

Synthesis and crystal structures of silver(I) halide complexes containing 1,3-diisopropyl-2-thiourea and triphenylphosphane ligands

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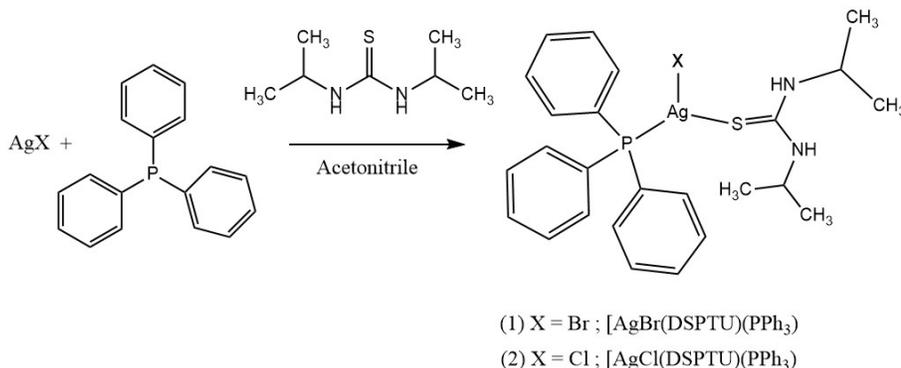
ABSTRACT: The reaction of silver(I) halide with triphenylphosphine (PPh₃) and 1,3-diisopropyl-2-thiourea (DSPTU) gave mononuclear complexes of formula [AgX(DSPTU)(PPh₃)], [where X = Br (**1**) and Cl (**2**)]. Complexes (**1**) and (**2**) were characterized by infrared (IR) spectroscopy and their structures determined by single crystal X-ray diffraction. The two complexes are isostructural and isomorphous, with the Ag(I) ion exhibiting a distorted trigonal planar coordination with one P atom from the PPh₃ ligand, one terminal S atom from the DSPTU ligand, and a halide ion. Intramolecular N–H···X hydrogen bonds are observed in both complexes (graph set motif S(6)). In the crystal, the amine and halide group are linked into a 1D zigzag chain along the *b* axis by N–H···X hydrogen bonds.

KEYWORDS: silver(I) bromide, silver(I) chloride, triphenylphosphane, 1,3-diisopropyl-2-thiourea, crystal structure, hydrogen bonding

INTRODUCTION

Thiourea and its derivatives belong to a class of N,S-donor ligands with the general formula (R₁R₂N)(R₃R₄N)C=S. The molecules readily act as ligands towards a wide number of metal ions and literally thousands of metal complexes of thiourea and its derivatives have been reported, with over 500 entries in the Cambridge Structural Database (CSD) [1] for unsubstituted thiourea (H₂N)C=S alone. This versatility of thiourea as ligand is in part facilitated by the presence of both soft sulfur and hard nitrogen donor atoms as defined by the HSAB (hard and soft acids and bases) concept, which allows them to easily coordinate to both soft as well as hard metals ions. A variety of chelating and bridging coordination modes have been observed such as chelating coordination via the S and one N atom (a very common motif), bridging coordination via the S and at least one N atom (this mode is relatively rare) [2], or also chelating via both N atoms (usually double deprotonated, not common) [3]. End-on coordination via one N atom (usually deprotonated) has also been described [4]. The by far most common end-on coordination of the thione S atom as a neutral soft ligand, usually to a soft transition metal [5–8]. Thiourea derivative complexes containing transition metals have played a considerable role as compounds that display antimicrobial, antiviral, antitumor, antimalarial, antifungal, and anticancer activities [9–13]. For example, two thiourea derivatives of methyl anthranilate with nickel(II) and platinum(II) exhibit antifungal activity against the major pathogens responsible for important

