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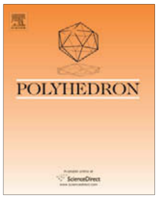

Synthesis, characterization and antimicrobial studies of mixed ligand silver(I) complexes of thioureas and triphenylphosphine; crystal structure of $\{[Ag(PPh_3)(thiourea)(NO_3)]_2{\cdot}[Ag(PPh_3)(thiourea)]_2(NO_3)_2\}$

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ABSTRACT

Mixed ligand silver(I) complexes of triphenylphosphine and thioureas (thiourea (Tu), *N*-methylthiourea (Metu), *N,N′*-dimethylthiourea (Dmtu) and *N,N′*-diethylthiourea (Detu)) with the general formulae, $[(Ph_3P)_2Ag(thione)]NO_3$ and $[(Ph_3P)Ag(thione)_2]NO_3$, have been prepared and characterized by elemental analysis, IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopic methods. The crystal structure of one of them has been determined by X-ray crystallography. The spectral data of the complexes are consistent with sulfur coordination of the thiones to silver(I). The single crystal X-ray structure of complex **1**, $\{[Ag(PPh_3)(thiourea)(NO_3)]_2{\cdot}[Ag(PPh_3)(thiourea)]_2(NO_3)_2\}$, shows that the complex consists of two independent centrosymmetric binuclear units, each having the silver atoms coordinated to one PPh_3 and two bridging thiourea molecules. In one of the independent units the silver atom is additionally bound to a nitrate ion, leading to a tetrahedral geometry, while in the other unit the silver atom adopts a trigonal planar environment. Antimicrobial activities of the complexes were evaluated by their minimum inhibitory concentration and the results showed that the complexes show a wide range of activity against two gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*) and molds (*Aspergillus niger, Penicillium citrinum*), while the activities were poor against yeasts (*Candida albicans, Saccharomyces cerevisiae*). However, the title complex did not show activity against any tested microorganism.

1. Introduction

The coordination chemistry of silver(I) complexes with phosphorus and sulfur donor ligands has attracted great interest in recent years because of the biological relevance of metal–sulfur interactions in the living systems and the potential applications of silver–phosphine complexes as antitumor/antibacterial agents [1–15]. In view of this, the crystal structures of several silver(I) complexes of phosphines and thioamides have been reported, which describe that these complexes are either mononuclear or dinuclear with the silver atom showing a distorted tetrahedral or trigonal configuration [2,3,9,16–23]. We are particularly interested in the spectral and structural chemistry of M–P and M–S complexes, and in this regard we have already reported the spectroscopic and structural characterization of a number of silver(I) and gold(I) complexes with phosphines and thiones [5,9,24–29]. In this work, our study is continued with the preparation, characterization and biological properties of silver(I) complexes of the general formula, $[Ag(PPh_3)_n(thioamide)_n]NO_3$, including the crystal structure of a tetranuclear silver(I) complex, $\{[Ag(PPh_3)(thiourea)(NO_3)]_2{\cdot}[Ag(PPh_3)(thiourea)]_2(NO_3)_2\}$. The structures of the thiourea ligands used in this study are given in Scheme 1.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$) was obtained from Panreac, Spain and triphenylphosphine (PPh_3) from Alfa Aesar, USA. Thiourea was a product of Merck, Germany. Other thiourea derivatives were purchased from Acros Organics, Belgium.

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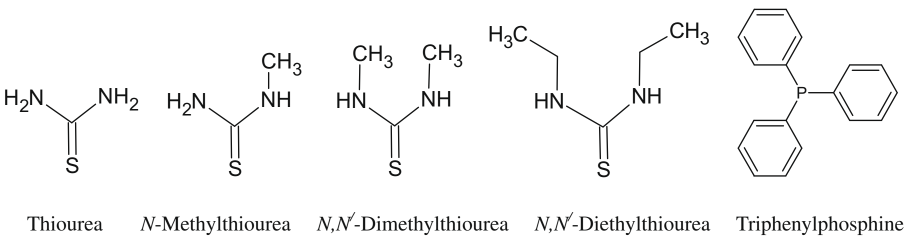

Scheme 1. Structures of the ligands used in this study.

