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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)BIS(*N*,*N*′-DIBUTYLTHIOUREA)SILVER(I) NITRATE

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A mixed-ligand silver(I) complex of triphenylphosphine and *N*,*N*′-dibutylthiourea (Dbtu), $[Ag(Ph_3P)_2(Dbtu)_2]NO_3$, is prepared and its structure in the solid state is determined by X-ray crystallography. X-ray structure of this complex shows that it is mononuclear with the silver atom coordinated by two PPh_3 and two dibutylthiourea ligands adopting a distorted tetrahedral geometry. The crystal structure shows the formation of 1-D chains through intermolecular hydrogen bonding interactions between N—H of Dbtu and nitrate ions. The new complex is also characterized by IR and NMR (^1H and ^{31}P) spectroscopy. The spectroscopic data are discussed in terms of the nature of bonding. A similar mixed-ligand complex is also prepared for tetramethylthiourea (Tmtu), but the structure of the resulting compound shows that it is a bis(phosphine) complex, $[Ag(PPh_3)_2NO_3]$ rather than a mixed-ligand complex.

Keywords: silver(I) complex, *N*,*N*′-dibuylthiourea, triphenylphosphine, crystal structure.

Silver(I) complexes of tertiary phosphine ligands have been widely studied in recent years because of their interesting luminescence properties and their potential applications as antitumor or antibacterial agents [1—8]. They have also been successfully employed as precursors for preparing mixed-ligand [(phosphine)(thione)silver(I)] complexes having different stoichiometries and geometries [9—16]. Structural studies on these complexes have shown that they are either mononuclear [9—12] or dinuclear [13—16]. The metal center in the majority of these complexes exhibits a tetrahedral coordination environment and thione ligands coordinate either as monodentate or bidentate bridging ligands through the sulfur atom. We have recently undertaken a work about this subject by reacting $[(PPh_3)AgNO_3]$ with a number of thiourea ligands, including the crystal structure of $\{Ag(PPh_3)(thiourea)(NO_3)\}_4$ [17]. In order to understand the influence of bulky ligands on the geometry of such compounds, we report here the synthesis and the characterization of bis(triphenylphosphine)bis(*N*,*N*′-dibutylthiourea)silver(I) nitrate, $[Ag(Ph_3P)_2(Dbtu)_2]NO_3$ (**1**).

Experimental. Materials. Silver nitrate ($AgNO_3$) was obtained from Panreac, Spain and triphenylphosphine (PPh_3) from Alfa Aesar, U.S. *N*,*N*′-Dibutylthiourea was purchased from Acros Organics, Belgium.

Synthesis of $[Ag(Ph_3P)_2(Dbtu)_2]NO_3$ (1). Compound **1** was prepared by adding one equivalent of Dbtu in 15 ml of methanol to a 1:1 mixture of $AgNO_3$ and PPh_3 dissolved in methanol (10 ml) and acetonitrile (15 ml) respectively. Mixing resulted in a clear solution that was further stirred for 30 minutes. The solution was filtered and 1—2 ml of water was added to the filtrate. When this solu-

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Table 1

Summary of crystal data and details of structure determination for **1**

Formula	$C_{54}H_{70}P_2S_2AgN_5O_3$
Formula Weight	1071.08
Crystal system	Monoclinic
Space group	$P2(1)/c$
a, b, c, Å	22.0280(7), 26.6486(5), 19.6624(5)
α, β, γ, deg.	90, 108.396(3), 90
V, Å^3	10952.3(5)
Z	8
ρ_{calc}, g·cm^{-3}	1.299
$\mu(MoK_\alpha)$, mm^{-1}	0.547
$F(000)$	4512
Crystal size, mm	0.30×0.30×0.25
Temperature, K	120
Wavelength (λ), Å	0.71073
2θ range, deg.	2.94—26.00
h, k, l limits	–27:24, –32:30, –24:20
Reflections; collected / Uniq.	52447 / 21300 (R_{int} = 0.0296)
T_{min}, T_{max}	1.00000, 0.81276
N_{ref}, N_{par}	21300, 1239
R_1, wR_2, S[$I > 2\sigma(I)$]	0.0292, 0.0532, 0.805
$w = [\sigma^2(F_0^2) + (0.0242P)^2 + 1.6454P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$	
Largest diff. peak, hole (e/Å^{-3})	0.518, –0.351