plant diseases [14]. Some Cu(II) complexes had been found to show higher activity against primary tumor cell lines than towards metastatic cell lines and also showed a significantly lower activity against normal cell lines [15]. Silver(I) ions are a typical soft metal ion that coordinates with thiourea predominantly via the thione sulfur atom in either an end-on or bridging mode (over 300 entries in the CSD). Coordination via a thiourea N atom towards a silver ion is exceedingly rare (just five entries in the CSD). The large size of the silver ion and the usually end-on coordination of the thiourea allow for more than one thiourea ligand or other additional ligands to be bound to the metal ion. Complexes are predominantly two-, three-, and four-coordinated and well known for their ability to readily form complexes with phosphane ligands and, like all thiourea complexes, adopt diversified coordination geometries in mononuclear, polynuclear and cluster complexes [16–18]. Ag(I) complexes showed selective cytotoxicity toward various types of cells, and this is dependent on the type of ligand linked to the silver(I) ions [19]. Silver(I) complexes with phosphane ligands were investigated as a highly effective positive apoptosis control for use in anticancer studies [20]. Silver(I) complexes with phosphorus and sulfur donor ligands have attracted considerable interest in antimicrobial activities. For example, [(PPh₃)₁Ag(Metu)₂]NO₃ shows a wide range of activity against two gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*) and molds (*Aspergillus niger*, *Penicillium citrinum*) [21]. In this context we report herein the synthesis and crystal structures of silver(I) halide complexes containing triphenylphos-



Scheme 1: Synthesis of compounds (1) and (2).

phine (PPh₃) and 1,3-diisopropyl-2-thiourea (DSPTU) ligands (Scheme 1).

MATERIALS AND METHODS

Materials

Reagents and solvents used in the synthesis were obtained from commercial suppliers and used directly without further purification. Silver(I) bromide (AgBr), silver(I) chloride (AgCl), triphenylphosphine (PPh₃) and 1,3-diisopropyl-2-thiourea (DSPTU) were purchased from Sigma Aldrich (USA). Infrared spectra were measured in the region 4000–400 cm⁻¹ on a Perkin-Elmer infrared spectrophotometer (Spectrum BX, England) using potassium bromide pellets.

Synthesis of [AgBr(DSPTU)(PPh₃)] (1)

PPh₃ (0.14 g, 0.53 mmol), was dissolved in 30 ml of acetonitrile at 336.15 K, and AgBr (0.10 g, 0.53 mmol), was added. The mixture was stirred for 3 h, and then DSPTU (0.09 g, 0.56 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 for several days at room temperature, leaving a crystalline complex, which was filtered off and dried in vacuo (0.27 g, 81% yield) M.p. 429.15–430.15 K.

Synthesis of [AgCl(DSPTU)(PPh₃)] (2)

Triphenylphosphine (0.18 g, 0.69 mmol) was dissolved in 30 ml of acetonitrile at room temperature and then silver(I) chloride (0.10 g, 0.70 mmol) was added. The mixture was stirred for 3 h and then 1,3-diisopropyl-2-thiourea (0.11 g, 0.69 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 crystalline complex, which was deposited upon standing for a day, was filtered off and dried in vacuo (0.30 g, 77% yield). M.p. 443–447 K.

X-ray crystallographic analysis

X-ray diffraction data for 1 and 2 were obtained on a Bruker Quest diffractometer with Mo-K_α (λ = 0.71073 Å) radiation at 150 K. Data were collected, and reflections were indexed and processed using APEX3 [20]. The space groups were assigned using XPREP within the SHELXTL suite of programs, the structures were solved by dual space methods using ShelXT and refined using ShelXL and ShelXle [21–24] (Table 1). Refinement for 1 and 2: 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 Å. Positions of nitrogen bound H atoms were refined and N–H distances refined to 0.806 (16)–0.854 (18) Å. U_{iso}(H) values were set to 1.2 or 1.5 U_{eq}(C/N). Reflections –1 0 2, –1 0 2 for 1 and 0 0 2, 0 1 1, –1 0 2, 10 0 0 for 2 were affected by the beam stop and were omitted from the refinement.