2.2. Synthesis of the complexes

The complexes were prepared by adding one or two equivalents of a thione dissolved in 15–20 mL methanol (Detu was taken in water) to a 1:1 mixture of $AgNO_3$ and PPh_3 in methanol–acetonitrile medium (10 mL and 15 mL, respectively). In each case, mixing resulted in a clear solution that was stirred for a further 30 min. The solutions were filtered and the filtrates were kept at low temperature for crystallization. The white crystalline products obtained were isolated and air-dried. The elemental analyses and melting points of the complexes are given in Table 1.

2.3. IR and NMR measurements

The IR spectra of the complexes were recorded on a Perkin–Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}. The ^1H NMR spectra of the complexes in DMSO-d_6 were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at a frequency of 500.00 MHz at 297 K using 0.10 M solution. The ^{13}C NMR spectra were obtained at a frequency of 125.65 MHz with ^1H broadband decoupling at 298 K. The spectral conditions were: 32 K data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{13}C chemical shifts were measured relative to TMS.

2.4. X-ray structure determination

Single crystal data collection for complex **1** was performed at 173 K (−100 °C) on a Stoe Mark II-Image Plate Diffraction System [30] equipped with a two-circle goniometer and using Mo Kα graphite monochromated radiation. Image plate distance 100 mm, ω rotation scans: $\omega = 0\text{–}180°$ at $\varphi = 0°$ and $\omega = 0\text{–}150°$ at $\varphi = 90.0°$, step $\Delta\omega = 1.0°$, exposures of 2 min per image, 2θ range = 2.29–59.53°, $d_{min} - d_{max} = 17.779 - 0.716$ Å. The structure was solved by direct methods using the program SHELXS-97 [31]. The refinement and all further calculations were carried out using SHELXL-97 [31]. The H-atoms were included in calculated positions and treated as riding atoms: N–H = 0.88 Å, C–H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}$ (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 [32]; transmission factors: $T_{min}/T_{max} = 0.685/0.849$. Crystal data and details of the data collection are summarized in Table 2.

2.5. Antimicrobial studies of the complexes

Antimicrobial activities of the silver(I) compounds prepared here were estimated by the minimum inhibitory concentration (MIC; μg mL^{-1}) [33]. Standard culture media of bacteria, *Escherichia coli*, (ATCC 13706) and *Pseudomonas aeruginosa* (MTCC 424), molds, *Aapergillus niger* (MTCC 1349) and *Penicillium citrinum* (MTCC 5215), and yeast, *Candida albicans* (MTCC 183) and *Saccharomyces cerevisiae* (MTCC 463), were obtained from Qingdao Yijia Huuyi Co., China. Bacteria were inoculated into 5 mL of liquid SCD medium (soybean, casein and digest) and cultured for 24 h at 35.5 °C. The cultured fluids were diluted, adjusted to a concentration of 10^5–10^6 microorganisms per mL and used for inoculation in the MIC test. In the case of the mold culture, the agar slant (potato and dextrose) medium for one week cultivation at 27 °C was gently washed with saline containing 0.05% Tween 80. The spore suspension obtained was adjusted to the concentration of 10^5 microorganisms per mL and used for inoculation in the MIC test. Yeast were inoculated into 5 mL of glucose polypeptone (GP) medium and cultured for 48 h at 30 °C. The cultured fluids were diluted, adjusted to a concentration of 10^6–10^7 mL^{-1} and used for inoculation in the MIC test. The test materials (silver(I) complexes) were suspended in water, and solutions were then diluted with SCD medium for bacteria and with GP medium (glucose and polypeptone) for mold and yeast. Using them, two-fold diluted solutions with concentrations of 1000–10 mg mL^{-1} were prepared. Each 1 mL of culture medium containing various concentrations of the test materials was inoculated with 0.1 mL of the microorganism suspension prepared above. Bacteria were cultured for one day at 35.5 °C, mold for 7 days at 25 °C and yeast for 2 days at 30 °C. Growth of the microorganisms was monitored during this period. When no growth of microorganism was observed in the medium containing the lowest concentration of test materials, the MIC of the test material was defined as being at this point of dilution.

