1)−Ag−S(3)	110.74(2)	S(2)−Ag−S(3^{i})	120.24(2)
S(1)−Ag−S(3^{i})	111.72(2)	S(3)−Ag−S(3^{i})	102.76(2)
Ag−S(3)−Ag^{i}	77.24(2)		
Hydrogen-Bonding Contacts within the Binuclear Cation (Å)			
N(12),H(12B)···S(2)	3.491(2), 2.6	N(32),H(32B)···S(1^{i})	3.448(3), 2.6
N(21),H(21B)···S(1)	3.591(3), 2.7		

[a] Coordinate transformation: (i) $1 - x$, $1 - y$, $\bar{z}$. The CN_2 planes of ligands 1−3 make dihedral angles of 83.07(8), 89.95(12), and 78.25(5)° with the central Ag_2S_2 plane; Ag−S−C angles are 104.15(9), 104.55(12), and 111.59(11)/102.49(9)° for S(1−3), respectively.

Table 4. Selected Geometries, $AgClO_4$/tu/H_2O (2:6:1), **6**[a]

atoms	parameter	atoms	parameter
Distances (Å)			
Ag(1)−S(1)	2.5070(7)	Ag(2)−S(4)	2.5629(7)
Ag(1)−S(2)	2.5536(7)	Ag(2)−S(5)	2.5366(7)
Ag(1)−S(3)	2.5209(10)	Ag(2)−S(3)	2.7037(10)
Ag(1)−S(6)	2.7942(9)	Ag(2)−S(6^{i})	2.5543(9)
Ag(1)···Ag(2)	4.1292(5)	Ag(1)···Ag(2^{i})	4.1899(5)
Angles (degrees)			
S(1)−Ag(1)−S(2)	106.31(2)	S(4)−Ag(2)−S(5)	107.23(2)
S(6)−Ag(1)−S(1)	111.89(3)	S(6^{i})−Ag(2)−S(4)	118.78(3)
S(6)−Ag(1)−S(2)	91.29(3)	S(6^{i})−Ag(2)−S(5)	118.28(3)
S(6)−Ag(1)−S(3)	103.77(3)	S(6^{i})−Ag(2)−S(3)	104.41(3)
S(3)−Ag(1)−S(1)	126.23(3)	S(3)−Ag(2)−S(4)	98.31(3)
S(3)−Ag(1)−S(2)	111.85(3)	S(3)−Ag(2)−S(5)	107.25(3)
Ag(1)−S(3)−Ag(2)	104.38(3)	Ag(1)−S(6^{ii})−Ag(2^{ii})	103.05(3)
Hydrogen-Bonding Contacts within the Cation (Å)			
N(11),H(11B)···S(4)	3.424(3), 2.5	N(41),H(41B)···S(1)	3.336(3), 2.5
N(12),H(12B)···S(4^{ii})	3.382(3), 2.5	N(42),H(42B)···S(1^{i})	3.393(3), 2.5
N(21),H(21B)···S(5)	3.431(3), 2.6	N(51),H(51B)···S(2)	3.389(3), 2.5
N(22),H(22B)···S(5^{ii})	3.378(3), 2.5	N(52),H(52B)···S(2^{i})	3.394(3), 2.5
N(31),H(31B)···S(6)	3.606(3), 2.7		

[a] Coordinate transformations: (i) x, y, $z - 1$; (ii) x, y, $z + 1$.

Table 5. Selected Bond Lengths, $AgNO_3$/tu (15: 23), **3**[a]

atoms	parameter	atoms	parameter
Distances (Å)			
Ag(1)−S(5)	2.5133(9)	Ag(2)−S(2)	2.5343(8)
Ag(1)−S(7)	2.5133(8)	Ag(2)−S(9)	2.5606(9)
Ag(1)−S(11)	2.7815(9)	Ag(2)−S(11)	2.8063(8)
Ag(1)−S(12)	2.5841(8)	Ag(2)−S(20)	2.5357(9)
Ag(3)−S(3)	2.5470(8)	Ag(4)−S(1)	2.5156(8)
Ag(3)−S(6)	2.5806(8)	Ag(4)−S(6^{ii})	2.5962(8)
Ag(3)−S(8^{i})	2.8136(8)	Ag(4)−S(8)	2.7201(8)
Ag(3)−S(13)	2.5507(8)	Ag(4)−S(20)	2.5451(9)
Ag(5)−S(4)	2.5318(8)	Ag(6)−S(11)	2.7383(8)
Ag(5)−S(5)	2.5077(9)	Ag(6)−S(12)	2.5721(8)
Ag(5)−S(8)	2.9456(8)	Ag(6)−S(17)	2.5707(8)
Ag(5)−S(22)	2.5515(9)	Ag(6)−S(19)	2.5507(8)
Ag(7)−S(9)	2.4449(8)	Ag(8)−O(31)	2.459(3)
Ag(7)−S(15)	2.5337(8)	Ag(8)−S(1)	2.4856(8)
Ag(7)−S(23)	2.5992(8)	Ag(8)−S(4)	2.9251(9)
Ag(9)−S(14)	2.6125(8)	Ag(8)−S(7)	2.4790(8)
Ag(9)−S(16)	2.6136(9)	Ag(10)−S(10)	2.8302(8)
Ag(9)−S(22^{iii})	2.4770(8)	Ag(10)−S(14)	2.6406(8)
Ag(11)−S(2)	2.4721(8)	Ag(10)−S(16)	2.5363(8)
Ag(11)−S(15)	2.7525(9)	Ag(10)−S(21)	2.4855(8)
Ag(11)−S(19)	2.4783(8)	Ag(12)−S(4^{iii})	2.4705(8)
Ag(13)−S(10)	2.5048(8)	Ag(12)−S(13^{iv})	2.4800(8)
Ag(13)−S(15)	2.7153(8)	Ag(12)−S(14)	2.7009(8)
Ag(13)−S(21)	2.8215(8)	Ag(12)−O(23^{iii})	2.666(2)
Ag(13)−S(23)	2.5294(8)	Ag(14)−S(3)	2.4947(8)
Ag(1)···Ag(6)	3.2659(4)	Ag(14)−S(10^{v})	2.5302(8)
Ag(3)···Ag(4^{i})	3.2224(4)	Ag(14)−S(18)	2.4619(9)
Ag(3)···Ag(14)	3.1199(4)	Ag(14)−O(21)	2.666(2)
Ag(6)···Ag(15)	3.1526(4)	Ag(15)−S(17)	2.4919(8)
Ag(7)···Ag(13)	2.9054(4)	Ag(15)−S(18)	2.4603(9)
Ag(9)···Ag(10)	2.9250(4)	Ag(15)−S(21)	2.5675(8)
Ag(10)···Ag(13)	3.0804(4)		

