Crystal Structures of Silver(I) Complexes with Phenylthiourea and Triphenylphosphine

Sofia Mekarat

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Thesis Title	Crystal Structures of Silver(I) Complexes with Phenylthiourea and Triphenylphosphine
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Major Program	Physical Chemistry

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ชื่อวิทยานิพนธ์ โครงสร้างผลึกของสารประกอบเชิงซ้อนซิลเวอร์(I) กับฟีนิลไธโอยูเรีย และไตรฟีนิลฟอสฟีน
ผู้เขียน นางสาวโซเฟีย เมฆารัฐ
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บทคัดย่อ

การศึกษาโครงสร้างผลึกสารประกอบเชิงซ้อนซิลเวอร์(I) กับลิแกนด์ไตรฟีนิลฟอสฟีน (PPh_3) และฟีนิลไธโอยูเรีย(ptu) คือ[$AgCl(PPh_3)_2$(ptu)](1), [$AgBr(PPh_3)_2$(ptu)](2) และ [$Ag(PPh_3)_2$(ptu)]NO_3(3) สารประกอบเหล่านี้เตรียมได้จากการทำปฏิกิริยาโดยตรงระหว่างเกลือซิลเวอร์(I) (AgCl, AgBr, $AgNO_3$) กับลิแกนด์ฟีนิลไธโอยูเรีย และไตรฟีนิลฟอสฟีนภายใต้สภาวะที่เหมาะสม และทำการศึกษาวิเคราะห์โครงสร้าง โดยการวิเคราะห์ปริมาณธาตุที่เป็นองค์ประกอบ เอกซเรย์ฟลูออเรสเซนซ์สเปกโทรเมตรี นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี และอินฟราเรดสเปกโทรสโกปี และหาโครงสร้างโดยใช้เทคนิคการเลี้ยวเบนรังสีเอกซ์บนผลึกเดี่ยว สารประกอบเชิงซ้อน [$AgCl(PPh_3)_2$(ptu)](1) และ [$AgBr(PPh_3)_2$(ptu)](2) ตกผลึกอยู่ในระบบไตรคลินิก หมู่ปริภูมิ $P\bar{1}$ มีเซลล์พารามิเตอร์ดังนี้ a = 10.5092(6), b = 11.3943(6), c = 17.2408(10) Å, α = 97.0180(10), β = 103.9100(10), γ = 103.2770(10)° และ a = 10.6748(11), b = 11.3434(12), c = 17.2296(18) Å, α = 97.358(2), β = 102.928(2), γ = 102.580(2)° ตามลำดับ โครงสร้างสารประกอบเชิงซ้อน (1) และ (2) เป็นแบบมอนอเมอร์และมีโครงสร้างเหมือนกัน โดยมีอะตอมซิลเวอร์จัดตัวเป็นทรงสี่หน้าที่บิดเบี้ยว โคออร์ดิเนตกับลิแกนด์ไตรฟีนิลฟอสฟีนสองโมเลกุล ฟีนิลไธโอยูเรียหนึ่งโมเลกุลและคลอไรด์หรือโบรไมด์หนึ่งอะตอม สารประกอบเชิงซ้อน [$Ag(PPh_3)_2$(ptu)]NO_3(3) ตกผลึกอยู่ในระบบโมโนคลินิก หมู่ปริภูมิ $P2_1/c$ มีเซลล์พารามิเตอร์ดังนี้ a = 13.6113(5), b = 10.6431(4) และ c = 26.4365(10) Å, β = 96.0680(10)° อะตอมของซิลเวอร์โคออร์ดิเนตแบบสามเหลี่ยมแบนราบที่บิดเบี้ยวกับลิแกนด์ไตรฟีนิลฟอสฟีนสองโมเลกุลและฟีนิลไธโอยูเรียหนึ่งโมเลกุล โดยมีไนเตรตทำหน้าที่เป็นแอนไอออน ตามลำดับ

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ABSTRACT

The silver(I) salt complexes containing triphenylphosphine (PPh_3) and phenylthiourea (ptu), $[AgCl(PPh_3)_2(ptu)]$(1) , $[AgBr(PPh_3)_2(ptu)]$(2) and $[Ag(PPh_3)_2(ptu)]NO_3$(3) have been prepared by direct reaction of silver(I) salt (AgCl, AgBr, $AgNO_3$) with triphenylphosphine and phenylthiourea under suitable conditions. The structures of these complexes have been characterized by elemental analysis, X-ray fluorescence spectrometry, Fourier transform nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy and single crystal X-ray diffraction methods. The complexes, $[AgCl(PPh_3)_2(ptu)]$(1) and $[AgBr(PPh_3)_2(ptu)]$(2) crystallized in triclinic system space group $P\bar{1}$ with cell parameters a = 10.5092(6), b = 11.3943(6), c = 17.2408(10) Å, α = 97.0180(10), β = 103.9100(10), γ = 103.2770(10)^o and a = 10.6748(11), b = 11.3434(12), c = 17.2296(18) Å, α = 97.358(2), β = 102.928(2), γ = 102.580(2)° respectively. Both structures are neutral monomer and isomorphous for which the coordination around silver is distorted tetrahedral and coordinated by two PPh_3 molecules, one ptu molecule and one chloride or bromide atom. The $[Ag(PPh_3)_2(ptu)]NO_3$(3) complex crystallized in monoclinic system space group $P2_1/c$ with cell parameters a = 13.6113(5), b = 10.6431(4) and c = 26.4365(10) Å, β = 96.0680(10)° . The structure is an ionic complex consisting of discrete independent $[Ag(ptu)(PPh_3)_2]^+$ cation and one NO_3^- anion. The cation part contains silver(I) atom trigonally coordinated by two phosphorus atoms from two PPh_3 molecules and one sulfur atom from ptu .

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Finally, love and understanding from teachers and friends take me to be strong today, that I would like to thank all of them.

Sofia Mekarat

THE RELEVANCY OF THE RESEARCH WORK TO THAILAND

Single crystal X-ray diffraction is the important technique in modern day chemistry. The structural studies of organic, organametallic and inorganic molecules have been established in this method.

The main propose of this work is to determine the crystal structures of silver(I) complexes containing N, S and P as donor atoms. The substituted thiourea ligand, phenylthiourea (ptu) is selected due to the interesting structure that might be formed coordinate bond with silver atom through both sulfur and nitrogen atom or via one of these atoms. In addition, triphenylphosphine(PPh_3) is a P donor atom ligand with different steric characteristics. This work examines systematically the structure variation of complexes of silver(I) salt (Cl, Br, NO_3^-) with mixed ligands of PPh_3 and ptu. The structure of these complexes would perhaps define more clearly the chemical properties of the coordination of this metal.

The knowledge of the molecular structure is one of fundamental aim of chemical properties of materials. The results of this research might be useful as scientific foundation for its application and may possibly be used to design and synthesize crystals with useful properties such as catalysts, semiconductors, superconductors and other materials for using in new technology.

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LIST OF ABBREVIATIONS AND SYMBOLS

° = degree
Å = Angstrom unit (1 Å = 10^{-10} metre)
A.R. = Analytical Reagent
$CDCl_3$ = Deuterium Chloroform
D_c = calculated density
D_m = measured density
DMSO-d_6 = hexadeutero-dimethyl sulphoxide
EDXRF = Energy Dispersive X-ray Fluorescence
h = hour
K = Kelvin
keV = kilo electron volt
L.R. = Lab Reagent
ml = millilitre
mm = millimetre
mmol = millimole
PPh_3 or Ph_3P = triphenylphosphine
ptu = *N*-phenylthiourea

CHAPTER 1

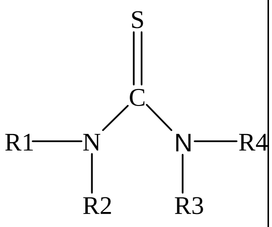
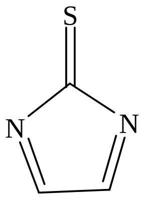
INTRODUCTION

1.1 Introduction

The element silver, symbol Ag, atomic number 47, is located in the periodic table between palladium and cadmium in the second row of the transition elements and in the same group as others known as coinage metals, copper and gold. The electronic configuration of silver is $[Kr]4d^{10}5s^{1}$. Silver has a single s electron outside the filled $4d$ shell but essentially has nothing in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled d shell is much less effective in shielding the outer s electron from the nuclear charge, so that the first ionization energy of Ag is higher than those of the alkalis. Since the electrons of the *d* shell are also involved in metallic bonding, the heat of sublimation and the melting point of Ag are also much higher than those of the alkalis. These factors are responsible for the more noble character of silver and the effect is to make the compounds more covalent and to give them higher lattice energies.

Thiourea and substituted thiourea ligands can form the coordinate covalent bond with silver either via both the sulfur and nitrogen or via one of these atoms. Hard and soft acid and base (HSAB) – hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases – can be applied here (Parr and Pearson, 1983). The silver(I) ion is regarded as an soft acid favoring coordinate to soft bases, such as ligands containing S and unsaturated N. However, S is rather softer than N. Accordingly, silver(I) complexes of these ligands were mostly bond with sulfur but the formation of the nitrogen-silver bond is somewhat difficult. The suspected coordination site of both these possibilities will be illustrated by the vibrational absorption spectra of the complexes. Coordination bond through sulfur will decrease the double bond character of the carbon-to-sulfur bond towards the value of a single bond whereas the bond order of the carbon-to-nitrogen bond is close to the value of a double bond. Therefore, in silver(I) complexes, the C-S stretching frequencies should shift to the lower frequencies while the C-N stretching should change to the higher frequencies. If, however, the coordination bond is through the nitrogen atom, it will attribute to the opposite result. Moreover, The N-H stretching should decrease if the metal is coordinated through the nitrogen and remain substantiallty unaffected if the bonding is through the sulfur (Suwaluk, 1999). Not only the effect from the coordinated site but also the effect from hydrogen bonding as well as the weak-interaction in the molecule leads to the decrease of the N-H stretching. Thus, the accurate molecular structures of Ag(I) complexes have determined by single crystal X-ray diffraction method.

Structure of thiourea and substituted thioureas : thiourea(tu), acetylthiourea(atu), *N*-ethylthiourea(ettu), *N*–ethylenethiourea(etu), *N*-methylthiourea(mtu), *N,N'*-dimethylthiourea(dmtu), *N,N'*-diethylthiourea(detu), *N*-phenylthiourea(ptu), *N,N'*-diphenylthiourea(dptu), N,N',N'',N'''-teramethylthiourea(tmtu), are shown in the table below : (Saithong, 2003).

Structures	Names	Remarks
	Thiourea(tu)	R1=R2=R3=R4=H
	acetylthiourea(atu)	R1=R2=R3=H R4=COCH$_3$
	N-ethylthiourea(ettu)	R1=R2=R3=H R4=C$_2$H$_5$
	N-methylthiourea(mtu)	R1=R2=R3=H R4=CH$_3$
	N,N’-dimethylthiourea(dmtu)	R1=R3=H R2=R4=CH$_3$
	N,N’-diethylthiourea(detu)	R1=R4=H R2=R3=C$_2$H$_5$
	N-phenylthiourea(ptu)	R1=R2=R3=H R4=C$_6$H$_5$
	N,N’-diphenylthiourea(dptu)	R1=R3=H R2=R4=C$_6$H$_5$
	N.N’,N’’,N’’’-tetramethylthiourea(tmtu)	R1=R2=R3=R4=CH$_3$
	*N*-ethylenethiourea(etu)	-

Thioamide are organic compounds containing the redical or group –CSNH$_2$. Thiourea and substituted thioureas have been shown to occur in the thione rather than the thiol form both in the solid state and in most of the common solvents, (Figure 1).

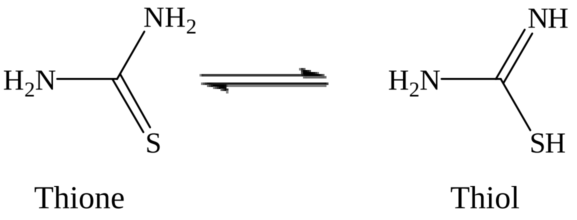


Figure 1 The tautomerism structure of thiourea.

Therefore *N*-phenylthiourea, the substituted thiourea in this work containing a thioamide structure has considerable potential is in thione form that indeed a considerable versatility in the coordination modes of these molecules which may include monodentate binding through S(I) or through N(II), bridging through a single S(III), bridging through both S and N(IV) or chelating via the S-to-N backbone (VI) (Akrivos, 2001, quoted in Nimtong, 2008: 3)(Figure 2).

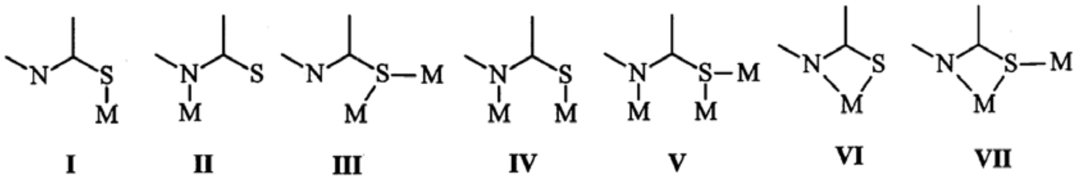


Figure 2 Various coordination modes of thioamides.

Triphenylphosphine (PPh_3) is a common organophosphorus compound with the formula $P(C_6H_5)_3$, often abbreviated to PPh_3 or Ph_3P. It is widely used in the synthesis of organic and organometallic compounds. PPh_3 exists as relatively air stable, colorless crystals at room temperature. It dissolves in non-polar organic solvents such as benzene, diethyl ether, etc.(Eadsongkram, 2010). The structure of triphenylphosphine is shown in Figure 3.

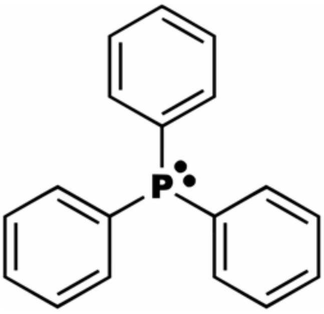


Figure 3 The structure of triphenylphosphine (PPh_3).

In this work, we prepared the single crystals of Ag(I)X (X= Cl, Br and NO_3^-) with triphenylphosphine (PPh_3) and phenylthiourea (ptu) complexes from the optimal conditions by means of varying mole ratios, type of solvent, volume of solvent and temperature to get the appropriate value. The functional groups in the structure were determined by infrared spectroscopy and the elemental compositions were specified by X-ray fluorescence spectroscopy technique. Finally, the structures of these complexes were determined by single crystal X-ray diffraction technique.

1.2 Literature reviews

Engelhard *et al.,* studied the crystal structures of silver(I) halide (AgX; X= Cl, Br, I) and triphenylphosphine(PPh_3), $[(PPh_3)_3AgCl]\cdot 2(CH_3)_2CO$, $[(PPh_3)_3AgBr]$ and $[(PPh_3)_3AgI]$ as shown in Figures 4. (Engelhard *et al.,* 1987).

Crystal data for chloride complex : triclinic system, space group $P\bar{1}$,

a = 13.654(4), b = 14.059(4), c = 13.970(4) Å, α = 84.82(2), β = 87.71(2), γ = 75.68(2)°, Z = 2; the structure was refined to residual R of 0.061 for N_o = 2428 which is independent observed reflections.

Crystal data for bromide complex : trigonal system, space group $P3$,

a = 19.366(6), c = 10.787(6) Å, Z = 3, R was 0.054 for N_o = 2362.

Crystal data for iodide complex : monoclinic system, space group $P2_1/n$,

a = 18.993(8), b = 13.807(4), c = 17.781(8) Å, β = 96.11(4)°, Z = 4, R was 0.042 for N_o = 3691

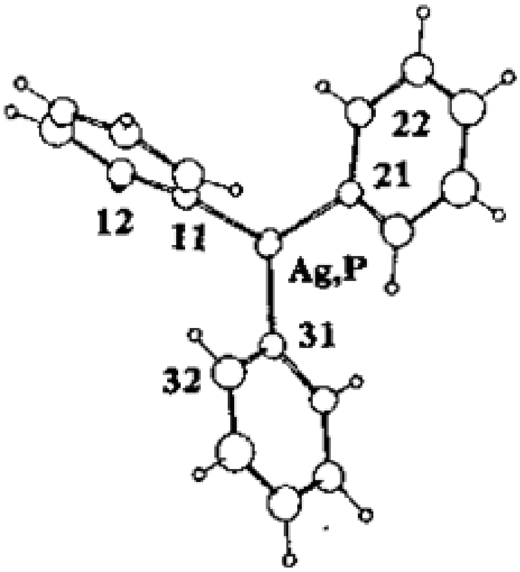


Figure 4 A phosphine ligand of the chloride structure viewed down the Ag-P bond.

Pakawatchai *et al.,* studied the structures of two different complexes of silver(I) and dimethylthiourea (dmtu) in the stoichiometric ratios 1:2, $[Ag(C_3H_8N_2S)_2]ClO_4$, and 1:3, $[Ag(C_3H_8N_2S)_3]C1O_4$. The 1:2 complex consists of polynuclear cationic chains, whereas the 1:3 complex contains discrete $[Ag_2(dmtu)_6]^{2+}$ cations. In both structures, Ag_2S_2 lozenges with different Ag—S bond lengths are observed. The structures are shown in Figures 5-6 (Pakawatchai *et al.,* 1996).

Crystal data of $[Ag(C_3H_8N_2S)_2]ClO_4$: triclinic system, space group $P\bar{1}$,

a = 6.397(1), b = 10.405(1), c = 12.347(1) Å, α = 69.78(1), β = 85.58(1),
γ = 78.77(1)°, Z = 2, D_x = 1.825 Mg/m^3, R = 0.0384.

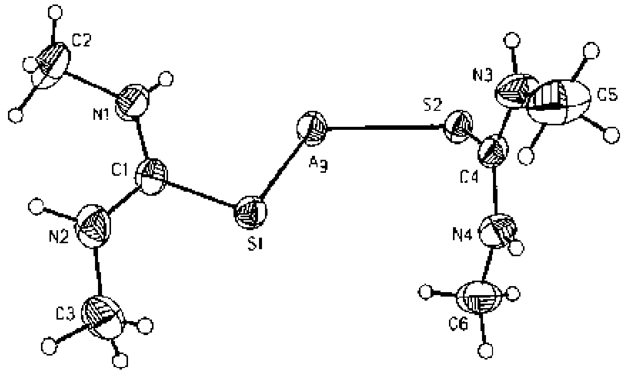


Figure 5 The structure of $[Ag(C_3H_8N_2S)_2]ClO_4$.

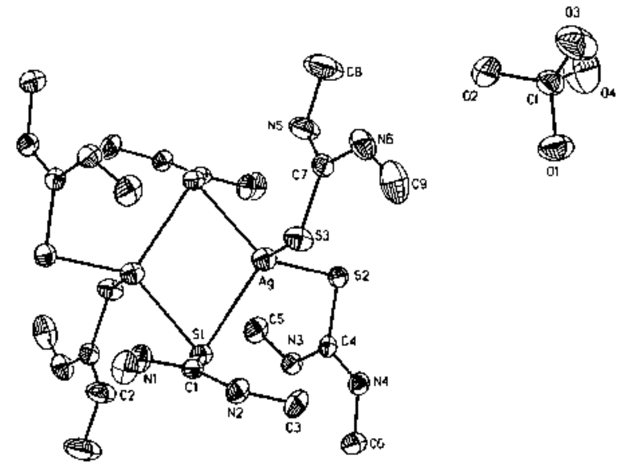


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Figure 6 The structure of $[Ag(C_3H_8N_2S)_3]ClO_4$.

Crystal data of $[Ag(C_3H_8N_2S)_3]C1O_4$: triclinic system, space group $P\bar{1}$, a = 9.887(1), b = 10.096(1), c = 10.687(1) Å, α = 90.96(1), β = 105.68(1), γ = 95.15(1)°, Z = 2, D_x = 1.689 Mg/m^3, R = 0.0318.

Aslanidis *et al.,* synthesised and studied the reaction of silver(I) nitrate with pyrimidine-2-thione and triphenylphosphine. The crystal structure of $[Ag(PPh_3)_2(pymtH)]NO_3$ was determined by single-crystal X-ray diffraction methods. The structure is shown in Figure 7 (Aslanidis *et al.,*1997). The complex is triclinic system, space group $P\bar{1}$, a = 10.084(2), b = 13.508(3), c = 14.326(3) Å, α = 77.43(2), β = 78.77(2), γ = 79.14(2)°, V = 1846 Å^3 and Z = 2.

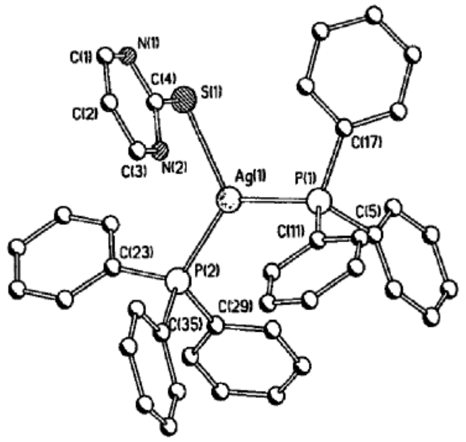


Figure 7 The structure of [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$.

Attilio *et al.,* studied silver(I) pyrazolate which was reacted with triphenylphosphine, leading to the dinuclear [Ag$_2$(pz)$_2$(PPh$_3$)$_2$] and [Ag$_2$(pz)$_2$(PPh$_3$)$_3$] complexes (Hpz = pyrazole), which were extensively characterized by ^{31}P-NMR methods and single crystal X-ray analyses. The structures are shown in Figures 8-9 (Attilio *et al.,* 1997).

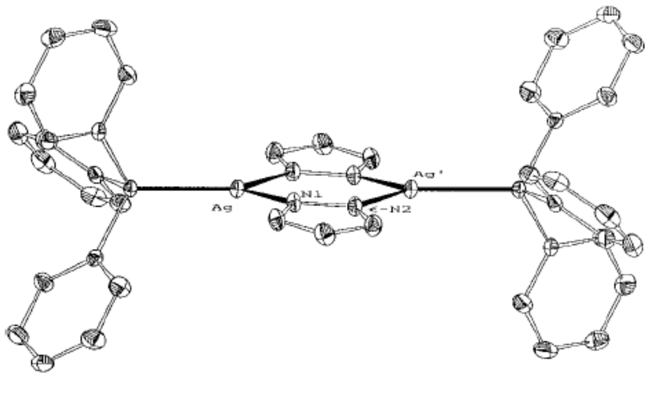


Figure 8 The structure of [Ag$_2$(pz)$_2$(PPh$_3$)$_2$].

Crystal data of [Ag$_2$(pz)$_2$(PPh$_3$)$_2$] : triclinic system, space group $P\bar{1}$, a = 9.567(2), b = 11.440(2), c = 10.073(2) Å, α = 93.59(4), β = 101.32(4), γ = 90.10(4)°, Z = 4, R = 0.0662.

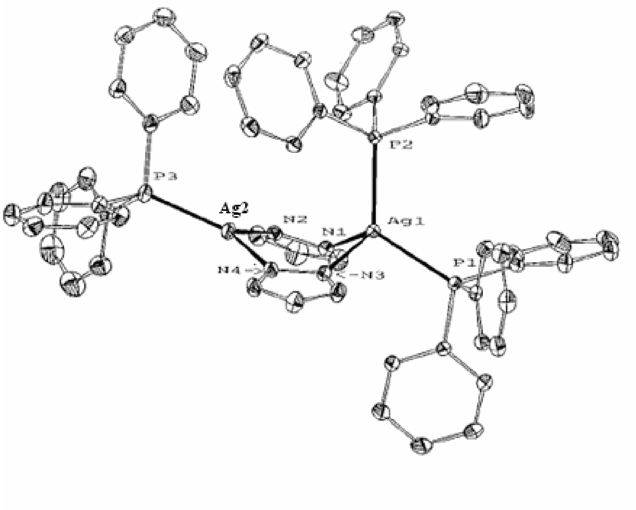


Figure 9 The structure of $[Ag_2(pz)_2(PPh_3)_3]$.

Crystal data of $[Ag_2(pz)_2(PPh_3)_3]$: triclinic system, space group $P\bar{1}$, a = 9.752(2), b = 14.136(2), c = 20.450(2) Å, α = 101.84(1), β = 99.83(2), γ = 100.68(2)° , Z = 2, R = 0.0225.

Fun *et al*., studied the reaction of the 1:3 mononuclear complexes of silver(I) iodide with diethylthiourea(detu). The crystal structure of $[AgI(C_2H_5)_2N_2S)_3]$ was determined by single-crystal X-ray diffraction methods. The structure is shown in Figure 10 (Fun *et al*., 1998). The complex is in trigonal system, space group $P31c$, a = 12.792(1), c = 9.3350(10) Å, Z = 2, R_w= 0.027.

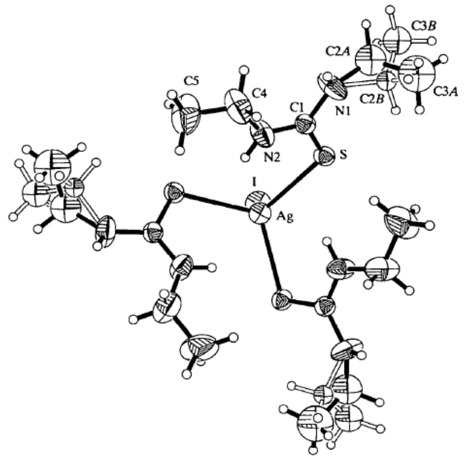


Figure 10 The structure of $[\mathrm{AgI(C_2H_5)_2N_2S)_3}]$.

Nomiya *et al.,* studied the reaction of $[\mathrm{Ag(tetz)}]_n$ with $\mathrm{PPh_3}$ (Htetz = tetrazole). The complex was characterized by TG/DTA, FT-IR and NMR spectroscopy. The crystal structure of $[\mathrm{Ag(tetz)(PPh_3)_3}]_\mathrm{n}$ was determined by single-crystal X-ray diffraction methods. The structure is shown in Figure 11 (Nomiya *et al.,* 2000).

Crystal data of $[\mathrm{Ag(tetz)(PPh_3)_3}]_\mathrm{n}$: monoclinic system, space group $P2_1/n$, a = 14.587(2), b = 9.471(3), c = 24.653(2) Å, β = 92.104(9)° , Z = 4, R = 0.044.

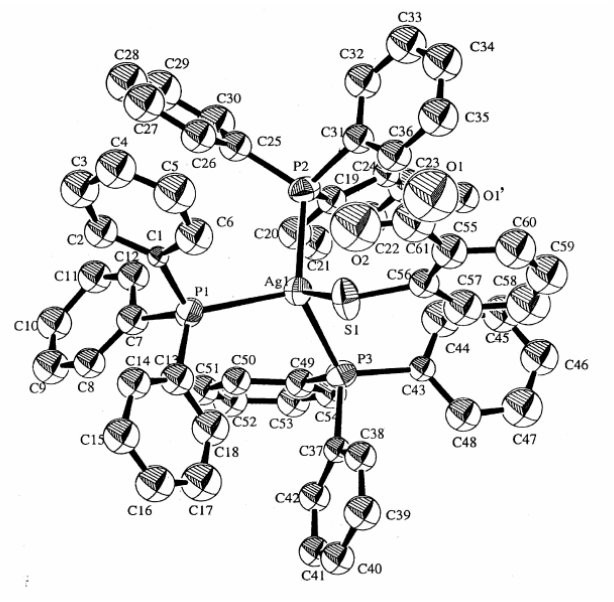


Figure 11 The structure of $[Ag(tetz)(PPh_3)_3]_n$.

Cox *et al.,* synthesised and studied the reaction of silver(I) bromide with pyrimidine-2-thione (pymtH) and triphenylphosphine. The crystal structure of $[Ag(PPh_3)(pymtH)Br]_2$ was determined by single-crystal X-ray diffraction methods. The structure is shown in Figure 12 (Cox *et al.,* 2000).