Table 1
Elemental analysis and melting points of silver(I) complexes of phosphines and thiones, $[(R_3P)_xAg(thione)_y]$.

Complex	Found (Calc.) (%)				M.p. (°C)
	C	H	N	S	
$[Ag(PPh_3)_1]NO_3$	50.24 (50.03)	3.39 (3.47)	3.87 (3.24)	–	206
$[(PPh_3)_1Ag(Tu)_1]NO_3$	44.41 (44.90)	3.66 (3.74)	9.27 (8.27)	7.56 (6.30)	192
$[(PPh_3)_2Ag(Metu)_1]NO_3$	56.97 (58.18)	4.33 (4.60)	4.81 (5.35)	3.53 (4.09)	175
$[(PPh_3)_1Ag(Metu)_2]NO_3$	44.70 (43.14)	4.52 (4.44)	10.97 (11.43)	9.98 (10.47)	110
$[(PPh_3)_2Ag(Dmtu)_1]NO_3$	55.94 (58.65)	4.23 (4.80)	5.34 (5.26)	3.79 (4.02)	155
$[(PPh_3)_1Ag(Dmtu)_2]NO_3$	45.46 (45.00)	4.92 (4.88)	11.44 (10.93)	10.0 (10.01)	160
$[(PPh_3)_1Ag(Detu)_1]NO_3$	48.42 (48.95)	4.91 (4.82)	7.88 (7.45)	5.02 (5.68)	140
$[(PPh_3)_2Ag(Detu)_2]NO_3$	58.95 (57.64)	5.75 (5.65)	7.69 (7.31)	5.76 (6.69)	140

Table 2
Summary of crystal data and details of the structure determination for **1**.

Crystal data	
Formula	$C_{38}H_{38}Ag_2N_6O_6P_2S_2$, $C_{38}H_{38}Ag_2N_4P_2S_2$, $2(NO_3)$
Formula weight	2033.13
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.5603(5)
b (Å)	15.3352(10)
c (Å)	18.0564(11)
α (°)	60.957(4)
β (°)	83.279(5)
γ (°)	84.782(5)
V (Å^3)	2056.4(2)
Z	1
ρ_{calc} (g cm^3)	1.642
μ (Mo Kα) (mm^{-1})	1.184
$F(0\,0\,0)$	1024
Crystal size (mm)	0.40 × 0.29 × 0.18
Data collection	
Temperature (K)	173(2)
λ Mo Kα (Å)	0.71073
θ Min–Max (°)	2.29–25.09
h limits	−10:10
k limits	−18:18
l limits	−21:21
Reflections: total, unique data, R_{int}	24202, 7329, 0.0487
Observed data [$I > 2\sigma(I)$]	6035
Absorption: T_{min}/T_{max}	0.685/0.849
Refinement	
N_{ref}, N_{par}	7329, 505
R, wR_2, S [$I > 2\sigma(I)$]	0.0344, 0.0745, 1.033
$w = [\sigma^2(F_o{}^2) + (0.0421P)^2 + 0.4103P]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$	
Min. and Max. Resd. Dens. [e Å^3]	−0.719, 0.869

Table 3
Selected IR absorptions (cm^{-1}) for the free ligands and their silver(I) complexes.

Species	ν(C=S)	ν(NH$_2$,NH)	ν(C–N)	ν(NO)$_3$
Tu	732	3156,3365	1473	–
$[(PPh_3)_1Ag(Tu)_1]\ NO_3$	694	3180	1477	1375
Metu	634	3245,3332	1488	–
$[(PPh_3)_2Ag(Metu)_1]\ NO_3$	625	3409	1478	1386
$[(PPh_3)_1Ag(Metu)_2]\ NO_3$	560	3197	1528	1354
Dmtu	641	3203	1521	
$[(PPh_3)_2Ag(Dmtu)_1]\ NO_3$	620	3245	–	1384
$[(PPh_3)_1Ag(Dmtu)_2]\ NO_3$	625	3244	1520	1355
Detu	642	3215	1445	
$[(PPh_3)_1Ag(Detu)_1]\ NO_3$	625	3274	1478	1377
$[(PPh_3)_2Ag(Detu)_2]\ NO_3$	620	3231	1478	1385

Table 4
^{1}H and ^{13}C NMR chemical shifts of the free ligands and their Ag(I) complexes in DMSO-d$_6$.