[a] Silver atom deviations (Å) from the ligand SCN_2 planes are 1/Ag(4,8) 0.350(5), 1.726(3); 2/Ag(2,11) 0.579(5), 1.856(3); 3/Ag(3,14) 1.625(4), −1.486(4); 4/Ag(5,8,12v^{i}) −0.770(4), 2.569(2), −1.449(4); 5/Ag(1,5) 1.895(4), −1.999(3); 6/Ag(3,4^{i}) −1.514(8), 1.705(4); 7/Ag(1,8) 0.067(6), 2.001(3); 8/Ag(3^{ii},4,5) 0.367(3), 2.682(3), −0.053(1); 9/Ag(2,7) −2.505(1), 0.066(6); 10/Ag(10,13,14^{iv}) 1.436(5), 2.338(2), −2,186(3); 11/Ag(1,2,6) −2.349(3), 1.947(5), −1.902(4); 12/Ag(1,6) −1.892(3), 1.345(4); 13/Ag(3,12^{v}) 1.279(4), 1.538(4); 14/Ag(9,10,12) 0.535(5), −2.119(3), 2.476(2); 15/Ag(7,11,13) 0.566(5), 2.314(3), −2.159(3); 16/Ag(9,10) 1.346(5), −1.549(4); 17/Ag(6,15) −2.028(3), 1.032(4); 18/Ag(14,15) −0.793(4), 0.383(4); 19/Ag(6,11) 0.882(4), 1.936(3); 20/Ag(2,4) 1.942(4), −2.107(3); 21/Ag(10,13,15) 2.322(2), 1.465(4), −2.283(2); 22/Ag(5,9^{vi}) 2.500(2), 0.094(6); 23/Ag(7,13) −1.888(4), 0.946(5). Coordinate transformations: (i) x, y, $z + 1$; (ii) x, y, $z - 1$; (iii) $x + 1$, y, $z + 1$; (iv) $x + 1$, y, z; (V) $x - 1$, y, z.

for the non-hydrogen atoms, the hydrogen atoms, where shown, having arbitrary radii of 0.1 Å. Full CIF depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC #696760, 696761, 706741, and 706742. Nonroutine features of the determinations of the 1:3 (Ag:tu) nitrate and sulfate complexes are mentioned in the Results and Discussion section.

Results and Discussion

Synthesis of Compounds. In a recent study of complexes of silver(I) halides with ethylenethiourea (imidazolidine-2-thione; etu), it was shown that the method of solvent-assisted mechanochemical synthesis in association with IR spectroscopy can be used to establish the composition of compounds of this type and to obtain information about their structures.[16] In view of the disagreement between different literature reports on the composition of complexes formed between $AgNO_3$ and thiourea,[14,15] we initially undertook a systematic solvent-assisted mechanochemical study of the $AgNO_3$/tu (1:n) system for $n = 1-4$. In addition, we investigated the $n = 1.5$ case on the basis of the previously reported existence of a corresponding etu complex.[5] The solvents used in the solvent-assisted processes were water and (in one case) methanol. The products were initially characterized by their IR spectra in the range 4000−650 cm^{-1}, which contain bands due to the tu ligand and the nitrate ion. The wavenumbers of selected bands in the spectra are listed in Table 6. Bands due to the thiourea ligand lie close to those previously reported for the uncomplexed tu molecule[11] and are assigned accordingly. Of the several tu bands observed in the spectra, the two assigned as ν(CS) and ν_a(CN) (the asymmetric C−N stretching mode)[11] proved to be the most sensitive to complex formation, and their wavenumbers are listed in Table 6. Bands due to the $\nu_3(E')$ mode of nitrate, which occurs at about 1380 cm^{-1} in the uncomplexed ion in KNO_3,[19] are obscured by a strong tu ligand band at 1410 cm^{-1}. However, the nitrate $\nu_2(A_2'')$ band that occurs at 828 cm^{-1} in KNO_3 is clearly visible in all cases, and its wavenumber for each complex is recorded in Table 6.

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(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., part A; Wiley: New York, 1997; p 182.

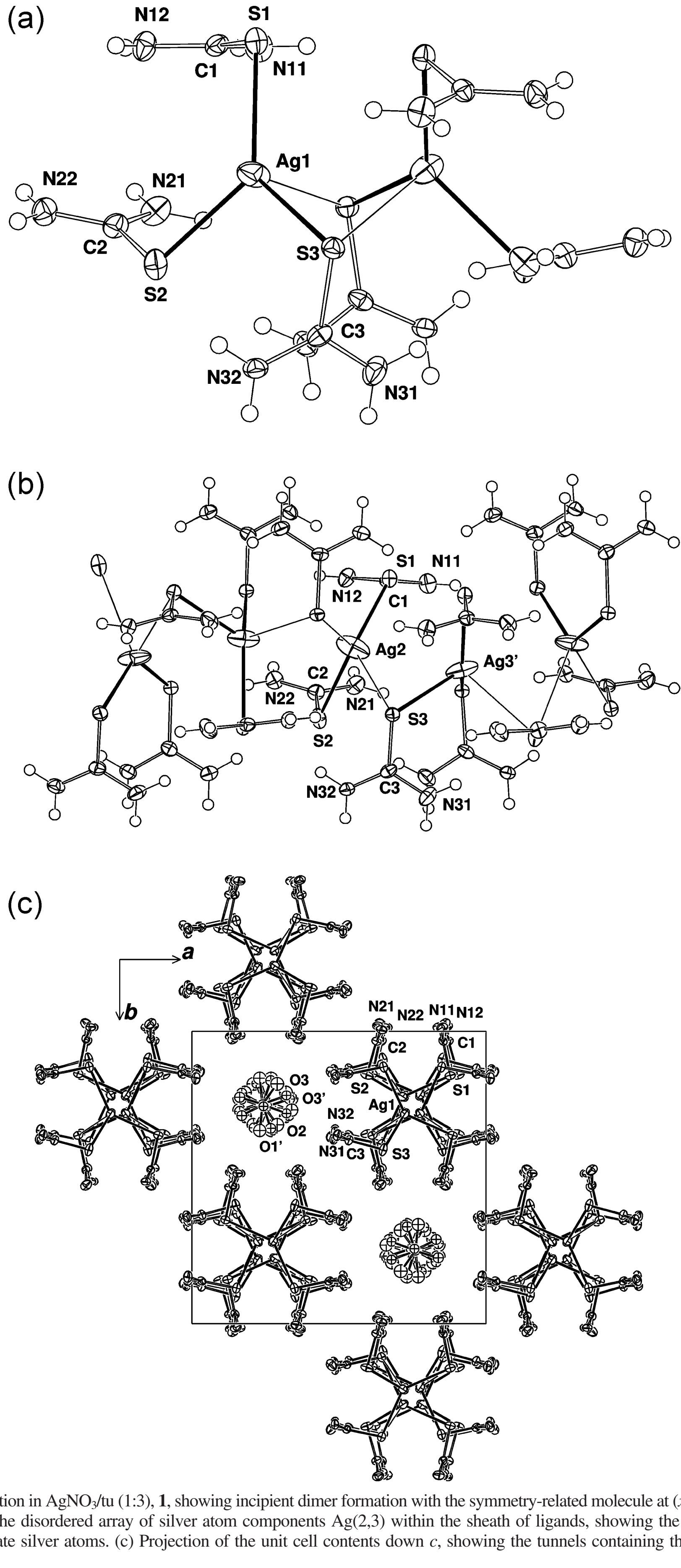

Figure 1. (a) The $[Ag(tu)_3]^+$ cation in $AgNO_3$/tu (1:3), **1**, showing incipient dimer formation with the symmetry-related molecule at (*x*, 1/2 − *y*, 1/4 − *z*) (Ag(1)···S(3′) 3.152(1) Å). (b) Projection of the disordered array of silver atom components Ag(2,3) within the sheath of ligands, showing the formation of a putative polymer along *c* involving four-coordinate silver atoms. (c) Projection of the unit cell contents down *c*, showing the tunnels containing the disordered nitrate anions.