tion was kept in refrigerator, a white crystalline product was obtained, which was air-dried. Yield of the product = 30 % (M.p = 120 °C).

IR and NMR Measurements. The IR spectrum of the title complex was recorded with a Perkin—Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000—400 cm^{-1}. The ^{1}H NMR spectrum in DMSO-d_6 was measured with a Jeol JNM-LA 500 NMR spectrometer operating at a frequency of 500.00 MHz at 297 K using a 0.10 M solution. The ^{31}P NMR spectrum was obtained at the frequency of 202.35 MHz with ^{1}H broadband decoupling, and ^{31}P NMR chemical shifts were measured relative to H_3PO_4.

X-ray Structure Determination. X-ray diffraction data of **1** were collected on an Oxford Gemini S diffractometer (MoK_α (λ = 0.71073 Å)) at 120 K. The structure of **1** was solved by direct methods with SHELXS-97 and refined by full-matrix least squares procedures on F^2 using the SHELXL-97 program [18, 19]. All *non*-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model. Hydrogen atoms on nitrogen were located in the difference Fourier map and refined isotropically. Crystal data and details of the data collection are summarized in Table 1.

Results and Discussion. Silver nitrate, triphenylphosphine, and *N*,*N'*-dibutylthiourea were treated in the molar ratios of 1:1:1 in the methanol-acetonitrile medium. The crystal structure of the expected $[(Ph_3P)Ag(Tmtu)]NO_3$ complex was also determined, but the measurements showed that the resulting complex was a bis(phosphine) complex, $[Ag(PPh_3)_2NO_3]$ rather than a mixed-ligand complex.

Spectroscopic Studies. In the IR spectrum of **1**, the characteristic bands due to Dbtu were observed at 691 cm^{-1} (ν(C=S)) and at 3245 cm^{-1} (ν(N—H)). For free Dbtu these bands are observed at

638 cm^{-1} and 3213 cm^{-1}, respectively. A band at 1329 cm^{-1} for NO_3^- bending was also observed indicating the presence of the non-coordinated NO_3^- ion [11, 12].

In the ^{1}H NMR spectrum of **1**, the N—H signal of Dbtu became less intense upon coordination and shifted downfield (7.27 ppm, 7.36 ppm, 7.48 ppm) compared to its position in the free ligand (2.265 ppm). Also three signals were observed for N—H protons showing that they became non-equivalent after coordination as observed for Ag—Dmtu complexes (Dmtu = *N*,*N*′-dimethylthiourea) [20, 21]. The deshielding of the N—H proton is related to an increase in the π electron density of the C—N bond upon complexation [20—23]. The appearance of an N—H signal shows that the ligands are coordinating to silver(I) via the thione group (proton loss changes this to the thiolate form).

In the ^{13}P NMR spectrum of **1**, a sharp singlet due to the presence of two Ph_3P groups was observed at 8.87 ppm, while for the precursor complex, $[Ag(Ph_3P)NO_3]$, a doublet was observed at 11.87 ppm. 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 in the title complex and only a singlet was observed. The ^{31}P NMR resonance signal of **1** is significantly downfield shifted compared to free Ph_3P (–5.5 ppm). This downfield shift is related to the dative-binding of the electron pair on phosphorus to silver, which reduces shielding at the phosphorus nucleus.