Species	δN–H	δC=S	δC–N	δC-5
Tu	6.98, 7.25	183.81	–	–
$[(PPh_3)_1Ag(Tu)_1]\ NO_3$	7.61, 8.05	180.06	–	–
Metu	6.99, 7.45, 7.65	181.10	29.90, 31.10	–
$[(PPh_3)_2Ag(Metu)_1]\ NO_3$	7.28, 7.83, 7.99	176.00	31.00	–
$[(PPh_3)_1Ag(Metu)_2]\ NO_3$	7.35, 7.75, 7.94	177.18	30.17	–
Dmtu	7.38	182.70	30.75	–
$[(PPh_3)_2Ag(Dmtu)_1]\ NO_3$	8.14, 8.49	177.20	29.90, 32.19	–
$[(PPh_3)_1Ag(Dmtu)_2]\ NO_3$	7.93, 8.20	177.80	29.80, 32.19	–
Detu	7.30	181.38	38.21	14.54
$[(PPh_3)_1Ag(Detu)_1]\ NO_3$	8.14, 8.22	174.49	37.85	13.60, 14.90
$[(PPh_3)_2Ag(Detu)_2]\ NO_3$	7.70	n.o.	38.0	13.90

n.o., not observed.

3. Results and discussion

The silver nitrate, triphenylphosphine and thioureas were treated in molar ratios of 1:1:1 or 1:1:2 in methanol–acetonitrile media. The elemental analyses of the resulting products correspond to the compositions $[(Ph_3P)_2Ag(thione)]NO_3$ and $[(Ph_3P)Ag(thione)_2]NO_3$, respectively. The elemental analysis of the starting Ag–PPh$_3$ complex corresponds to the formula $[Ag(PPh_3)NO_3]$. A similar product was also prepared for tetramethylthiourea (Tmtu) by reacting $[Ag(PPh_3)NO_3]$ with tetramethylthiourea (Tmtu) (1:1), but it is interesting to note that the compound analyzed was found to be a bis(phosphine) complex, $[Ag(PPh_3)_2NO_3]$ rather than a mixed ligand complex.

3.1. Spectroscopic studies

Selected IR spectroscopic vibration bands for the free ligands and their silver(I) complexes are given in Table 3. A low frequency shift in the ν(C=S) band and a high frequency shift in the ν(N–H) band of the complexes compared to the free ligands are indicative of the coordination of the ligands to the metal ion. A sharp band around 1300 cm^{-1} for $NO_3{}^-$ bending was observed for all the complexes, indicating the presence of a non-coordinated $NO_3{}^-$ ion [18,19]. A characteristic peak due to ν(P–C$_{Ph}$) around 1090 cm^{-1} indicated the presence of PPh$_3$ in the complexes.

The ^{1}H and ^{13}C NMR chemical shifts of the complexes in DMSO-d$_6$ are summarized in Table 4. In the ^{1}H NMR spectra of the complexes, the N–H signal of the thiones became less intense upon coordination and shifted downfield by 0.5–1.0 ppm from their positions in the free ligands. The deshielding of the N–H proton is related to an increase of the π electron density in the C–N bond upon complexation [24,25]. The appearance of a N–H signal shows that the ligands are coordinating to silver(I) via the thione group (proton loss will change this to the thiolate form).

