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CRYSTAL STRUCTURE OF A SILVER(I) COMPLEX $\{[Ag(N\text{-METHYLTHIOUREA})_2]NO_3\}_n$ EXHIBITING INFINITE CHAINS OF AgS_4 TETRAHEDRA© 2011 **Habib-ur-Rehman**¹, **S. Ahmad***², **H. Ajaz**², **M. Hanif**², **M. Altaf**³, **H. Stoeckli-Evans**³¹*Exxelis Limited, ETTC/Biospace, Mayfield Road, Edinburgh EH9 3JF, UK*²*Department of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan*³*Institute of Physics, University of Neuchâtel, CH-2009 Neuchâtel, Switzerland*

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A polymeric silver(I) complex, bis(*N*-methylthiourea)silver(I) nitrate, $\{[Ag(Metu)_2]NO_3\}_n$ is prepared and its crystal structure is determined by X-ray crystallography. The compound crystallizes in the monoclinic *C2/c* space group. In the structure, distorted AgS_4 tetrahedra are linked through the sulfur atoms of the Metu ligand to form isolated infinite chains of the type $[Ag(SR)_2]_n^{n+}$. The cationic chains are separated from each other by nitrate ions that do not coordinate to the metal ion. The chains are bridged via N—H...O hydrogen bonds involving the nitrate ions. The complex exhibits an Ag---Ag separation of ~ 3.21 Å indicating the existence of significant argentophilic interactions. An upfield shift in the $>C=S$ resonance of Metu in ^{13}C NMR and downfield shift in the N—H resonance in 1H NMR are consistent with sulfur coordination to silver(I).

Key words: Silver(I) complexes, *N*-methylthiourea, crystal structure.**INTRODUCTION**

The study of the coordination behavior of thiones is of considerable interest due to their variable binding modes and the relevance of their binding sites to those in living systems [1—18]. Moreover, thiourea complexes are starting materials in chemical spray pyrolysis processes used to produce sulfide thin films [19]. Structural studies on silver(I) complexes of thiourea and its derivatives have shown that silver(I) is quite variable in the geometries of its sulfur coordination, which can vary between linear, trigonal planar and tetrahedral [4, 8—13]. These studies demonstrate that thiones can act both as terminal [8—10] or bridging [4, 11, 12] ligands to form polymeric structures, such as $[Ag_2(Tmtu)(CN)_2]_n$ (Tmtu = tetramethylthiourea) [4]. The versatility in bonding modes is attributed to a large size of the sulfur atom, which makes it easier to adopt different angles at this atom in complexes [20, 21]. The importance of these compounds also motivated us to investigate their structural properties and consequently, we reported the crystal structures of several such complexes [2—5]. Here, we report the crystal structure of bis(*N*-methylthiourea)silver(I) nitrate $[Ag\{SC(NH_2)\times(HN(CH_3))_2\}_2]NO_3$ (**1**) that crystallizes in the form of a linear polymeric chain.

EXPERIMENTAL

Materials. Silver nitrate was obtained from Panreac Chemical Company, Spain and *N*-Methylthiourea (Metu) was purchased from Acros Organics, Belgium.

Synthesis of $\{[Ag(Metu)_2]NO_3\}_n$ (1**).** Complex **1** was prepared by adding 2 mmolar methanolic solution of Metu to 0.17 g (1 mmol) $AgNO_3$ in methanol followed by the addition of one equivalent of PPH_3 (taken in 15 ml acetonitrile). A clear solution was obtained, which was stirred for 25—30 mi-

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Table 1

Summary of crystal data and details of structure determination

Crystal data	
Formula	$\text{C}_4\text{H}_{12}\text{AgN}_5\text{O}_3\text{S}_2$
Formula weight	350.18
Crystal system	Monoclinic
Space group	$C2/c$
$a, b, c, \text{\AA}$	19.2430(16), 6.4315(4), 18.4142(15)
$\alpha, \beta, \gamma, \text{deg.}$	90, 90.884(7), 90
$V, \text{\AA}^3$	2278.7(3)
Z	8
$\rho_{\text{calc}}, \text{g/cm}^3$	2.041
$\mu(\text{MoK}\alpha), \text{mm}^{-1}$	2.132
$F(000)$	1392
Crystal size, mm	0.50×0.24×0.22
Data collection	
Temperature, K	173
$\lambda\text{MoK}\alpha, \text{\AA}$	0.71073
$\theta\text{Min—Max}, \text{deg.}$	2.12—29.25
h, k, l limits	−26:26, −8:8, −25:25
Reflns: Total, Uniq. Data, R_{int}	21253, 3083, 0.0289
Observed data [$I > 2\sigma(I)$]	2720
Absorption: $T_{\text{min}}/T_{\text{max}}$	0.4325/0.6696
Refinement	
Nref, Npar	3083, 138
$R, wR2, S$	0.0194, 0.0463, 1.053
$w = [\sigma^2(F_o^2) + (0.0242P)^2 + 1.6454P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$	
Max. and Av. Shift/Error	<0.001, <0.001
Min. and Max. Resd. Dens., e/\AA^3	−0.380, 0.507