Crystal data of $Ag(PPh_3)(pymtH)Br]_2$: monoclinic system, space group *C*2/c, a = 27.284(3), b = 9.219(2), c = 18.465(2) Å, $\beta = 108.44(2)^{\circ}$, $Z = 4$, $R = 0.033$.

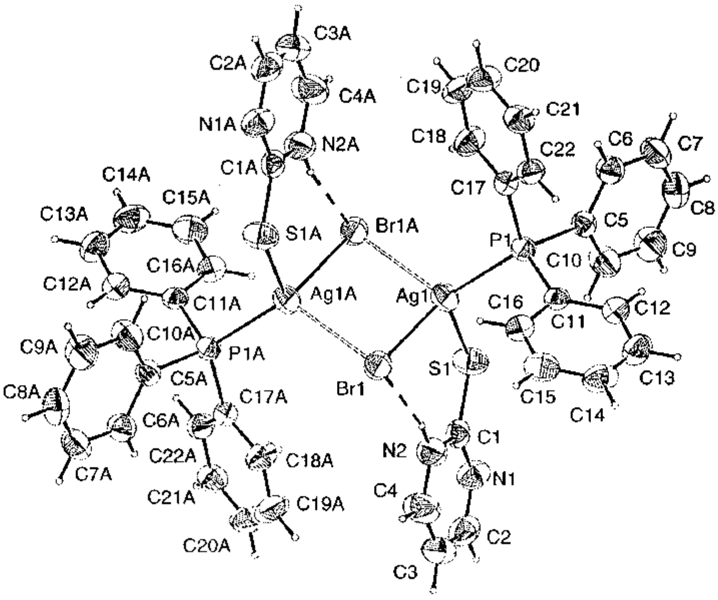


Figure 12 The structure of [Ag(PPh_3)(pymtH)Br]$_2$.

Ngo *et al.,* synthesised and studied the reaction of silver(I) nitrate with 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH), 5, mercapto-2,2,6,6-tetramethyl-4-hepten-3-one (S-tmhdH) and triphenylphosphine. The crystal structure of [Ag(tmhd)(PPh_3)](1) and [Ag(S-tmhd)(PPh_3)](2) was determined by single-crystal X-ray diffraction methods. The structures are shown in Figures 13-14 (Ngo *et al.,* 2002).

Crystal data of [Ag(tmhd)(PPh_3)] : monoclinic system, space group $P2_1/c$, a = 13.253(6), b = 11.756(3), c = 17.722(5) Å, α = 90, β = 102.40(3)°, γ = 90, Z = 4, R = 0.0422.

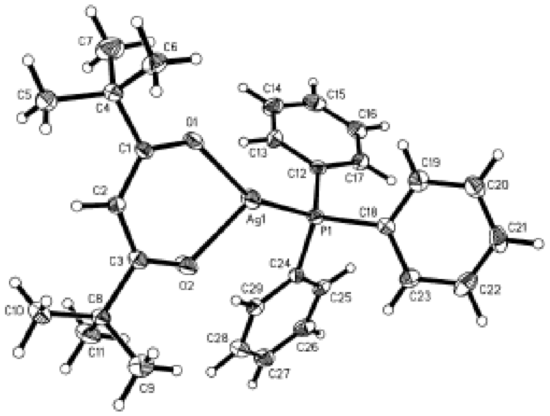


Figure 13 The structure of [Ag(tmhd)(PPh_3)].

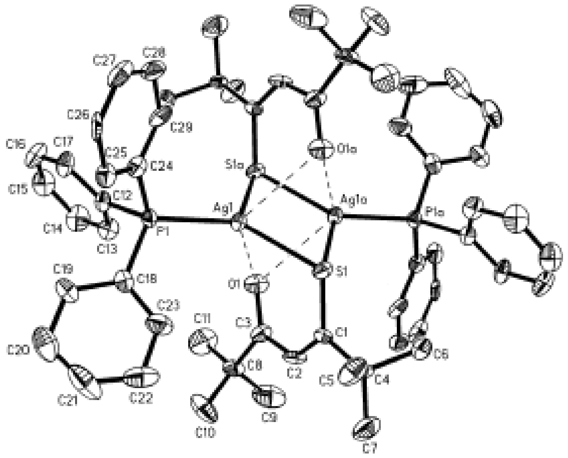


Figure 14 The structure of [Ag(S-tmhd)(PPh_3)].

Crystal data of [Ag(S-tmhd)(PPh_3)] : triclinic system, space group $P\bar{1}$, a = 11.194(3), b = 13.639(3), c = 20.431(5) Å, α = 75.32(2), β = 78.37(2), γ = 72.37(2)°, Z = 2, R = 0.0817.

Gassemzadeh *et al.,* synthesized [Ag(PPh_3)$_2$$NO_3$] with 6-methyl-4-[thiophene-2-yl-methylene-amino]-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2H)-5-one(TAMTTO) and 4-[furan-2-yl-methylene-amino]-6-methyl-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2H)-5-one(FAMTTO) yielded mononuclear complexes of the formula, [Ag(TAMTTO)(PPh_3)$_2$]NO_3 and [Ag(FAMTTO)(PPh_3)$_2$]NO_3 . The complexes were characterized by single-crystal X-ray diffraction methods. The structures are shown in Figures 15-16 (Gassemzadeh *et al.,* 2004).

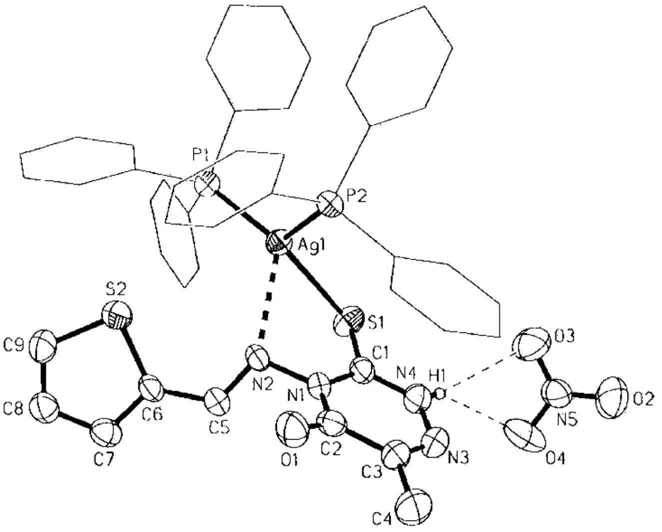


Figure 15 The structure of [Ag(TAMTTO)(PPh_3)$_2$]NO_3 .

Crystal data of [Ag(TAMTTO)(PPh_3)$_2$]NO_3 : triclinic system, space group $P\bar{1}$, a = 1151.1(1), b = 1225.1(2), c = 1887.4(3) Å, α = 78.04(1), β = 86.20(1), γ = 76.03(1)°, Z = 2 , R= 0.0662.

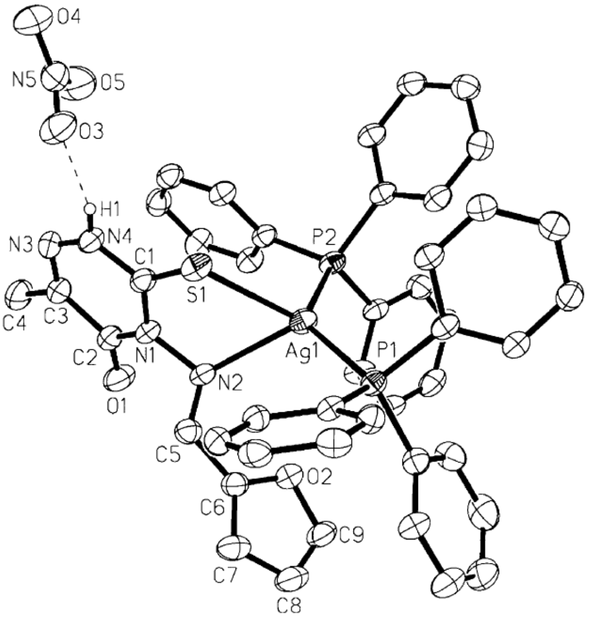


Figure 16 The structure of [Ag(FAMTTO)$(PPh_3)_2$]NO_3.

Crystal data of [Ag(FAMTTO)$(PPh_3)_2$]NO_3 : triclinic system, space group $P\bar{1}$, a = 1151.1(1), b = 1225.1(2), c = 1887.4(3) Å, α = 78.04(1), β = 86.20(1), γ = 76.03(1)°, Z = 2 , R = 0.0511.

Wei *et al.,* synthesised and studied the reaction [$Ag(PPh_3)_2NO_3$] with 2-(4 dimethylaminophenyl)imidazo(4,5-f)(1,10)phenanthroline) (NMP) yielded the complex, [$Ag(PPh_3)_2$(NMP)] and the complex was characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction methods. The structure is shown in Figure 17 (Wei *et al.,* 2005).

Crystal data of [$Ag(PPh_3)_2$(NMP)] : triclinic system, space group $P\bar{1}$, a = 10.971(4), b = 14.472(5), c = 20.053(1) Å, α = 96.475(3), β = 97.895(2), γ = 111.252(5)°, Z = 2 , R = 0.0726.

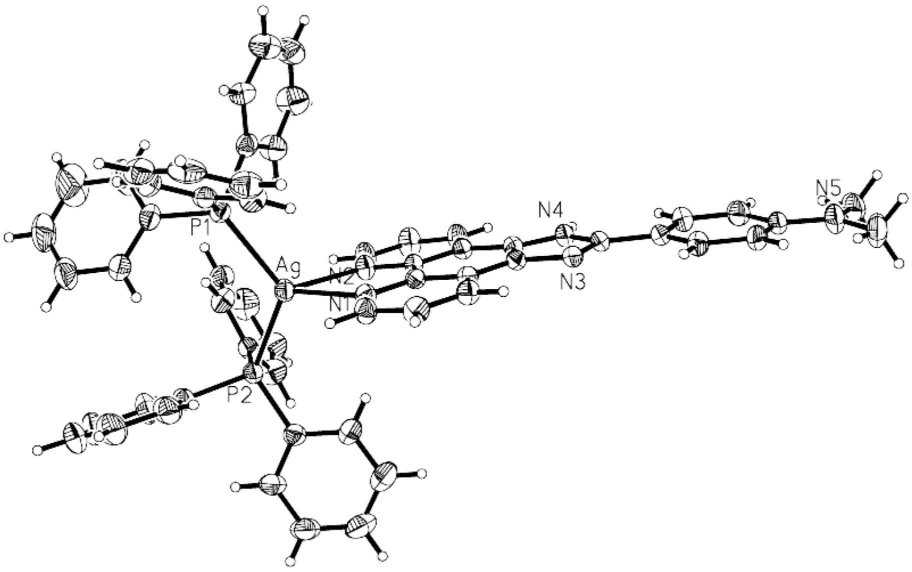


Figure 17 The structure of $[Ag(PPh_3)_2(NMP)]$.

Han *et al.,* synthesised and studied the reaction of silver α, β - unsaturated carboxylate with triphenylphosphine yielded the complex, $[Ag_2(O_2CCH{=}C(CH_3)_2(PPh_3)_2]$. The complex was characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectroscopic data and the structure was determined by single crystal X-ray diffraction methods. The structure is shown in Figure 18 (Han *et al.,* 2005).

Crystal data of $[Ag_2(O_2CCH{=}C(CH_3)_2(PPh_3)_2]$: monoclinic system, space group $P2_1/c$, a = 16.766(2), b = 7.1793(13), c = 21.026(3) Å, β = 107.89(2)°, Z = 4 ,
R = 0.0473.

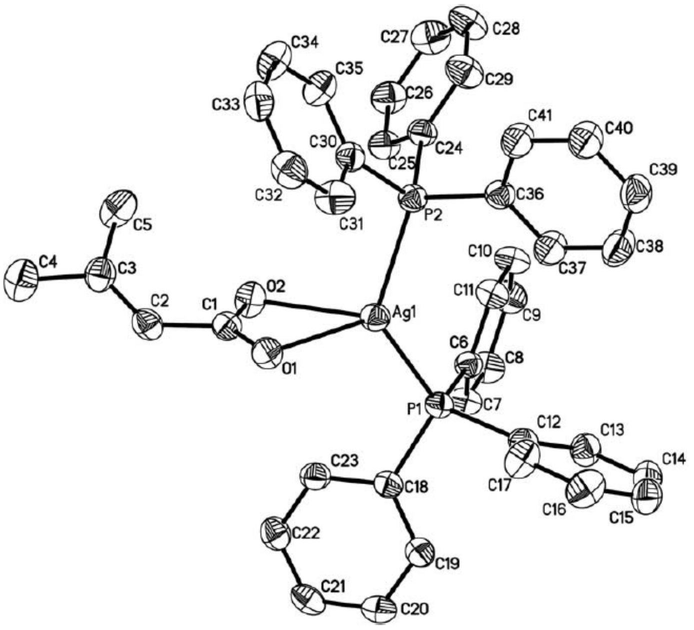


Figure 18 The structure of [$Ag_2(O_2CCH{=}C(CH_3)_2(PPh_3)_2$].

Li *et al.,* synthesized and characterized silver(I) sulfonate complexes with PPh_3, namely $Ag(L1)(PPh_3)_2$ (1), $Ag(L2)(PPh_3)_3$ (2), $[Ag_2(L3)(PPh_3)_4(H_2O)]\cdot 1.5CH_3CN\cdot 0.5H_2O$ (3) and $[Ag_4(L4)(PPh_3)_{10}]\cdot 8H_2O$ (4), where L1 = *p*-toluenesulfonate, L2 = 1-naphthalenesulfonate, L3 = 3-carboxylate-4-hydroxybenzenesulfonate, L4 = 1, 3, 6, 8-pyrenetetrasulfonate and PPh_3 = triphenylphosphine. The crystal structures were determined by single-crystal X-ray diffraction method. The structures are shown in Figures 19-22 (Li *et al.,* 2006).

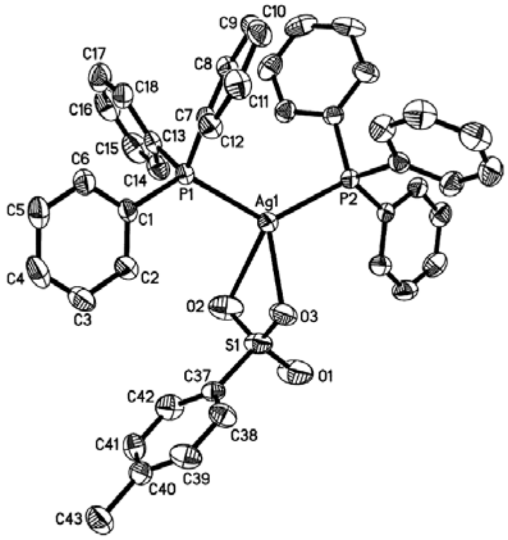


Figure 19 The structure of [Ag(L1)$(PPh_3)_2$].

Crystal data of [Ag(L1)$(PPh_3)_2$] : monoclinic system, space group $P2_1/c$, a = 15.619(5), b = 12.921(5), c = 19.429(5) Å, α = 90°, β = 108.572(5)°, γ = 90° , Z = 4 , R = 0.0359.

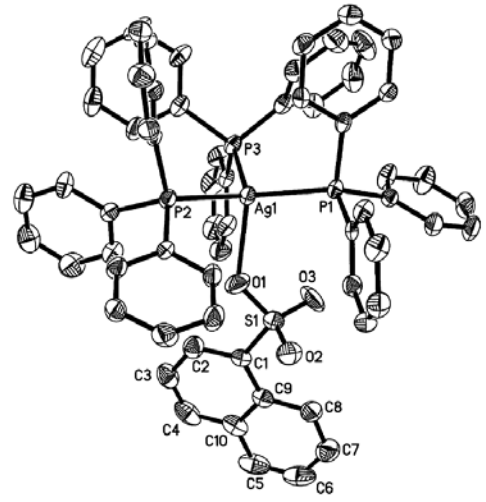


Figure 20 The structure of [Ag(L2)$(PPh_3)_3$].

Crystal data of [Ag(L2)$(PPh_3)_3$] : monoclinic system, space group $P2_1/n$, a = 13.020(2), b = 24.695(4), c = 16.425(3) Å, α = 90°, β = 95.623(4)°, γ = 90° , Z = 4 , R = 0.0977.

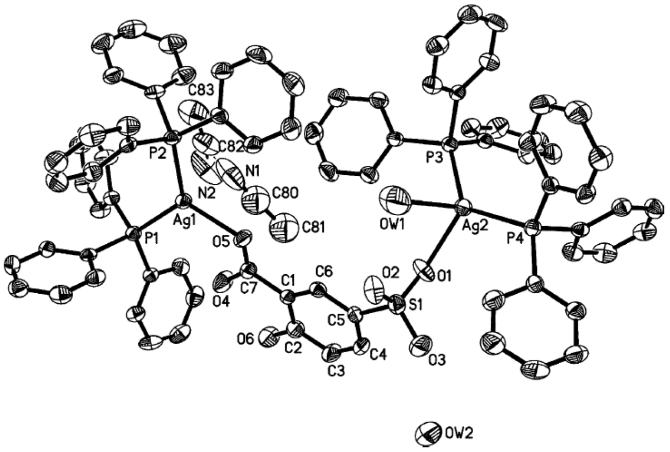


Figure 21 The structure of $[Ag_2(L3)(PPh_3)_4(H_2O)].1.5CH_3CN.0.5H_2O$.

Crystal data of $[Ag_2(L3)(PPh_3)_4(H_2O)].1.5CH_3CN.0.5H_2O$: triclinic system, space group $P\bar{1}$, a = 13.020(2), b = 24.695(4), c = 16.425(3) Å, α = 90°, β = 95.623(4)°, γ = 90° , Z = 4 , R = 0.0421.

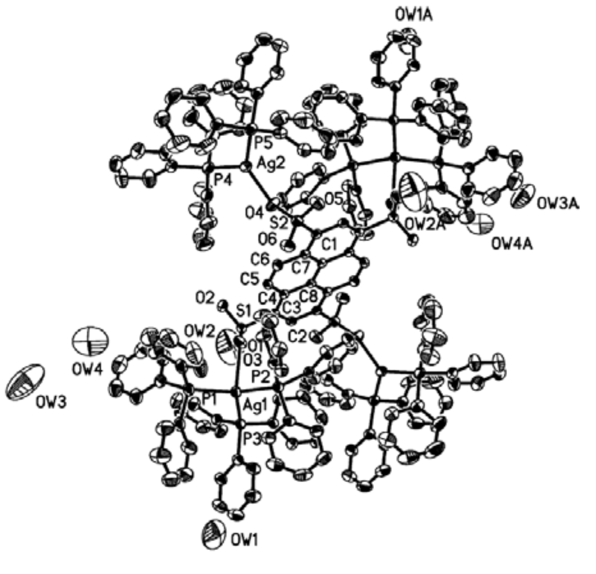


Figure 22 The structure of $[Ag_4(L4)(PPh_3)_{10}]\cdot 8H_2O$.

Crystal data of $[Ag_4(L4)(PPh_3)_{10}]\cdot 8H_2O$: triclinic system, space group $P\bar{1}$, a = 13.3518(6), b = 19.6573(8), c = 20.0069(1) Å, α = 60.943(1), β = 85.559(1), γ = 80.269(1)°, Z = 1 , R = 0.0437.

Jia *et al.,* studied the reaction of Ag_2SO_4 with ethylenethiourea (etu) yielded the complex, $[Ag(etu)_3]_2SO_4$. The complex was characterized by single crystal X-ray crystallography. In crystallographically independent Ag^+ ions are trigonally coordinated by three monodenate etu ligands. The structure is shown in Figure 23 (Jia *et al.,* 2007).

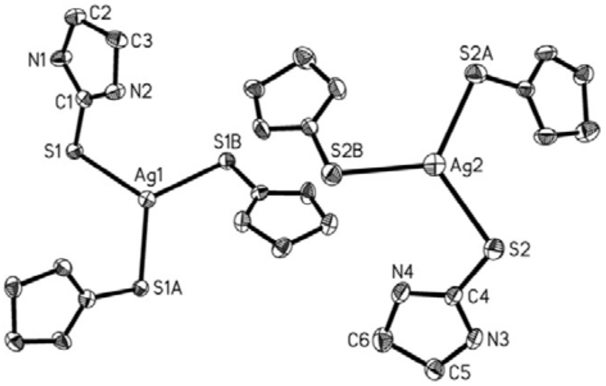


Figure 23 The structure of $[Ag(etu)_3]_2SO_4$.

Crystal data of $[Ag(etu)_3]_2SO_4$: trigonal system, space group *R3c*, a = 12.983(3), b = 12.983(3), c = 34.894(7) Å, Z = 6 , R = 0.0446.

Stey *et al.,* synthesized and characterized silver(I) with tropolonate and triphenylphosphine yielded the complex, $[Ag(C_7H_5O_2)(C_{18}H_{15}P)_2]{\cdot}CH_2Cl_2$. Crystal structure of the this complex was determined by X-ray analysis. The structure is shown in Figure 24 (Stey *et al.,* 2009).

Crystal data of $[Ag(C_7H_5O_2)(C_{18}H_{15}P)_2]{\cdot}CH_2Cl_2$: triclinic system, space group $P\bar{1}$, a = 12.0175 (3), b = 12.9925 (4), c = 13.8394 (7)Å, α = 100.487 (2), β = 93.760 (2), γ = 116.809 (1)°, Z = 2 , R = 0.046.

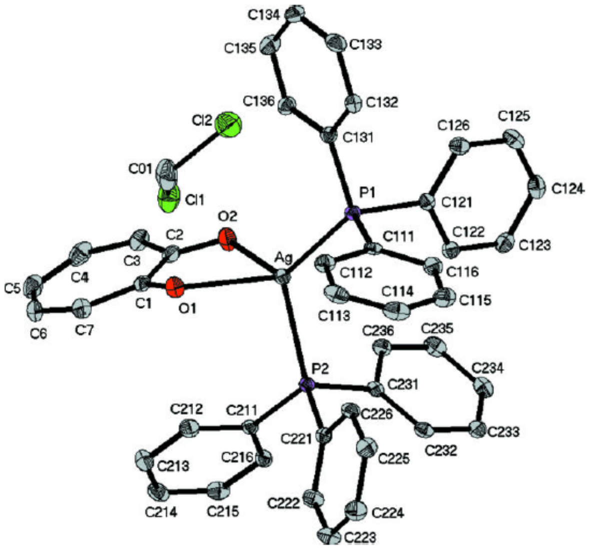


Figure 24 The structure of $[Ag(C_7H_5O_2)(C_{18}H_{15}P)_2]{\cdot}CH_2Cl_2$

Wu *et al.,* studied the reaction of silver(I) trifluoromethanesulfonate with 1,10-Phenanthroline and triphenylphosphine yielded the complex, $[Ag(C_{12}H_8N_2)(C_{18}H_{15}P)]CF_3SO_3$. The crystal structures were determined by single-crystal X-ray diffraction method. The structure is shown in Figure 25 (Wu *et al.,* 2009).

Crystal data of $[Ag(C_{12}H_8N_2)(C_{18}H_{15}P)]CF_3SO_3$: triclinic system, space group $P\bar{1}$, a = 10.9832(2), b = 11.7533(2), c = 12.2642 (3)Å, α = 77.711 (1), β = 76.183 (1), γ = 73.440 (1)°, Z = 2 , R = 0.

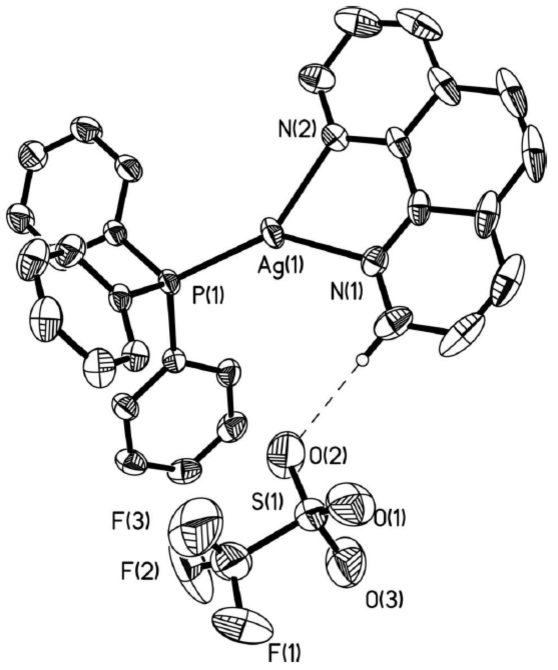


Figure 25 The structure of $[Ag(C_{12}H_8N_2)(C_{18}H_{15}P)]CF_3SO_3$.

1.3 Objectives

1. To study the method and find the optimum condition for synthesizing silver(I) complexes with mixed ligands of triphenylphospine and phenylthiourea by varying mole ratio of reactants, solvents, temperature of reaction and so on.
2. To synthesize and characterize the structures of these complexes by single crystal X-ray diffraction technique, IR, NMR and XRF spectroscopies.
3. To study molecular structure, arrangement of the molecules in unit cell, including crystal system, cell parameters and space group of the complexes.
4. To be the fundamental informations for other researcher who take them to find more applications.
5. To present the research in academic conference or publish in chemistry journal.

CHAPTER 2

Experiment

2. Method of Study

2.1 Materials and Instruments

1. Thermometer, Gallenkamp, England, 0-360 °C
2. Capillary tube
3. Capillary melting point apparatus, Thomas Hoover, Unimelt 0-360 °C
4. Hot plate stirrer with magnetic bar
5. X-ray fluorescence spectrometer model PW 2400, Philips
6. Fourier transform infrared spectrometer, model 783, Perkin – Elmer
7. Fourier transform NMR spectrometer 500 MHz, model UNITY INOVA, Varian
8. Bruker SMART APEX CCD diffractometer
9. UHU epoxy adhesive
10. Fiber glass, 0.4-0.7 mm. (in diameter)
11. Bee wax

2.2 Chemicals

Products of Fluka Chemical, Buchs, Switzerland

N-phenylthiourea, $C_7H_8N_2S$, purum

Triphenylphosphine, $C_{18}H_{18}P$, purum

Silver(I) bromide, AgBr, L.R. grade

Silver(I) chloride, AgCl, L.R. grade

Silver(I) nitrate, $AgNO_3$, L.R. grade

Products of Lab-Scan Analytical Science
Acetonitrile, CH_3CN, A.R. grade
Ethanol, C_2H_5OH, A.R. grade

2.3 Preparation of Complexes

2.3.1 Preparation of [AgCl(PPh$_3$)$_2$(ptu)] Complex

Triphenylphosphine (0.36g, 1.39 mmol) was dissolved in 30 cm^3 of acetonitrile at 70-75 °C and then AgCl (0.1g, 0.69 mmol) was added. The mixture was stirred for 2 hours during that time a greenish precipitate was formed. *N*-phenylthiourea (0.10g, 0.69 mmol) was added and the new reaction mixture was heated under reflux for 5 hours where upon the precipitate gradually disappeared. The resulting clear solution was filtered off and left to evaporate at room temperature. The microcrystalline solids, which were deposited upon standing for several days, were filtered off and dried in vacuo.

2.3.2 Preparation of [AgBr(PPh$_3$)$_2$(ptu)] Complex

Triphenylphosphine (0.27g, 1.06 mmol) was dissolved in 30 cm^3 of acetonitrile at 70-75 °C and then AgBr (0.10g, 0.53 mmol) was added. The mixture was stirred for 2 hours during that time a greenish precipitate was formed. *N*-phenylthiourea (0.08g, 0.53 mmol) was added and the new reaction mixture was heated under reflux for 5 hours where upon the precipitate gradually disappeared. The resulting clear solution was filtered off and left to evaporate at room temperature. The microcrystalline solids, which were deposited upon standing for several days, were filtered off and dried in vacuo.