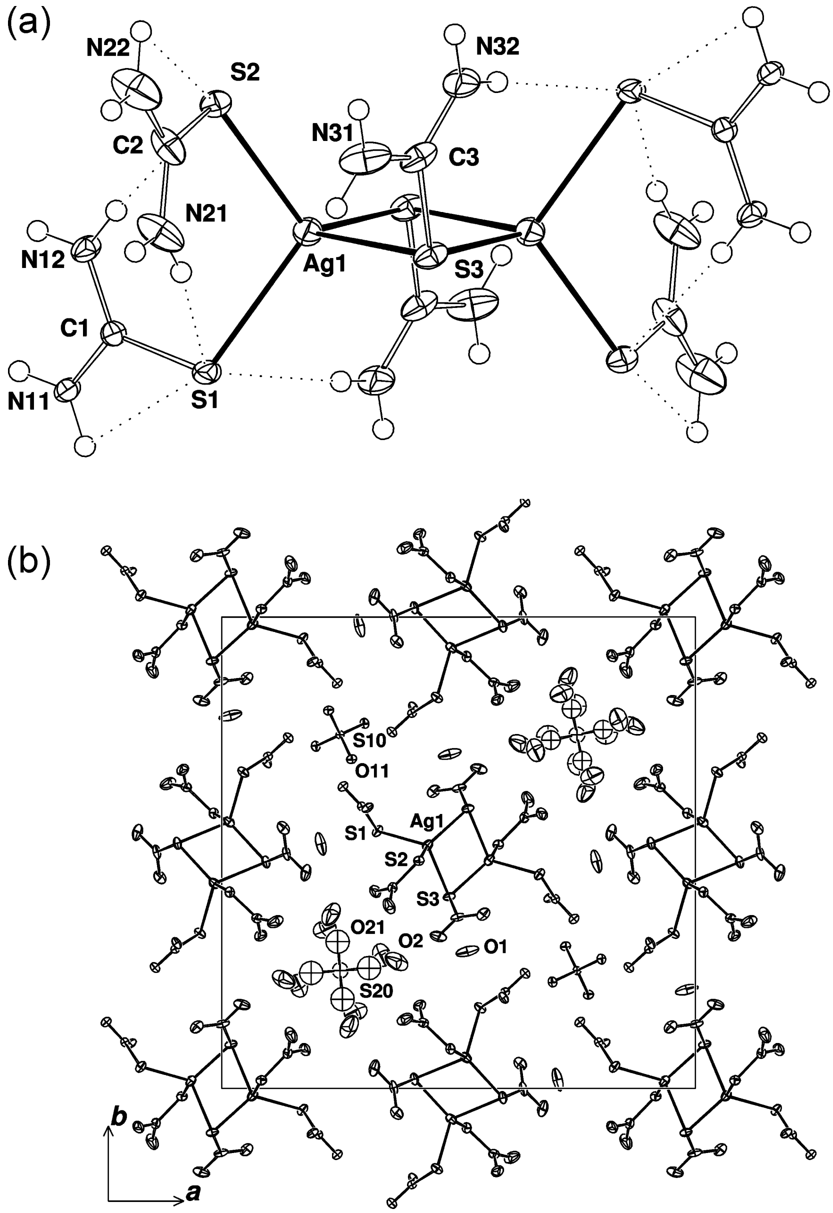

Figure 2. (a) The binuclear cation of Ag_2SO_4/tu/H_2O (1:6:4), **5**, $[(\text{tu-}S)_2Ag(\mu\text{-}S\text{-tu})_2Ag(S\text{-tu})_2]^{2+}$. (b) Unit cell contents, projected down *c*.

These studies clearly establish the existence of $AgNO_3$/tu (1:3), which was confirmed by subsequent synthesis of this compound, **1**, from aqueous solution (see the Experimental Section) and a determination of its crystal structure (see below). This result is in agreement with an early report[15] but contradicts a more recent claim, based on solid-state NMR measurements, that only the 1:1 and 1:4 complexes exist.[14]

Mechanochemical Treatment of $AgNO_3$/tu (1:4). Mechanochemical treatment of a $AgNO_3$/tu (1:4) mixture resulted in a product that was shown by IR spectroscopy to be a mixture of the 1:3 complex and unreacted tu. In the previously reported solid-state NMR study that claimed the existence of a 1:4 complex, an acetonitrile/methanol solvent mixture was used rather than water, raising the possibility that the compositions of complexes in this system might be solvent-dependent. However, it was shown in the present work that the 1:3 complex is the only product obtained from a reaction carried out in an acetonitrile/methanol mixture in which the tu/$AgNO_3$ ratio is as high as 5 (see the Experimental Section). Also, mechanochemical treatment of a $AgNO_3$/tu (1:4) mixture with methanol resulted in a mixture of the 1:3 complex and unreacted tu, as in the case of the reaction carried out in water. These results conclusively prove the nonexistence of a 1:4 complex.

Mechanochemical Treatment of $AgNO_3$/tu (1:1). Mechanochemical treatment of a $AgNO_3$/tu (1:1) mixture resulted in a product that was shown by IR spectroscopy to be the same as that obtained from the 1:1 reaction in solution (see the Experimental Section), with IR bands that are clearly different from those of the 1:3 complex (Table 6). The product of the reaction from homogeneous aqueous solution was significantly contaminated by a black decomposition product. This contrasts with the result of

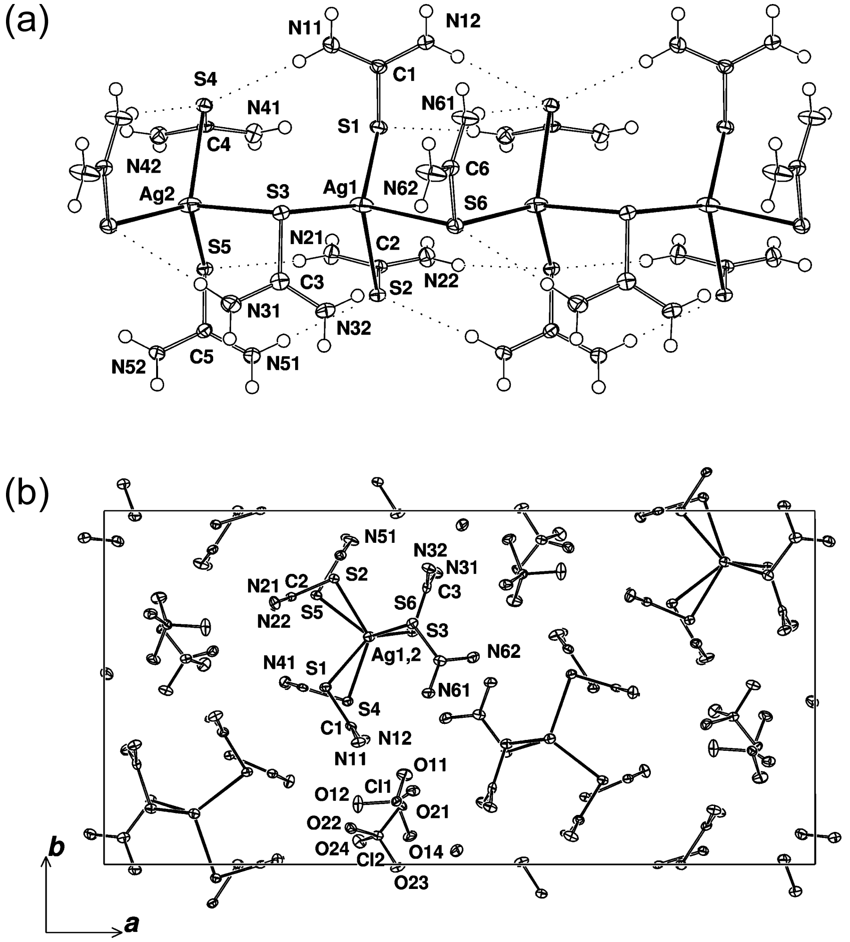

Figure 3. (a) The single-stranded polymer (*c* horizontal in the page) of $AgClO_4$/tu/H_2O (2:6:1), **6**. (b) Unit cell contents, projected down *c*.