CCDC 2225733 (for 1) and 2225734 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (<https://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The two [AgX(DSPTU)(PPh₃)], [X = Br (1) and Cl (2)] complexes were prepared by reacting the silver(I) halide with DSPTU, followed by addition of PPh₃, in acetonitrile in 1:1:1 molar ratios (Scheme 1). The complexes are isostructural and crystallize in the monoclinic system with space group P21/c with four formula units (Z = 4) in a crystallographic unit cell.

In 1 and 2, the DSPTU ligand coordinates in a monodentate manner to the Ag via the terminal S donor, and no coordination of the silver with amine moiety was observed. The second and third coordination positions at the silver ion are taken up by the P atom from the PPh₃ ligand and by the halide atom, respectively, leading to a distorted trigonal pla-

Table 1 Crystal data and structure refinement details for **1** and **2**.

Crystal data		
Chemical formula	$C_{25}H_{31}AgBrN_2PS$	$C_{25}H_{31}AgClN_2PS$
<i>M_r</i>	610.33	565.87
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.1556 (7), 8.7609 (4), 18.3325 (8)	16.0838 (7), 8.7047 (3), 18.2118 (7)
β (°)	93.140 (2)	93.386 (2)
<i>V</i> (Å ³)	2590.8 (2)	2545.29 (17)
<i>Z</i>	4	4
Radiation type	Mo K_{α}	Mo K_{α}
μ (mm ⁻¹)	2.48	1.06
Crystal size (mm)	0.52 × 0.42 × 0.29	0.44 × 0.42 × 0.29
Data collection		
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan	Multi-scan
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	97572, 9895, 8574	68105, 9710, 8872
<i>R</i> _{int}	0.039	0.031
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.770	0.770
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.021, 0.052, 1.06	0.020, 0.050, 1.08
No. of reflections	9895	9710
No. of parameters	291	291
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.69, -0.72	0.45, -0.54

Computer programs: Apex4 v2021.10-RC6, SAINT V8.40B [22], SHELXT [25], SHELXL2018/3 [23, 26], SHELXL Rev1275 [27], Mercury [28] and publCIF [29].

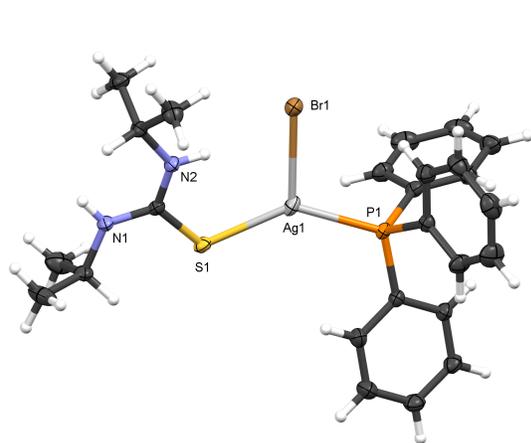


Fig. 1 Molecular structure of $[AgBr(DSPTU)(PPh_3)]$ (**1**), with ellipsoid displacement drawn at the 50% probability level.

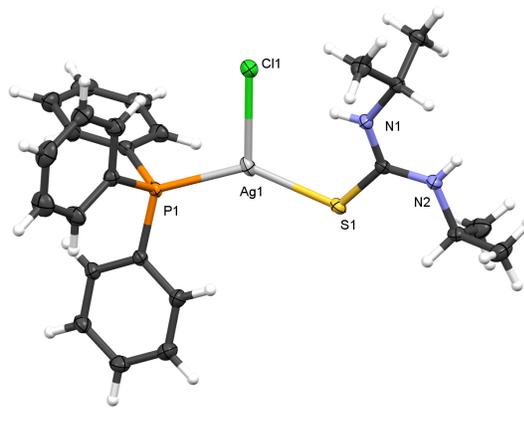


Fig. 2 Molecular structure of $[AgCl(DSPTU)(PPh_3)]$ (**2**), with ellipsoid displacement drawn at the 50% probability level.