As shown in Table 4, in all the complexes the C=S resonance appears upfield compared to the free ligands, in accordance with the data observed for other complexes of Cu(I), Ag(I) and Au(I) with thiones [24–29,34]. The upfield shift is attributed to a lowering of the >C=S bond order upon coordination and a shift of N → C electron density producing partial double bond character in the C–N bond [24–29]. The upfield shift decreases as the number of ligands attached to silver(I) increases from one in $[(Ph_3P)_2Ag(thione)]NO_3$ to two in $[(Ph_3P)Ag(thione)_2]NO_3$. This is because in the bis(thione) complexes each thione is sharing about half a silver atom rather than one as in the mono(thione) complexes. A small shift of ~1 ppm is observed in other carbon atoms, which shows that the nitrogen atoms are not involved in coordination. The difference in shielding at C=S is related to the strength of the metal–sulfur bond, which arises from the back donation of silver(I) to sulfur [24]. So the Dmtu complexes with the most significant shift in C=S are found to be the most stable.

The resonances for the triphenylphosphine ring carbons of the complexes were observed in the region 128–134 ppm (Table 5). The carbon atoms C(-P), C-2, C-3 and C-4 of the free triphenylphosphine resonate at 137.2, 133.6, 128.4 and 128.5 ppm, respectively. In the complexes, the C–P resonance is shifted upfield, while the other resonances remain almost unshifted. Upfield shifts of about 4–5 ppm in the C–P resonance compared to free Ph$_3$P are consistent with its coordination to a metal center [35]. The upfield shift is attributed to the shift of electron density from the metal ion towards C(-P), because of the π-accepting nature of PPh$_3$. The C(-P),

Table 5
^{31}P and ^{13}C chemical shifts of the PPh$_3$ part of the complexes.

Species	δ(^{31}P)	δC-1	δC-2	δC-3	δC-4
PPh$_3$	−5.5	137.20	133.60	128.40	128.60
[Ag(PPh$_3$)NO$_3$]	10.20, 13.55	131.52	133.62	129.38	131.21
[Ag(PPh$_3$)$_2$NO$_3$][a]	9.26	131.47	133.60	129.40	131.06
[(PPh$_3$)$_1$Ag(Tu)$_1$] NO$_3$	9.21	132.06	133.84	129.57	131.14
[(PPh$_3$)$_2$Ag(Metu)$_1$] NO$_3$	10.37	131.57	133.64	129.45	131.11
[(PPh$_3$)$_1$Ag(Metu)$_2$] NO$_3$	8.01	132.20	133.49	129.27	130.76
[(PPh$_3$)$_2$Ag(Dmtu)$_1$] NO$_3$	10.42	131.51	133.65	129.44	131.11
[(PPh$_3$)$_1$Ag(Dmtu)$_2$] NO$_3$	8.75	132.03	133.50	129.34	130.89
[(PPh$_3$)$_1$Ag(Detu)$_1$] NO$_3$	10.10	131.46	133.62	129.43	131.11
[(PPh$_3$)$_2$Ag(Detu)$_2$] NO$_3$	7.31	132.29	133.44	129.22	130.69

[a] The product is actually isolated from the reaction of [Ag(PPh$_3$)NO$_3$] and tetramethylthiourea.

Table 6
Selected geometric parameters for compound **1**.

Bond lengths (Å)

Bond	Distance	Bond	Distance
Ag1···Ag1^a	2.9027(10)	Ag2···Ag2^b	2.8704(4)
Ag1–S1	2.5478(10)	Ag2–S2	2.6272(11)
Ag1–P1	2.4029(10)	Ag2–P2	2.4157(10)
Ag1–S1^a	2.6542(9)	Ag2–S2^b	2.6179(10)
Ag1–O1	2.519(3)		

Bond angles (°)

Bond	Angle	Bond	Angle
S1–Ag1–P1	120.86(3)	S2–Ag2–P2	127.58(3)
S1–Ag1–P1^a	120.60(3)	S2–Ag2–P2^b	118.56(3)
S1–Ag1–S1^a	112.18(5)	S2–Ag2–S2^b	113.64(3)
S1–Ag1–O1	96.52(3)	Ag1–S1–Ag1^a	67.80(2)
S1–Ag1–O1^a	91.77(7)	Ag2–S2–Ag2^b	66.36(3)
P1–Ag1–O1	106.15(8)		

Symmetry codes: (a) 1 − *x*, 1 − *y*, 1 − *z*; (b) −*x*, −*y*, −*z*.