the mechanochemical reaction, also carried out in the presence of water, where the product showed absolutely no sign of such decomposition. This is probably due to the fact that, in the mechanochemical reaction, the reactants spend very little time in solution, so that the opportunity for side reactions is greatly reduced. This phenomenon may be of wider applicability and can be added to the previously noted advantages of solvent-assisted mechanochemical synthesis.[16,17]

Mechanochemical Treatment of $AgNO_3$/tu (1:1.5). Mechanochemical treatment of a $AgNO_3$/tu (1:1.5) mixture resulted in a product that was shown by IR spectroscopy to be the same as that initially obtained from the 1:1.5 reaction in solution and established by elemental analysis to be of 1:1.5 stoichiometry (see the Experimental Section), with IR bands that are clearly different from those of the 1:1 and 1:3 complexes (Table 6). However, this IR spectrum developed only after three successive mechanochemical treatments. The spectrum observed after the first mechanochemical treatment was the same as that observed for $AgNO_3$/tu (15:23 = 1:1.5333), the second product obtained from a $AgNO_3$/tu (1:1.5) reaction in a homogeneous aqueous solution, following the initial separation of a 1:1.5 complex. The $AgNO_3$/tu (15:23) product, **3**, obtained from solution was characterized by elemental analysis (see the Experimental Section) and by X-ray crystallography (see below). The fact that the 15:23 complex was observed in the initial mechanochemical treatment of a 1:1.5 mixture implies that this formed preferentially to the 1:1.5 complex, leaving a small amount of unreacted $AgNO_3$, which reacted upon subsequent treatments to produce the 1:1.5 complex. Multiple mechanochemical treatments of the pure 15:23 complex with water resulted in no change in its IR spectrum. These observations show that the 1:1.5 and 15:23 complexes do in fact have distinct chemical compositions, rather than being different polymorphs of the same composition, which could, in principle, be interconverted by mechanochemical treatment.[17]

Mechanochemical Treatment of $AgNO_3$/tu (1:2). Mechanochemical treatment of a $AgNO_3$/tu (1:2) mixture resulted in a product that was shown by IR spectroscopy to be a mixture of the 1:3 complex and another compound, possibly unreacted $AgNO_3$, with $\nu_2(A_2'' \ NO_3^-) = 824$ cm^{-1}. The nonexistence of a 1:2 complex is in agreement with a recent NMR study[14] but does not agree with earlier synthetic/IR studies, which claimed the existence of a crystalline 1:2 adduct.[20,21] The considerable discrepancy between the properties (e.g., mp, $\nu(CS)$) reported for the 1:2 compound in these two studies is consistent with our finding that the 1:2 product is a mixture rather than a pure compound.

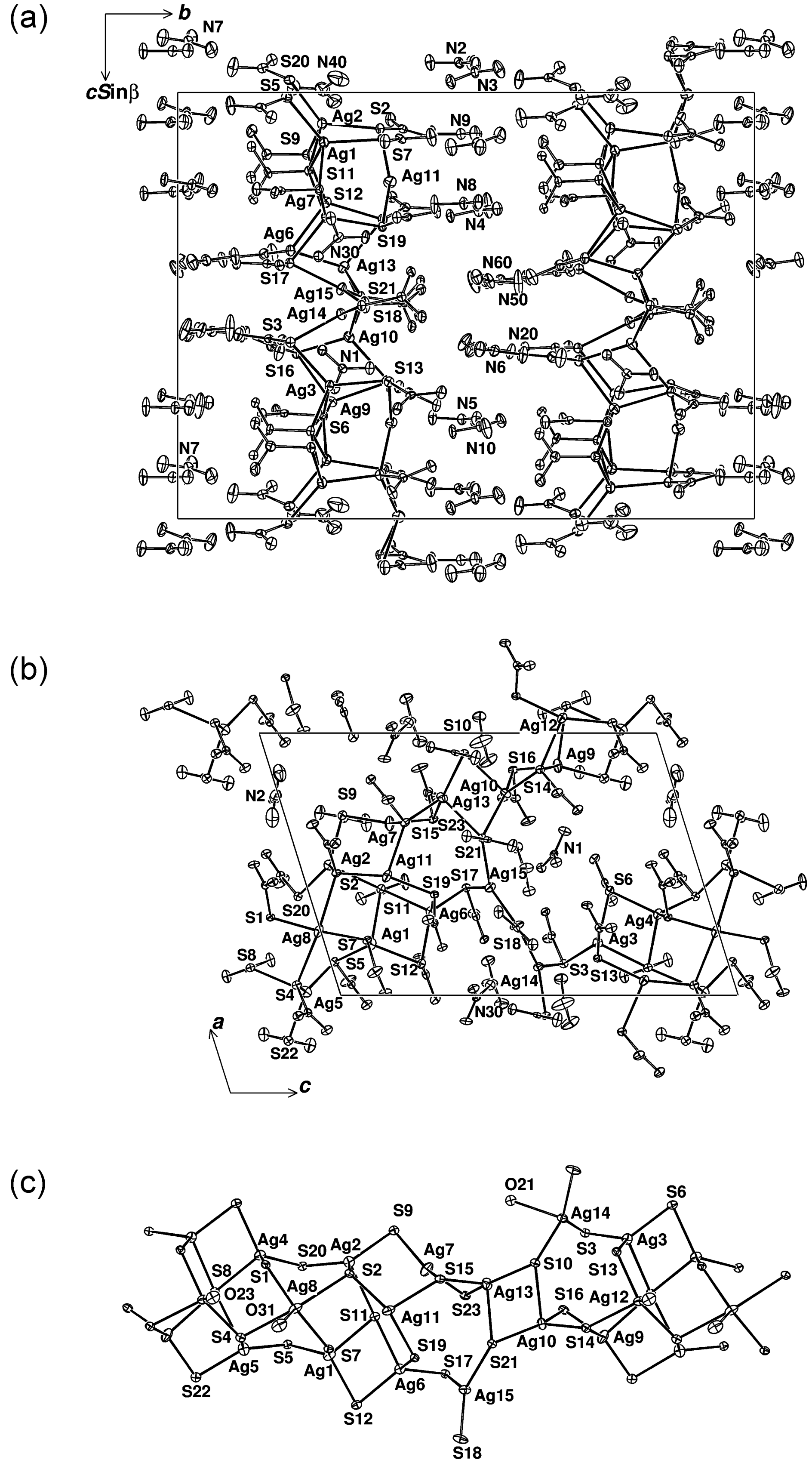

Figure 4. (a) Unit cell contents of $AgNO_3$/tu (15:23), **3**, down *a*, showing the partitioning of the cell contents at $y = 0$, 0.5. (b) Projections of the unit cell contents down *b*, showing cross-linking of the polymer strands by tu(18). (c) A single strand of the cation polymer, showing the Ag,S(,O) framework only. Within the Ag/S framework, the following rings are identified (Ag,S by number, *S italicized*, primed atoms related by the unit *c* translation): (a) four-membered rings, a_1 3, 4′, *6*, *8′*; a_2 7, 13, *15*, *23*; a_3 1, 6, *11*, *12*; a_4 10, 13, *10*, *21*; a_5 9, 10, *14*, *16*; (b) six-membered rings, b_1 5′, 9, 12, *4′*, *14*, *22′*; b_2 3, 5′, 12, *4′*, *13*, *8′*; b_3 1, 5, 8, *4*, *5*, *7*; b_4 2, 7, 11, *2*, *9*, *15*; b_5 2, 6, 11, *2*, *11*, *19*; (c) eight-membered rings, c_1 1, 4, 5, 8, *1*, *5*, *7*, *8*; c_2 1, 2, 4, 8, *1*, *7*, *11*, *20*; c_3 6, 11, 13, 15, *15*, *17*, *19*, *21*; c_4 3, 10, 12, 14, *3*, *10*, *13*, *14*.