nar AgXSP environment (Fig. 1 and Fig. 2). The Ag–S bond length in (**1**) and (**2**) are similar to the values of 2.482 (2) Å for Ag(Tu)₂SCN [30]. The Ag1–P1 bond

lengths of 2.4198 (3) Å for **1** and 2.4128 (3) Å for **2** are close to the values of 2.4703 (3)–2.4750 (4) Å found in $[AgCl(4-PTSC)(PPh_3)_2]$ [31]. The angle at the Ag(I) ion in **1** and **2** varies from 106.949 (9) °

Table 2 Selected bond lengths and angles for (\AA , $^\circ$) [AgBr(DSPTU)(PPh₃)] (**1**) and [AgCl(DSPTU)(PPh₃)] (**2**).

Bond length (\AA)		Bond angle ($^\circ$)	
Compound (1)			
Ag1—P1	2.4198 (3)	P1—Ag1—S1	138.425 (10)
Ag1—S1	2.4452 (3)	P1—Ag1—Br1	106.949 (9)
Ag1—Br1	2.6562 (2)	S1—Ag1—Br1	114.623 (8)
Compound (2)			
Ag1—P1	2.4128 (3)	P1—Ag1—S1	140.524 (9)
Ag1—S1	2.4457 (3)	P1—Ag1—Cl1	107.057 (9)
Ag1—Br1	2.5626 (3)	S1—Ag1—Cl1	112.418 (9)

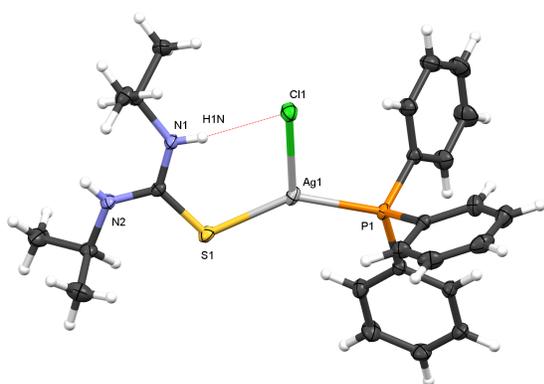


Fig. 3 Part of the crystal structure of [AgCl(DSPTU)(PPh₃)] (**2**), showing intramolecular N—H \cdots Cl hydrogen bonds (shown as dashed lines).

to 140.524 (9) $^\circ$. Other bond angles and lengths of structural importance are summarized in Table 2.

The molecular structures are stabilized by intramolecular N2—H2NN \cdots Br1 (for **1**) and N1—H1N \cdots Cl1 (for **2**) hydrogen bonds between the DSPTU and halide atom with a graph set motif of S(6) (Fig. 3) [32]. In the crystals of (**1**) and (**2**), the amine NH moieties of DSPTU and halide atom of neighboring molecules are linked through intermolecular N1—H1NN \cdots Br1ⁱ (for **1**) and N2—H2B \cdots Cl1ⁱⁱ (for **2**) hydrogen bonds, leading to the formation of 1D chains along [010] (Fig. 4, Table 3).

In the IR spectra of complexes **1** and **2**, bands at 3287 and 3199 cm^{-1} regions, respectively are due to the stretching frequency for different types of NH groups. The band from the SH group is not present between 2600–2800 cm^{-1} indicating the absence of thiol form of the ligands. The characteristic peak of $\nu(\text{C}=\text{S})$ of both complexes is at a lower energy compared to the stretching absorption observed in the free DSPTU ligand (878 cm^{-1}) supporting the coordination of the thione sulfur to the metal center.