2.3.3 Preparation of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$ Complex

Triphenylphosphine (0.31g, 1.17 mmol) was dissolved in 30 cm^3 of ethanol at 75-80 °C and then $AgNO_3$ (0.1g, 0.58 mmol) was added. The mixture was stirred for 2 hours after that a complete clear solution was formed. *N*-phenylthiourea (0.08g, 0.58 mmol) was added slowly and the new reaction mixture was heated with continuous stirring for 5 hours. The resulting clear solution was filtered off and left to evaporate at room temperature. The colorless crystals deposited upon standing for several days were filtered off and dried in vacuo.

2.4 Methods for Determination Structures

2.4.1 Melting Point Measurement

Melting points of the complexes were measured on capillary Melting Point Apparatus, Thomas Hoover, Unimelt 0-360 °C.

2.4.2 Elemental Analysis

Carbon, hydrogen, nitrogen, sulfur and phosphorus contents in the synthetic crystals were determined by CE Instruments flash 1112 Series EA CHNS-O Analyser.

2.4.3 X-ray Fluorescence Spectrometry

Ag, S, P and halides (Cl and Br) qualitative analyses of $[AgCl(ptu)(PPh_3)_2]$ $[AgBr(ptu)(PPh_3)_2]$ and $[Ag(ptu)(PPh_3)_2]NO_3$ were performed by X-ray Fluorescence spectrometer (Perkin Elmer, PW2400).

2.4.4 Fourier Transfrom Infrared Spectroscopy (FT-IR)

Infrared spectra in the region 4000-400 cm^{-1} were measured on a Perkin-Elmer 783 Infrared Spectrophotometer and Perkin-Elmer Spectrum GX FTIR-Spectrophotometer using potassium bromide disc.

2.4.5 Fourier Transfrom NMR Spectroscopy (FT-NMR)

^{1}H and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Varian Inova spectrometer at 500 MHz. The chemical shift values are on δ scale and the coupling constants (*J*) are in Hz.

2.5 Crystal Structure Determination

The X-ray diffraction data of [AgCl(ptu)(PPh$_3$)$_2$], [AgBr(ptu)(PPh$_3$)$_2$] and [Ag(ptu)(PPh$_3$)$_2$]NO$_3$ were collected using SMART APEX CCD at the Department of Chemistry, Prince of Songkla University.

The structures of the synthesized crystals were determined by following steps in Figure 26. (Clegg, 1998)

Figure 26. shows an outline of crystal structure determination in a simplified form as a schematic flowchart. The involved steps are in the boxes. To the right of each is listed the information obtained and to the left an indication of the time-scale involved in carrying out the operation.

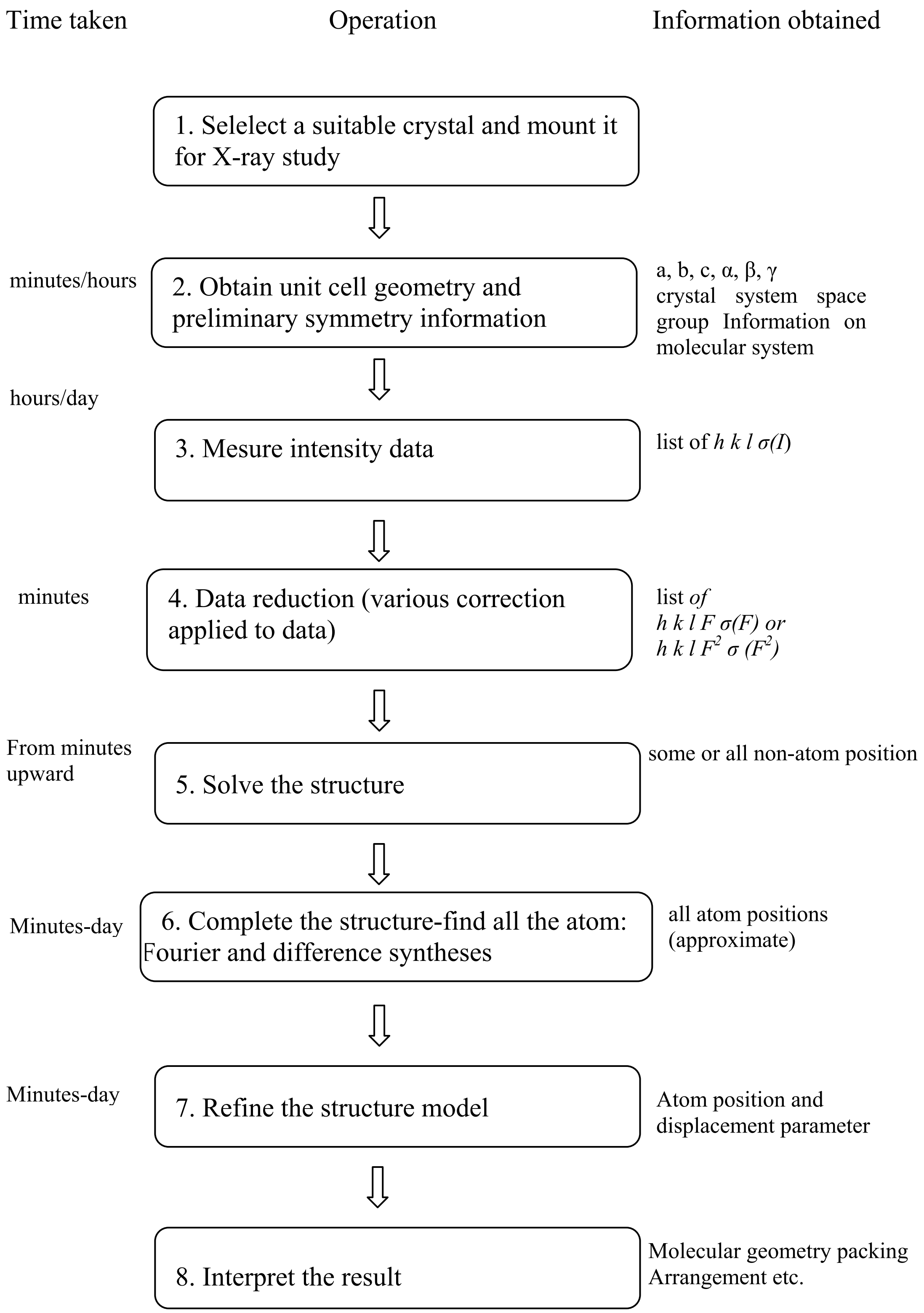


Figure 26 A flowchart for the step involved in a crystal structure determination (Clegg, 1998).

2.5.1 Selection of a Suitable Crystal

If a crystal is satisfactory for collecting X-ray diffraction data, the following characterizations must be required :

(1) A crystal must be pure at the molecular, ionic or atomic levels. it must be a single crystal. It should not be grossly fractured, bent or otherwise physically distorted.

(2) It must be of proper size and shape, 0.2 - 0.4 mm

(3) Check crystals under a polarizing microscope. A good single crystal will extinguish completely on a distinct position on the crossed polarization filters.

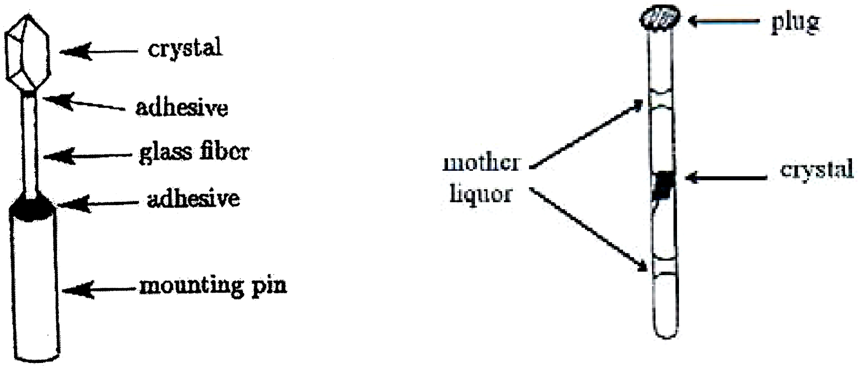
(4) Scan crystal with the Apex CCD, i.e. make a few quick exposures and check the images visually on spot shape, spacing and distribution.

2.5.2 Crystals Mounting

For single-crystal X-ray diffractometry it is convenient to have the crystal mounted so that it can be moved for proper alignment and centering in the camera. Crystals need to be mounted in such a way that they can be manipulated in various devices used for intensity measurement. Two methods are commonly used to mount crystals :

(1) Crystals that are not volatile or sensitive to the environment are glued onto a thin glass fiber with an epoxy glue (Figure 27a). All studied crystals were mounted by this method.

(2) Crystals that are air-sensitive or that degrade by loss of loosely bound solvent require special treatment. They may be sealed in thin-walled glass capillary tubes (Figure 27b). Alternatively, the crystals can be coated with an inert viscous oil and then manipulated without difficulty under a normal microscope in the open atmosphere.



(a) (b)

Figure 27 Crystal mounting.

2.5.3 Optical Alignment

The mounted crystal was attached to a goniometer head (Figure 28). The goniometer head is a delicate instrument that can be translationally adjusted (in 3 dimensions) to bring the crystal into the X-ray beam and center it on an axis of rotation (phi) defined by the goniometer. The goniometer rotates omega slowly during data collection to bring different reflections into diffraction position. It is absolutely critical that the translation screws on the goniometer head be adjusted so that the crystal is centered in the X-ray beam throughout 360 degrees of rotation in phi.

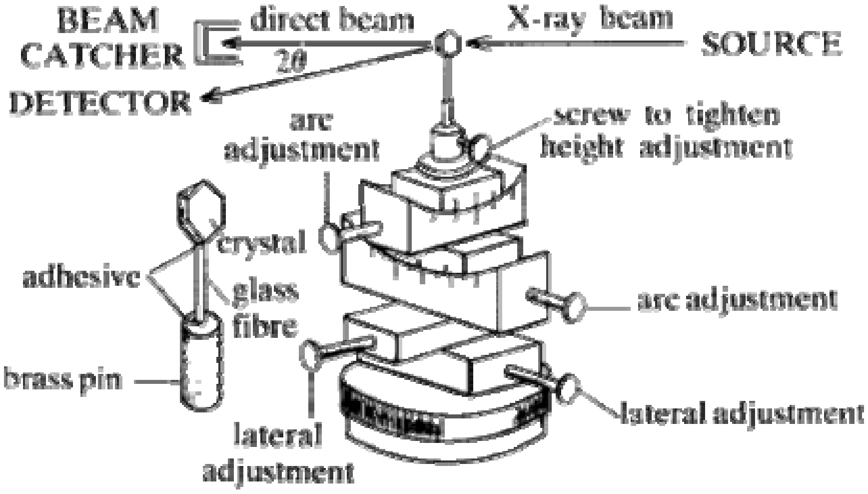


Figure 28 The goniometer head.

2.5.4 Data Collection

The good of data collection is to determine the indices and record the intensities of as many reflections, as rapidly and efficiently as possible. For this work, the device used for data collection is the SMART APEX CCD area detector with the Bruker platform diffractometer at Prince of Songkla University Crystallography Lab.

2.5.5 Obtaining Unit Cell Geometry and Symmetry

Some reflections of high intensity are located by simply driving the various motor while monitoring the detector output for a single significantly above background (a blind search, all under computer control). From these positions, the crystal orientation, unit cell geometry and reflection indices have to be determined simultaneously, by calculations which are not simple and are usually regarded as computer black-box methods, but they are all based essentially on the Bragg equation (Appendix B). A diffractometer will often give a unit cell and orientation for a crystal in less than an hour.

2.5.6 The Measurement of Intensities

The diffractometer with CCD detector measures intensities of diffracted beam in an automatic, computer-controlled process

The result of this process is a list of reflections, usually thousands of them, each with *hkl* indices and measured intensity. In addition, from diffractometer measurements each intensity I has an associated standard uncertainly (s.u.), $\sigma\ (I)$, which is calculated from the known statistical properties of the X-ray generation and diffraction processes, and is a measure of the precision or reliablilty of the measurement.

2.5.7 Data Reduction

The intensity of an X-ray beam is proportional to the square of the wave amplitude, $[\mathrm{I}(hkl)\ \alpha\ |F(hkl)|^2]$. The measured intensity is affected by various factors, eg. Lorenz-polarisation factors, absorption problems etc., however, for which corrections must be applied. The conversion of intensities I to 'observed structure amplitudes' $|F_o|$ (o = observed) or F^2_{o} and, correspondingly, of s.u.'s $\sigma(I)$ to $\sigma\ (F_o)$ or $\sigma\ (F^2_o)$ is known as data reduction and has several components.

The various corrections for the intensities are applied also to their s.u.'s. The result of this whole process, which usually takes only a matter of minutes on a computer, is a list of reflection as $h, k, l,\ |F_o|$, $\sigma(F_o)$ [or h, k, l, F^2_o, $\sigma(F^2_o)$; the advantage of retaining the squared form is that no special treatment is required for intensities measured as negative.

2.5.8 Structure Determination and Refinement

The intergration process (SAINT) has produced two important files- compid.p4p, containing the final unit cell parameters and important information on how the experiment was carried out, and compid.raw, containing the actual intensity data where compid is the compound identification code. These files are all that required to begin the structure solution and refinement process. The various steps in solving and refining the structure are carried out using the programs of the SHELXTL package (Sheldrick, 2000).

A simplified flow chart is shown in Figure 29.

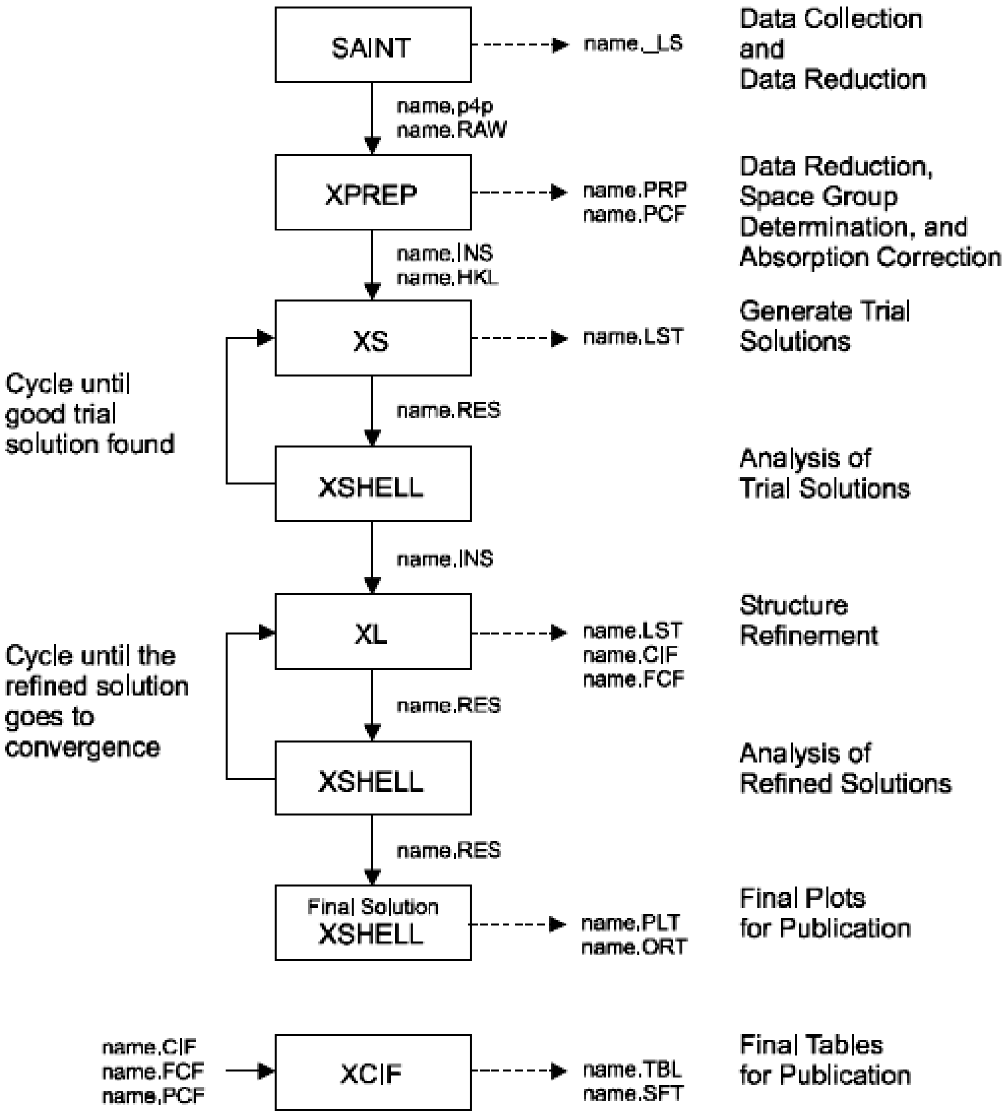


Figure 29 A flowchart of structure determination and refinement.

The refinement process uses a well-established mathematical procedure called least-squares analysis, which define the best fit two sets of data (here $|F_o|$ and $|F_c|$) to be that which minimizes one of the least-squares sum : $\sum w(F_o^2 - F_c^2)$

w = Reflection weights

F_o = Observed structure factors

F_c = Calculated structure factors

If atoms of the model structure are approximately in the right positions, there should be at least some degree of resemblance between the sets of calculated structure factors, $|F_c|$, and observed structure factors, $|F_o|$. This is the most widely used assessment is a so-called residual factor or R-factor, define as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)}{\sum w(F_o^2)^2}}$$

For a correct and complete crystal structure determination from well measured data, *R* is typically around 0.02-0.05 or 2-5 %.

CHAPTER 3

RESULTS

3.1 Preparation of Complexes

The optimum condition of preparation complexes for which X-ray crystal structures have been determined in the course of this study are shown in Table 1. Some of their physical properties together with reacting ligands are summarized in Tables 2, 3 and 4.

Table 1. The condition of preparation compounds.

Reactants	Mole ratio	Solvent	Temp* (°C)	Complex
AgCl : PPh_3 : ptu	1:2:1	acetonitrile	70-75	$[AgCl(PPh_3)_2(ptu)]$
AgBr : PPh_3 : ptu	1:2:1	acetonitrile	70-75	$[AgBr(PPh_3)_2(ptu)]$
$AgNO_3$: PPh_3 : ptu	1:2:1	ethanol	75-80	$[Ag(PPh_3)_2(ptu)]NO_3$

Temp* = temperature

Table 2. The physical properties of ligands and complexes.

Compound	Physical properties		
	Appearance	Color	Melting point (°C)
Ligand ptu	Powder	White	145-150
Ligand PPh_3	Powder	White	79-81
$[AgCl(PPh_3)_2(ptu)]$	Block	Colorless	204-206
$[AgBr(PPh_3)_2(ptu)]$	Block	Colorless	194-196
$[Ag(PPh_3)_2(ptu)]NO_3$	Block	Colorless	192-194

Table 3. The solubility of complexes at room temperature (28-29 ºC)

Complexes Solvent	[AgCl(PPh_3)$_2$(ptu)]	[AgBr(PPh_3)$_2$(ptu)]	[Ag(PPh_3)$_2$(ptu)]NO_3
H_2O	-	-	-
CH_3OH	-	-	-
C_2H_5OH	-	-	-
CH_3CN	-	-	-
CH_3COCH_3	+	+	+++
$CHCl_3$	++	++	+++
CH_2Cl_2	+++	++	+++
DMSO	+	+	+++
DMF	+	+	+++

Remark:

The weight of samples for testing solubility is 0.0032-0.0040 g.

-	:	insoluble
+	:	partially soluble
++	:	soluble
+++	:	highly soluble

3.2 Elemental analysis

Table 4. The partial elemental analyses of the complexes.

Complex	%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	%S Found (Calcd.)
[AgCl(PPh$_3$)$_2$(ptu)]	62.75 (62.97)	4.62 (4.66)	2.91 (3.41)	3.40 (3.90)
[AgBr(PPh$_3$)$_2$(ptu)]	59.18 (59.73)	4.34 (4.42)	2.74 (3.24)	3.20 (3.70)
Ag(PPh$_3$)$_2$(ptu)]NO$_3$	65.16 (65.99)	4.96 (4.52)	4.46 (4.96)	3.28 (3.78)

3.3 X-ray Fluorescence Spectrometry

The X-ray fluorescence spectra of the compounds are shown in Figure 30-36.

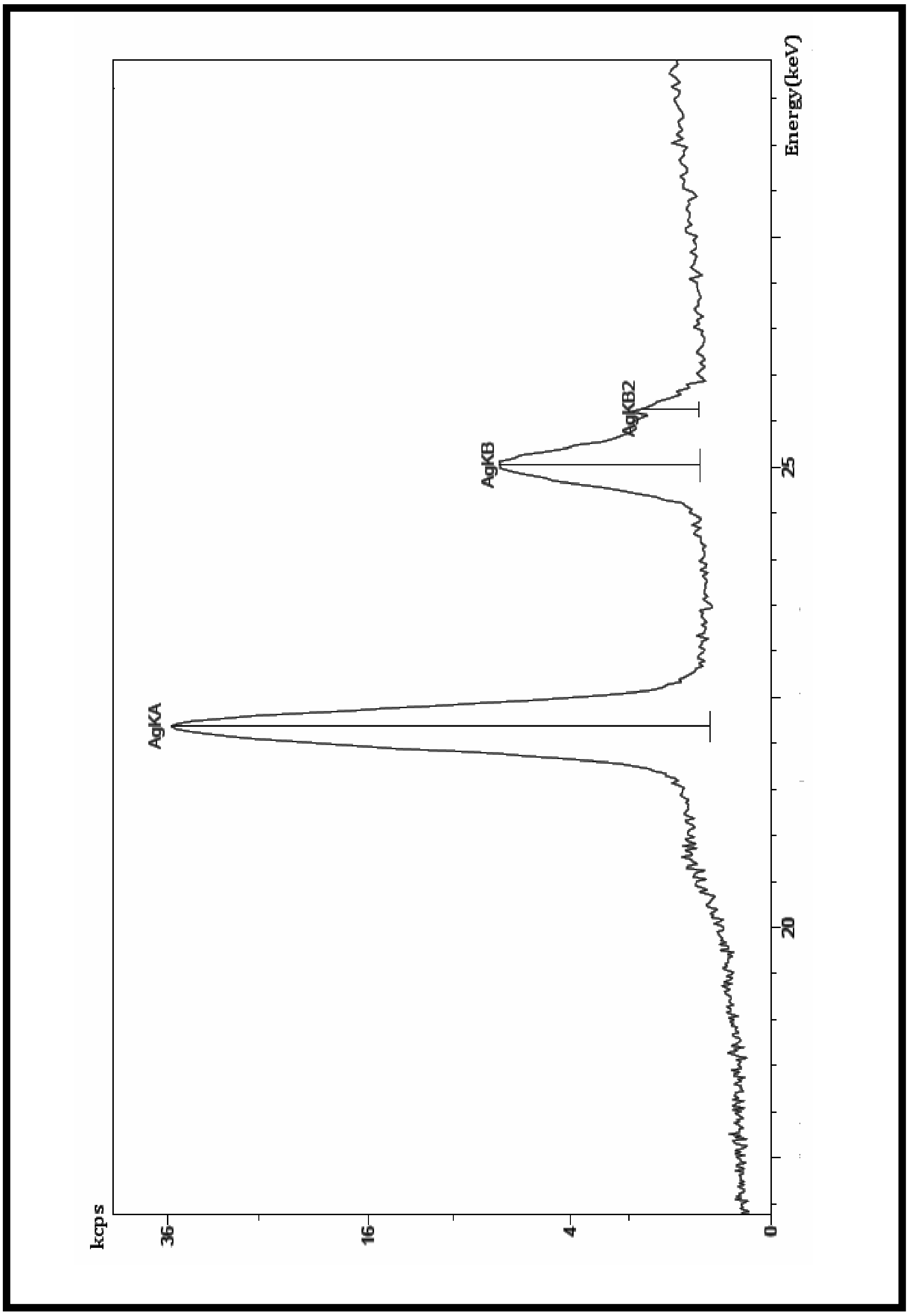


Figure 30 The XRF spectrum of Ag in [$AgCl(PPh_3)_2(ptu)$].

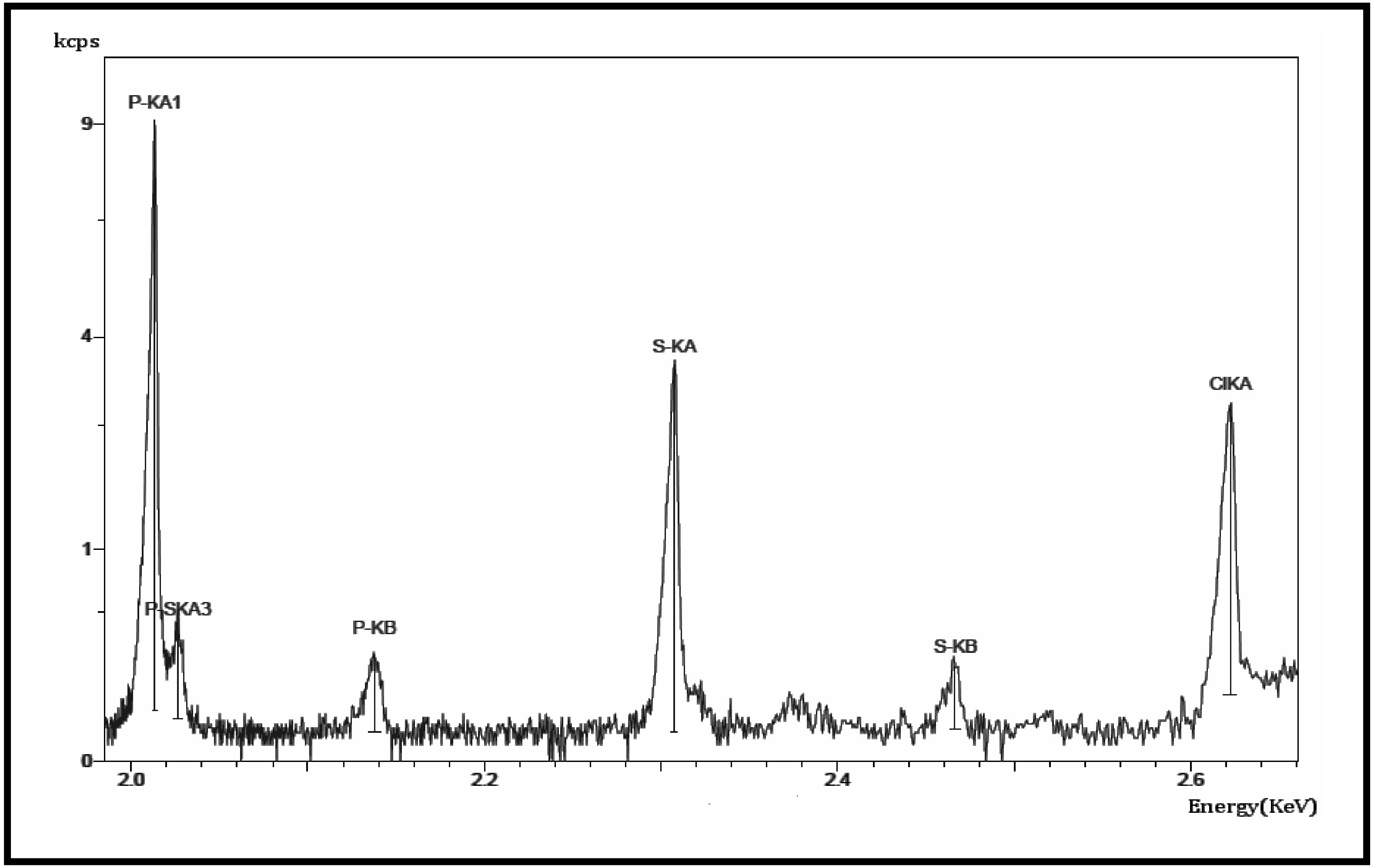


Figure 31 The XRF spectrum of Cl, S, and P in [AgCl(PPh$_3$)$_2$(ptu)].

