

Crystal structure of metal (I) bromide complexes containing 1-(4-nitrophenyl)thiourea and triphenylphosphine ligands

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ABSTRACT: Two metal(I) complexes containing triphenylphosphine (PPh₃) and 1-(4-nitrophenyl)thiourea (NPTU) ligands were prepared, namely, [MBr(NPTU)(PPh₃)₂] (M = Cu (1) and Ag (2)). Both compounds (1) and (2) exhibit a distorted tetrahedral metal coordination environment with two P atoms from two PPh₃ ligands, one terminal S atom from the NPTU ligand and a bromide ion. An intramolecular N–H···Br hydrogen bond is observed (graph set motif S(6)). Amine and bromide units from neighbouring molecules are linked via bifurcated (N–H)₂···Br hydrogen bonds forming 1D zigzag chains along [001] with an R₁²(6) graph set motif. Neighbouring chains are connected through C–H···O hydrogen bonds leading to the formation of a three-dimensional network.

KEYWORDS: silver(I) bromide, copper(I) bromide, 1-(4-nitrophenyl)thiourea, hydrogen bonding, intra- and inter-molecular hydrogen bonding

INTRODUCTION

Thiourea and thiourea derivatives have attracted considerable attention in recent years as a class of ligands that bear both soft sulfur and hard nitrogen donor atoms, as defined by the HSAB (hard and soft acids and bases) concept. This gives thiourea and its analogues a wide range of possible coordination modes towards metal ions, allowing both coordination towards soft metals, such as copper [1], silver [2], gold [3] and palladium [4] via its sulfur donor site. The acidic hydrogen atoms of the amine moiety provide additional means of inter- or intramolecular interactions via formation of hydrogen bonds, giving this class of compounds, an even wider range of structural diversity.

Thiourea and thiourea derivatives including its metal complexes are also relevant due to their observed biological properties, such as antiproliferative activity against lung cancer cells and antitumor agents [5]. Some derivatives were also found to exhibit a moderate inhibitory potency on the diphenolase activity of tyrosinase [6] and against biofilm formation [7]. Copper(I) and silver(I) complexes of thiourea derivatives have been studied for their antimycobacterial, antileishmanial, antibacterial [8] and antifungal activities [9]. Keeping

these potential applications in mind we recently reported a series of metal thiourea complexes prepared by reacting copper or silver(I) chloride with triphenylphosphane and 1-(4-nitrophenyl)thiourea, NPTU [10, 11]. Herein, we report the synthesis and crystal structures of analogue bromide compounds [MBr(NPTU)(PPh₃)₂] (M = Cu and Ag).

MATERIALS AND METHODS

Materials

Reagent and solvents in the synthesis were obtained from commercial suppliers and used directly without further purification. Copper(I) bromide, silver(I) bromide, triphenylphosphine and 1-(4-nitrophenyl)thiourea were purchased from Sigma Aldrich. Infrared spectra were measured in the region 4000–400 cm⁻¹ on a Perkin-Elmer 783 Infrared Spectrophotometer using potassium bromide pellets.

Synthesis of [CuBr(NPTU)(PPh₃)₂](1)

Triphenylphosphane (0.16 g, 0.61 mmol) was dissolved in 30 mL of acetonitrile at 339 K and then copper(I) bromide (0.04 g, 0.28 mmol) was added. The mixture was stirred for 2 h and then 1-(4-nitrophenyl)thiourea, (0.06 g, 0.30 mmol) was

added. The resulting reaction mixture was heated under reflux for 6 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to evaporate at room temperature. A yellow crystalline precipitate was obtained upon standing for three days, and was filtered off and dried in vacuo (0.11 g, 42% yield). M.p. 469–471 K. IR bands (KBr, cm^{-1}): 3248 (m), 3134 (m), 2673 (m), 1963 (w), 1893 (w), 1816 (w), 1774 (w), 1597 (s), 1577 (s), 1511 (s), 1478 (s), 1400 (s), 1328 (m), 1178 (w), 1154 (w), 1093 (w), 1027 (w), 996 (w), 887 (w), 849 (s), 745 (s), 693 (s).