Crystal Structure Description. Complex **1** crystallizes in the centrosymmetric monoclinic space group *P*2(1)/*c* with two crystallographically independent molecules (**1a** and **1b**) in the asymmetric unit. The molecular structure of **1a** and **1b** together with the atomic labeling scheme is shown in Fig. 1. Selected bond lengths and angles are presented in Table 2. The structure consists of two crystallographically independent molecules each comprising $[Ag(Ph_3P)_2(Dbtu)_2]^+$ cations and NO_3^- counter ions. The silver atom in each molecule adopts a distorted tetrahedral geometry with the angles at Ag varying from 101.802(17)° to 120.298(17)° in **1a** and from 100.254(17)° to 118.629(17)° in ° **1b**. The deviation from the tetrahedral geometry is apparently due to the steric interactions between bulky phosphine ligands. The high values of the P—Ag—P angles are counterbalanced by the smaller S—Ag—S bond angles. The crystallographically independent thiourea molecules bonded to the central silver atom are not co-planar. Dbtu ligands coordinate in terminal mode, although bridging mode

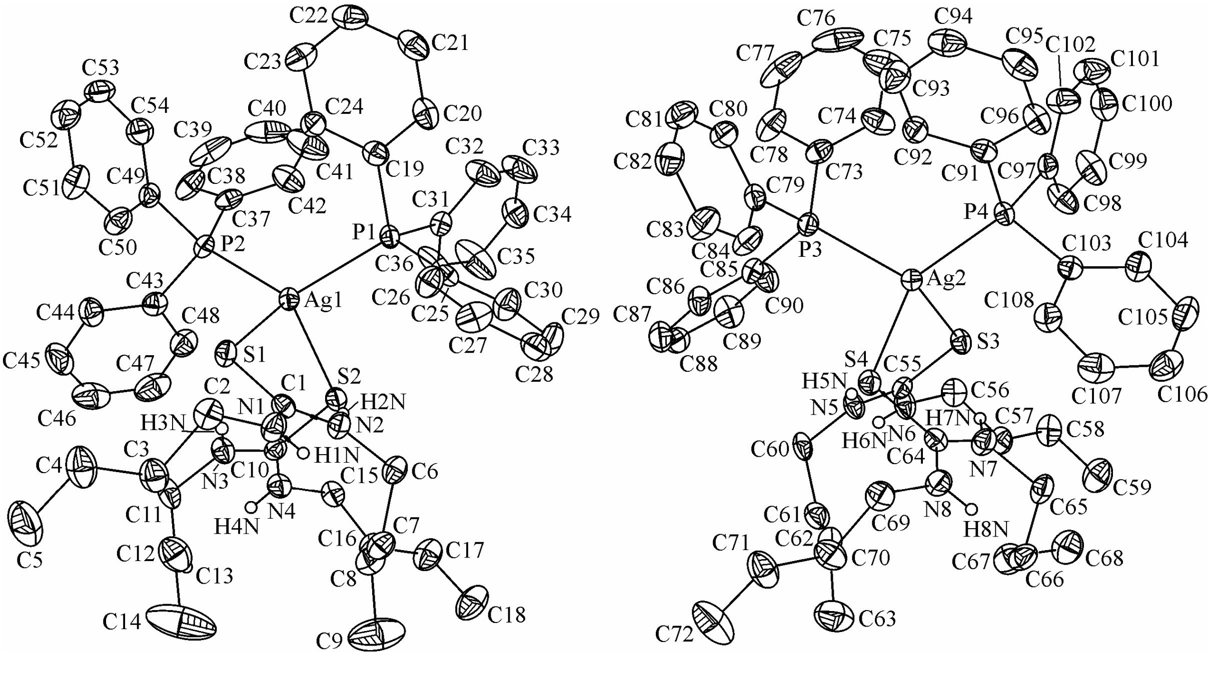

Fig. 1. ORTEP diagrams (50 % probability level) of the molecular structure of **1a** (*left*) and **1b** (*right*). All C-bonded hydrogen atoms and the NO_3^- anions have been omitted for clarity