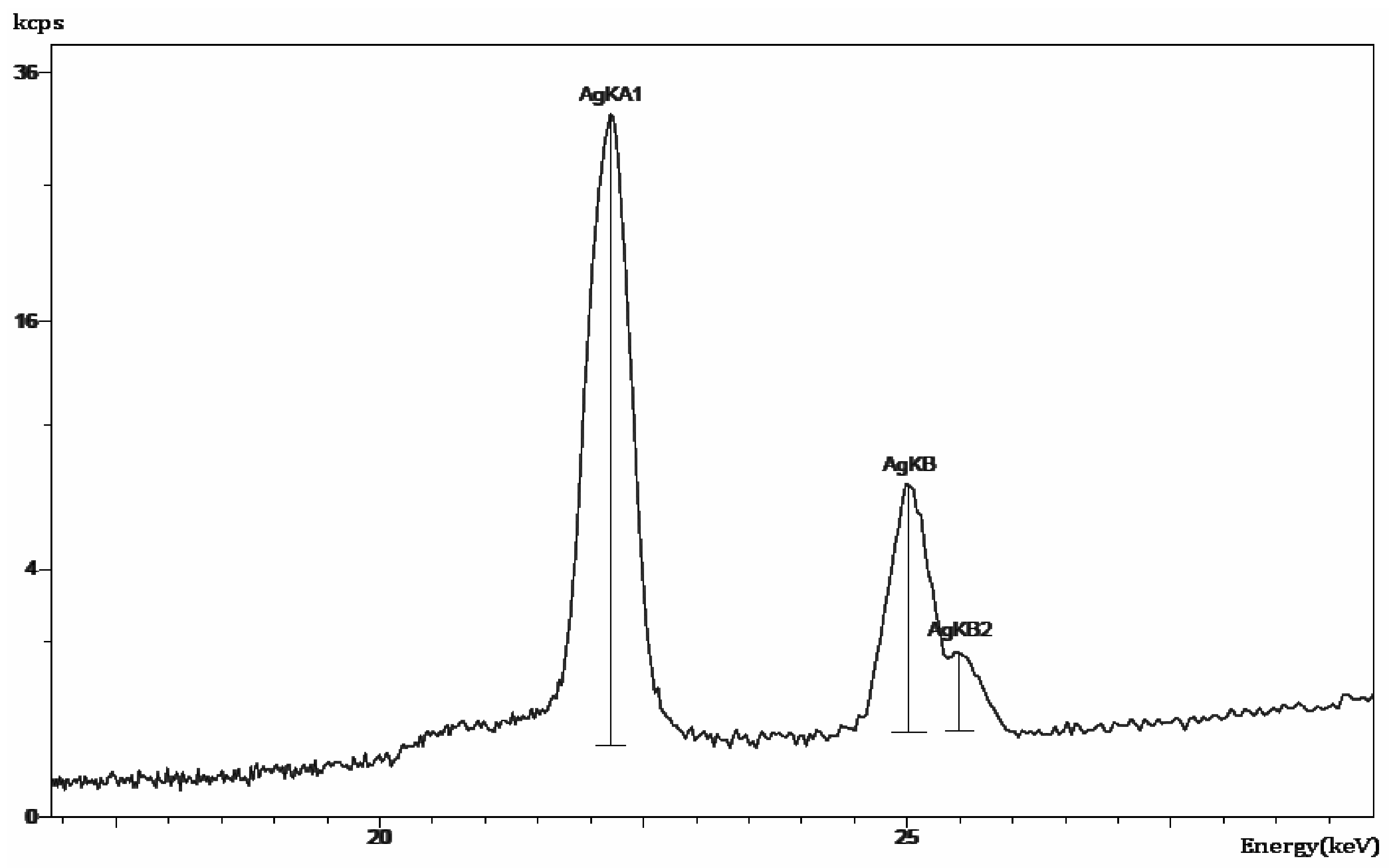


Figure 32 The XRF spectrum of Ag in [$AgBr(PPh_3)_2(ptu)$].

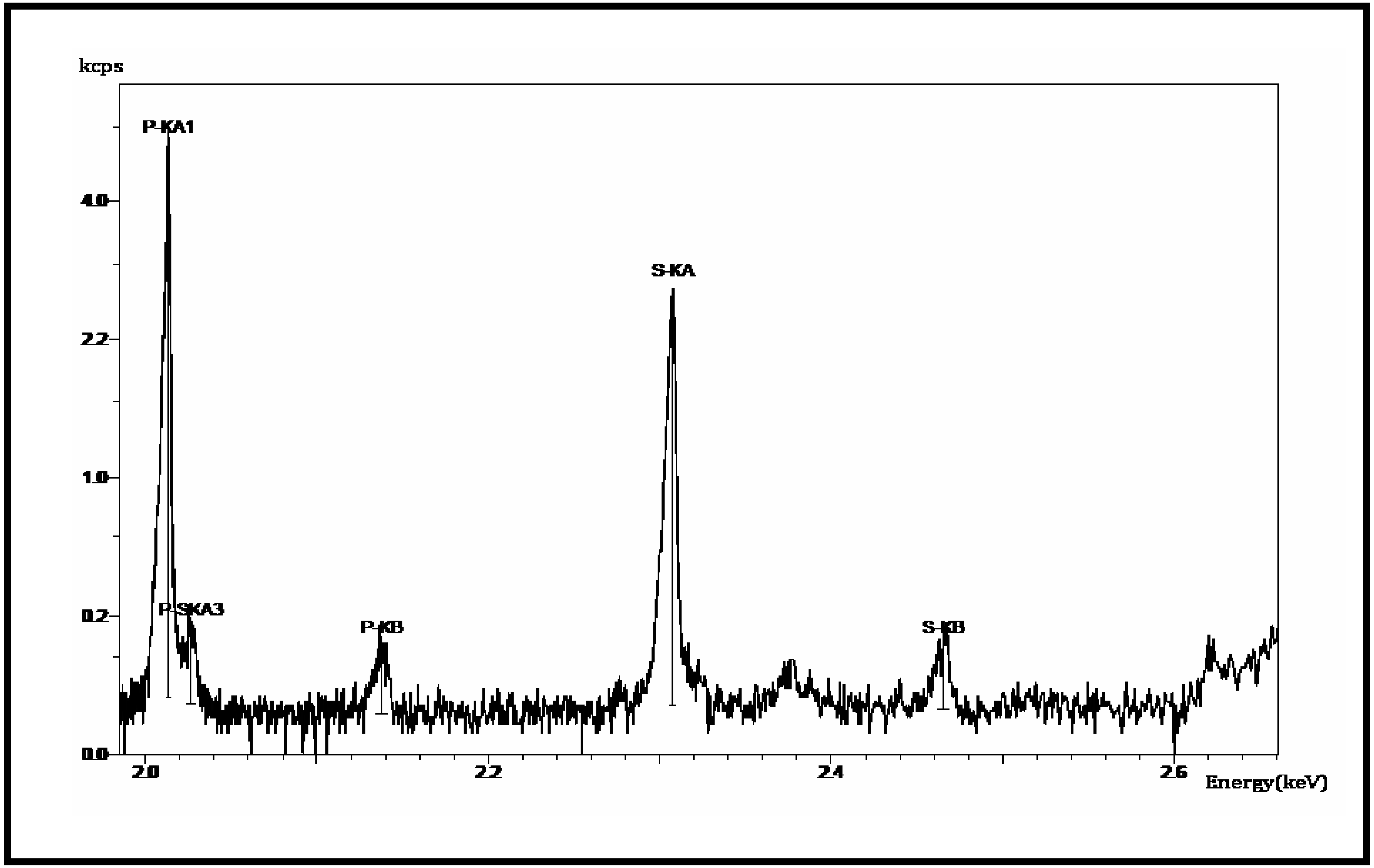


Figure 33 The XRF spectrum of S and P in [$AgBr(PPh_3)_2(ptu)$].

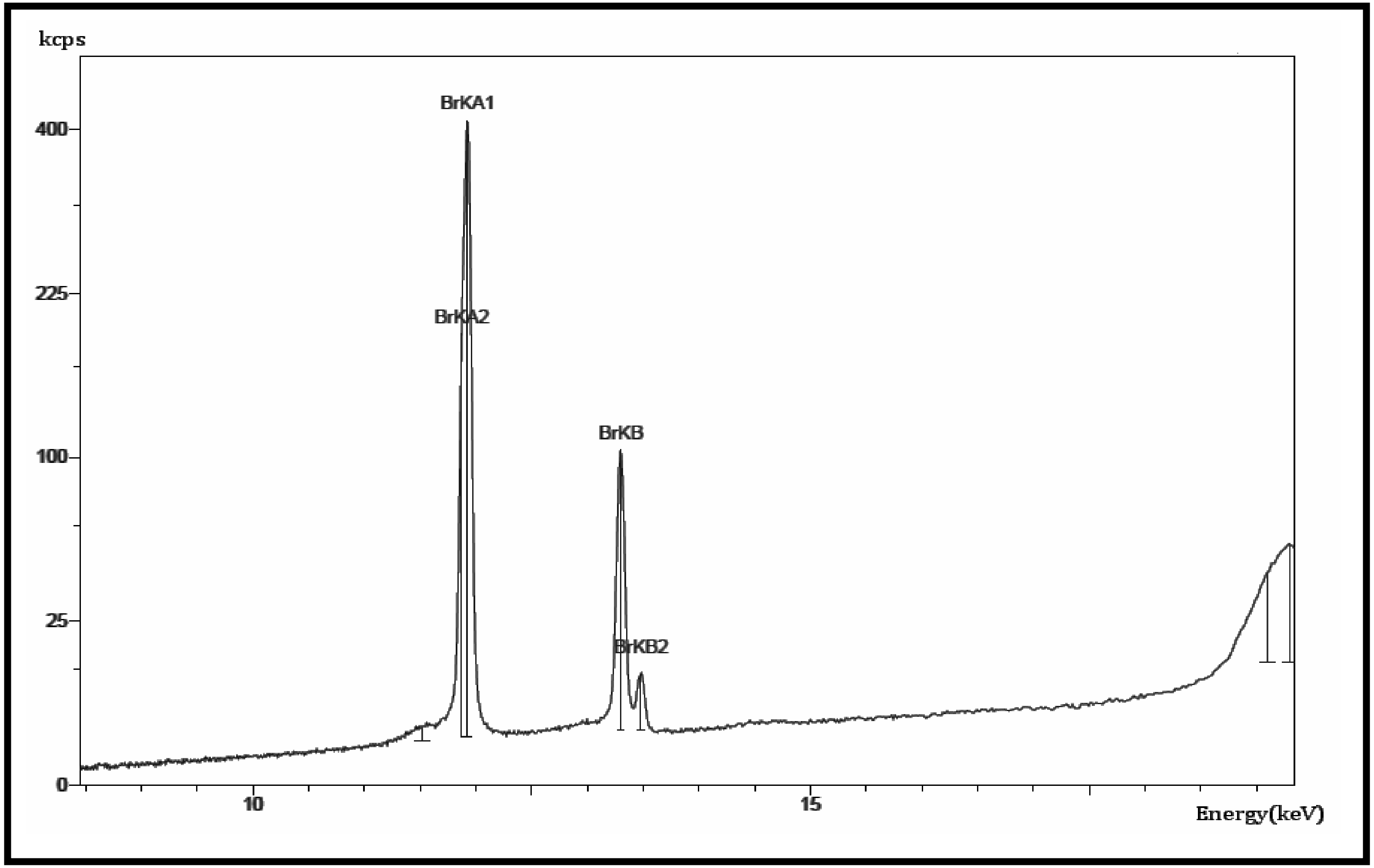


Figure 34 The XRF spectrum of Br in [AgBr$(PPh_3)_2$(ptu)].

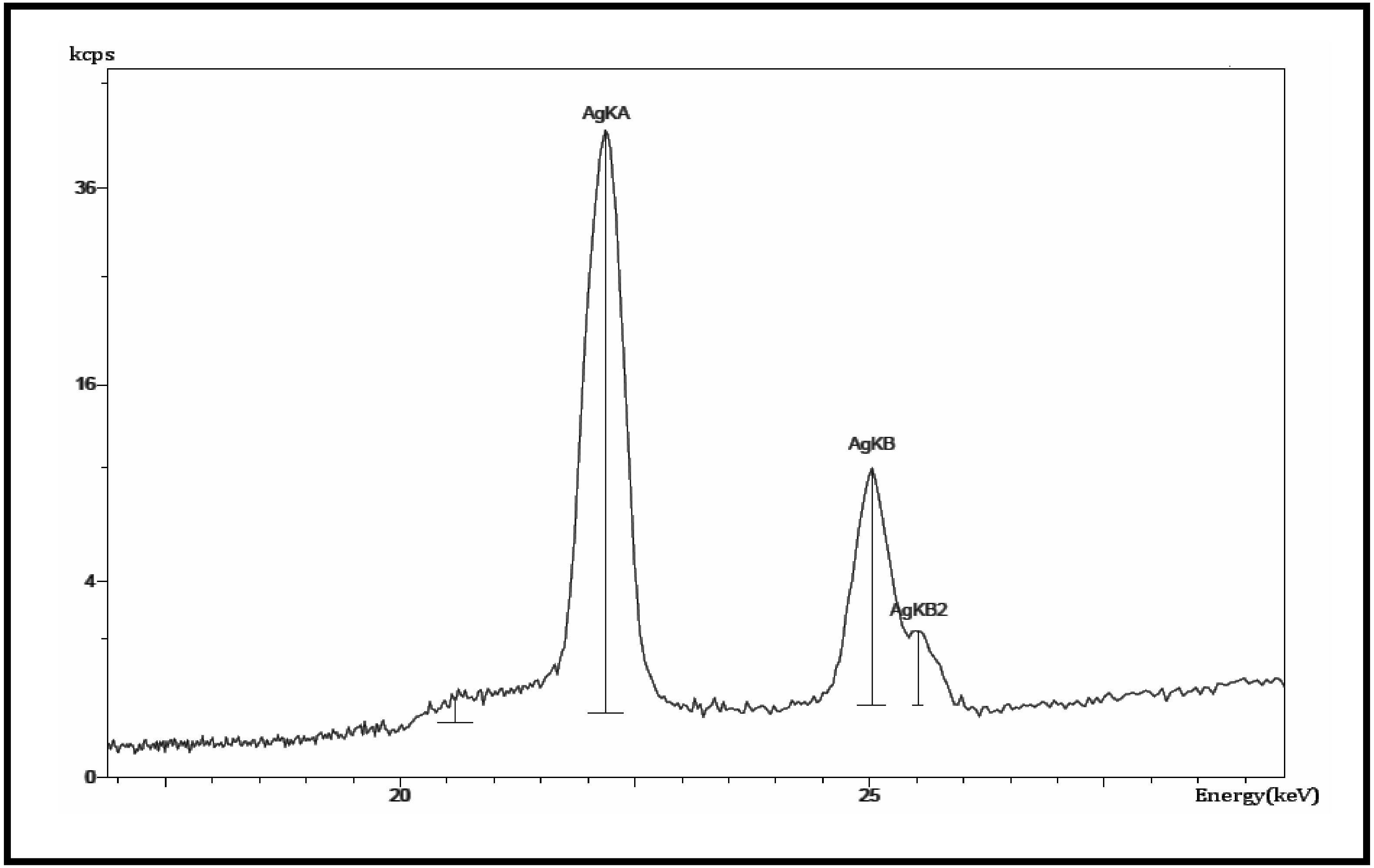


Figure 35 The XRF spectrum of Ag in $[Ag(PPh_3)_2(ptu)]NO_3$.

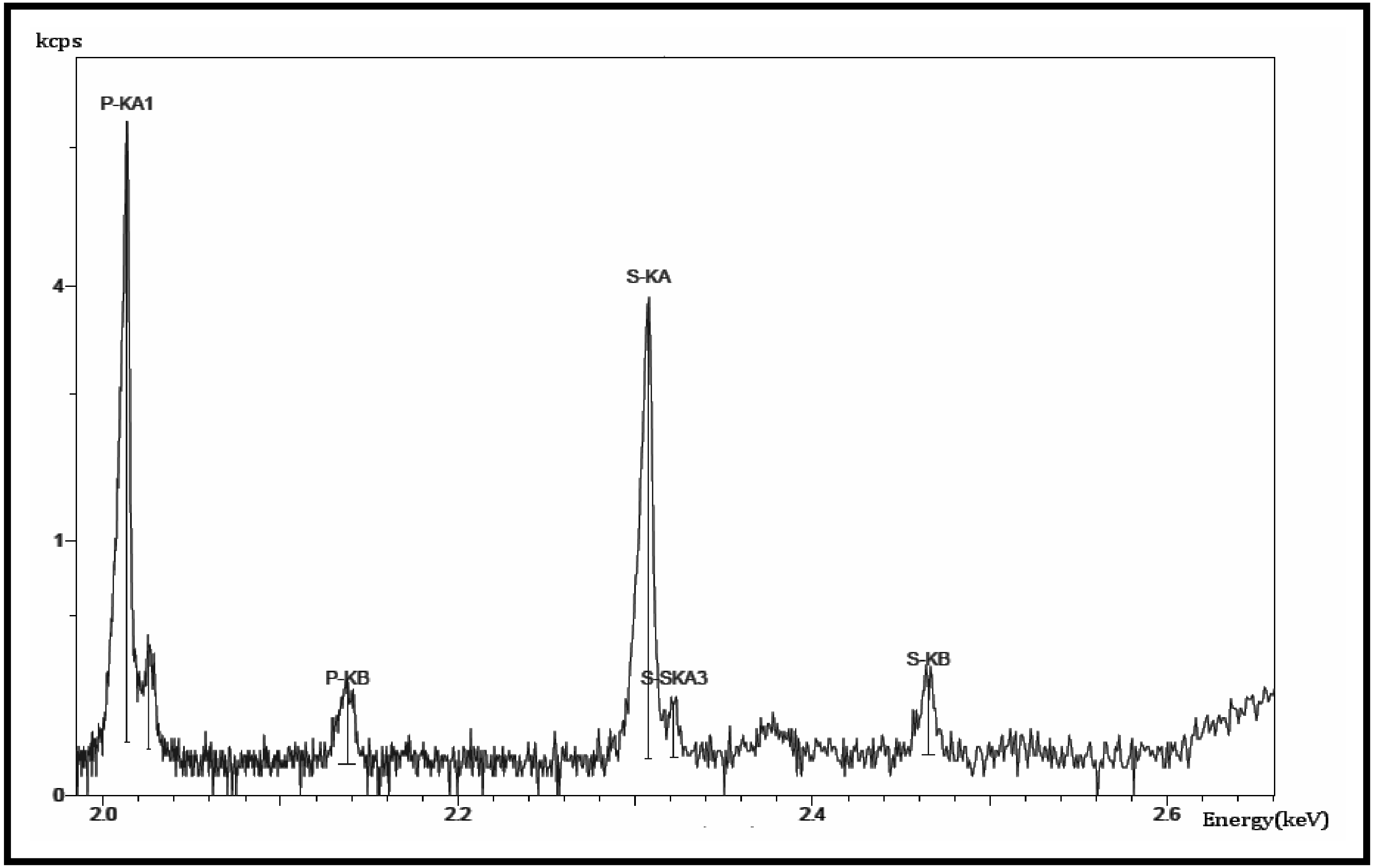


Figure 36 The XRF spectrum of S and P in $[Ag(PPh_3)_2(ptu)]NO_3$.

3.4 Infrared Spectroscopy

The infrared spectrum of the ligands and compounds are shown in Figures 37-41.

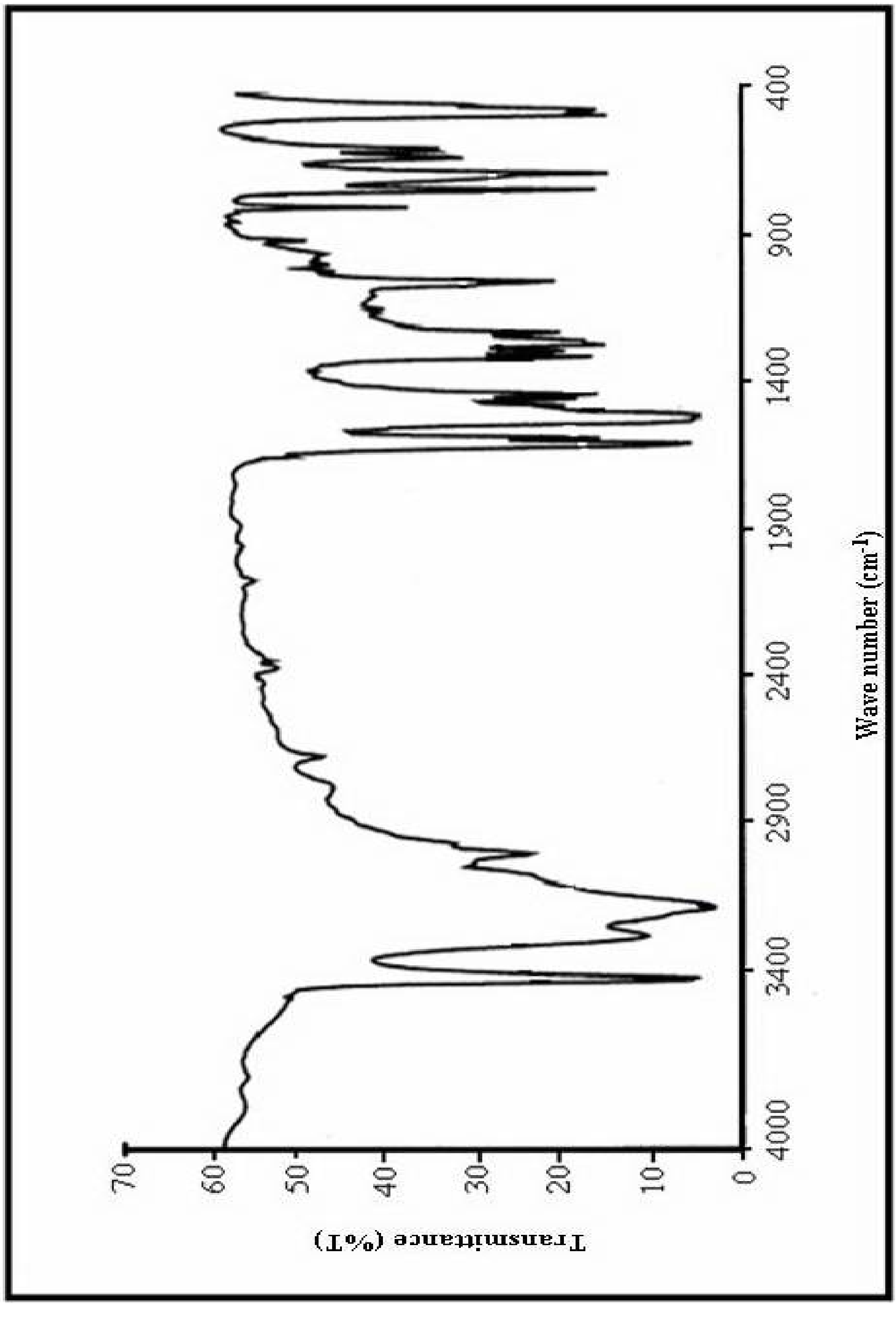


Figure 37 The infrared spectrum of *N*-phenylthiourea(ptu).

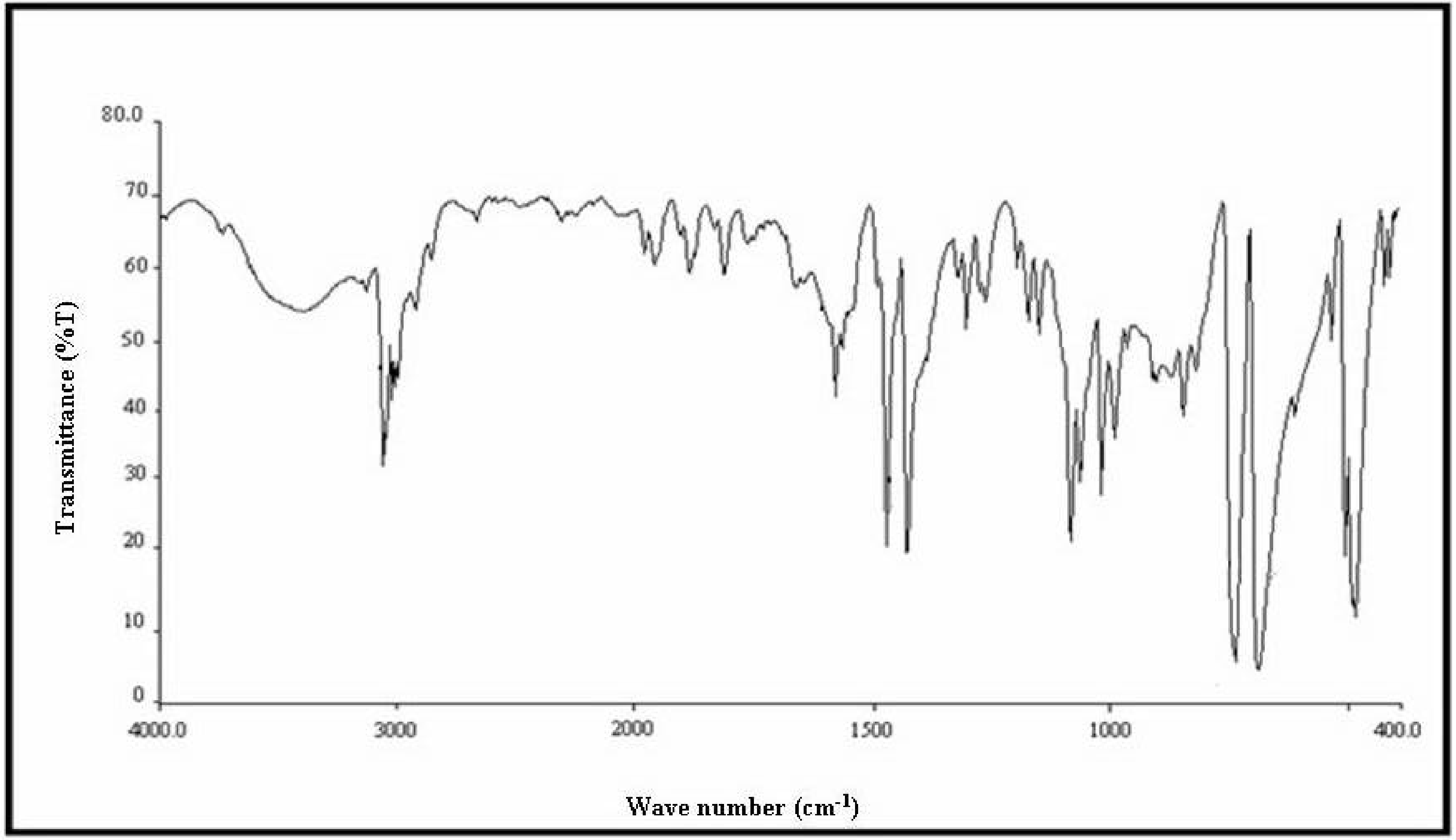


Figure 38 The infrared spectrum of triphenylphosphine(PPh$_3$).