Synthesis of $[\text{AgBr}(\text{NPTU})(\text{PPh}_3)_2](2)$

Triphenylphosphane (0.16 g, 0.61 mmol) was dissolved in 30 mL of acetonitrile at 339 K and then silver(I) bromide (0.06 g, 0.30 mmol) was added. The mixture was stirred for 3 h and then 1-(4-nitrophenyl)thiourea, (0.05 g, 0.25 mmol) was added. The resulting reaction mixture was heated under reflux for 7 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to evaporate at room temperature. The yellow crystalline complex, which deposited upon standing for a day, was filtered off and dried in vacuo (0.18 g, 67% yield). M.p. 451–453 K. IR bands (KBr, cm^{-1}): 3296 (m), 3248 (m), 3135 (m), 2346 (w), 1578 (w), 1508 (w), 1492 (w), 1478 (w), 1432 (m), 1399 (m), 1333 (s), 1296 (w), 1255 (w), 1180 (w), 1156 (w), 1094 (m), 1026 (w), 997 (w), 849 (m), 745 (s), 693 (s).

X-ray crystallographic analysis

X-ray diffraction data for 1 and 2 was obtained on a Bruker Quest diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K and 100 K, respectively. Data were collected; reflections were indexed and processed using APEX3 [12]. The space groups were assigned and the structures were solved by direct methods using XPREF within the SHELXTL suite of programs [13, 14] and refined using Shelxl [15] and Shelxle [16] (Table 1). Refinement for 1: crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95 \AA . The nitrogen bound H atoms were located in difference-Fourier maps and were refined with an N–H = 0.84 (2)–0.85 (2) \AA . $U_{\text{iso}}(\text{H})$ values were set to $1.2U_{\text{eq}}(\text{C/N})$. Refinement for 2:

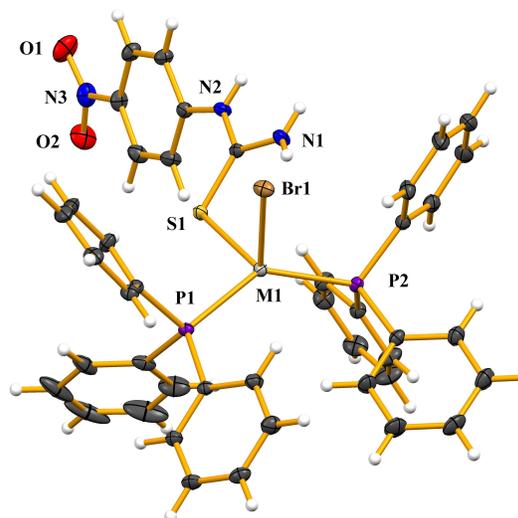


Fig. 1 The molecular structure of $[\text{MBr}(\text{NPTU})(\text{PPh}_3)_2]$ ($\text{M} = \text{Cu}$ (1) and Ag (2)), with displacement ellipsoids drawn at the 50% probability level.

crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95 \AA . The nitrogen bound H atoms were located in difference-Fourier maps and were refined with an N–H = 0.83 (2)–0.85 (2) \AA . $U_{\text{iso}}(\text{H})$ values were set to $1.2U_{\text{eq}}(\text{C/N})$. Reflections 0 4 0, 0 3 1, -3 0 2, -1 3 1, 1 3 0, -8 10 18, -10 3 17, and -9 2 17 were affected by the beam stop and were omitted from the refinement. CCDC 1981594 (for 1) and 1981339 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

The $[\text{MBr}(\text{NPTU})(\text{PPh}_3)_2]$ ($\text{M} = \text{Cu}$ (1) and Ag (2)) complexes as well as their chloride counterparts are isostructural and isomorphous. The thiourea is coordinated to both Cu and Ag solely via the soft sulfur donor, and no interaction of the metal with the amine moiety is observed. The complexes are monomeric, metal ions are not bridged via either the sulfur or bromide ions, and in both compounds, the M(I) ion is coordinated to exactly two P atoms from two PPh_3 ligands, one terminal S atom from the NPTU ligand and one bromide ion, leading to a distorted tetrahedral

Table 1 Experimental details.