C-2 and C-3 resonances are in the form of doublets, while C-4 appears as a singlet.

The ^{31}P NMR chemical shifts are given in Table 5. In the ^{13}P NMR spectra of the complexes, a sharp singlet was observed for Ph$_3$P except for [Ag(Ph$_3$P)NO$_3$], where a doublet was observed. The doublet shows that ^{31}P–$^{109/107}$Ag coupling is partially resolved for [Ag(PPh$_3$)NO$_3$], with a coupling constant of 678 Hz. The P–Ag coupling could not be detected for the other complexes and only singlets are observed due to rapid exchange of PPh$_3$ at various positions in solution. The ^{31}P resonance in the complexes is significantly downfield shifted compared to free Ph$_3$P. A downfield shift in the ^{31}P resonance of the complexes is related to the donation of the electron pair on the phosphorus to the metal, which reduces the shielding at the phosphorus nucleus. The shifts are found to be smaller for bis(thione) complexes than for mono(thione) complexes.

3.2. Crystal structure description

The molecular structure of compound **1** is shown in Fig. 1, and selected bond lengths and angles are given in Table 6. The complex consists of two independent centrosymmetric binuclear units, each consisting of two silver(I) ions. In each binuclear unit the two silver centers are bridged by the sulfur atoms of two thiourea molecules to form a four-membered Ag–S–Ag–S ring. There are two kinds of coordination environment around the silver atoms. In one of the binuclear units, the silver atom, Ag1, is tetrahedrally coordinated to one P atom of PPh$_3$, two S atoms of bridging thiourea ligands and one oxygen atom of the nitrate ion. The two S1–Ag1–P1 angles have values of 120.60(3)° and 120.86(3)°, which are larger than the normal tetrahedral value of 109.5°. This large angle is counter balanced by the S1–Ag1–O1 bond angles of 91.77(7)° and 96.52(7)°. This tetrahedral distortion is probably due to the steric imposition of the bulky phosphine ligands. In the second independent molecule, the silver atom, Ag2, is bound to one PPh$_3$ and two sulfur atoms of the bridging thiourea units in a trigonal planar environment. In the two units the Ag–P [2.4029(10)–2.4157(10) Å] and Ag–S [2.5478(10)–2.6542(9) Å] distances are comparable to the values reported for similar silver(I) complexes [9,17–21,36,37], while the Ag–O bond length [2.519(3) Å] is somewhat longer than that found in other silver–oxygen bonding complexes [38,39]. The Ag–P distances of the tetrahedrally coordinated Ag1 atoms are similar to those in the trigonally coordinated center, Ag2. However, while the Ag–S bonds involving the atom Ag2 are similar [2.6272(11) and 2.6179(19) Å], those involving atom Ag1 are considerably different [2.5478(10) and 2.6542(9) Å]. The nitrate ions in both units are strictly planar but exhibit low symmetry owing to rather strong hydrogen bonding interactions with the NH$_2$ groups of the thione ligands.