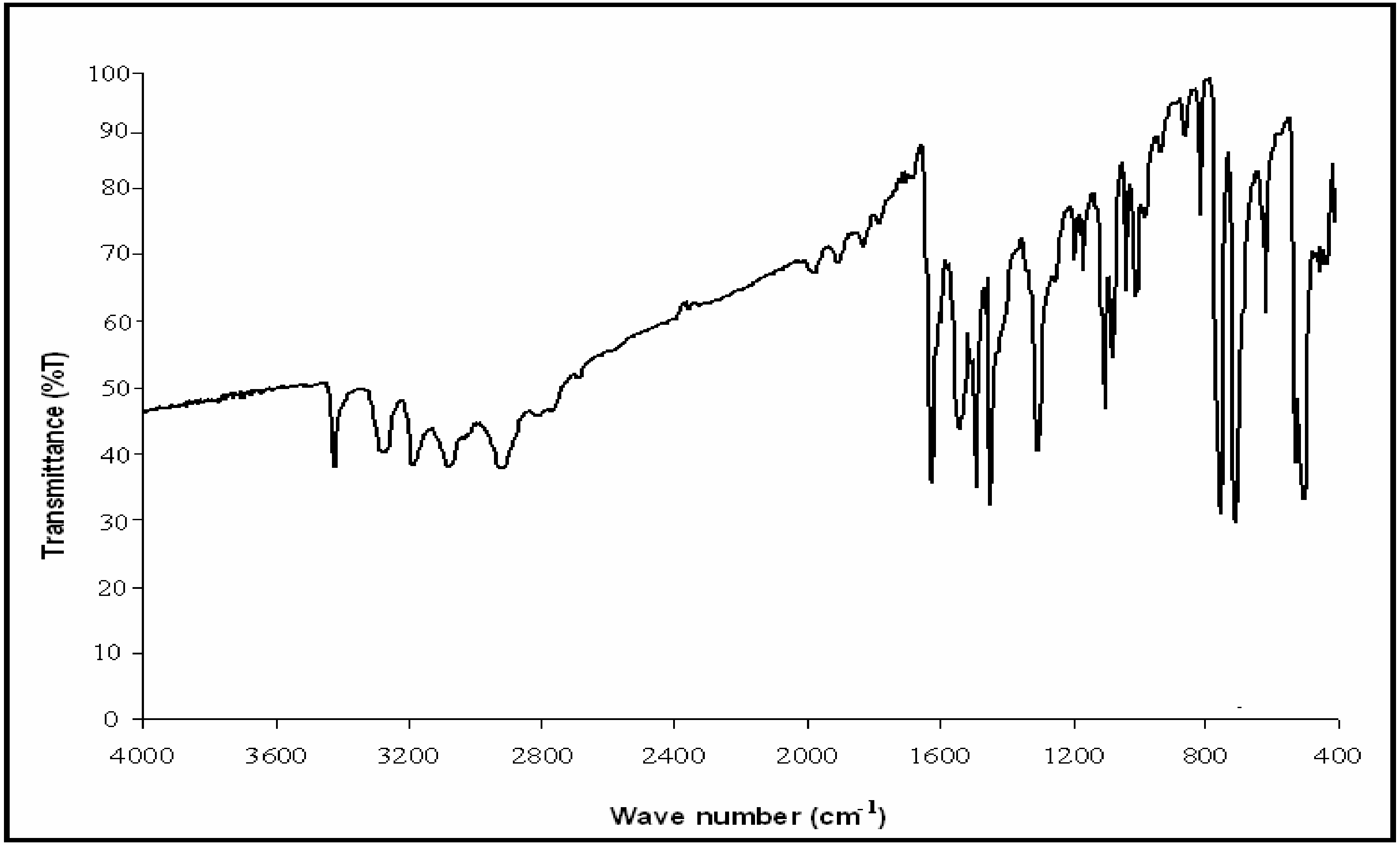


Figure 39 The infrared spectrum of [AgCl(PPh_3)$_2$(ptu)].

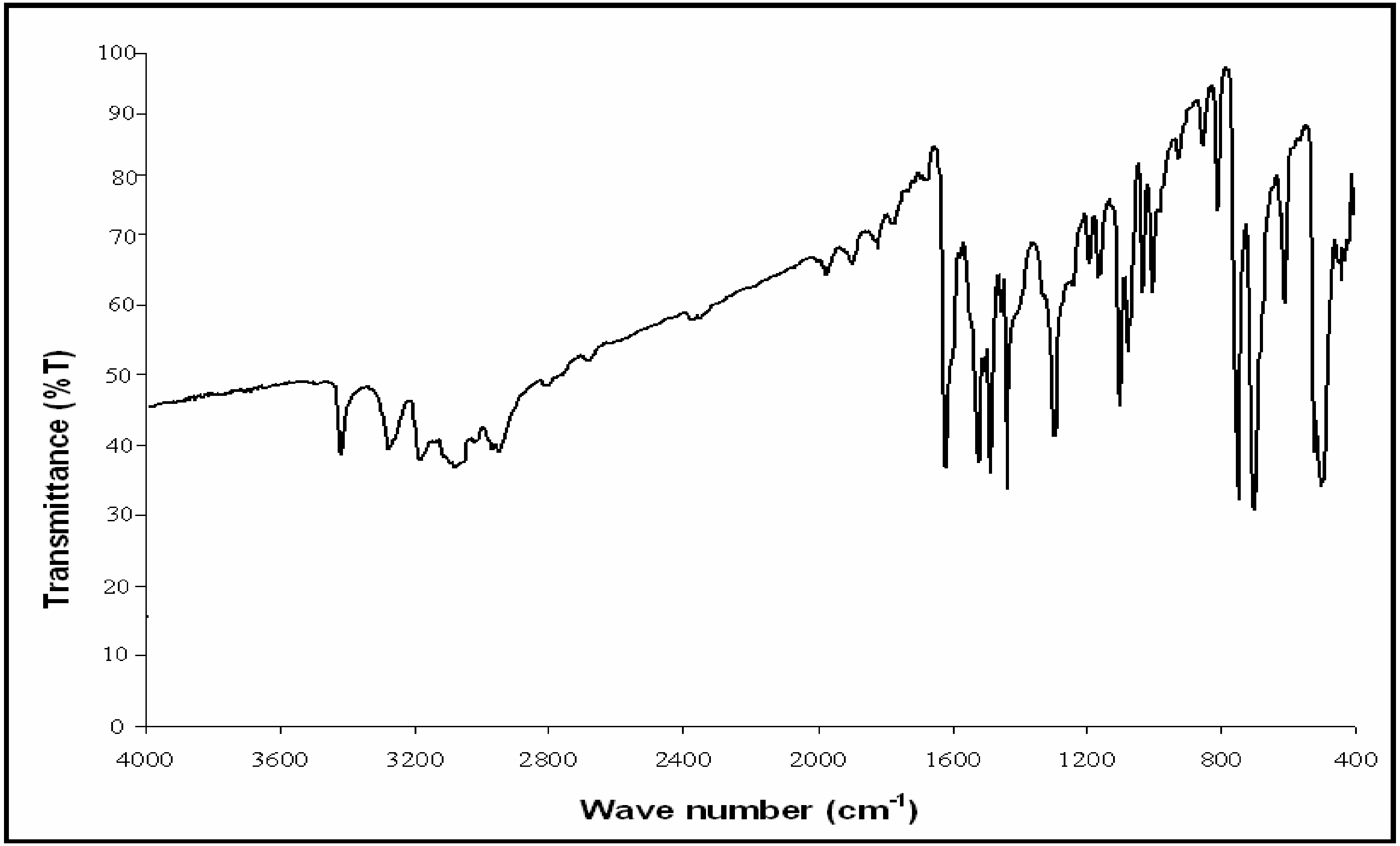


Figure 40 The infrared spectrum of [AgBr(PPh$_3$)$_2$(ptu)].

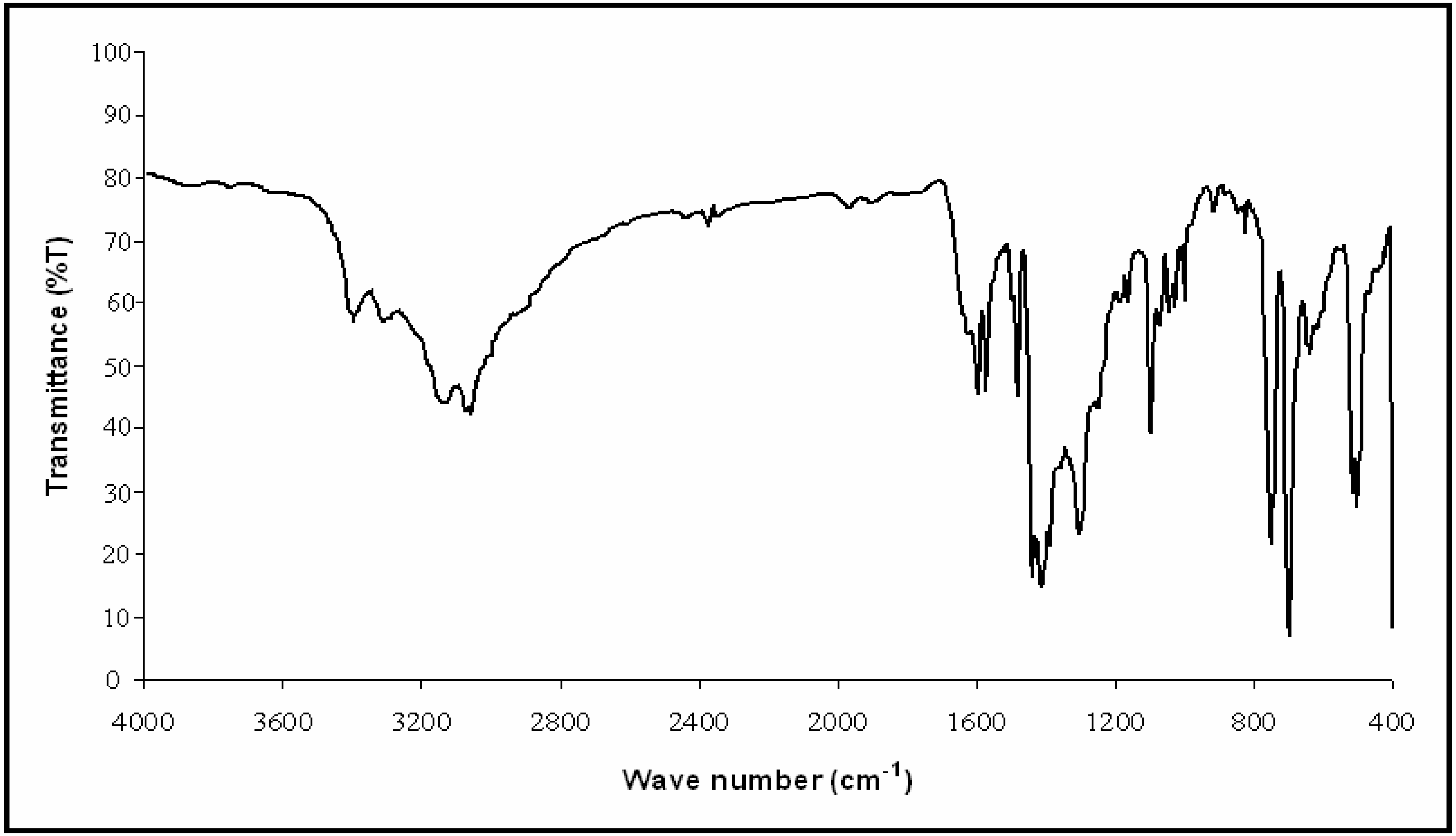


Figure 41 The infrared spectrum of [Ag(PPh_3)$_2$(ptu)]NO_3.

3.5 ^{1}H NMR and ^{13}C NMR Spectroscopy

The ^{1}H NMR and ^{13}C NMR Spectra of the ligands and compounds are shown in Figures 42-51.

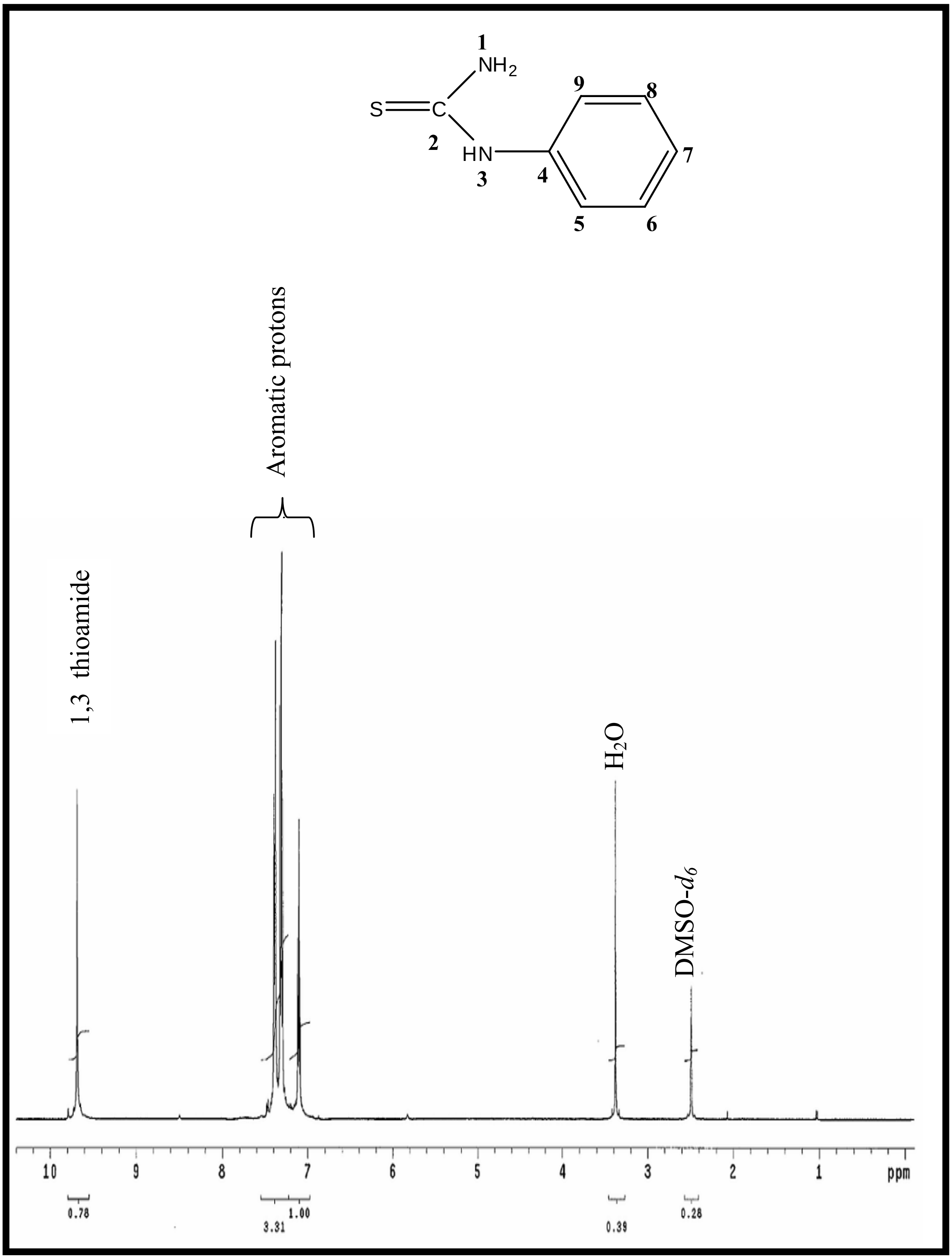


Figure 42 ^{1}H NMR spectrum of *N*-phenylthiourea(ptu).

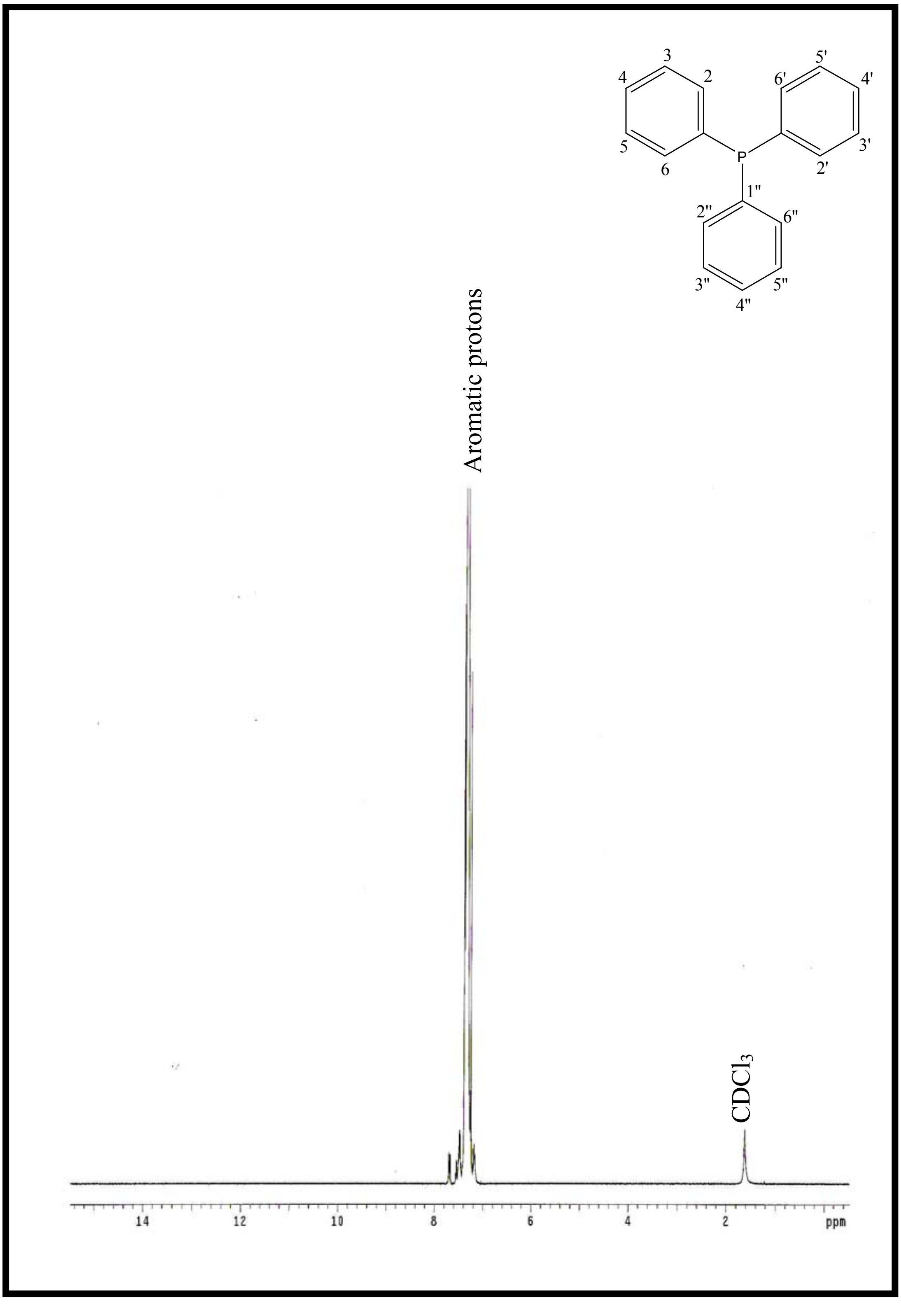


Figure 43 ^{1}H NMR spectrum of triphenylphosphine (PPh_3).

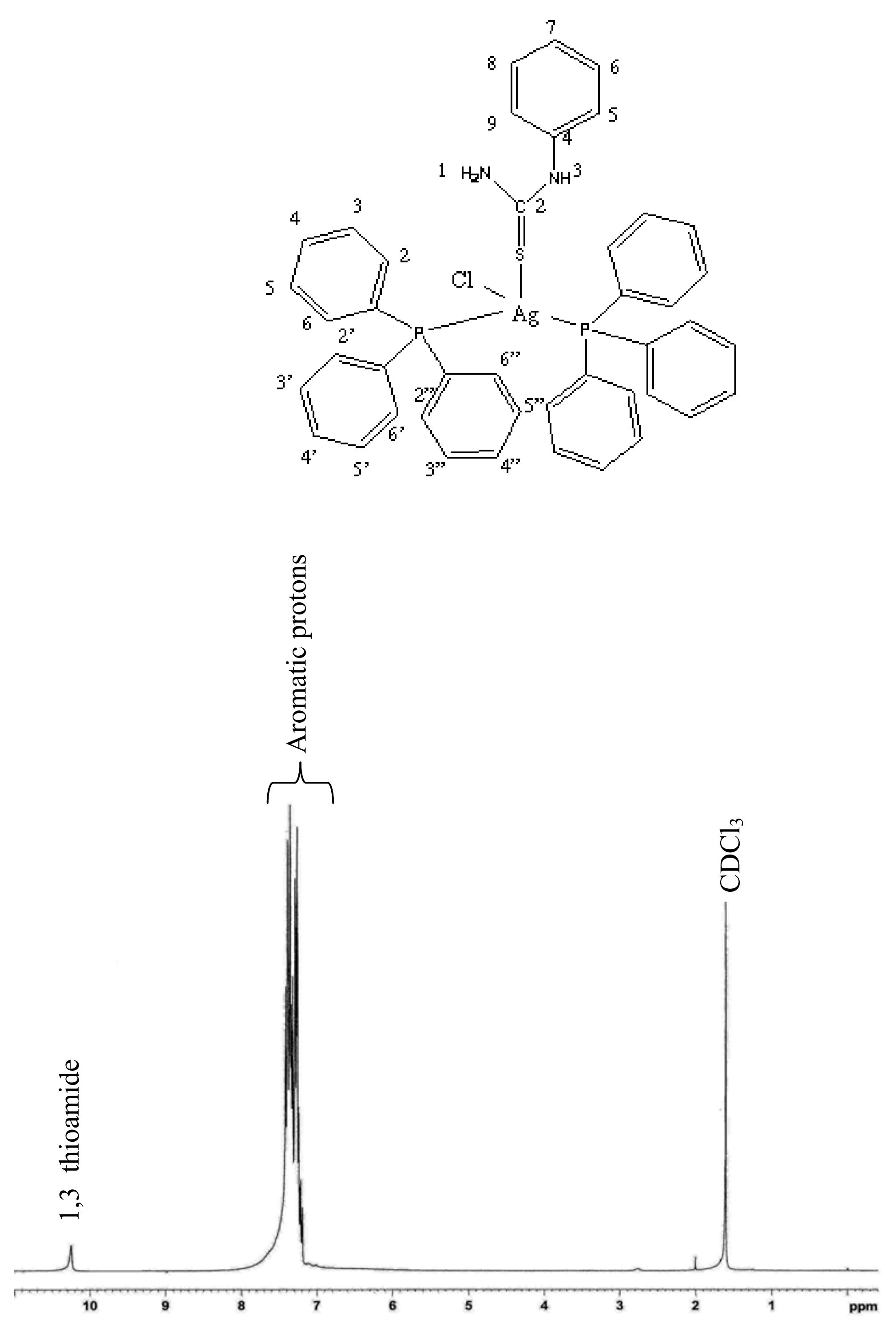


Figure 44 ^{1}H NMR spectrum of [AgCl(PPh$_3$)$_2$(ptu)].

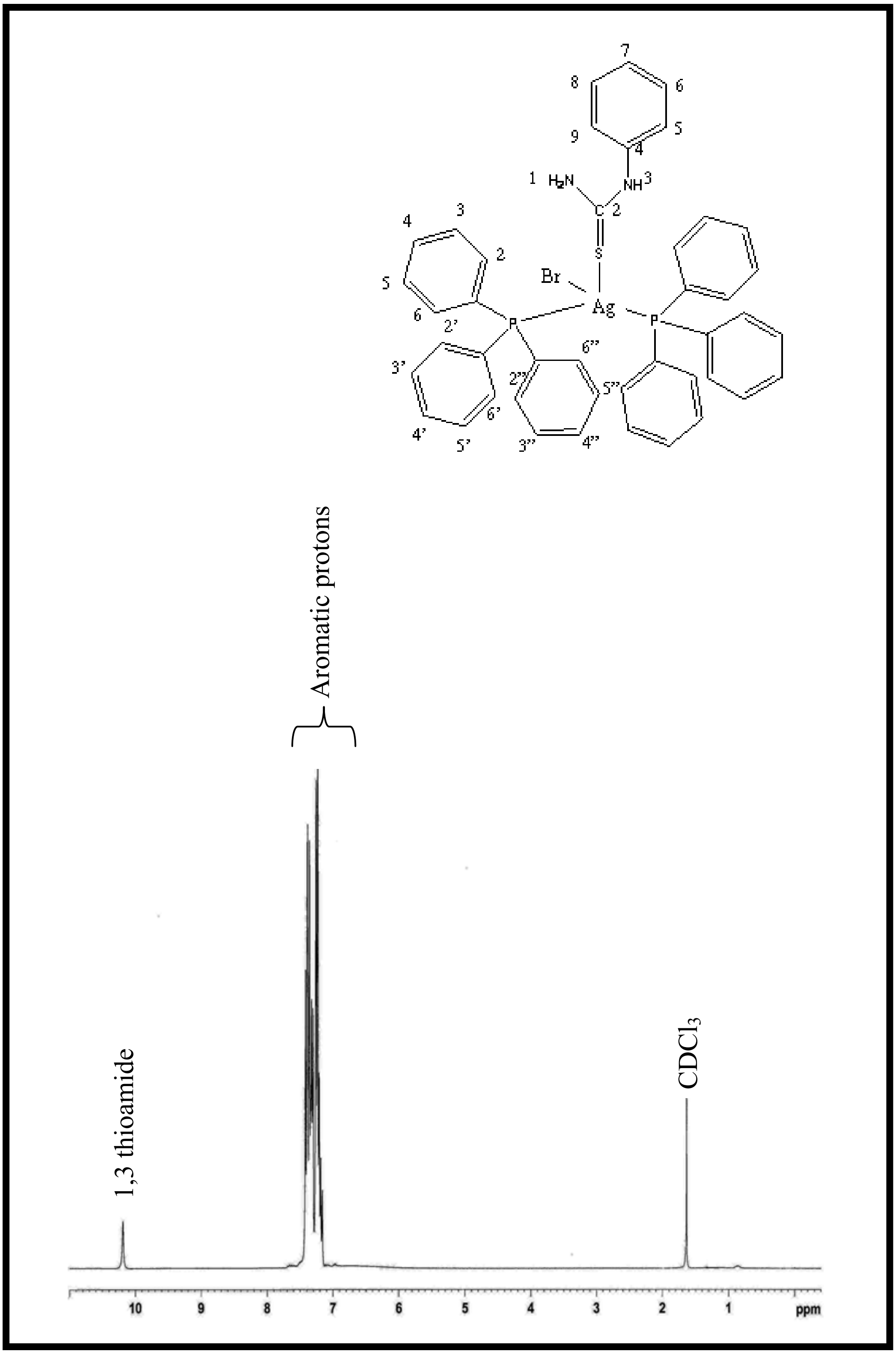


Figure 45 ^{1}H NMR spectrum of [AgBr(PPh$_3$)$_2$(ptu)].