Table 6. Selected Bands (cm^{-1}) in the IR Spectra of $AgNO_3$/tu, $AgClO_4$/tu, and Ag_2SO_4/tu Complexes

compound	ν (CS)	ν_a (CN)	ν ($A_2''NO_3^-$)	ν (AgS)
tu	729	1462		
KNO_3			828	
$AgNO_3$/tu (1:3), **1**	710	1490	815	190, 157, 146
$AgNO_3$/tu (15:23), **3**	698	1510	813	255, 211
$AgNO_3$/tu (1:1.5), **2**	700	1513	819	230, 177
$AgNO_3$/tu (1:1), **4**	694	1532	815	213, 175
$AgClO_4$/tu/H_2O (2:6:1), **6**	711	1491		164 (broad)
Ag_2SO_4/tu/H_2O (1:6:4), **5**	711	1500, 1478		186, 154, 95

In order to investigate the effect of the anion on the structure of complexes with a given Ag/tu ratio, 1:3 complexes involving sulfate and perchlorate counterions were also prepared.

Mechanochemical Treatment of Ag_2SO_4/tu (1:6). Mechanochemical treatment of a Ag_2SO_4/tu (1:6) mixture with water produced a product that showed the same IR spectrum (Table 6) as that of $[Ag_2(tu)_6](SO_4)\cdot 4H_2O$, **5**, produced in an aqueous solution reaction (see the Experimental Section). In the case of the latter reaction, an excess of tu was required to obtain an analytically pure product, and the product initially obtained was an oil, which solidified only upon cooling, whereas the mechanochemical reaction yielded the pure solid product directly, in one treatment. The yield of product from the mechanochemical synthesis was greater than the sum of the masses of the reactants, and consistent with the formation of the tetrahydrate.

An attempted synthesis of the previously reported $AgClO_4$/tu $(1:3)_2$[22] resulted in the isolation of a new hemihydrate form $AgClO_4$/tu/H_2O (2:6:1), **6**, with a different structure for the cation (see below).

Single Crystal X-Ray Studies. $AgNO_3$/tu (1:3), 1. The results of the single-crystal X-ray study are consistent with the present formulation, one such formula unit comprising the asymmetric unit of the structure. To a first approximation, the complex may be described as ionic, comprising a quasi-trigonal planar mononuclear $[Ag(tu)_3]^+$ cation (Table 2) and a nitrate anion; the latter is well-removed from any interaction with the silver atom and was modeled as disordered over two sets of sites (N$\cdots$N′ 0.57(1) Å), with occupancies set at 0.5 after trial refinement. There is a long Ag$\cdots$S contact (3.152(1) Å; cf. van der Waals 3.5 Å) which may be ascribed to a weak dimer formation (Figure 1a). As in a significant number of silver(I) coordination complexes, there is some ambiguity concerning the silver atom location and its coordination environment and number. A pair of significant residues, designated Ag(2,3), are located to either side of the primary silver atom Ag(1); refinement of the site occupancies within a total constraint of unity results in Ag(1,2,3) of 0.78(1), 0.11(1), 0.11(1), respectively, suggesting the disorder involving the Ag(2,3) components to possibly be concerted. Ag(2)$\cdots$Ag(2) $(1 - x, 1 - y, \bar{z})$ and Ag(3)$\cdots$Ag(3) $(x, 1/2 - y, 1/4 - z)$ are 1.99(2) and 2.12(2) Å, respectively, too close for simultaneous occupancy within each pair. However, alternate occupancy results in a plausible one-dimensional polymer about a crystallographic 4-axis along *c*, with Ag(2,3) both having plausible four-coordinate environments (Figure 1b; Table 2), the nitrate ions occupying tunnels about the alternative set of 4-axes (Figure 1c). As is usual in tu complexes, hydrogen bonds are a significant determinant of the lattice array. Somewhat unusually, there are no NH$\cdots$S interactions within the primary $[Ag(tu)_3]^+$ unit. However, from every NH_2 group, there is one NH$\cdots$S interaction to an adjacent unit in the columnar array up *c*, with the other hydrogen atom from each NH_2 group directed outward from the column, so that all disordered oxygen atom components of the adjacent anionic nitrate column are contacted.

Ag_2SO_4/tu/H_2O (1:6:4), 5. Very few (x)tu complexes have been defined with silver(I) sulfate and none at all structurally defined with thiourea as the ligand. Remarkably, despite the noncoordinating nature of the anion in all three 1:3 silver(I) oxoanion/tu complexes defined in the present work, the resulting cations are all different, perhaps an indicator of the extent to which, as participants in hydrogen-bonding, this may be a determinant of the nature of the resulting lattice, even to the detail of the cation component. In the present complex, the cation is binuclear; one-half of the formula unit comprises the asymmetric unit of the structure, the cation being centrosymmetric $[(tu\text{-}S)_2Ag((\mu\text{-}S\text{-}tu)_2Ag(S\text{-}tu)_2]^{2+}$, each silver atom being four-coordinated by a pair of terminal and a pair of bridging *S*-thiourea ligands (Table 3, Figure 2a). There are two independent sulfate groups: sulfate 1 lies with the sulfur atom disposed on a $\bar{4}$ axis; unlike sulfate 2, it is nicely ordered with the one independent oxygen atom involved in strong hydrogen bonding (Figure 2b). The sulfur atom of sulfate 2 is similarly disposed, but the oxygen atom is modeled as disposed over two equally populated sets of sites, both also involved in hydrogen bonding, in a number of situations to residues assigned and refined as water molecule oxygen atom fragments, O(1) ordered, fully occupied, and with hydrogen atoms sensibly located, the other disordered over a pair of equally occupied sites O(2,3). (No associated hydrogen atoms were located for these, but they are disposed at reasonable notionally hydrogen-bonding distances from other oxygen atom components.) There are also intracation hydrogen bonds of the usual type (Table 3). The present binuclear $[M_2tu_6]^{2+}$ cation form has a precedent, defined in the recently reported $AgNO_3$/etu $(1:3)_2$ adduct;[5] the dimensions in that array are similar, with the bridging sulfur atom similarly disposed in respect to the asymmetry in its Ag−S distances, perhaps induced by unsymmetrical (intracation) hydrogen-bonding associations, since the geometry remains more nearly four- rather than three-coordinate.

Numerous counterpart arrays for M = Cu have been summarized in Table 1 of ref 1.

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The structure of anhydrous $AgClO_4$/tu (1:3) has been previously reported[23] as having a similar binuclear cation, being $[Ag_2(tu)_6](ClO_4)_2$. The present synthesis, following that of ref 23, has surprised by yielding a different product of novel form, a hemihydrate.