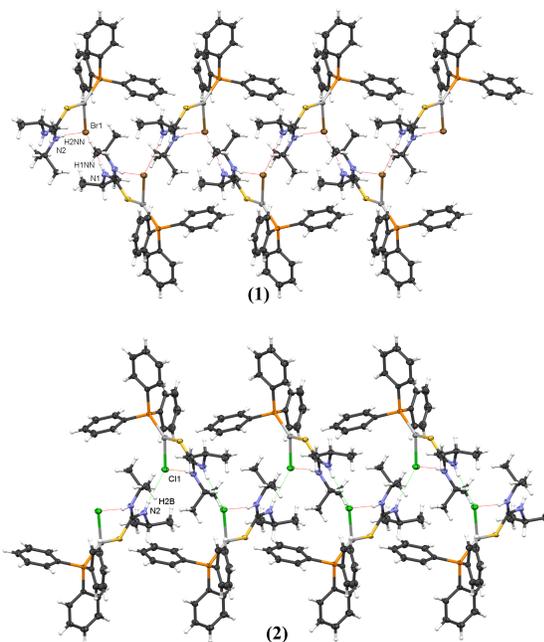


Fig. 4 Part of the crystal structure of [AgX(DSPTU)(PPh₃)], [where X=Br (**1**) and Cl (**2**)], showing the 1D zigzag chain formed by intermolecular N—H \cdots X bond (shown as dashed lines).

The bands in the range 1309–1069 cm^{-1} are characteristics for the skeletal vibrations of $\nu(\text{P-C}_{\text{ph}})$ which confirmed the presence of the phosphane ligand in both complexes. The results from IR spectroscopy are corresponding to the X-ray crystallographic data. IR bands for **1** (KBr, cm^{-1}): 3287(w), 2501(m), 2362(m), 2338(m), 2258(m), 1699(m), 1684(m), 1652(m), 1541(s), 1478(s), 1309(m), 1094(s), 1069(m), 1027(m), 982(m), 929(m), 877(m), 846(s), 738(s) (see Fig. 5). IR bands for **2** (KBr, cm^{-1}): 3199(w), 2360(m), 1981(m), 1904(m), 1829(m), 1699(m), 1683(m), 1653(m), 1560(s), 1477(s), 1433(s), 1307(s), 1268(s), 1157(m), 1095(s), 1069(m), 1026(m), 996(m), 972(m), 950 (m), 846(m), 740(s) (see Fig. 6).