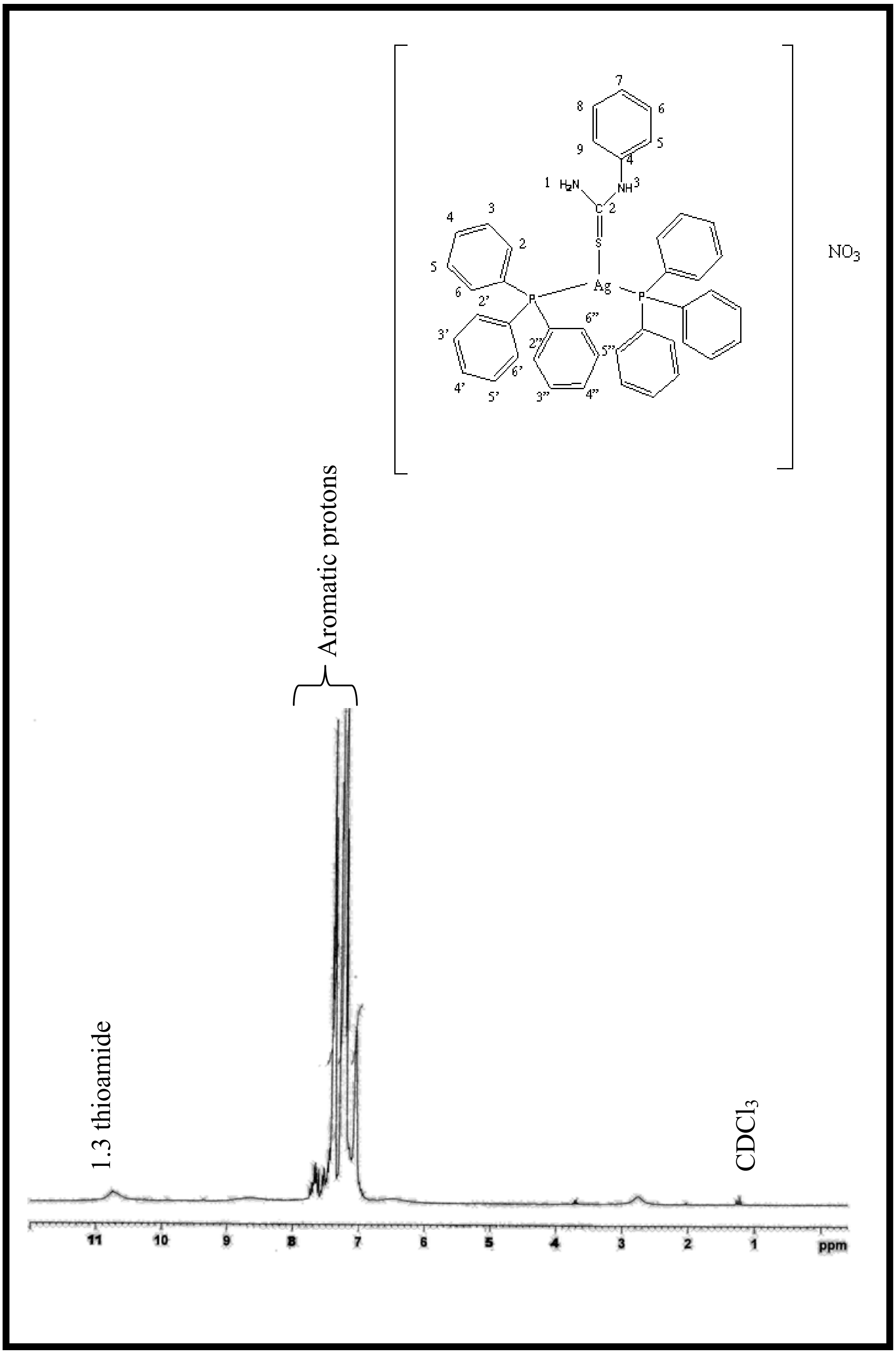


Figure 46 ^{1}H NMR spectrum of $[Ag(PPh_3)_2(ptu)]NO_3$.

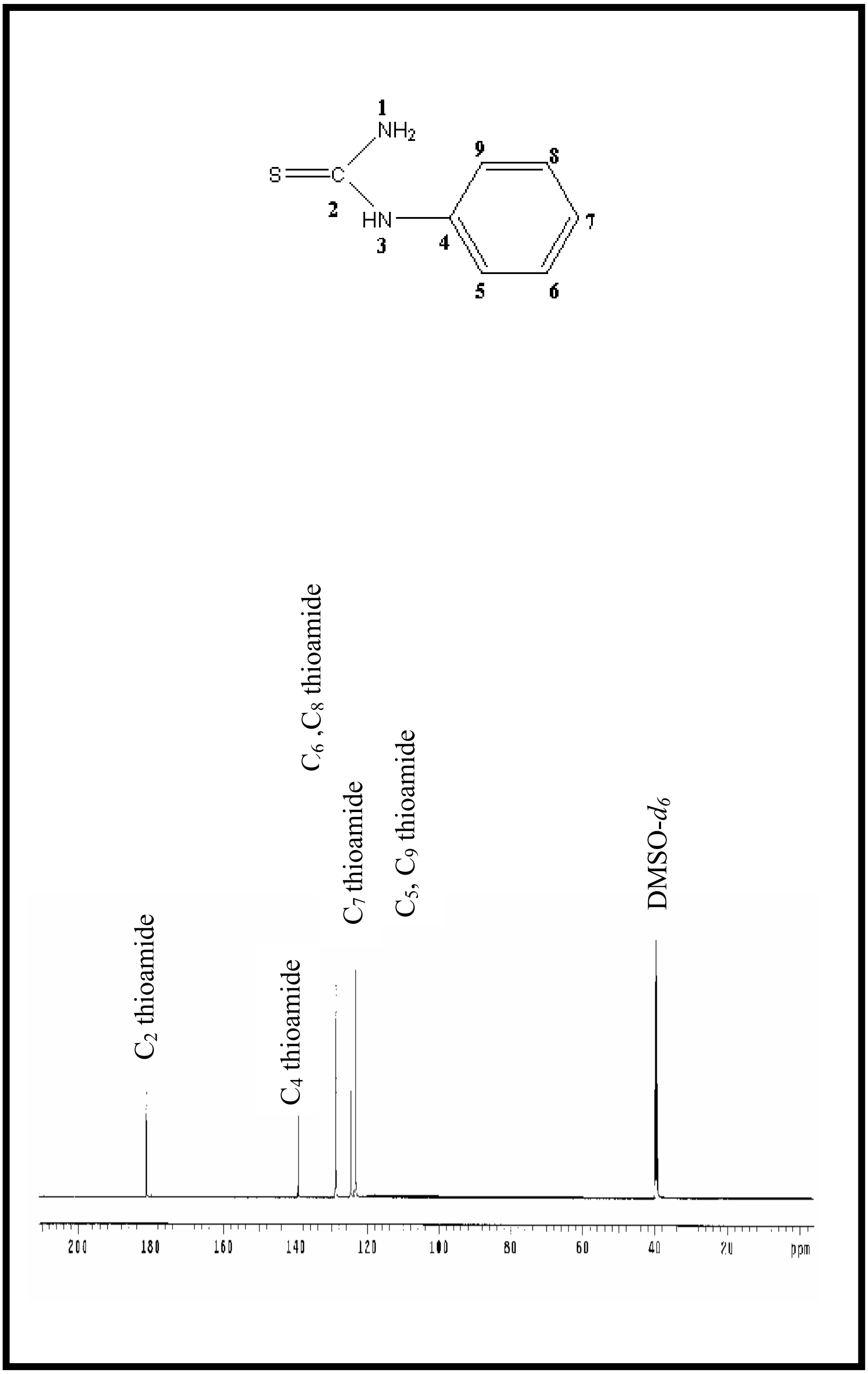


Figure 47 ^{13}C NMR spectrum of *N*-phenylthiourea (ptu).

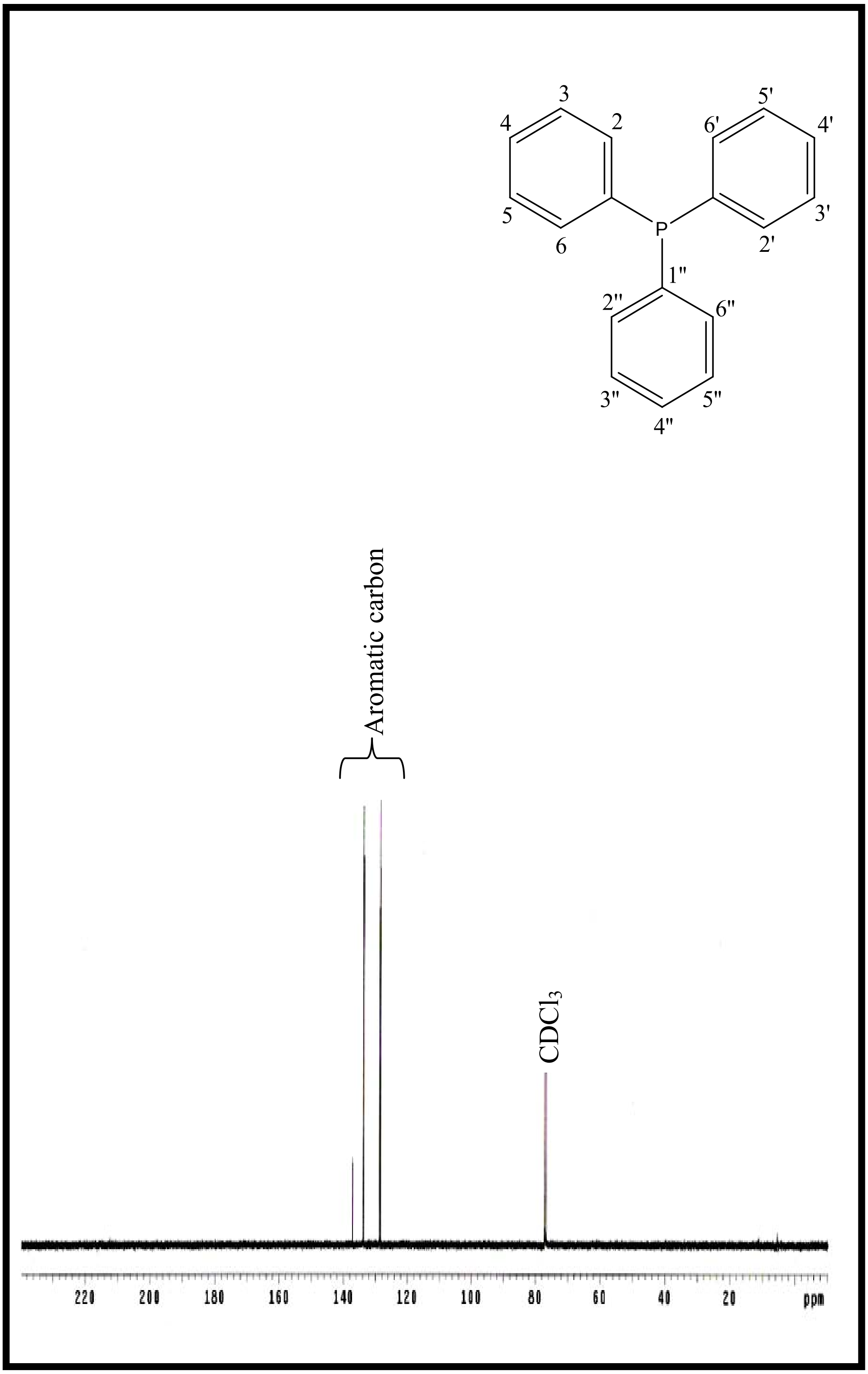


Figure 48 ^{13}C NMR spectrum of triphenylphosphine (PPh_3).

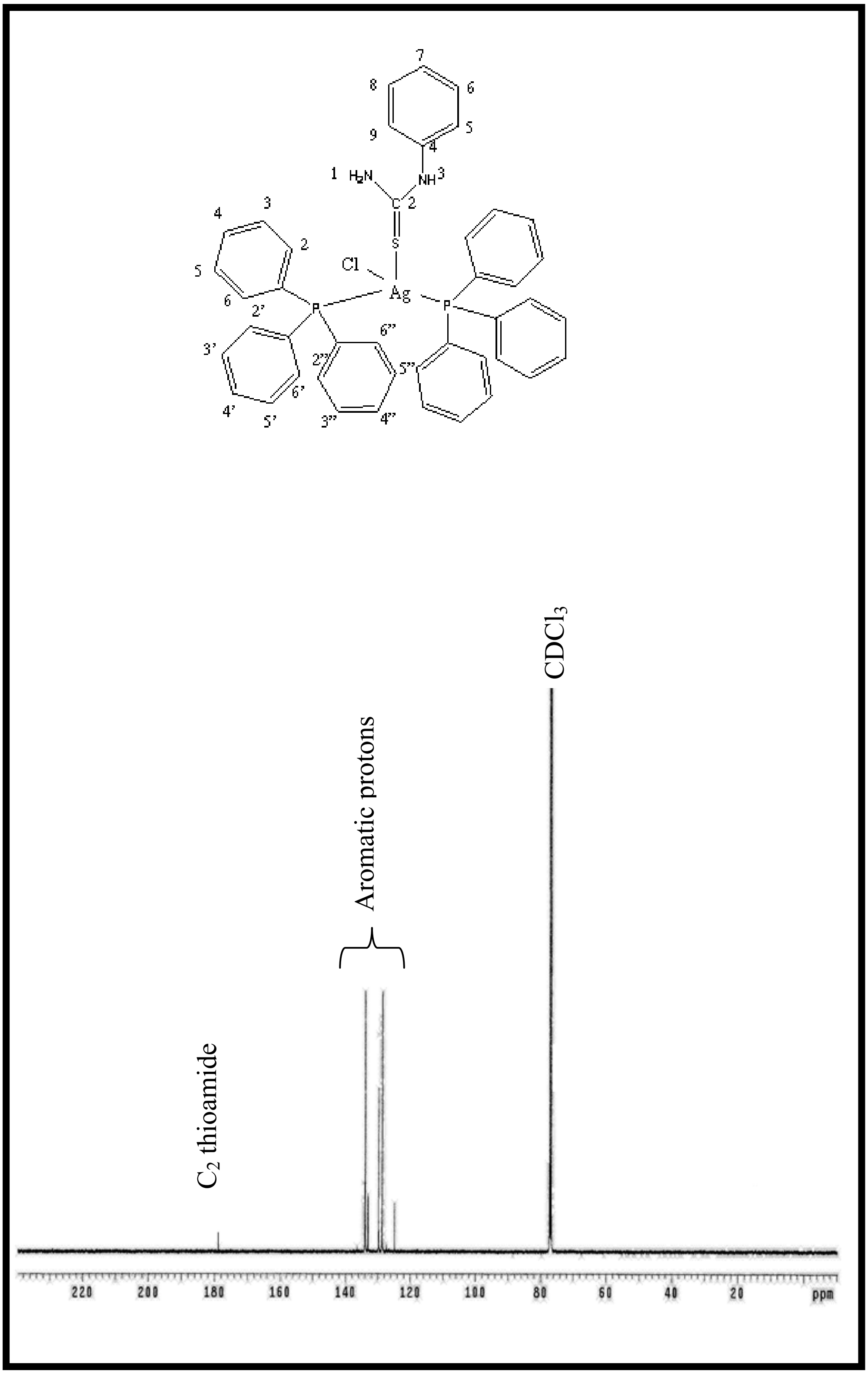


Figure 49 ^{13}C NMR spectrum of [AgCl(PPh$_3$)$_2$(ptu)].

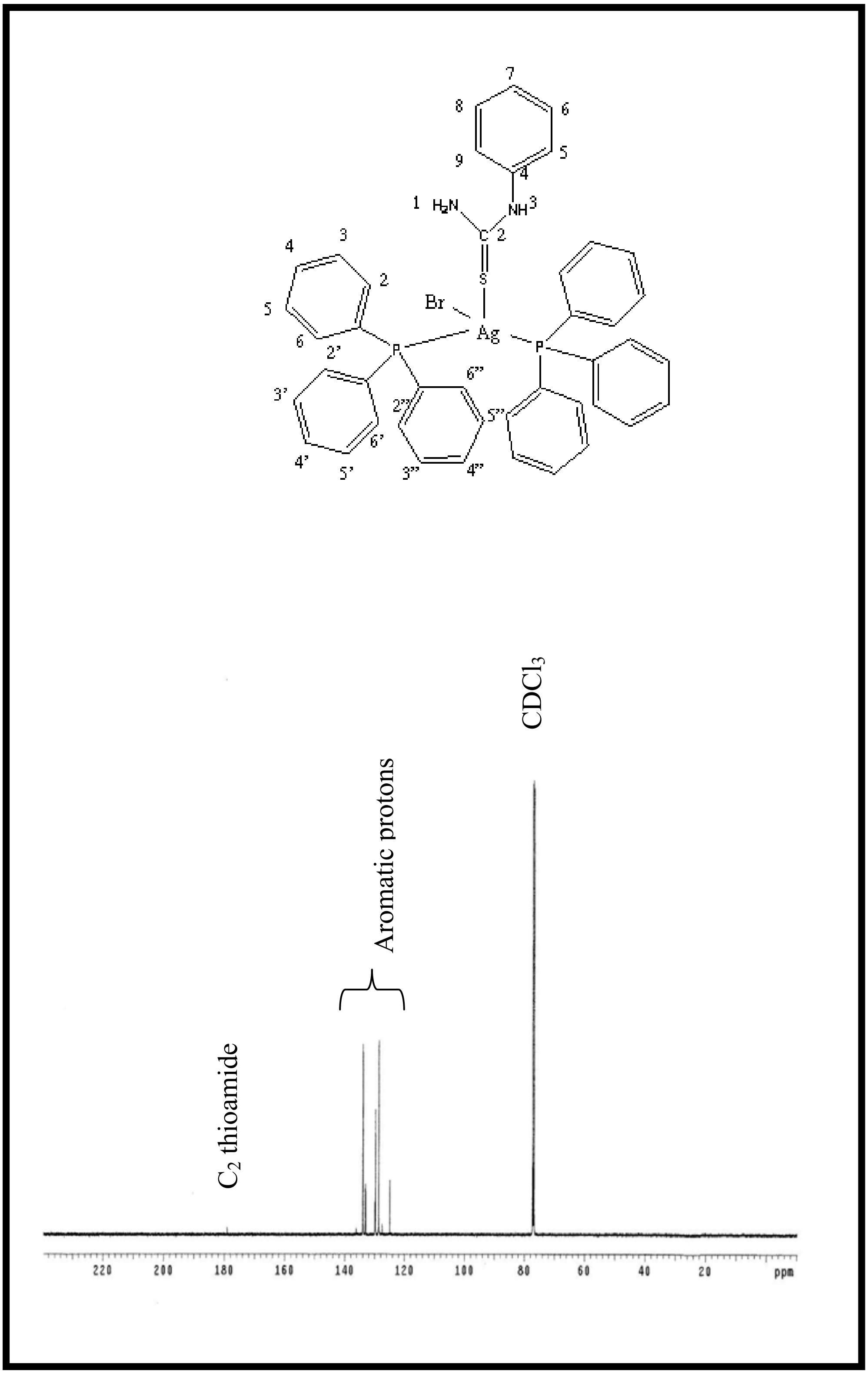


Figure 50 ^{13}C NMR spectrum of [AgBr(PPh$_3$)$_2$(ptu)].

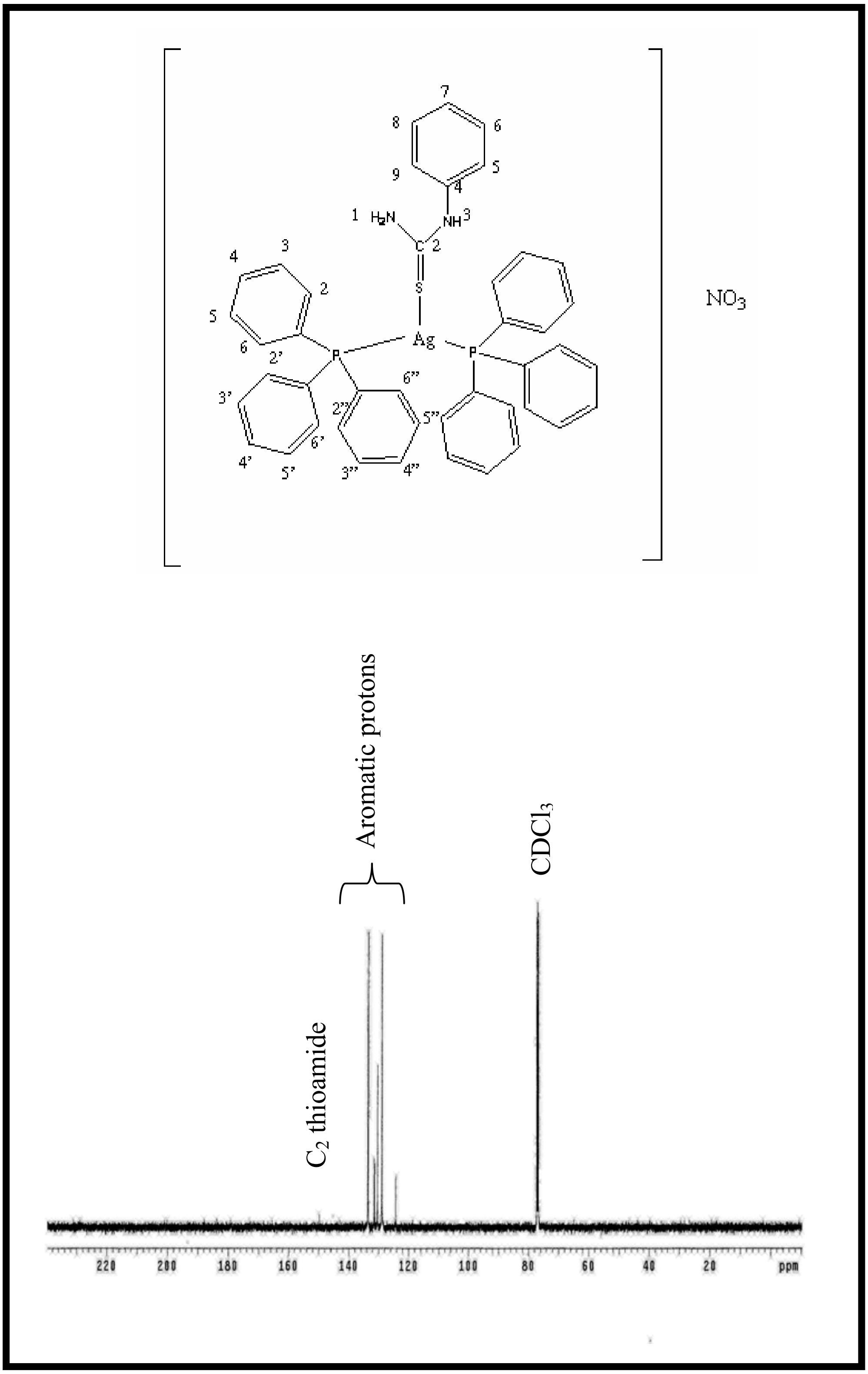


Figure 51 ^{13}C NMR spectrum of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$.

3.6 Single crystal X-ray diffractometry

3.6.1 Crystal Structures

These results from crystal structure determination using WinGX and SHELXTL program system (Sheldrick, 2000) are shown in Table 5-13 and Figures 52-66.

Table 5 The crystallograpraphic data for [AgCl(PPh$_3$)$_2$(ptu)].

Empirical formula	C43H38AgClN2P2S	
Formula weight	820.07	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.5092(6) Å	α = 97.0180(10)°
	b = 11.3943(6) Å	β = 103.9100(10)°
	c = 17.2408(10) Å	γ =103.2770(10)°
Volume	1915.70(19) Å^3	
Z	2	
Density (calculated)	1.422 Mg/m^3	
Absorption coefficient	0.767 mm^{-1}	
F(000)	840	
Crystal size	0.225 x 0.156 x 0.080 mm^3	
Theta range for data collection	1.87 to 28.03°	
Index ranges	-13<=h<=13, -15<=k<=15, -22<=l<=22	
Reflections collected	26428	
Independent reflections	9236 [R(int) = 0.0248]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9236 / 3 / 460	
Goodness-of-fit on F^2	1.036	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0327, wR2 = 0.0758	
R indices (all data)	R1 = 0.0388, wR2 = 0.0787	
Largest diff. peak and hole	0.611 and -0.265 e. Å^{-3}	

Table 6 Non-hydrogen interatomic distances of [AgCl($(PPh_3)_2$(ptu)].

Atom	Distance (Å)	Atom	Distance (Å)
Ag(1)-P(1)	2.4742(5)	Ag(1)-P(2)	2.4869(5)
Ag(1)-Cl(1)	2.5492(6)	Ag(1)-S(1)	2.7309(5)
S(1)-C(1)	1.710(2)	P(1)-C(21)	1.820(2)
P(1)-C(11)	1.824(2)	P(1)-C(31)	1.827(2)
P(2)-C(61)	1.824(2)	P(2)-C(41)	1.826(2)
P(2)-C(51)	1.829(2)	N(1)-C(1)	1.320(3)
N(2)-C(1)	1.327(3)	N(2)-C(2)	1.435(3)
C(2)-C(3)	1.368(3)	C(2)-C(7)	1.381(3)
C(3)-C(4)	1.377(3)	C(4)-C(5)	1.366(4)
C(5)-C(6)	1.365(4)	C(6)-C(7)	1.380(4)
C(11)-C(16)	1.386(3)	C(11)-C(12)	1.390(3)
C(12)-C(13)	1.390(4)	C(13)-C(14)	1.365(5)
C(14)-C(15)	1.364(4)	C(15)-C(16)	1.386(3)
C(21)-C(22)	1.376(3)	C(21)-C(26)	1.391(3)
C(22)-C(23)	1.391(4)	C(23)-C(24)	1.359(4)
C(22)-C(23)	1.391(4)	C(23)-C(24)	1.359(4)
C(24)-C(25)	1.367(4)	C(25)-C(26)	1.370(3)
C(31)-C(36)	1.383(3)	C(31)-C(32)	1.392(3)
C(32)-C(33)	1.389(3)	C(33)-C(34)	1.362(5)
C(34)-C(35)	1.368(5)	C(35)-C(36)	1.387(4)
C(41)-C(42)	1.385(3)	C(41)-C(46)	1.387(3)
C(42)-C(43)	1.395(3)	C(43)-C(44)	1.363(4)
C(44)-C(45)	1.370(4)	C(45)-C(46)	1.381(3)
C(51)-C(52)	1.364(3)	C(51)-C(56)	1.383(3)
C(52)-C(53)	1.383(4)	C(53)-C(54)	1.343(5)
C(54)-C(55)	1.364(5)	C(55)-C(56)	1.385(4)
C(61)-C(62)	1.383(3)	C(61)-C(66)	1.392(3)
C(62)-C(63)	1.387(3)	C(63)-C(64)	1.361(4)
C(64)-C(65)	1.381(4)	C(65)-C(66)	1.384(3)

Table 7 Non-hydrogen interbond angles of [AgCl(PPh$_3$)$_2$(ptu)].

Atom	Angle (°)
P(1)-Ag(1)-P(2)	121.252(18)
P(1)-Ag(1)-Cl(1)	117.04(2)
P(2)-Ag(1)-Cl(1)	111.08(2)
P(1)-Ag(1)-S(1)	95.992(17)
P(2)-Ag(1)-S(1)	110.893(18)
Cl(1)-Ag(1)-S(1)	95.813(18)
C(1)-S(1)-Ag(1)	103.96(7)
C(21)-P(1)-C(11)	108.60(10)
C(21)-P(1)-C(31)	103.44(9)
C(11)-P(1)-C(31)	100.64(9)
C(21)-P(1)-Ag(1)	107.00(6)
C(11)-P(1)-Ag(1)	118.25(7)
C(31)-P(1)-Ag(1)	117.75(7)
C(61)-P(2)-C(41)	104.25(9)
C(61)-P(2)-C(51)	104.59(10)
C(41)-P(2)-C(51)	102.39(9)
C(61)-P(2)-Ag(1)	111.43(7)
C(41)-P(2)-Ag(1)	117.98(7)
C(51)-P(2)-Ag(1)	114.77(7)
C(1)-N(2)-C(2)	125.82(18)
N(1)-C(1)-N(2)	118.82(19)
N(1)-C(1)-S(1)	120.87(16)
N(2)-C(1)-S(1)	120.30(15)
C(3)-C(2)-C(7)	119.9(2)
C(3)-C(2)-N(2)	120.0(2)
C(7)-C(2)-N(2)	120.0(2)
C(2)-C(3)-C(4)	120.1(2)
C(5)-C(4)-C(3)	120.1(3)

Table 7 (continued).