nute. The solution was filtered and the filtrate was kept at room temperature for crystallization. As a result, a white crystalline product was obtained, that was washed with methanol and dried. Yield 0.1 g (30 %); m.p. 171—172 °C.

IR and NMR Measurements. The IR spectrum of complex **1** was recorded as KBr pellets on a Perkin Elmer Spectrum One FTIR spectrophotometer in the 4000—450 cm^{-1} range. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX 350 MHz using $\text{DMSO-}d_6$ as solvent. TMS was used as the internal standard.

X-ray Structure Determination. Single crystal data collection for complex **1** was performed at 173 K on a Stoe Mark II-Image Plate Diffraction System [22] equipped with a two-circle goniometer and using $\text{MoK}\alpha$ graphite monochromated radiation. Diffraction data for **1** were collected using image plate distance 100 mm, ω rotation scans 0—180° at ϕ 0°, and 0—79° at ϕ 90°, step $\Delta\omega = 1.0^\circ$, exposures of 4 min per image, 2θ range 2.29—59.53°, $d_{\text{min}}—d_{\text{max}} = 17.779—0.716 \text{\AA}$. The structure was solved by direct methods using the SHELXS-97 program [23]. The refinement and all further calculations were carried out using SHELXL-97 [23]. The H atoms were included in calculated positions and treated as riding atoms: N—H = 0.88 \AA , C—H = 0.98—0.99 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (parent N or C atom). The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . An empirical absorption correction was applied using the MULscanABS routine in PLATON [24]; transmission factors: $T_{\text{min}}/T_{\text{max}} = 0.4325/0.6696$. Crystal data and details of the data collection are summarized in Table 1.

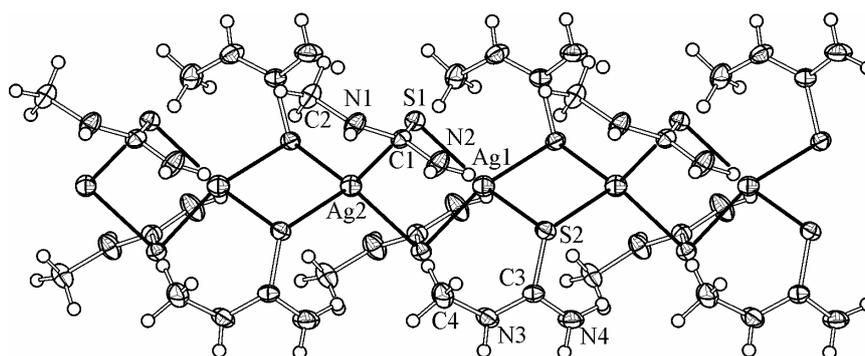


Fig. 1. A view of the molecular structure of $\{[Ag(Metu)_2]^{n+}\}_n$ (**1**), with complete atom labeling scheme and anions have been omitted for the clarity of structure. Displacement ellipsoids are drawn at the 50 % probability level

RESULTS AND DISCUSSION

IR and NMR Studies. The reaction of $AgNO_3$ with Metu and PPh_3 in a 1:2:1 molar ratio resulted in a product of the composition $[Ag(Metu)_2]NO_3$. The absence of PPh_3 in the bulk of the sample was verified by ^{31}P NMR that gave no signal for PPh_3 . Triphenylphosphine probably assisted the formation of the title complex, because the same product could not be obtained when $AgNO_3$ was treated with Metu alone. In the IR spectrum of **1**, the characteristic bands were observed in three frequency regions; $\nu(C=S)$ at 676 cm^{-1} , $\nu(C-N)$ at 1570 cm^{-1} and $\nu(N-H)$ at 3279 & 3176 cm^{-1} . For free Metu these bands are observed at 634 , 1488 and 3245 & 3163 cm^{-1} respectively. A sharp band at 819 cm^{-1}

Table 2

Selected bond distances (Å) and bond angles (deg.)