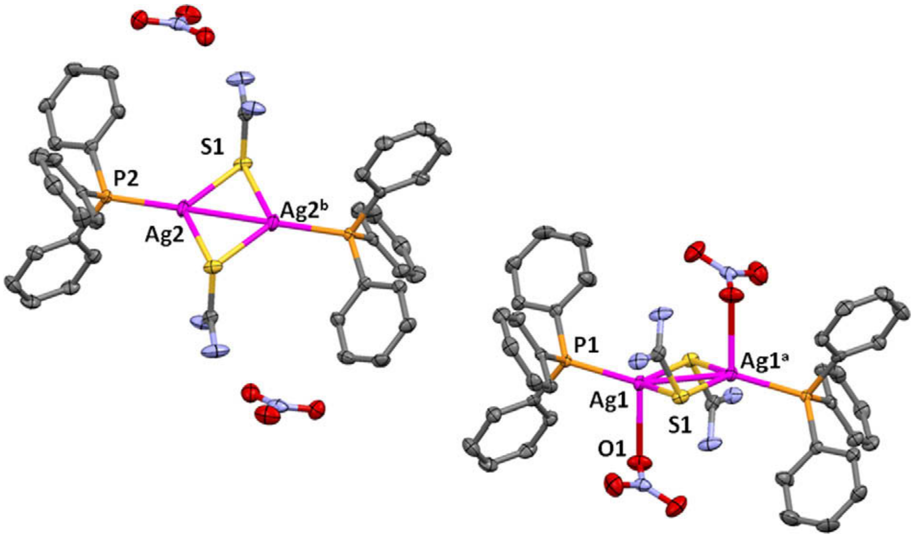

Fig. 1. A view of the molecular structure of compound **1**, with displacement ellipsoids drawn at the 50% probability level [H-atoms have been omitted for clarity; symmetry operations (a) 1 − *x*, 1 − *y*, 1 − *z*; (b) −*x*, −*y*, −*z*].

The Ag1···Ag1^a and Ag2···Ag2^b distances of 2.9027(10) and 2.8704(4) Å, respectively, indicate that the complex is stabilized by significant argentophilic interactions. The Ag···Ag distances are comparable to reported values [40–43]. Due the presence of these Ag···Ag interactions, the Ag1–S1–Ag1^a and Ag2–S2–Ag2^b bond angles [68.80(2)° and 66.36(3)°, respectively], are considerably smaller than the C–S–Ag bond angles [95.75(12)–112.59(14)° involving Ag1, and 108.20(12)–110.44(11)° involving Ag2].

In the crystal, N–H···O hydrogen-bonding interactions are present. They involve all four –NH_2 groups in each independent unit and all six nitrate oxygen atoms (Table 7). This results in the formation of a two-dimensional hydrogen bonded network propagating in (0 1 1), as shown in Fig. 2.

3.3. Antimicrobial activities

The antimicrobial activities of the silver(I) complexes (average of three measurements) estimated by minimum inhibitory concentrations (MIC; μg mL^{-1}) are listed in Table 8. Table 8 shows that the tested complexes showed a wide range of activity against two gram-negative bacteria (*E. coli*, *P. aeruginosa*). However, the title complex, $\{(PPh_3)_1Ag(Tu)_1NO_3\}_4$, did not show activity against any of the tested microorganisms. The Metu complex, $[(PPh_3)_1Ag(Mtu)_2]NO_3$, exhibits the most significant activity among these complexes, especially its activity against bacteria is remarkable. $[(PPh_3)_1Ag(Detu)_1]NO_3$ is only effective against bacteria and is inactive against all other tested microorganisms. The other complexes, particularly $[(PPh_3)_1Ag(Dmtu)_2]NO_3$ and $[(PPh_3)_2Ag(Detu)_2]NO_3$, display a moderate activity.

The antibacterial activities of the complexes are due to a direct interaction of the metal ions with biological ligands such as proteins, enzymes and membranes [1,6,44]. The activities of the silver(I) complexes given in Table 8 may be attributed to their tendency to undergo further ligand replacement reactions with the biological ligands such as proteins and DNA. The poor activity of the title complex shows that the chelate is highly stable due to which the ligands could not be displaced easily by biological ligands.

Table 7
Hydrogen bonding details in compound **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N1–H1A···O2^a	0.88	2.16	2.940(4)	147
N1–H1B···O6	0.88	1.97	2.841(4)	170
N2–H2A···O2^a	0.88	2.09	2.887(5)	150
N2–H2B···O1	0.88	2.06	2.847(5)	148
N4–H4A···O5^b	0.88	2.31	2.975(4)	132
N4–H4B···O4^c	0.88	2.07	2.924(4)	165
N5–H5A···O6^b	0.88	2.3	2.910(5)	127
N5–H5B···O2^d	0.88	2.13	2.969(4)	159
N5–H5B···O3^d	0.88	2.51	3.159(5)	131

Symmetry codes: (a) 2 – *x*, 1 – *y*, 1 – *z*; (b) *x*, *y* – 1, *z*; (c) 1 – *x*, 1 – *y*, –*z*; (d) 1 – *x*, –*y*, 1 – *z*.