Table 2

Selected bond distances (Å) *and angles* (deg.) *of* $\{[Ag(PPh_3)_2(Dbtu)_2]NO_3\}_2$

Bonds lengths

Ag(1)—P(1)	2.4749(5)	Ag(2)—S(3)	2.5982(6)	N(9)—O(1)	1.248(2)
Ag(1)—P(2)	2.4772(5)	Ag(2)—S(4)	2.6618(5)	N(9)—O(2)	1.238(2)
Ag(1)—S(1)	2.6117(6)	C(1)—S(1)	1.728(2)	N(9)—O(3)	1.242(2)
Ag(1)—S(2)	2.6552(6)	C(1)—N(1)	1.333(3)	N(10)—O(4)	1.248(2)
Ag(2)—P(3)	2.4770(5)	C(2)—N(1)	1.457(3)	N(10)—O(5)	1.233(2)
Ag(2)—P(4)	2.4723(5)	C(1)—N(2)	1.324(3)	N(10)—O(6)	1.238(2)

Bonds Angles

S(1)—Ag(1)—S(2)	101.802(17)	P(3)—Ag(2)—S(3)	114.019(18)	C(55)—S(3)—Ag(2)	106.45(7)
P(1)—Ag(1)—P(2)	120.298(17)	P(3)—Ag(2)—S(4)	102.414(18)	C(64)—S(4)—Ag(2)	109.86(7)
P(1)—Ag(1)—S(1)	114.641(18)	P(4)—Ag(2)—S(3)	106.397(18)	C(19)—P(1)—Ag(1)	114.60(7)
P(1)—Ag(1)—S(2)	102.893(18)	P(4)—Ag(2)—S(4)	113.744(18)	C(25)—P(1)—Ag(1)	115.51(6)
P(2)—Ag(1)—S(1)	103.201(18)	N(1)—C(1)—S(1)	120.76(16)	C(31)—P(1)—Ag(1)	113.80(6)
P(2)—Ag(1)—S(2)	112.752(18)	N(1)—C(1)—N(2)	119.31(19)	O(1)—N(9)—O(2)	120.24(19)
S(3)—Ag(2)—S(4)	100.254(17)	C(1)—S(1)—Ag(1)	106.65(7)	O(1)—N(9)—O(3)	119.35(18)
P(3)—Ag(2)—P(4)	118.629(17)	C(10)—S(2)—Ag(1)	108.69(7)	O(2)—N(9)—O(3)	120.40(17)

has also been observed in some other metal-thione complexes [13—16]. The Ag—P, Ag—S and other distances are comparable to the reported values for similar silver(I) complexes [9—16]. However, they are somewhat longer than those in the trigonally coordinated silver atoms [11, 17] showing that an increase in coordination number lengthens the bond distance. The nitrate ions in both units are strictly planar, but exhibit low symmetry owing to rather strong hydrogen bonding interactions with