Bond distances			
Ag(1)—S(1)	2.5881(4)	S(1)—C(1)	1.7296(16)
Ag(1)—S(2)	2.6117(4)	S(2)—C(3)	1.7308(15)
Ag(1)—Ag(2)#2	3.2151(3)	N(1)—H(1N)	0.8800
Ag(1)—Ag(2)	3.2164(3)	N(2)—C(1)	1.321(2)
Ag(2)—S(2)#2	2.5869(4)	N(2)—H(2NA)	0.8800
Ag(2)—S(1)	2.6046(4)	N(2)—H(2NB)	0.8800
N(1)—C(1)	1.314(2)	N(3)—C(3)	1.319(2)
N(1)—C(2)	1.444(2)	N(3)—C(4)	1.443(2)
Bond angles			
S(1)#1—Ag(1)—S(1)	103.918(19)	S(1)—Ag(2)—Ag(1)#4	128.503(9)
S(1)—Ag(1)—S(2)#1	112.129(13)	S(2)#3—Ag(2)—Ag(1)	127.857(9)
S(1)—Ag(1)—S(2)	113.039(13)	C(1)—S(1)—Ag(1)	109.17(5)
S(2)#1—Ag(1)—S(2)	102.901(18)	C(1)—S(1)—Ag(2)	99.79(5)
S(1)#1—Ag(1)—Ag(2)#2	128.041(9)	Ag(1)—S(1)—Ag(2)	76.544(12)
S(2)—Ag(1)—Ag(2)	128.550(9)	C(3)—S(2)—Ag(2)#2	111.34(5)
Ag(2)#2—Ag(1)—Ag(2)	180	C(3)—S(2)—Ag(1)	97.30(5)
S(2)#3—Ag(2)—S(2)#4	104.287(19)	Ag(2)#2—S(2)—Ag(1)	76.406(13)
S(2)#3—Ag(2)—S(1)	112.006(13)	C(1)—N(1)—C(2)	125.75(15)
S(2)#4—Ag(2)—S(1)	112.918(13)	C(3)—N(3)—C(4)	125.77(15)
S(1)—Ag(2)—S(1)#1	102.994(18)	O(2)—N(5)—O(1)	117.94(15)

Symmetry operators: #1: $x, -1+y, z$, #2: $x, 1+y, z$, #3: $-x, -1+y, 1/2-z$, #4: $-x, y, 1/2-z$.

was observed for the non-coordinated NO_3^- ion [25]. A peak at 3405 cm^{-1} indicates the presence of hydrogen bonds in the complex.

In ^1H NMR spectra of the complexes, the N—H signals of Metu became less intense upon coordination and shifted downfield from their positions in free ligands (7.81, 8.36, 8.54 Vs 6.99, 7.51, 7.70 ppm). The spectrum further showed that N—H protons of Metu were nonequivalent (NH_2 appeared as a doublet). The appearance of a N—H signal shows that Metu is coordinated to silver(I) via a thione group. In ^{13}C NMR, the $>\text{C}=\text{S}$ resonance shifted upfield by 4—5 ppm as compared to the free ligand resonances in accordance with the data observed for other complexes of silver(I) with thiones [25—29]. The upfield shift is attributed to a lowering of the C—S bond order upon coordination and a shift of the $\text{N}\rightarrow\text{C}$ electron density producing partial double bond character in the C—N bond [25]. A small deshielding effect is observed in methyl carbon atoms, which is due to an increase in the π character of the C—N bond. It should be noted that Metu gives two signals for both $>\text{C}=\text{S}$ (176.0, 180.0 ppm) and N— CH_3 (30.7, 32.1 ppm) carbons showing that Metu exists in two different forms. However, the downfield signals are of less intensity. For free Metu these resonances appear at 181.0 & 184.0 and 29.8 & 31.0 ppm respectively.