Crystal data		
Chemical formula	C ₄₃ H ₃₇ AgBrN ₃ O ₂ P ₂ S	C ₄₃ H ₃₇ CuBrN ₃ O ₂ P ₂ S
Mr	909.53	865.20
Crystal system, space group	Monoclinic <i>P</i> 2 ₁ / <i>c</i>	Monoclinic <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100	150
a, b, c (Å)	11.7913 (5), 28.6891 (11), 12.1416 (5)	11.6696 (5), 29.0515 (10), 12.0068 (5)
β (°)	105.1249 (16)	106.351(2)
V (Å ³)	3965.0 (3)	3905.9 (3)
Z	4	4
Radiation type	Mo-Kα	Mo-Kα
μ (mm ⁻¹)	1.69	1.76
Crystal size (mm)	0.45 × 0.43 × 0.36	0.38 × 0.36 × 0.30
Data collection		
Diffractometer	Bruker AXS D8 Quest CMOS	Bruker AXS D8 Quest CMOS
Absorption correction	Multi-scan Apex3 v2016.9-0	Multi-scan Apex3 v2016.9-0
No. of measured, independent, observed [<i>I</i> > 2σ(<i>I</i>)] reflections	53040, 17948, 15843	46975, 11816, 9571
Rint	0.021	0.043
(sin θ/λ) max(Å ⁻¹)	0.834	0.770
Refinement		
R[F ² > 2σ(F ²)], wR(F ²), S	0.027, 0.069, 1.15	0.032, 0.087, 1.07
No. of reflections	17948	11816
No. of parameters	487	490
H-atom treatment	a mixture of independent and constrained refinement	a mixture of independent and constrained refinement
Δρ max, Δρ min(e Å ⁻¹)	0.62, -1.00	0.42, -0.83

Computer programs: Apex3, SAINT [12], SHELXS9 [13], SHELXL2014/7 [15], SHELXLE Rev714 [16], Mercury [19], SHELXL97, and publCIF [20].

Table 2 Hydrogen-bond geometry (Å, °) for [MBr(NPTU)(PPh₃)₂] (M = Cu (1) and Ag (2)).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
Compound (1)				
N1—H1A···Br1 ⁱ	0.85 (2)	2.48 (2)	3.3027 (15)	165 (2)
N1—H1B···Br1	0.84 (2)	2.54 (2)	3.3412 (15)	160 (2)
N2—H2···Br1 ⁱ	0.84 (2)	2.63 (2)	3.4355 (15)	160 (2)
C24—H24···O2 ⁱⁱ	0.95	2.61	3.33	134
C33—H33···O1 ⁱⁱⁱ	0.95	2.72	3.40	129
Compound (2)				
N1—H1A···Br1 ⁱ	0.83 (2)	2.53 (2)	3.3186 (12)	158.3 (19)
N1—H1B···Br1	0.85 (2)	2.60(2)	3.3989 (12)	157.3 (18)
N2—H2···Br1 ⁱ	0.83 (2)	2.57 (2)	3.3734 (11)	162.8 (19)
C24—H24···O2 ⁱⁱ	0.95	2.62	3.277	127
C33—H33···O1 ⁱⁱⁱ	0.95	2.68	3.398	133

Symmetry codes: (i) *x*, -*y* + 1/2, *z* - 1/2; (ii) -*x* + 1, -*y* + 1, -*z* + 1; (iii) *x* - 1, *y*, *z*.

environment (Fig. 1). The monomeric structures are stabilized by an intramolecular N1—H1B···Br1 hydrogen bond between the NPTU NH₂ and the Br atom, thus saturating the donor sites of the bromide ions and making them unavailable for possible dimer formation via bridging halogens

as often observed in other silver(I) or copper(I) species where no such hydrogen bonds are observed. The graph-set motif of the N—H···Br hydrogen bond is S(6) (Table 2). The Cu—S distance in (1) is similar to the values of 2.382 (2) Å reported in [CuCl(C₇H₇N₃O₂S)(C₁₈H₁₅P)₂]. The

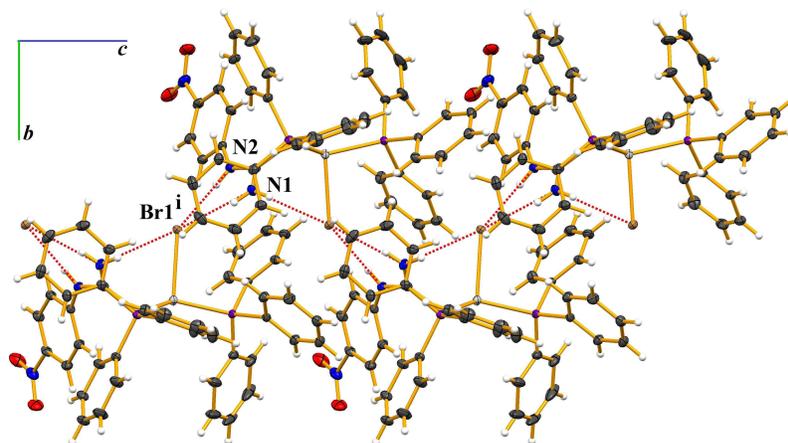


Fig. 2 Part of the crystal structure of $[\text{AgBr}(\text{NPTU})(\text{PPh}_3)_2]$, showing the 1D zigzag chain along $[001]$ axis formed by intermolecular $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds (dashed lines).