4. Conclusion

The present report describes that thioureas in the presence of PPh_3 react with $AgNO_3$ to form complexes of the type $[(Ph_3P)_2Ag(thione)]NO_3$ and $[(Ph_3P)Ag(thione)_2]NO_3$, in which the thione ligands coordinate through the sulfur atom. The crystal structure of the complex (**1**) presented here represents a novel silver(I) cluster that consists of two different types of binuclear molecules, with the nitrate ions present in the form of a ligand as well as a non-coordinated counter ion. One of the complexes exhibits significant biological activity, showing the potential for its use as an antibacterial agent.

5. Supplementary data

CCDC 745856 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

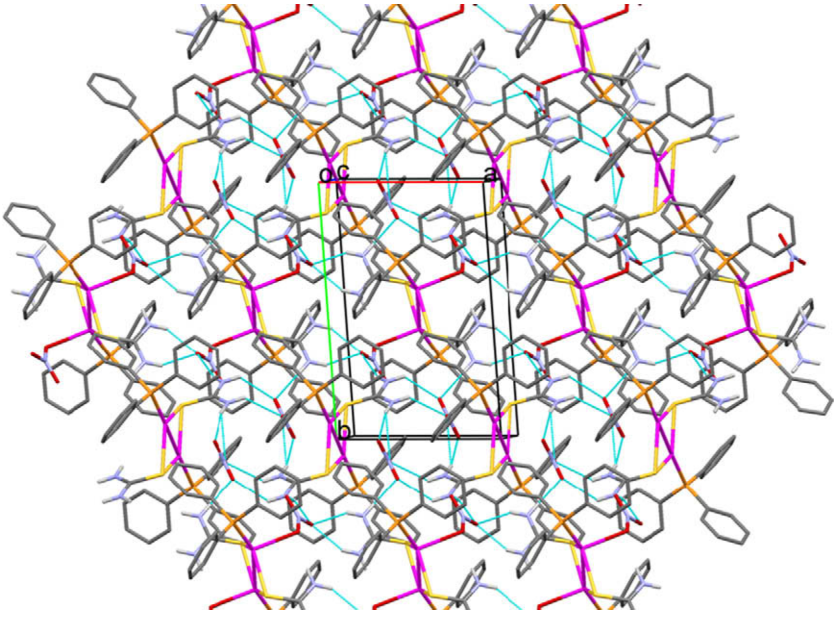

Fig. 2. View along the *c*-axis of the crystal packing in compound **1** showing the N–H···O hydrogen bonds.

Table 8

Antimicrobial activities of the Ph_3P–silver(I)–thione complexes evaluated by the minimum inhibitory concentration (MIC: μg mL^{-1}).

	Microbial activity (in terms of MIC: μg mL^{-1})					
Complexes	*E. coli*	*P. aeruginosa*	*A. niger*	*P. citrinum*	*C. albicans*	*S. cerevisiae*
$[(PPh_3)_1Ag(Tu)_1]\ NO_3$	>1000	>1000	>1000	>1000	>1000	>1000
$[(PPh_3)_2Ag(Metu)_1]\ NO_3$	480	390	810	970	>1000	>1000
$[(PPh_3)_1Ag(Metu)_2]\ NO_3$	50	40	210	320	440	410
$[(PPh_3)_2Ag(Dmtu)_1]\ NO_3$	420	470	910	840	>1000	930
$[(PPh_3)_1Ag(Dmtu)_2]\ NO_3$	180	220	390	410	720	630
$[(PPh_3)_1Ag(Detu)_1]\ NO_3$	510	620	>1000	>1000	>1000	>1000
$[(PPh_3)_2Ag(Detu)_2]\ NO_3$	170	210	570	610	630	580

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