X-Ray Structure Description. The molecular structure of **1**, along with the crystallographic numbering scheme, is shown in Fig. 1. Selected bond distances and bond angles are given in Table 2. The structure is ionic and consists of $[\text{Ag}(\text{Metu})_2]^+$ cationic units and nitrate counter ions. The cationic units are linked through sulfur atoms of bridging Metu ligands to form a linear chain of the type $[\text{Ag}(\text{SR})_2]_n^{n+}$ running parallel to the c axis, as shown in Fig. 2. These chains are separated from each other by nitrate anions that do not coordinate to the metal atoms. The silver atom is tetrahedrally coordinated to four sulfur atoms from Metu molecules with S---Ag---S angles varying from $102.901(18)^\circ$ to $113.918(19)^\circ$. The values are indicative of some distortion of the AgS_4 tetrahedra. The compound is

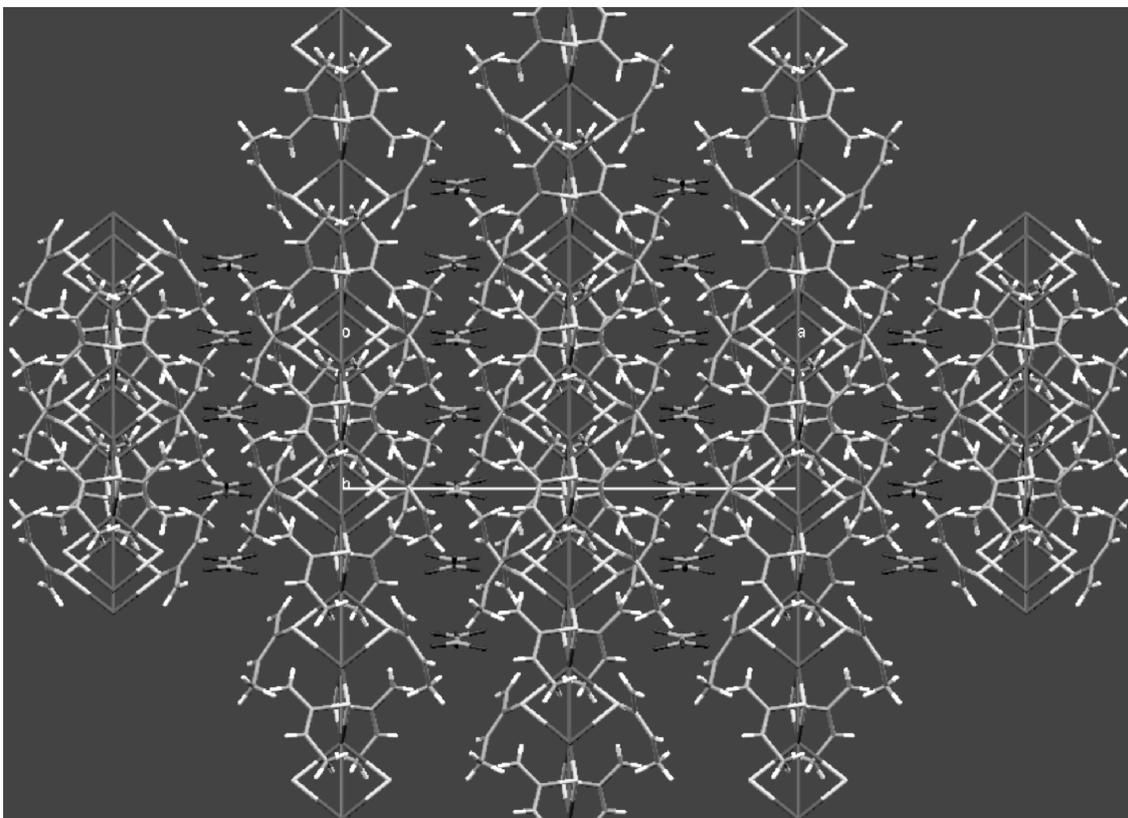


Fig. 2. A view of the molecular structure of compound **1** along c -axis, showing the parallel polymeric chains separated by nitrate counter ions