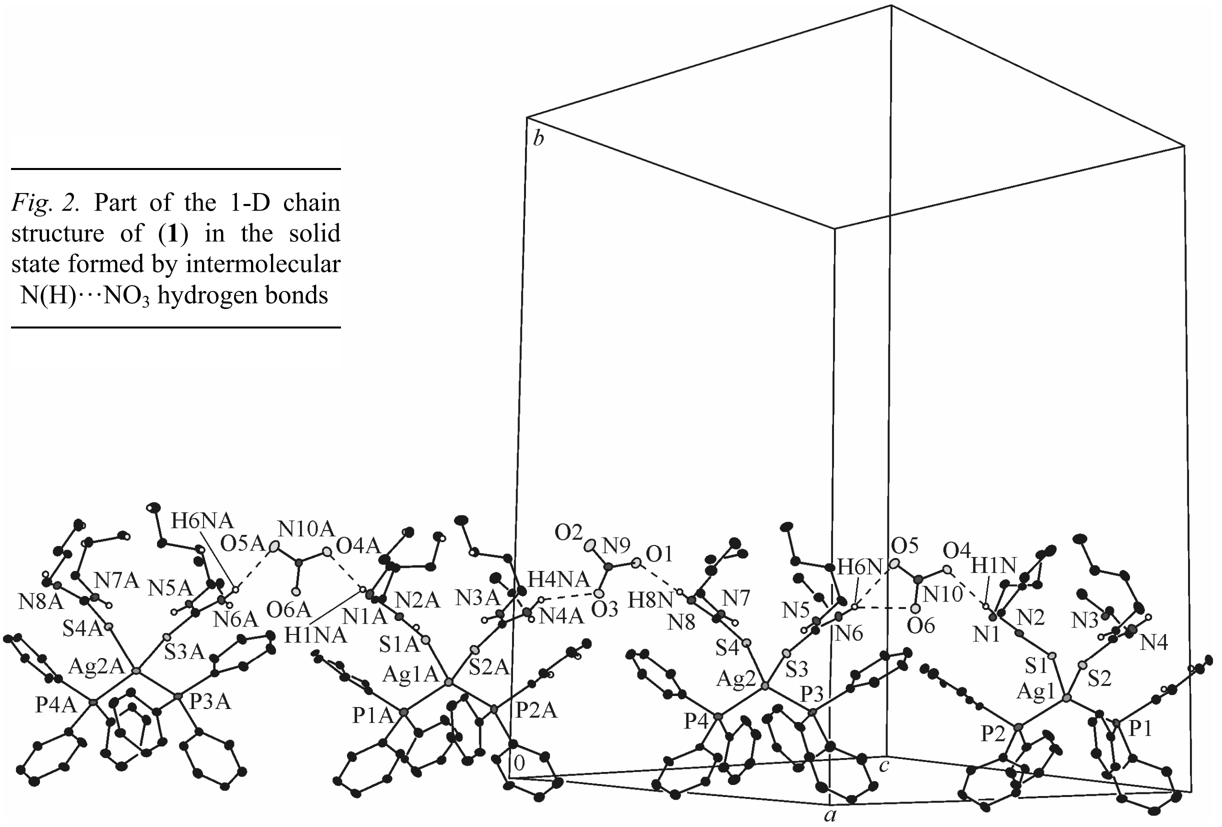

Fig. 2. Part of the 1-D chain structure of (**1**) in the solid state formed by intermolecular N(H)···NO_3 hydrogen bonds

Table 3

Selected geometrical details (*bond lengths* (Å) *and bond angles* (deg.) *of the intermolecular hydrogen bonds formed by* **1** *in the solid state*

Donor—H···Acceptor	D—H	H···A	D···A	∠D—H···A
N1—H1N···O4	0.79(2)	2.22(2)	2.956(2)	155(2)
N4—H4N···O3	0.80(2)	2.73(2)	3.010(3)	147(2)
N6—H6N···O5	0.80(2)	2.46(2)	3.224(3)	161(2)
N6—H6N···O6	0.80(2)	2.46(2)	3.127(3)	143(2)
N8—H8N···O1	0.80(2)	2.15(2)	2.913(2)	160(2)

the NH group of the Dbtu ligand. The compound is isostructural to two other silver(I) complexes, $[Ag(Ph_3P)_2(pyridine\text{-}2\text{-}thione)_2]NO_3$ [11] and $[Ag(Ph_3P)_2(benzoxazolin\text{-}2\text{-}thione)_2]NO_3$ [12].

Within the crystal structure, the formation of 1D chains due to intermolecular hydrogen bonds of the NH groups of the $[Ag(Ph_3P)_2(Dbtu)_2]^+$ cations and the NO_3^- counter ions has been observed, cf. Fig. 2. Hydrogen bonding details are given in Table 3.

Supplementary material. Supplementary crystallographic data of **1** (CCDC No. 757402) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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