$AgClO_4$/tu/H_2O (2:6:1), 6. The full formula unit comprises the asymmetric unit of the structure. Again, the complex is ionic, but in this, the third independent cationic form of 1:3 stoichiometry of the present paper, the form taken is that of a single-stranded polymer,...−tu)Ag(*S*-tu)$_2$(μ-*S*-tu)Ag(*S*−..., with two crystallographically independent...(μ-*S*-tu)Ag(tu)$_2$... units alternating in the strand, and in the asymmetric unit (Figure 3a). This is the first such example incorporating silver(I); with copper(I), three isomorphous examples are found, unexpectedly in the isomorphous arrays CuX/tu (1:3) (X = Cl, Br, I), where the anions are "softer".[1] Again, each silver atom is four-coordinated, by a pair of terminal *S*-tu and a pair of bridging μ-*S*-tu ligands; again, the pairs of Ag-(μ-*S*) distances show differences which are comparable with those found in the preceding dimer, despite the quite different Ag−S−Ag angles. The thiourea ligands are all oriented quasi-parallel to the polymer axis (*c*) with one exception (Figure 3b), so that five out of the six are involved in H···S hydrogen bonds along the polymer, presumably stabilizing it (Table 4). For the copper(I) arrays (averages over Cl, Br, I), Cu−S (bridging) distances are 2.371(12) and 2.412(21) and Cu−S (terminal-tu) are 2.285(4) and 2.349(3) Å. The Cu···Cu distances range between 4.379(1) and 4.4366(3) Å with concomitant divergence in (μ-)S−Cu−(μ-)S (113.87(2)−116.24(5)°), Cu−S−Cu being remarkably constant (<>134.44(11)°) and much larger than the silver(I) counterpart values (Table 4).

$AgNO_3$/tu (15:23), 3. A recent survey of structurally defined complexes found between simple silver(I) salts, AgX, and simple (substituted) thiourea ligands, (x)tu,[5] shows a variety of adducts of generally simpler form than their copper(I) counterparts,[1] of composition AgX/(x)tu (*x*:*y*), *x* and *y* being simple integers overwhelmingly of the form 1:*n*, *n* = 1, 2, 3, 4(,0.5), with complexity rarely greater than binuclear, except for small *x*:*y* ratios, where polymers may be found.[7] With this latter example in mind, there would be an overwhelming temptation on the basis of analysis alone to formulate the present material as a 1:1.5 complex. However, the results of the single-crystal X-ray study show the stoichiometry to be 15:23, one such formula unit comprising the asymmetric unit of the structure; the structure is nicely ordered and unsolvated. Selected bond lengths are given in Table 5. The complex is essentially an ionic polymer; interestingly, most anions have no interaction with silver atoms—the strongest, NO_3(3), has a single interaction, Ag(8)−O(31) = 2.459(3) Å, and the complex might thus be formulated as $[Ag_{15}(tu)_{23}(\mathit{O}NO_2)]^{14+}_{(\infty|\infty)}(NO_3^-)_{14}$, although there are weaker *O*NO_2 interactions with Ag(12,14), both at 2.666(2) Å. Nine of the silver atoms are four-coordinate, eight with AgS_4 coordination environments and one (or three) with AgS_3O, with Ag−S ranging widely between 2.4790(8) and 2.9456(8) Å. The other six are three-coordinate (AgS_3), Ag−S more tightly constrained between 2.4449(8) and 2.7525(9) Å. Angle sums at the latter are (Ag(7,9,11,12,14,15)) 357.6, 354.1$_4$, 350.3$_6$, 353.5$_7$, 359.6$_2$, and 359.9$_1$°, indicative of approaches, more or less effective, toward a trigonal planar stereochemistry for these atoms. A projection of the unit cell contents down *a* (Figure 4a) shows the partitioning of the cell contents, the polymeric cation components being disposed about $y = 1/4, 3/4$, the (majority of the) anions about $y = 0, 0.5$. Projection down *b* (Figure 4b) shows the cationic component to be primarily a one-dimensional polymer lying across the short cell diagonal, adjacent strands linked by a single bridging thiourea sulfur atom (S(18)) in a second dimension. All thiourea sulfur atoms are bridging between silver atoms; seven (S(4,8,10,11,14,15,21)) are triply bridging (μ_3), the remainder doubly (μ_2), although the assignment in a number of cases is not clear-cut, with 'μ_3'-S−Ag distances ranging upward toward 3 Å (see above). In complexes of the type AgX/(x)tu (*x*:*y*) in which X is (as is essentially the case here with the one exception) a noncoordinating anion, the structural types/motifs which have been defined are quite limited, confined to mononuclear $[Ag(\mu\text{-S-(x)tu})_n]^+$ and binuclear $[((x)tu\text{-}S)_nAg(\mu\text{-}S\text{-}(x)tu))_2Ag(S\text{-}(x)tu)_n]^{2+}$; the systems which have been defined all have AgX/(x)tu ratios greater than the present, being 1:2,[23−25] 3,[22,26−29] and 4.[5] With copper(I), lower ratios are found, leading to oligonuclear forms, in which tetranuclear species $[Cu_4((x)tu)_x]^{4+}$ predominate,[1] and it would not surprise to find parallels between the motifs found in species of that type and silver(I) complexes of low AgX/(x)tu ratios such as the present. The present polymer, the Ag/S/(O) framework of which is shown in Figure 4c, is comprised of four-, six-, and eight-membered $(AgS)_{2n}$ rings—five four-membered ('a$_n$'), five six-membered rings ('b$_n$'), and four eight-membered ('c$_n$'). The four-membered rings generally deviate appreciably from planarity, with "fold" angles (across their S···S lines) of 32.13(6), 39.64(6), 31.54(6), 45.88(6), and 40.33(6)° for rings a_1−a_5, respectively; the pyramidalizations of the three-coordinate sulfur atoms and the proto-tetrahedral four-coordinate silver atoms result in considerable folding throughout the polymer, resulting in incipient formation of three-dimensional motifs, none of which, however, is closed, in the manner found in the $[Cu_4((x)tu)_x]^{4+}$ forms.

Given the bridging nature of the sulfur atoms in the present structure, it is not surprising to find that, among the 90 hydrogen bonds ascribed to the 92 hydrogen atoms, only 10 hydrogen-bond to sulfur atoms (eight of these μ_2), all others being to nitrate oxygen atoms. All of the latter (except O(31),

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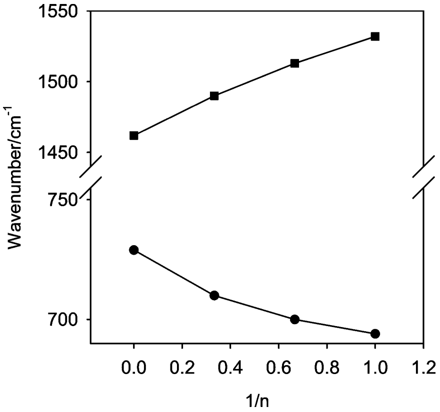

Figure 5. Plot of the ν(CS) and ν_a(CN) wavenumbers for $AgNO_3$/tu (1:*n*) (*n* = 1, 1.5, and 3; **4**, **2**, and **1**) and uncomplexed tu (*n* = ∞) as a function of 1/*n*.

the most strongly coordinated to a silver atom) are involved in at least one hydrogen bond.