Atom	Angle (°)
C(6)-C(5)-C(4)	120.0(2)
C(5)-C(6)-C(7)	120.4(2)
C(6)-C(7)-C(2)	119.4(2)
C(16)-C(11)-C(12)	119.4(2)
C(16)-C(11)-P(1)	117.94(16)
C(12)-C(11)-P(1)	122.38(18)
C(13)-C(12)-C(11)	119.7(3)
C(14)-C(13)-C(12)	120.2(3)
C(15)-C(14)-C(13)	120.7(3)
C(14)-C(15)-C(16)	120.3(3)
C(11)-C(16)-C(15)	119.9(2)
C(22)-C(21)-C(26)	117.7(2)
C(22)-C(21)-P(1)	126.14(17)
C(26)-C(21)-P(1)	116.12(16)
C(21)-C(22)-C(23)	120.1(2)
C(24)-C(23)-C(22)	121.0(2)
C(23)-C(24)-C(25)	119.5(2)
C(24)-C(25)-C(26)	119.9(2)
C(25)-C(26)-C(21)	121.7(2)
C(36)-C(31)-C(32)	118.6(2)
C(36)-C(31)-P(1)	124.48(17)
C(32)-C(31)-P(1)	116.87(17)
C(33)-C(32)-C(31)	120.4(3)
C(34)-C(33)-C(32)	120.3(3)
C(33)-C(34)-C(35)	119.8(2)
C(34)-C(35)-C(36)	120.9(3)
C(31)-C(36)-C(35)	120.0(3)
C(42)-C(41)-C(46)	118.6(2)

Table 7 (continued).

Atom	Angle (°)
C(42)-C(41)-P(2)	123.72(16)
C(46)-C(41)-P(2)	117.70(16)
C(41)-C(42)-C(43)	120.1(2)
C(44)-C(43)-C(42)	120.4(2)
C(43)-C(44)-C(45)	119.8(2)
C(44)-C(45)-C(46)	120.5(2)
C(45)-C(46)-C(41)	120.5(2)
C(52)-C(51)-C(56)	117.8(2)
C(52)-C(51)-P(2)	119.49(17)
C(56)-C(51)-P(2)	122.65(19)
C(51)-C(52)-C(53)	121.8(3)
C(54)-C(53)-C(52)	120.0(3)
C(53)-C(54)-C(55)	119.7(3)
C(54)-C(55)-C(56)	120.8(3)
C(51)-C(56)-C(55)	119.9(3)
C(62)-C(61)-C(66)	118.5(2)
C(62)-C(61)-P(2)	123.84(17)
C(66)-C(61)-P(2)	117.59(16)
C(61)-C(62)-C(63)	120.0(2)
C(64)-C(63)-C(62)	121.2(3)
C(63)-C(64)-C(65)	119.8(2)
C(64)-C(65)-C(66)	119.6(3)
C(65)-C(66)-C(61)	121.0(2)

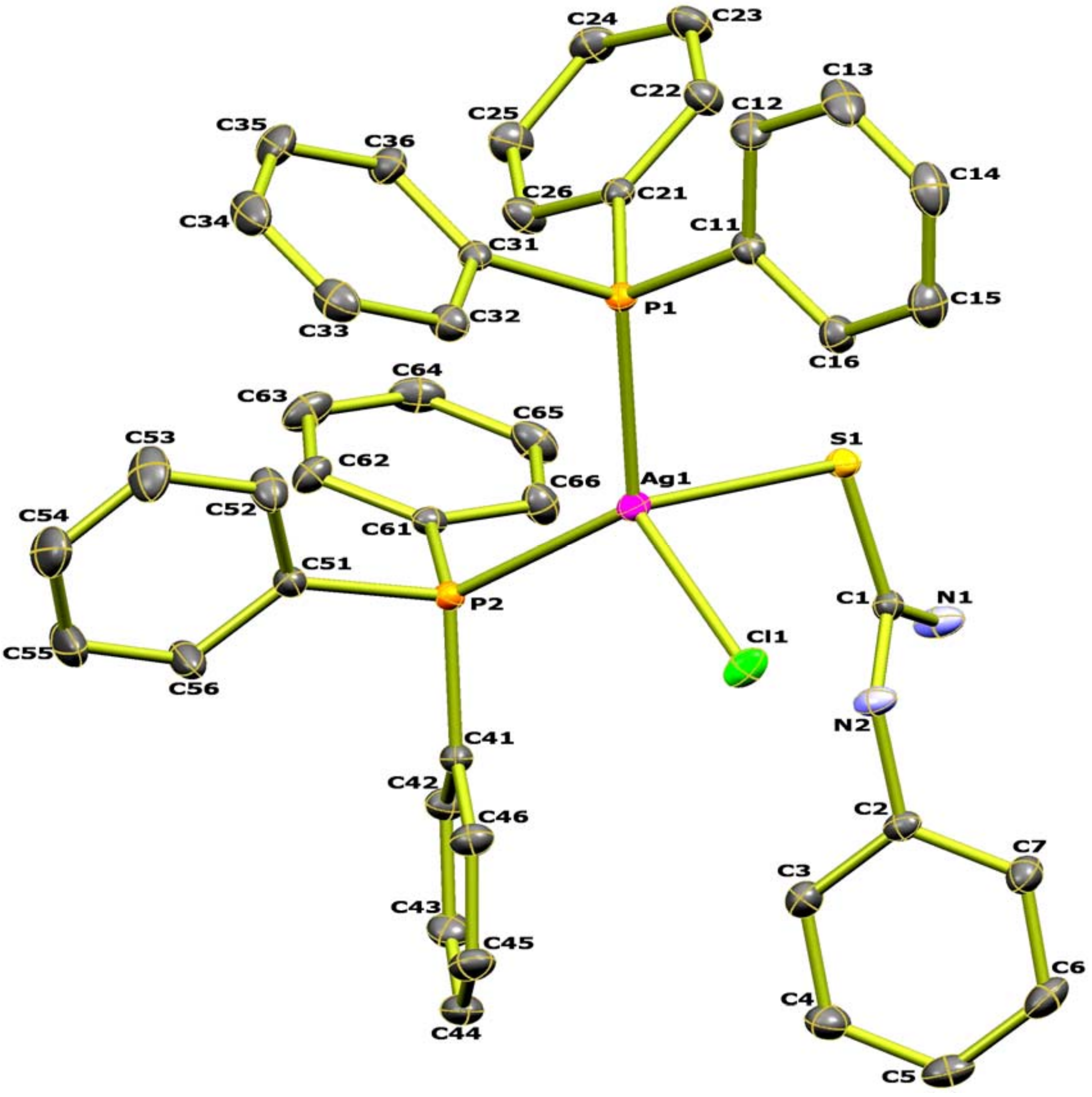


Figure 52 The structure of $[AgCl(PPh_3)_2(ptu)]$.

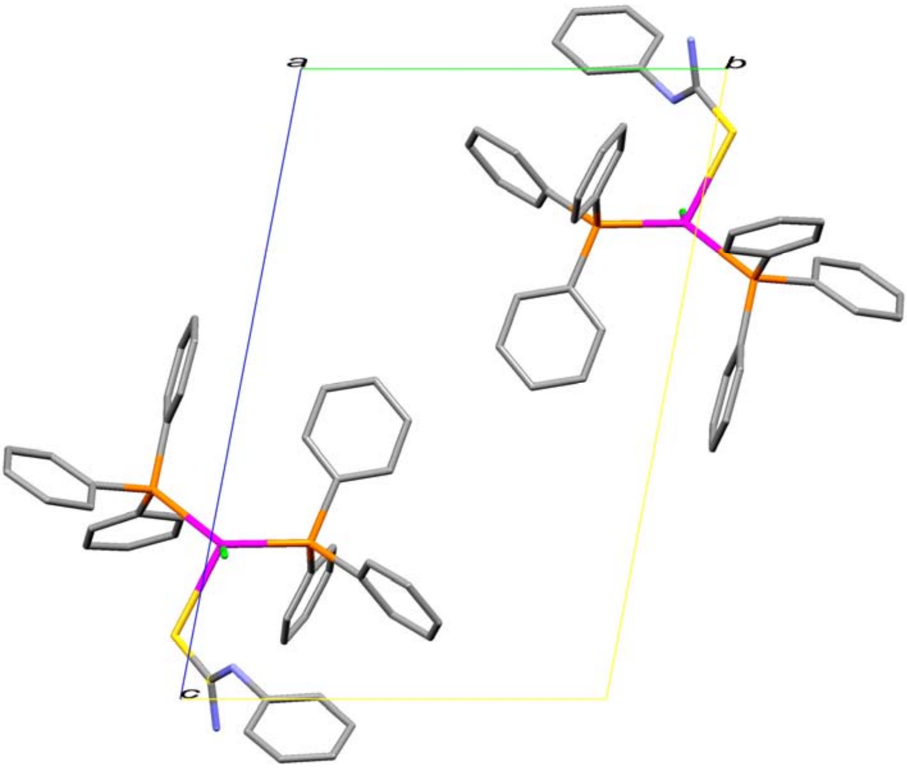


Figure 53 Unit cell contents of [AgCl(PPh_3)$_2$(ptu)] projected down *a*.

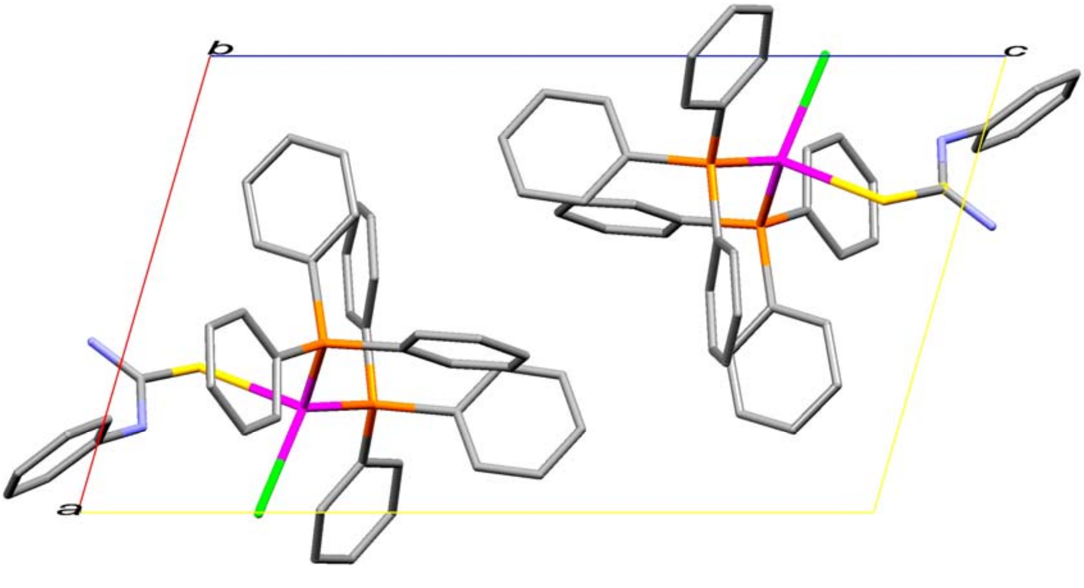


Figure 54 Unit cell contents of [AgCl(PPh_3)$_2$(ptu)] projected down *b*.

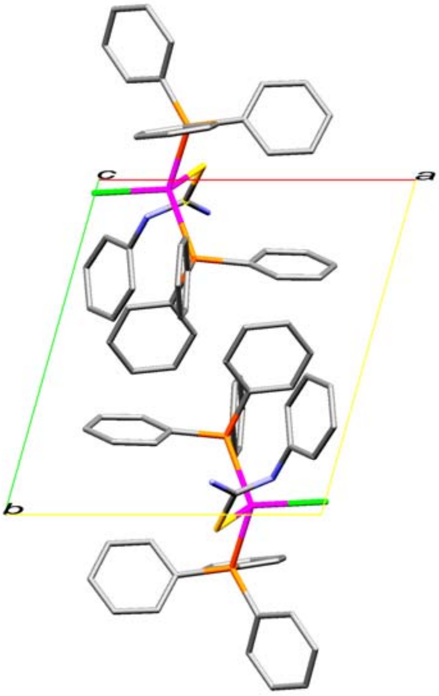


Figure 55 Unit cell contents of [AgCl(PPh$_3$)$_2$(ptu)] projected down *c*.

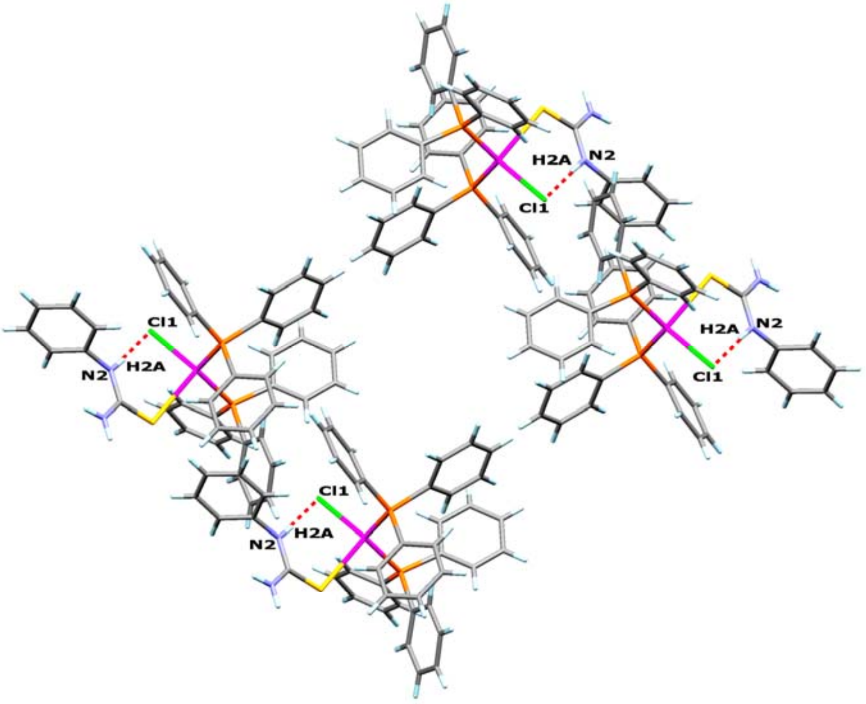


Figure 56 Hydrogen bonding the intraction of [AgCl(PPh$_3$)$_2$(ptu)].

Table 8 The crystallograpraphic data for [AgBr(PPh_3)$_2$(ptu)].

Empirical formula	C43H38AgBrN2P2S	
Formula weight	864.53	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No.2)	
Unit cell dimensions	a = 10.6748(11) Å	α = 97.358(2) °
	b = 11.3434(12)Å	β =102.928(2)°
	c = 17.2296(18)Å	γ = 102.580(2)°
Volume	1950.0(4)Å^3	
Z	2	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	1.710 mm^{-1}	
F(000)	876	
Crystal size	0.263 x 0.189 x 0.080 mm^3	
Theta range for data collection	1.87 to 28.07°	
Index ranges	-12<=h<=12, -14<=k<=14, -22<=l<=22	
Reflections collected	26911	
Independent reflections	9404 [R(int) =0.0243]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9404 / 3 / 461	
Goodness-of-fit on F^2	1.036	
Final R indices [$I>2\sigma(I)$]	$R1$ =0.0291, $wR2$ = 0.0724	
R indices (all data)	$R1$ = 0.0376, $wR2$ = 0.0763	
Largest diff. peak and hole	0.568 and -0.386 e. Å^{-3}	

Table 9 Non-hydrogen interatomic distances of [AgBr$(PPh_3)_2$(ptu)].

Atom	Distance (Å)	Atom	Distance (Å)
Ag(1)-P(1)	2.4776(5)	Ag(1)-P(2)	2.4886(6)
Ag(1)-Br(1)	2.6528(4)	Ag(1)-S(1)	2.7114(6)
S(1)-C(1)	1.709(2)	P(1)-C(21)	1.817(2)
P(1)-C(11)	1.824(2)	P(1)-C(31)	1.829(2)
P(2)-C(61)	1.825(2)	P(2)-C(41)	1.829(2)
P(2)-C(51)	1.831(2)	N(1)-C(1)	1.313(3)
N(2)-C(1)	1.328(3)	N(2)-C(2)	1.431(3)
C(2)-C(3)	1.365(3)	C(2)-C(7)	1.376(3)
C(3)-C(4)	1.379(3)	C(4)-C(5)	1.366(4)
C(5)-C(6)	1.358(4)	C(6)-C(7)	1.380(4)
C(11)-C(16)	1.381(3)	C(11)-C(12)	1.389(3)
C(12)-C(13)	1.390(4)	C(13)-C(14)	1.360(5)
C(14)-C(15)	1.355(5)	C(15)-C(16)	1.393(3)
C(21)-C(22)	1.373(3)	C(21)-C(26)	1.390(3)
C(22)-C(23)	1.397(4)	C(23)-C(24)	1.356(4)
C(24)-C(25)	1.370(4)	C(25)-C(26)	1.372(3)
C(31)-C(32)	1.382(3)	C(31)-C(36)	1.384(3)
C(32)-C(33)	1.400(4)	C(33)-C(34)	1.366(5)
C(34)-C(35)	1.355(5)	C(35)-C(36)	1.390(4)
C(41)-C(46)	1.384(3)	C(41)-C(42)	1.389(3)
C(42)-C(43)	1.392(3)	C(43)-C(44)	1.360(4)
C(44)-C(45)	1.372(4)	C(45)-C(46)	1.383(3)
C(51)-C(52)	1.360(3)	C(51)-C(56)	1.376(3)
C(52)-C(53)	1.396(4)	C(61)-C(66)	1.397(3)
C(62)-C(63)	1.388(4)	C(63)-C(64)	1.366(4)
C(64)-C(65)	1.365(4)	C(65)-C(66)	1.389(3)

Table 10 Non-hydrogen interbond angles of [AgBr$(PPh_3)_2$(ptu)].

Atom	Angle (°)
P(1)-Ag(1)-P(2)	121.417(18)
P(1)-Ag(1)-Br(1)	115.325(15)
P(2)-Ag(1)-Br(1)	110.383(15)
P(1)-Ag(1)-S(1)	96.674(18)
P(2)-Ag(1)-S(1)	110.766(18)
Br(1)-Ag(1)-S(1)	98.662(14)
C(1)-S(1)-Ag(1)	104.86(7)
C(21)-P(1)-C(11)	108.60(10)
C(21)-P(1)-C(31)	103.63(10)
C(11)-P(1)-C(31)	100.33(9)
C(21)-P(1)-Ag(1)	107.08(6)
C(11)-P(1)-Ag(1)	119.32(7)
C(31)-P(1)-Ag(1)	116.66(7)
C(61)-P(2)-C(41)	104.11(9)
C(61)-P(2)-C(51)	105.30(10)
C(41)-P(2)-C(51)	101.68(9)
C(61)-P(2)-Ag(1)	112.27(7)
C(41)-P(2)-Ag(1)	117.66(7)
C(51)-P(2)-Ag(1)	114.41(7)
C(1)-N(2)-C(2)	126.38(18)
N(1)-C(1)-N(2)	118.94(19)
N(1)-C(1)-S(1)	120.98(16)
N(2)-C(1)-S(1)	120.07(15)
C(3)-C(2)-C(7)	119.9(2)
C(3)-C(2)-N(2)	119.9(2)
C(7)-C(2)-N(2)	120.1(2)
C(2)-C(3)-C(4)	120.1(2)
C(5)-C(4)-C(3)	120.0(3)

Table 10 (continued).

Atom	Angle (°)
C(6)-C(5)-C(4)	120.1(2)
C(5)-C(6)-C(7)	120.4(2)
C(2)-C(7)-C(6)	119.6(3)
C(16)-C(11)-C(12)	119.8(2)
C(16)-C(11)-P(1)	118.09(17)
C(12)-C(11)-P(1)	121.84(18)
C(11)-C(12)-C(13)	119.4(3)
C(14)-C(13)-C(12)	120.5(3)
C(15)-C(14)-C(13)	120.4(3)
C(14)-C(15)-C(16)	120.8(3)
C(11)-C(16)-C(15)	119.2(3)
C(22)-C(21)-C(26)	118.0(2)
C(22)-C(21)-P(1)	126.18(17)
C(26)-C(21)-P(1)	115.66(16)
C(21)-C(22)-C(23)	119.8(2)
C(24)-C(23)-C(22)	121.1(2)
C(23)-C(24)-C(25)	119.5(2)
C(24)-C(25)-C(26)	119.8(2)
C(25)-C(26)-C(21)	121.5(2)
C(32)-C(31)-C(36)	119.0(2)
C(32)-C(31)-P(1)	116.73(17)
C(36)-C(31)-P(1)	124.25(18)
C(31)-C(32)-C(33)	120.2(3)
C(34)-C(33)-C(32)	119.8(3)
C(35)-C(34)-C(33)	120.2(3)
C(34)-C(35)-C(36)	120.9(3)
C(31)-C(36)-C(35)	119.8(3)
C(46)-C(41)-C(42)	118.9(3)

Table 10 (continued).

Atom	Angle (°)
C(46)-C(41)-P(2)	117.27(16)
C(42)-C(41)-P(2)	123.84(16)
C(41)-C(42)-C(43)	119.9(2)
C(44)-C(43)-C(42)	120.6(2)
C(43)-C(44)-C(45)	119.7(2)
C(44)-C(45)-C(46)	120.6(2)
C(45)-C(46)-C(41)	120.2(2)
C(52)-C(51)-C(56)	118.1(2)
C(52)-C(51)-P(2)	119.58(17)
C(56)-C(51)-P(2)	122.30(18)
C(51)-C(52)-C(53)	121.3(3)
C(54)-C(53)-C(52)	120.0(3)
C(53)-C(54)-C(55)	120.1(3)
C(54)-C(55)-C(56)	120.1(3)
C(51)-C(56)-C(55)	120.4(3)
C(62)-C(61)-C(66)	118.1(2)
C(62)-C(61)-P(2)	124.67(18)
C(66)-C(61)-P(2)	117.19(16)
C(61)-C(62)-C(63)	120.3(2)
C(64)-C(63)-C(62)	121.0(3)
C(65)-C(64)-C(63)	119.7(2)
C(64)-C(65)-C(66)	120.2(3)
C(65)-C(66)-C(61)	120.7(2)

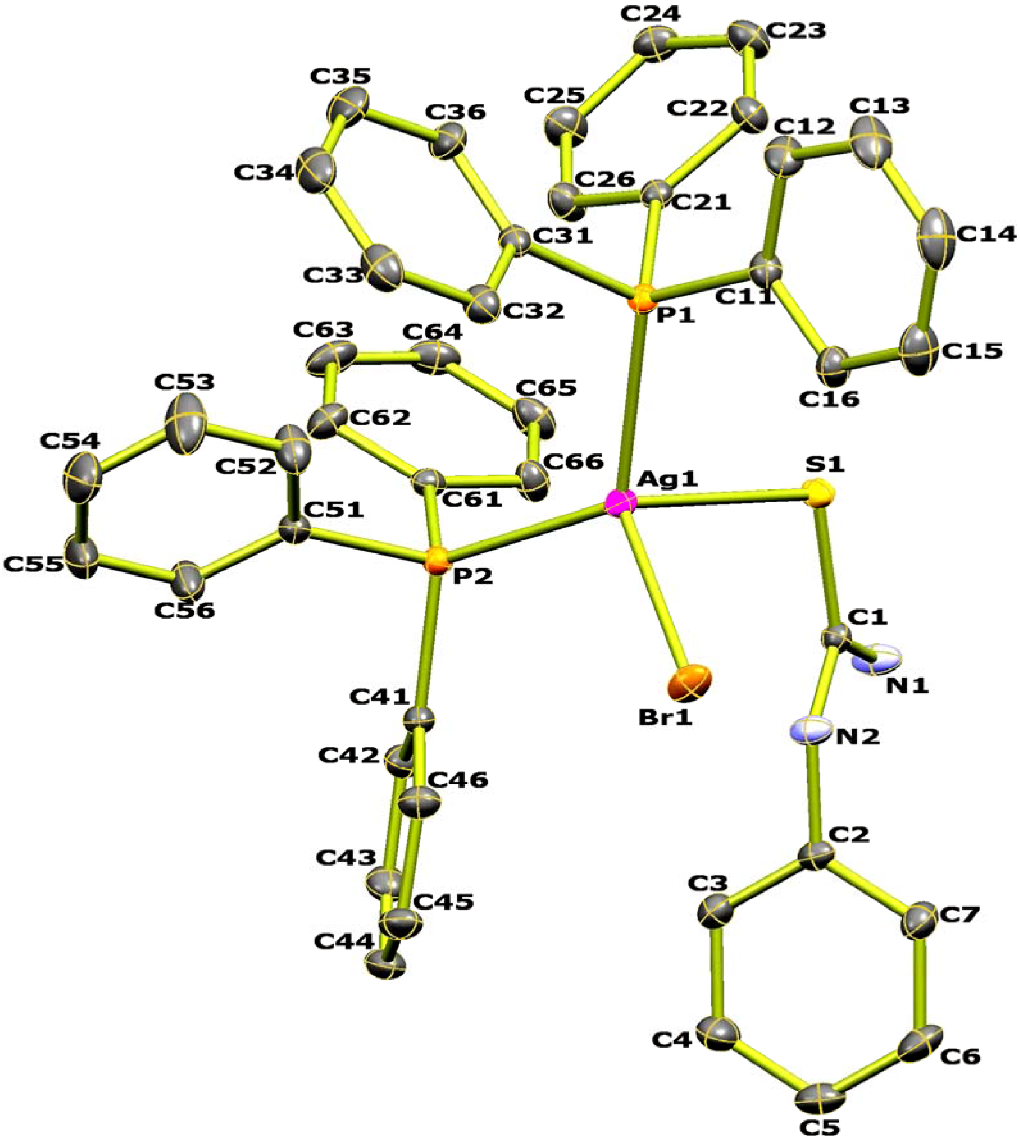


Figure 57 The structure of $[AgBr(PPh_3)_2(ptu)]$.

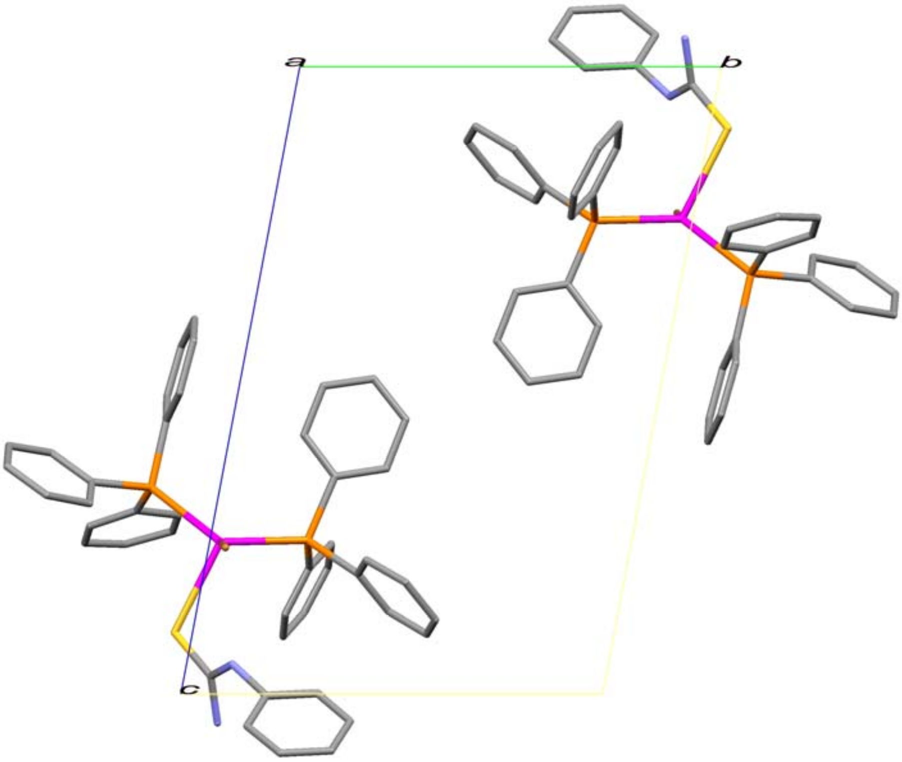


Figure 58 Unit cell contents of [AgBr(PPh$_3$)$_2$(ptu)] projected down *a*.