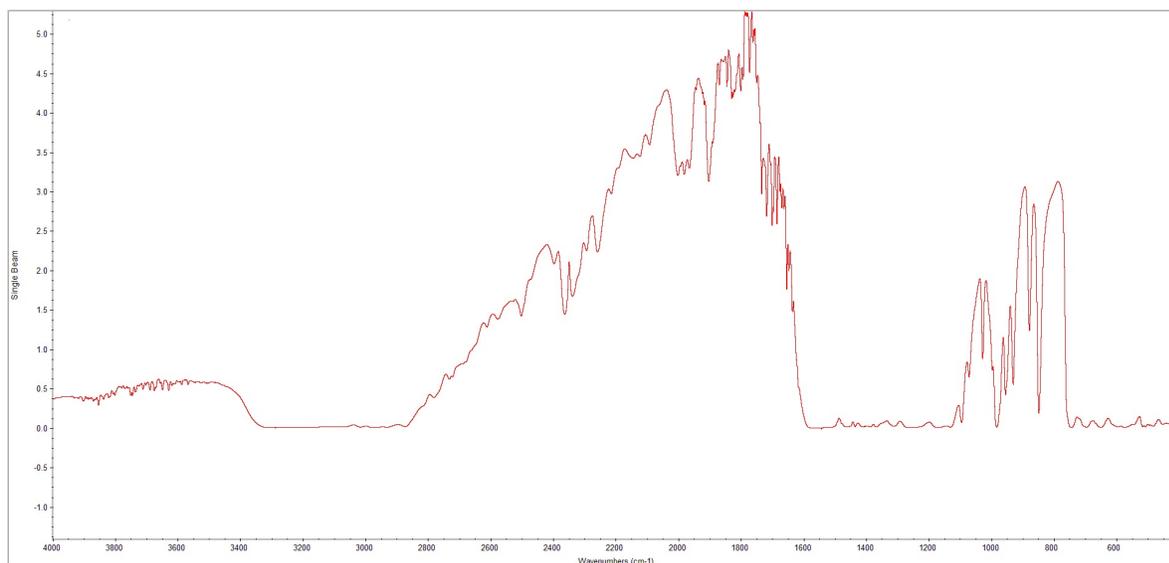
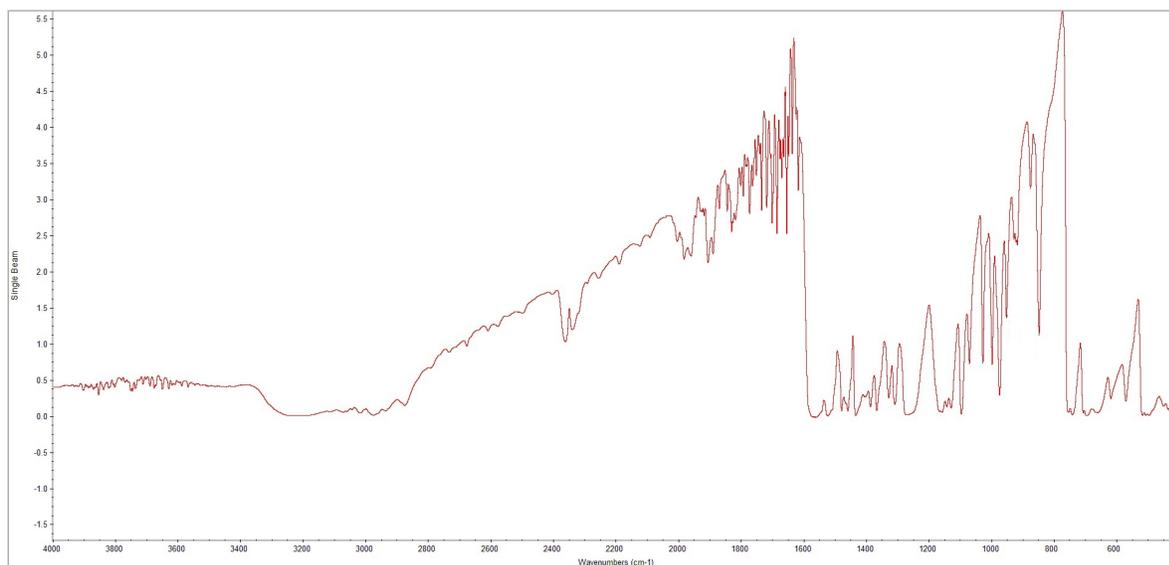
CONCLUSION

Two isostructural [AgX(DSPTU)(PPh₃)], [X= Br (**1**) and Cl (**2**)] were prepared from AgX:DSPTU:PPh₃ in 1:1:1 molar ratios in acetonitrile. The structure of complexes were characterized by IR spectroscopy and X-ray single crystal analysis methods. The geometry of both complexes is a distorted trigonal planar comprising Ag(I) as a center linked with one P atom of PPh₃ ligand, one S atom of DSPTU ligand and one halide ion. In the crystals, there are intra and inter-molecular

Table 3 Hydrogen-bond geometry (\AA , $^\circ$) for $[\text{AgBr}(\text{DSPTU})(\text{PPh}_3)]$ (**1**) and $[\text{AgCl}(\text{DSPTU})(\text{PPh}_3)]$ (**2**).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
Compound (1)				
N1—H1N \cdots Br1 ⁱ	0.852 (19)	2.711 (19)	3.5327 (10)	162.3 (16)
N2—H2N \cdots Br1	0.854 (18)	2.552 (18)	3.3925 (10)	168.3 (16)
Compound (2)				
N1—H1N \cdots Cl1	0.806 (16)	2.444 (16)	3.2378 (9)	168.4 (15)
N2—H2B \cdots Cl1 ⁱⁱ	0.822 (17)	2.613 (17)	3.4195 (9)	167.3 (15)

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

**Fig. 5** IR spectra of $[\text{AgBr}(\text{DSPTU})(\text{PPh}_3)]$ (**1**).**Fig. 6** IR spectra of $[\text{AgCl}(\text{DSPTU})(\text{PPh}_3)]$ (**2**).

hydrogen bonds leading to a 1D zigzag chain.

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