Vibrational Spectroscopy. The ν(CS) and ν_a(CN) wavenumbers for $AgNO_3$/tu (1:*n*) (*n* = 1, 1.5, 3) show a monotonic increase and decrease, respectively, with increasing *n* (Table 6). Plotting the wavenumbers as a function of 1/*n* allows a comparison of these with the values for uncomplexed tu (*n* = ∞), and this plot is shown in Figure 5. From this, it is apparent that coordination of the tu ligand results in a decrease in the strength of the C−S bond and an increase in the strength of the C−N bonds, and this effect increases with decreasing *n*. The latter trend is entirely as expected, since the ability of the silver atom to coordinate to the tu ligand is greater when the number of such ligands is smaller with increased tendency toward the formation of μ_2- and μ_3-*S* coordination modes. Of the tu ligand vibrational modes, the ν_a(CN) mode is the most sensitive to coordination. In the case of $AgNO_3$/tu (1:*n*) (*n* = 1, 1.5, 3), the band associated with this mode is fairly sharp, but for $AgNO_3$/tu (15:23), this band, which shows a maximum at 1510 cm^{-1}, is rather broad, with shoulders at 1500 and 1530 cm^{-1}. This is consistent with the crystal structure (see above), which shows a large number of different Ag/tu interactions. A larger effect of this kind is seen in a comparison of the ν_a(CN) wavenumbers for $AgNO_3$/tu (1:3) and Ag_2SO_4/tu/H_2O (1:6: 4); in the latter case, the ν_a(CN) band is split into two components at 1500 and 1478 cm^{-1} (Table 6). The average of these, 1489 cm^{-1}, is very close to the value of 1490 cm^{-1} observed for $AgNO_3$/tu (1:3; Table 6), which is appropriate for the Ag/tu ratio 1:3 that applies to both compounds. However, the primary structural unit in the nitrate is the $[Ag(tu)_3]^+$ unit (see above), in which all three tu ligands are terminally bound to the silver, which is consistent with the presence of a single ν_a(CN) band in the IR. The presence of two such bands in the sulfate might be considered to be due to the presence of both bridging and terminal tu ligands in the dimeric $[Ag_2(tu)_6]^{2+}$ cation present in this compound. However, the factor that is most likely to affect the vibrational frequency is the strength of interaction of the tu ligand with the Ag atom, as reflected in the Ag−S bond length. The crystal structure (see above) shows that that there is not a close relationship between the Ag−S bond length and the terminal or bridging nature of the ligand. There are two short bonds (Ag−S(2) = 2.5148(7) (terminal); Ag−S(3^i) = 2.5204(7) Å (bridging)) and two longer bonds (Ag−S(1) = 2.5857(7) (terminal); Ag−S(3) = 2.7363(7) Å (bridging); Table 3, Figure 2a), and the presence of two ν_a(CN) bands is attributed to the presence of these two groups of short and longer Ag−S bonds. This interpretation is supported by the fact that the perchlorate complex does not show a resolved splitting of the ν_a(CN) band, despite the presence of both terminal and bridging tu ligands in the complex (Figure 3a). There are eight Ag−S distances from Ag−S(1) = 2.5070(7) to Ag(1)−S(6) = 2.7942(9) Å in this complex (Table 4, Figure 3a), and this apparently results in a greater number of ν_a(CN) frequencies for the coordinated tu, so that only a relatively broad, unresolved band is observed with a maximum absorbance at 1491 cm^{-1} (Table 6). This, however, is exactly at the position expected for a complex of 1:3 Ag^+/tu stoichiometry (Figure 5). Similar behavior to that described above is observed for the ν(AgS) bands in the far-IR spectra of the sulfate and perchlorate complexes (see below).

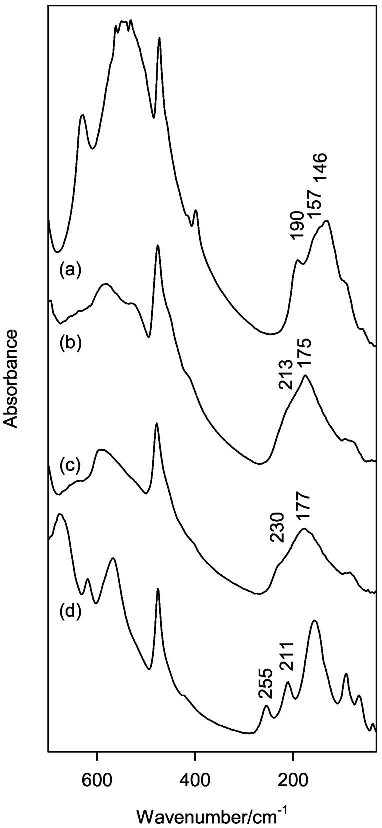

Figure 6. Far-IR spectra of $AgNO_3$/tu adducts (a) 1:3, **1**; (b) 15:23, **3**; (c) 1:1.5, **2**; (d) 1:1, **4**. Bands assigned to ν(AgS) are labeled with their wavenumbers.

The far-IR spectra of $AgNO_3$/tu (1:3, 15:23, 1:1.5, and 1:1) are shown in Figure 6. The region above 400 cm^{-1} contains bands due to coordinated thiourea, and these can readily be assigned in accordance with previous studies.[11] The region below 300 cm^{-1} contains bands due to the presence of Ag−S linkages. We have previously shown that a good correlation exists between ν(CuS) and the Cu−S distance *d*(CuS) in a number of copper(I) thiourea complexes, and this is illustrated in Figure 7 for the complexes

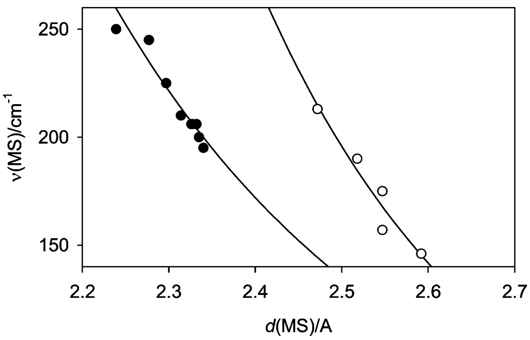

Figure 7. Correlation between ν(MS) and the M−S bond length d(MS) for $AgNO_3$/tu (1:3), **1**, abd $AgNO_3$/tu (15:23), **3** (○) (M = Ag; this work), and for Cu_2SO_4/tu/H_2O (1:5:3) and Cu_2SO_4/tu/H_2O (1:6:1) (•) (M = Cu; data from ref 11).

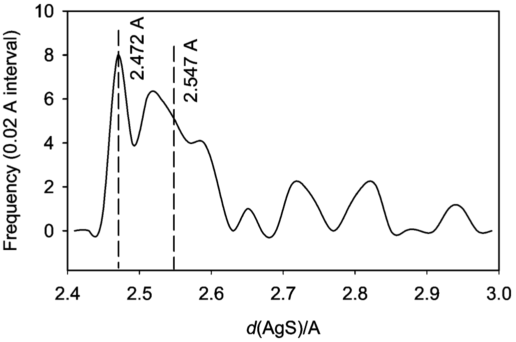

Figure 8. Frequency of occurrence of Ag−S bond lengths (within a 0.02 Å interval) as a function of the bond length for $AgNO_3$/tu (15:23), **3** (data from Table 5).