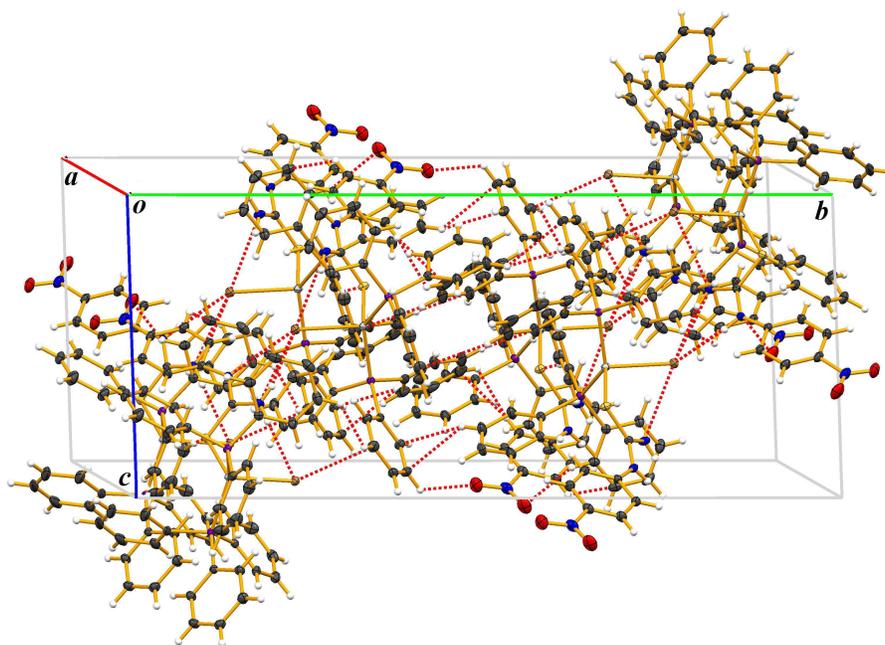


Fig. 3 Part of the crystal structure of $[\text{AgBr}(\text{NPTU})(\text{PPh}_3)_2]$, showing intermolecular $\text{N}-\text{H}\cdots\text{Br}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (dashed lines).

Cu–P bond lengths of 2.2687 (4)–2.2758 (5) are similar to the values of 2.2602 (4)–2.2671 (4) Å for $[\text{CuCl}(\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S})(\text{C}_{18}\text{H}_{15}\text{P})_2]$ [10]. In compound (2), the Ag–S bond length of 2.6231 (3)

is similar to the bond length of 2.6316 (5) found in $[\text{AgCl}(\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S})(\text{C}_{18}\text{H}_{15}\text{P})_2]$ [11]. The Ag–P bond lengths of 2.4327 (3)–2.4373 (3) are close to the values of 2.4807 (9)–2.4657 (9) Å for

[AgBr(C₃H₆N₂OS)(C₁₈H₁₅P)₂] [17].

In the crystals of (1) and (2), the amine NH₂ moieties of NPTU and Br atom of neighboring molecules are linked through bifurcated intermolecular N—H...Br hydrogen bonds, N1—H1...Br1 and N2—H2A...Br1 for (1) and N1—H1A...Br1 and N2—H2...Br1 (2), forming 1D zigzag chain along [001] (graph set motif (R₁² (6) [18]) (Fig. 2). The chains are in turn connected by C—H...O hydrogen bonds, C12—H12...O2 and C35—H35...O1 hydrogen bonds for (1) and C24—H24...O2 and C33—H33...O1 hydrogen bonds for (2), leading to the formation of a three-dimensional network (Fig. 3 and Table 2).

CONCLUSIONS

The compounds [MBr(NPTU)(PPh₃)₂] (M = Cu (1) and Ag (2)) were prepared from MBr:NPTU:PPh₃ in 1:1:2 molar ratios in acetonitrile. Structures of the complexes were determined using single crystal X-ray diffraction analysis which display a distorted tetrahedral coordination with two PPh₃ ligands, NPTU ligand and bromide ion. In the crystals, there are intra and inter-molecular hydrogen bonds leading to the formation of a three-dimensional network.

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