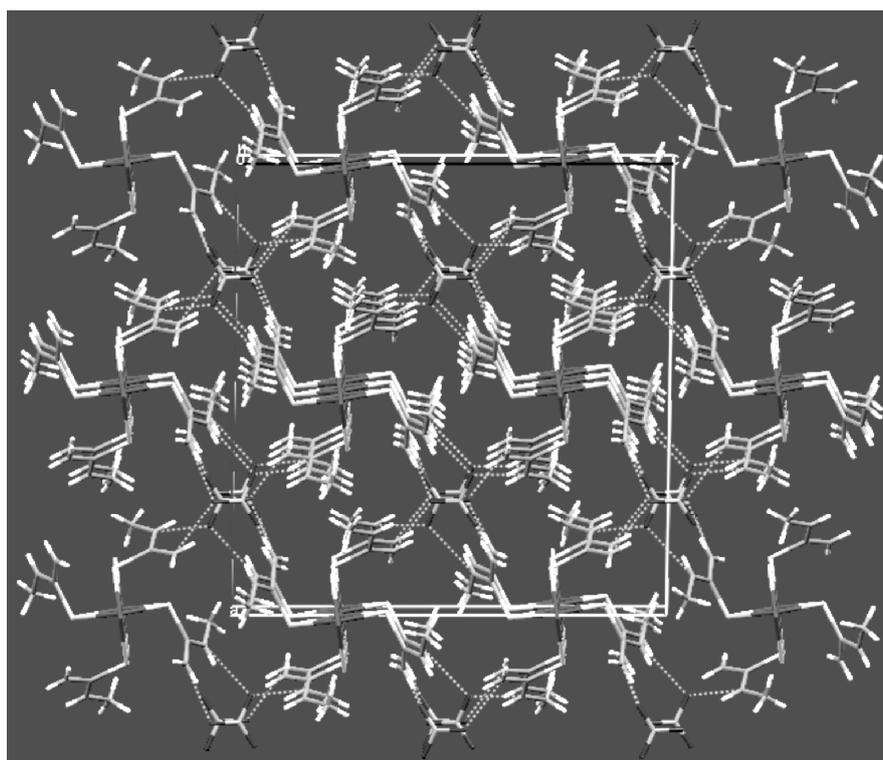


Fig. 3. A view of the molecular structure of compound **1** along *b*-axis, showing the N—H...O hydrogen bonds as dotted lines

isostructural to copper(I) complex bis(*N,N'*-dimethylthiourea)copper(I) nitrate $\{[\text{Cu}(\text{Dmtu})_2]\text{NO}_3\}_n$ [30].

In a previously reported silver(I) complex with three Metu molecules chlorotris(methylthiourea)silver(I) [9], the Metu ligand behaves as a terminal ligand, and the structure consists of independent distorted tetrahedral Ag(I) moieties with only weak hydrogen bonds and/or van der Waals interactions between molecules. On the other hand, in the title complex, the Metu ligand binds to two silver atoms in a bridging mode, and as a result, a polymeric structure is formed. The average Ag---S---Ag bond angle is $76.475(9)^\circ$, and the average Ag...Ag distance in the four-membered Ag---S---Ag---S rings is $3.2157(2)$ Å. This value is considerably shorter than the sum of the van der Waals radii of two Ag(I) centers (3.44 Å), which is considered to be the upper limit of the distance for viable argentophilic interactions [31–34]. Other bond lengths observed in the title complex are comparable to those in the reported complexes [2, 7–12]. The two crystallographically independent Metu molecules bonded to the central metal atom are not co-planar, having a dihedral angle of $80.60(7)^\circ$.

Within the crystal package, $[\text{Ag}(\text{Metu})_2]^+$ units and NO_3^- ions are connected through hydrogen bonds. All N—H bonded hydrogen atoms are involved in hydrogen bonding. Bridging of the individual chains of edge sharing AgS_4 tetrahedra occurs via these hydrogen bonds only. Both intermolecular and intramolecular hydrogen bonds are observed in the solid state structure of complex **1**. These non-covalent intermolecular interactions result in a two-dimensional hydrogen bonded polymeric chain architecture as shown in Fig. 3. Hydrogen bond length details are listed in Table 3.

SUPPLEMENTARY DATA

Crystallographic data (excluding structure factors) for structure **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. 691143 CCDC (**1**). Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3

Hydrogen bond distances and angles (Å, deg.)

Donor-H...Acceptor	D—H	H...A	D...A	D—H...A	Donor-H...Acceptor	D—H	H...A	D...A	D—H...A
N2—H2NA...O2	0.88	2.09	2.9394	161	N4—H4NA...O2	0.88	2.09	2.8556	145
N2—H2NA...O3	0.88	2.58	2.9273	105	N3—H3N...O1	0.88	2.36	2.9748	127
N1—H1N...O1	0.88	2.11	2.9160	152	N3—H3N...O2	0.88	2.35	3.0725	140
N2—H2NB...S2	0.88	2.67	3.5172	162	N4—H4NB...S1	0.88	2.72	3.5876	169

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