$[Cu_2(tu)_5](SO_4)\cdot 3H_2O$ and $[Cu_2(tu)_6](SO_4)\cdot H_2O$. The present results for the $AgNO_3$/tu complexes provide an opportunity to investigate the possibility of a similar relationship for silver(I) complexes. The situation is not as straightforward as it was for the copper(I) complexes, due to the greater complexity of the structures of the $AgNO_3$/tu complexes. However, it is possible to get some indication of the nature of the relationship between ν(AgS) and d(AgS) in $AgNO_3$/tu (1:3) and $AgNO_3$/tu (15:23) from the following considerations. Although the structure of $AgNO_3$/tu (1:3) shows a degree of disorder, the predominant Ag site occupancy (corresponding to the $[Ag(tu)_3]^+$ cationic form) is Ag(1) (78%). This has the coordination environment shown in Figure 1a, with Ag(1)−S(1,2,3) = 2.547(2), 2.518(2), 2.592(1) Å respectively. Ag(1)−S(2) is the shortest Ag−S distance in the complex, and we associate this with the band at 190 cm^{-1}, the highest wavenumber band in the region below 300 cm^{-1} (Figure 6a). Two partially resolved shoulders at 157 and 146 cm^{-1} are assigned to the Ag(1)−S(1) and Ag(1)−S(3) bonds, respectively. The situation for $AgNO_3$/tu (15:23) is potentially far more complex, but the far-IR spectrum shows a single band at 175 cm^{-1}, with a shoulder at 213 cm^{-1} (Figure 6b). The Ag−S bond lengths in this compound cover a wide range (Table 5), but most of the values may be considered as falling into two groups: 11 in the range below 2.49 Å (<>2.472(12) Å) and 29 in the range 2.49−2.62 Å (<>2.55(3) Å) (see Figure 8). We therefore assign the 213 cm^{-1} shoulder to the former and the 175 cm^{-1} band to the latter of these groups. The ν(AgS) versus d(AgS) correlation that results from the assignments discussed above for $[Ag(tu)_3](NO_3)$ and $AgNO_3$/tu (15:23) is shown in Figure 7. Also shown in Figure 7 are the fits of the ν(MS) data to the equation

$$\nu/\mathrm{cm}^{-1} = b(r/\text{Å})^{-m} \tag{1}$$

where $r = d$(MS) and b = 31 180 and 374 110 and m = 5.94 and 8.25 for M = Cu and Ag, respectively. Similar relationships have been recorded previously for ν(MX) (X = Cl, Br, I) in a wide range of copper(I), silver(I), and gold(I) halide complexes,[30−32] and the above results for copper(I)/thiourea complexes were reported previously, together with corresponding results for copper(I)/ethylenethiourea compounds.[11] While the band assignments that form the basis of the above correlation for the silver(I)/thiourea compounds are rather less certain because of the complicated structures of the complexes involved, comparison of the curves in Figure 7 for the copper(I) and silver(I) complexes suggests that these assignments are reasonable. The decrease in ν(MS) and the increase in d(MS) from M = Cu to Ag is entirely in line with expectations based on the greater atomic mass and size of Ag relative to Cu, and the relative slopes of the curves and positions of the data points in Figure 7 are very similar to those for copper(I) and silver(I) ethylenethiourea complexes.[5]

The far-IR spectra of $AgNO_3$/tu (1:1.5) and (1:1) (Figure 6c,d) show bands at 230 and 177 (1:1.5) and at 255 and 211 cm^{-1} (1:1) that can be assigned as ν(AgS). It is perhaps not surprising that the spectrum of the 1:1.5 complex is very similar to that of the 15:23 (= 1:1.5333) compound, given the close similarity in their composition. However, there is a definite upward shift in the ν(AgS) wavenumbers with decreasing $AgNO_3$/tu ratio, implying the presence of significantly shorter Ag−S bonds in the 1:1.5 compound. This trend continues in the 1:1 complex, which shows two well-resolved ν(AgS) bands at 255 and 211 cm^{-1}.

The structure of this compound is not known, but a one-dimensional polymeric structure involving a linear chain of two-coordinate silver atoms with doubly bridging thiourea ligands alternating above and below the chain has been proposed.[20] This structure would appear to be ruled out by the far-IR data because all of the Ag−S bond lengths should be equal in such a structure, whereas the far-IR spectrum suggests the presence of two quite different bond lengths. The band at 156 cm^{-1} is assigned to δ(AgSC) bending, the counterpart of δ(CuSC) bands that occur at about 170 cm^{-1} in copper(I)/tu complexes.[11] This probably contributes to absorption on the low wavenumber side of the broad ν(AgS) bands observed in the other $AgNO_3$/tu compounds (Figure 6).

The far-IR spectra of Ag_2SO_4/tu/H_2O (1:6:4) and $AgClO_4$/tu/H_2O (2:6:1) are shown in Figure 9. According to the relationship shown in Figure 7 for the M = Ag case, the

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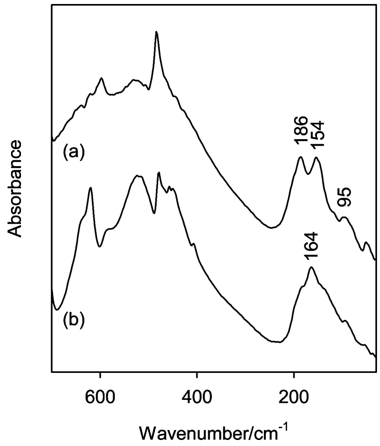

Figure 9. Far-IR spectra of (a) Ag_2SO_4/tu/H_2O (1:6:4), **5**, and (b) $AgClO_4$/tu/H_2O (2:6:1), **6**. Bands assigned to ν(AgS) are labeled with their wavenumbers.

four Ag−S bond lengths in the sulfate complex correspond to ν(AgS) = 93, 148, 183, and 187 cm^{-1}. This agrees well with the observed spectrum (Figure 9a), which shows ν(AgS) bands at 95, 154, and 186 cm^{-1}. A corresponding analysis for the structurally more complex perchlorate compound yields eight ν(AgS) values in the range 80−190 cm^{-1}, with the most frequently occurring bond length (Ag(1)−S(2), Ag(2)−S(6) = 2.554 Å) corresponding to ν(AgS) = 164 cm^{-1}. This agrees well with the observed spectrum (Figure 9b), which shows a broad ν(AgS) band in the range 80−200 cm^{-1}, with a peak at 164 cm^{-1}.

Conclusion

An investigation of the silver(I) nitrate/thiourea system, exploiting the uniquely powerful access provided by the recently developed combination of mechanochemical synthesis coupled with vibrational spectroscopy, has resulted in the identification of solid adducts $AgNO_3$/tu (x:y) for x:y = 1:1, 1:1.5, 15:23 (= 1:1.5333), and 1:3. This contrasts with previously published claims for the existence of 1:2 and 1:4 complexes and was confirmed in the case of the 1:3 and 15:23 complexes by X-ray crystal structure determinations on samples prepared by crystallization from aqueous solution. The mechanochemical study demonstrated a previously unknown advantage of solvent-assisted mechanochemical synthesis, namely, the suppression of unwanted side reactions that lead to impure products in conventional solution-based synthesis, and exploitation of this technique in the present work has been fundamental in enabling the access of new and surprising stoichiometries and forms, such as the remarkable, essentially ionic 15:23 nitrate complex $[Ag_{15}(tu)_{23}(ONO_2)]^{14+}_{(\infty|\infty)}(NO_3^-)_{14}$. The ν(CS) and ν_a(CN) bands in the infrared spectra of the complete series of adducts show a monotonic wavenumber decrease and increase, respectively, with decreasing tu content of the adduct, indicating a decrease in the C−S bond strength and a concomitant increase in the C−N bond strength with increasing Ag−S bond strength. The increase in Ag−S bond strength with decreasing tu content is also indicated by an increase in the wavenumbers of the bands assigned to ν(AgS) in the 140−200 cm^{-1} region in the far-IR. These and the structural data for the 1:3 and 15:23 complexes provide the basis for establishing a correlation between ν(AgS) and the Ag−S bond length d(AgS) for silver complexes involving the tu ligand. We have defined three different cation forms for complexes of 1:3 Ag/tu stoichiometry, with distinctive IR spectra for each, which are of potential value in identifying the form taken in other 1:3 complexes.

Supporting Information Available: Expanded versions of Tables 2−5 containing additional structural parameters (bond angles and H-bonding distances). This material is available free of charge via the Internet at http://pubs.acs.org.

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