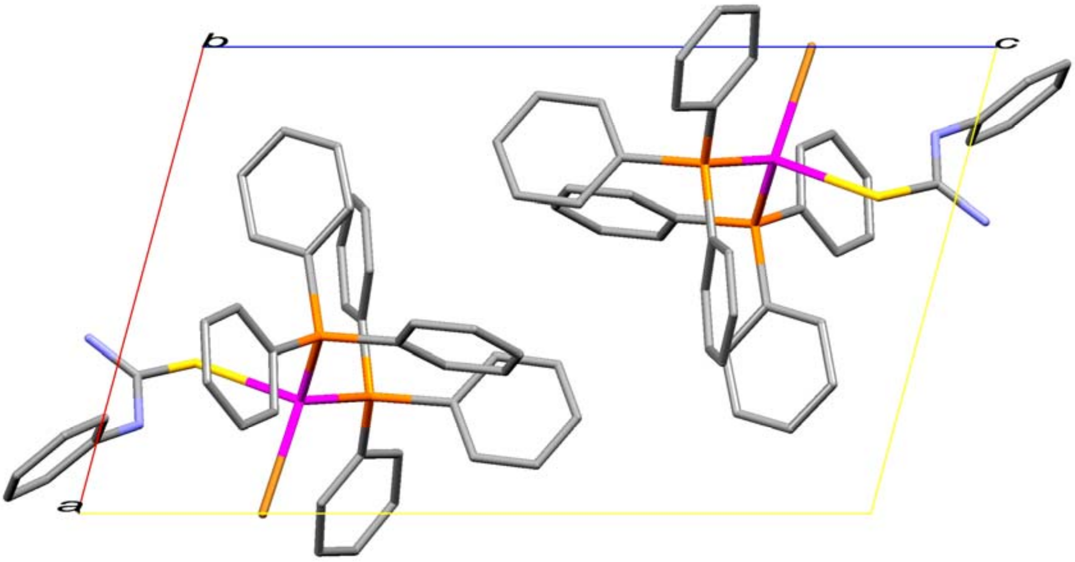


Figure 59 Unit cell contents of [AgBr(PPh$_3$)$_2$(ptu)] projected down *b*.

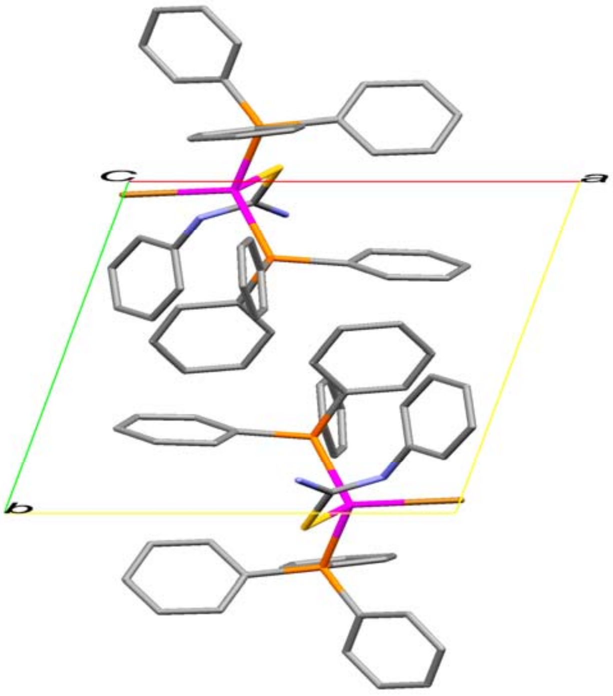


Figure 60 Unit cell contents of [AgBr(PPh$_3$)$_2$(ptu)] projected down *c*.

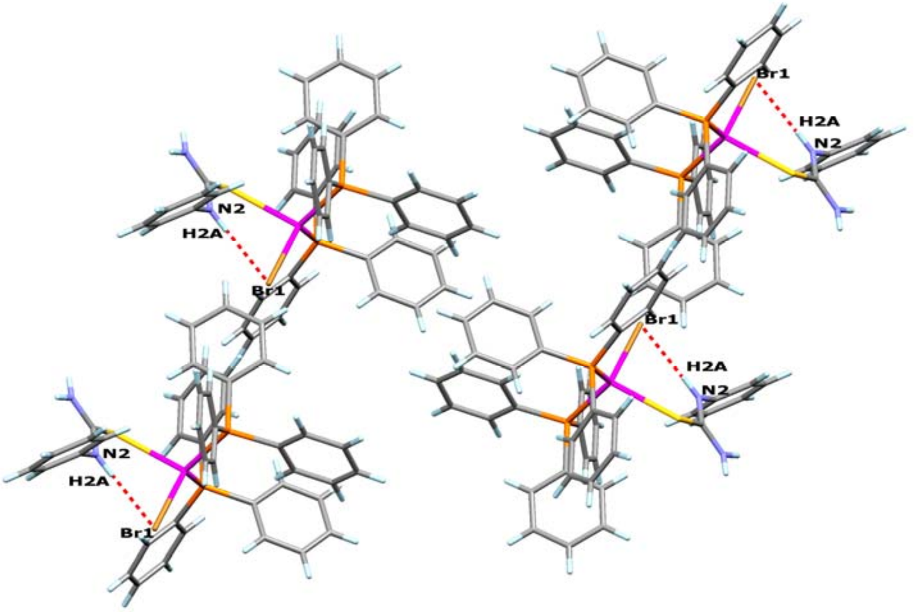


Figure 61 Hydrogen bonding the intraction of [AgBr(PPh$_3$)$_2$(ptu)].

Table 11 The crystallograpraphic data for [Ag(PPh$_3$)$_2$(ptu)]NO$_3$.

Empirical formula	C43H38AgN3O3P2S	
Formula weight	846.63	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/c	
Unit cell dimensions	*a* =13.6113(5)Å	α =90°
	b=10.6431(4)Å	β=96.0680(10)°
	c=26.4365(10)Å	γ =90°
Volume	3808.3(2) A^3	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	0.713 mm^{-1}	
F(000)	1736	
Crystal size	0.271 x 0.135 x 0.080 mm^3	
Theta range for data collection	1.50 to 28.02°.	
Index ranges	-17<=h<=17, -14<=k<=14, -34<=l<=34	
Reflections collected	44417	
Independent reflections	9196 [*R*(int) = 0.0332]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9196 / 320 / 481	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	$R1$ = 0.0276, $wR2$ = 0.0622	
R indices (all data)	$R1$ = 0.0622, $wR2$ = 0.0642	
Largest diff. peak and hole	0.546 and -0.262 e.Å^{-3}	

Table 12 Non-hydrogen interatomic distances of $[Ag(PPh_3)_2(ptu)]NO_3$.

Atom	Distance (Å)	Atom	Distance (Å)
Ag(1)-P(1)	2.4645(7)	Ag(1)-P(2)	2.4693(7)
Ag(1)-S(1)	2.5307(7)	S(1)-C(1)	1.710(3)
P(1)-C(31)	1.826(3)	P(1)-C(21)	1.826(3)
P(2)-C(41)	1.822(3)	P(2)-C(51)	1.824(3)
P(2)-C(61)	1.824(3)	N(1)-C(1)	1.332(3)
N(2)-C(1)	1.340(3)	N(2)-C(2)	1.426(3)
N(3)-O(2)	1.231(3)	N(3)-O(1)	1.257(3)
N(3)-O(3)	1.264(3)	C(2)-C(3)	1.387(4)
C(2)-C(7)	1.389(4)	C(3)-C(4)	1.392(4)
C(4)-C(5)	1.380(4)	C(5)-C(6)	1.384(4)
C(6)-C(7)	1.389(4)	C(11)-C(16)	1.396(4)
C(11)-C(12)	1.404(4)	C(12)-C(13)	1.383(4)
C(13)-C(14)	1.389(4)	C(14)-C(15)	1.386(4)
C(15)-C(16)	1.391(4)	C(21)-C(22)	1.388(4)
C(21)-C(26)	1.397(4)	C(22)-C(23)	1.394(4)
C(23)-C(24)	1.387(4)	C(24)-C(25)	1.389(4)
C(25)-C(26)	1.387(4)	C(31)-C(32)	1.392(4)
C(31)-C(36)	1.398(4)	C(32)-C(33)	1.387(4)
C(33)-C(34)	1.389(4)	C(34)-C(35)	1.384(4)
C(35)-C(36)	1.389(4)	C(41)-C(42)	1.385(4)
C(41)-C(46)	1.394(4)	C(42)-C(43)	1.392(4)
C(43)-C(44)	1.379(5)	C(44)-C(45)	1.385(5)
C(45)-C(46)	1.390(4)	C(51)-C(56)	1.395(4)
C(51)-C(52)	1.396(4)	C(52)-C(53)	1.382(4)
C(53)-C(54)	1.382(4)	C(54)-C(55)	1.388(4)
C(55)-C(56)	1.388(4)	C(61)-C(66)	1.390(4)
C(61)-C(62)	1.397(4)	C(62)-C(63)	1.393(4)

Table 12 (continued).

Atom	Distance (Å)	Atom	Distance (Å)
C(63)-C(64)	1.386(4)	C(64)-C(65)	1.385(4)
C(65)-C(66)	1.386(4)		

Table 13 Non-hydrogen interbond angles of [Ag(PPh_3)$_2$(ptu)]NO_3.

Atom	Angle (°)
P(1)-Ag(1)-P(2)	127.56(2)
P(1)-Ag(1)-S(1)	113.03(2)
P(2)-Ag(1)-S(1)	112.69(2)
C(1)-S(1)-Ag(1)	109.30(9)
C(11)-P(1)-C(31)	105.61(12)
C(11)-P(1)-C(21)	99.63(12)
C(31)-P(1)-C(21)	105.30(12)
C(11)-P(1)-Ag(1)	118.36(9)
C(31)-P(1)-Ag(1)	111.81(9)
C(21)-P(1)-Ag(1)	114.64(8)
C(41)-P(2)-C(51)	103.41(12)
C(41)-P(2)-C(61)	106.55(12)
C(51)-P(2)-C(61)	101.37(12)
C(41)-P(2)-Ag(1)	117.14(9)
C(51)-P(2)-Ag(1)	104.48(9)
C(61)-P(2)-Ag(1)	121.15(9)
C(1)-N(2)-C(2)	127.8(2)
O(2)-N(3)-O(1)	120.5(2)
O(2)-N(3)-O(3)	120.5(2)
O(1)-N(3)-O(3)	119.0(2)
N(1)-C(1)-N(2)	115.8(2)
N(1)-C(1)-S(1)	119.1(2)
N(2)-C(1)-S(1)	125.1(2)
C(3)-C(2)-C(7)	120.2(3)
C(3)-C(2)-N(2)	122.1(2)
C(7)-C(2)-N(2)	117.6(2)
C(2)-C(3)-C(4)	119.4(3)
C(5)-C(4)-C(3)	120.4(3)
C(4)-C(5)-C(6)	120.2(3)

Table 13 (continued).

Atom	Angle (°)
C(5)-C(6)-C(7)	119.7(3)
C(2)-C(7)-C(6)	120.1(3)
C(16)-C(11)-C(12)	119.0(2)
C(16)-C(11)-P(1)	120.3(2)
C(12)-C(11)-P(1)	120.6(2)
C(13)-C(12)-C(11)	120.6(2)
C(12)-C(13)-C(14)	120.0(3)
C(15)-C(14)-C(13)	119.9(2)
C(14)-C(15)-C(16)	120.5(2)
C(15)-C(16)-C(11)	119.9(2)
C(22)-C(21)-C(26)	119.2(2)
C(22)-C(21)-P(1)	124.3(2)
C(26)-C(21)-P(1)	116.6(2)
C(21)-C(22)-C(23)	120.2(2)
C(24)-C(23)-C(22)	120.3(3)
C(23)-C(24)-C(25)	119.7(3)
C(26)-C(25)-C(24)	120.1(3)
C(25)-C(26)-C(21)	120.5(3)
C(32)-C(31)-C(36)	118.9(2)
C(32)-C(31)-P(1)	123.8(2)
C(36)-C(31)-P(1)	117.3(2)
C(33)-C(32)-C(31)	120.5(3)
C(32)-C(33)-C(34)	120.2(3)
C(35)-C(34)-C(33)	119.7(3)
C(34)-C(35)-C(36)	120.2(3)
C(35)-C(36)-C(31)	120.4(3)
C(42)-C(41)-C(46)	119.2(3)
C(42)-C(41)-P(2)	123.5(2)
C(46)-C(41)-P(2)	117.3(2)

Table 13 (continued).

Atom	Angle (°)
C(41)-C(42)-C(43)	120.2(3)
C(44)-C(43)-C(42)	120.5(3)
C(43)-C(44)-C(45)	119.5(3)
C(44)-C(45)-C(46)	120.3(3)
C(45)-C(46)-C(41)	120.2(3)
C(56)-C(51)-C(52)	119.1(2)
C(56)-C(51)-P(2)	124.1(2)
C(52)-C(51)-P(2)	116.8(2)
C(53)-C(52)-C(51)	120.6(3)
C(52)-C(53)-C(54)	120.2(3)
C(53)-C(54)-C(55)	119.6(3)
C(56)-C(55)-C(54)	120.5(3)
C(55)-C(56)-C(51)	119.9(3)
C(66)-C(61)-C(62)	119.0(3)
C(66)-C(61)-P(2)	119.0(2)
C(62)-C(61)-P(2)	121.9(2)
C(63)-C(62)-C(61)	120.1(3)
C(64)-C(63)-C(62)	120.2(3)
C(65)-C(64)-C(63)	119.9(3)
C(64)-C(65)-C(66)	120.0(3)
C(65)-C(66)-C(61)	120.7(3)

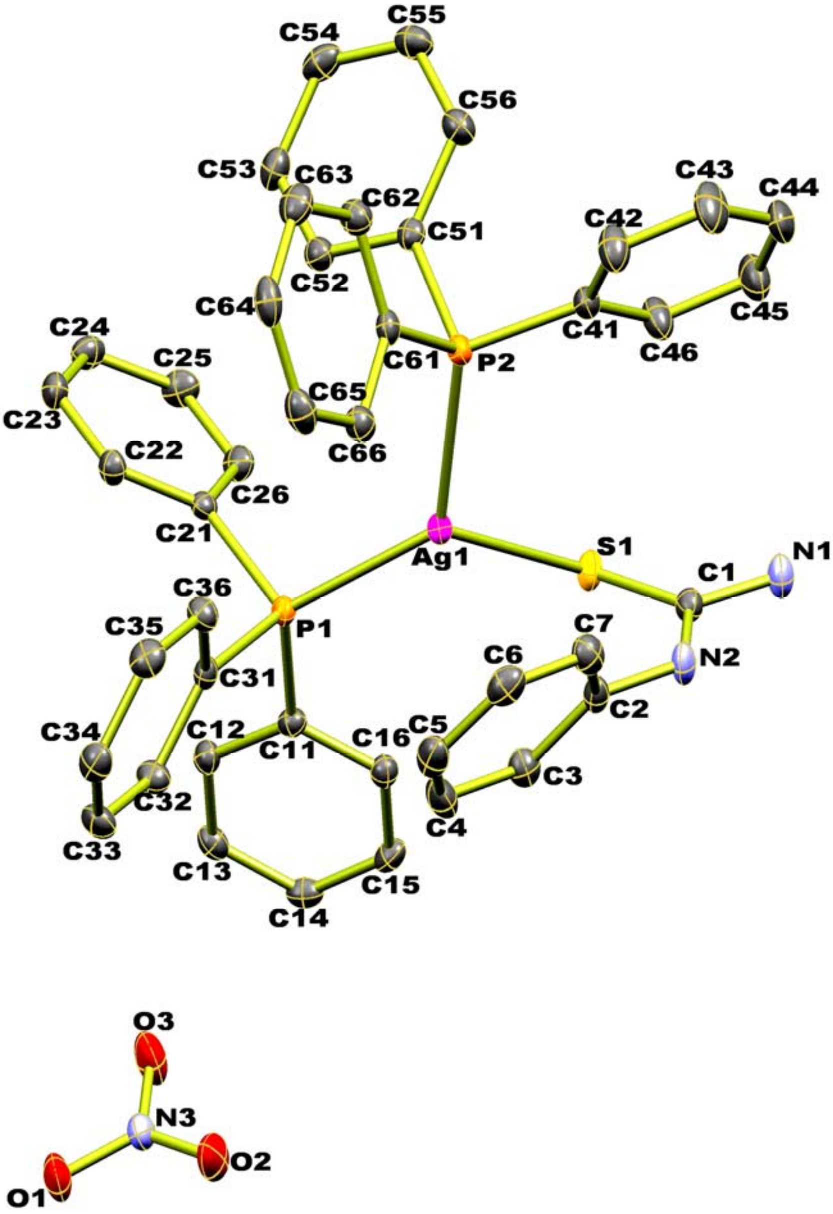


Figure 62 The structure of $[Ag(PPh_3)_2(ptu)]NO_3$.

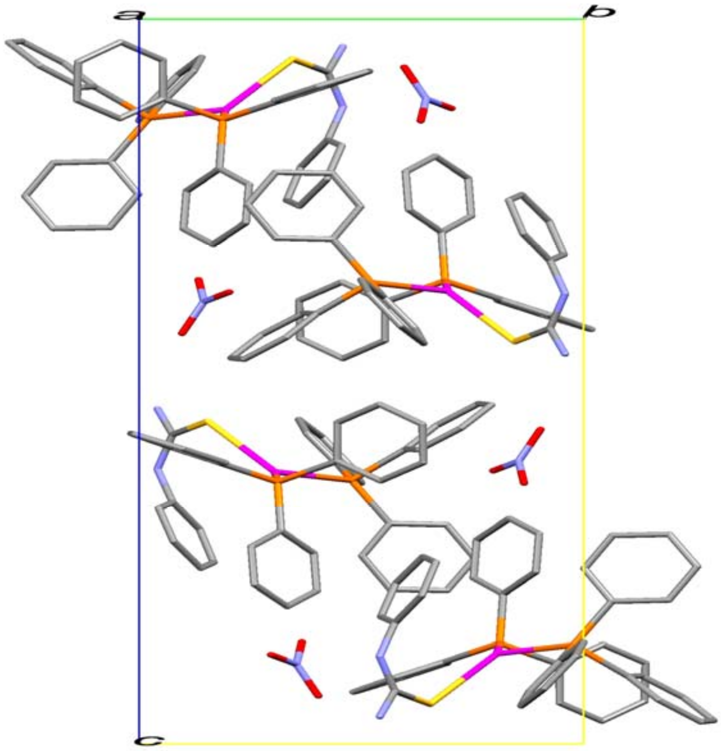


Figure 63 Unit cell contents of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$ projected down *a*.

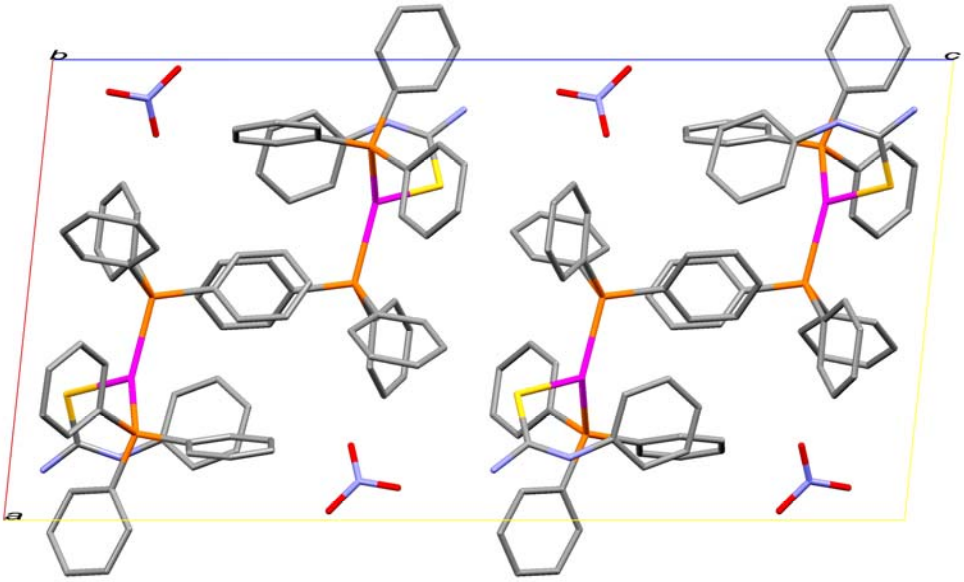


Figure 64 Unit cell contents of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$ projected down *b*.

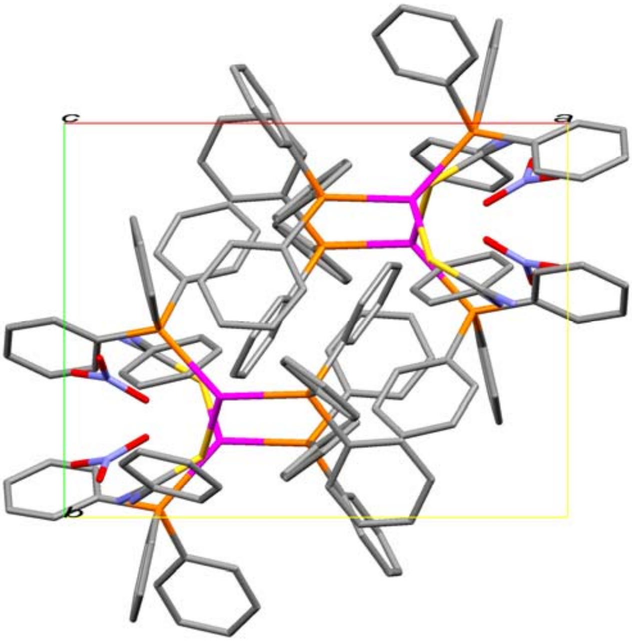


Figure 65   Unit cell contents of $[Ag(PPh_3)_2(ptu)]NO_3$ projected down *c.*

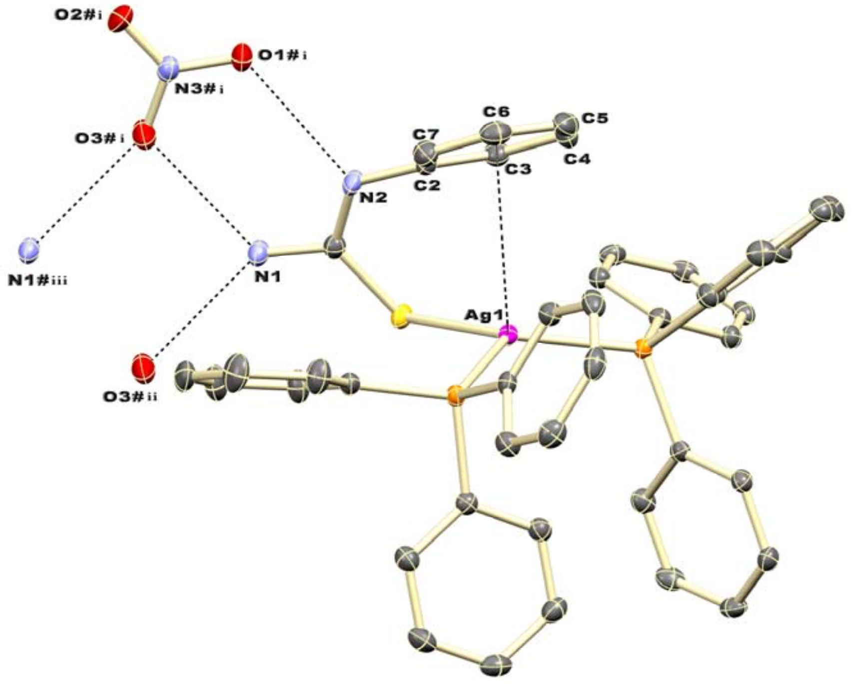


Figure 66   The inter-molecular interactions of $[Ag(PPh_3)_2(ptu)]NO_3$ complex.

CHAPTER 4

Discussion

4.1 Preparation of complexes

The purpose of this research is to study the structures of silver(I) complexes with mixed ligands of triphenylphosphine (PPh_3) and *N*-phenylthiourea (ptu) by single X-ray diffraction method. The preparation of these complexes have been carried out from direct reactions of silver(I) salt (AgX, X = Cl, Br, NO^-_3) with *N*-phenylthiourea and triphenylphosphine by varying mole ratio of reactants, solvent types, reaction temperation and time. The suitable conditions for preparing all complexes are shown in Table 1. However in this research the most suitable mole ratio of AgX (X = Cl, Br, NO^-_3) with PPh_3 and ptu for preparation of all complexes is 1:2:1. In addition, most reaction can form more complex at reaction temperature in the range of 70-80° because reactants tend to be more soluble in solvents especially silver salts and crystallization of these complexes was obtained by slow solvent evaporation. The complexes are colorless solids soluble in acetone, chloroform, dichloromethane, DMSO and DMF but insoluble in water, methanol, ethanol and acetonitrile.

4.2 Elemental Analysis

The method to determine the content of carbon, hydrogen, nitrogen and sulfur in complexes by CHN Elemental Analyzer is reported. The accepted experiment results must be close to calculated data. In practice, the experimental data are usually slightly different from the calculated data because of the impurity, the moisture and how sensitive of samples to the air. The experimental and calculated data are compared in Table 4.

4.3 X-ray Fluorescence Spectrometry

This technique was used for measuring the elemental composition of compounds such as Ag, S and halides (Cl and Br). It was only fundamentally qualitative analyses. The Ag, Cl and Br are represented for silver(I) salts, the K_α spectrum of Ag, Cl, and Br appear at 22.25, 2.62 and 11.92 keV, respectively. In addition, S and P atoms are represented for ptu and PPh_3, respectively in which the K_α spectrum appears at 2.31 and 2.01 keV for S and P, respectively. The XRF spectra for all complexes are shown in Figures 32-38.

4.4 Infrared spectrometry

Infrared spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. (Sherman Hsu, 1997).

Because of *N*-phenylthiourea (ptu) ligand consists of the NHC=S group as shown Figure 1 in which may be adopt either the thione from (H-N-C=S) or the thiol from (N=C-S-H)

However, sulfur atom or nitrogen atom of ptu ligand can coordinate to silver(I) atom. From the previous study found that IR spectra exhibit the dominance of the thione form of the ligands which was deduced by the presence of ν(N-H) bands at 3200-3130 cm^{-1}, the absence of any evidence for ν(S-H) bands in the 2600-2500 cm^{-1} region and the production of characteristic “thioamide band” as well as the characteristic medium ν(Cu-S) bands at 370-340 cm^{-1} (Hadjikakov *et al*., 1991).

Yamaguchi assigned the infrared absorption bands for some metal thiourea complexes such as tetrakis(thiourea)platinum(II) chloride, tetrakis(thiourea) palladium(II) chloride, dichlorobis(thiourea)zinc(II), dithiocyanatobis(thiourea) nickel(II), dichlorobis(thiourea)platinum(II). This investigation was undertaken to assign the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule, (Yamaguchi *et al.*, 1958).

Table 14 The previous studies of infrared absorption spectra for some metal thiourea and substituted thiourea.

Region (cm^{-1})	**Mode of vibration**	**References**
3350	ν(N-H)	Yamaguchi *et al.*, 1958
1600	$\delta(NH_2)$	
1500	ν_s(C-N)	
1100	ν (C-S)	
700	ν(C=S) + ν_s(C-N)	
3000	ν(N-H)	Lane *et al.*, 1959
2900	ν(C-H)	
1600	δ(N-H)	
1500	ν(N-H) + ν_{as}(C-N)	
1000	ν(C-N) + ν(N-H) + ν(C=S)	
700	ν(C=S) + ν(C-N)	
3180-3130	ν(N-H)	Lecomte *et al.*, 1989
1505-1515	$\nu(NH_2)$	
1330-1250	ν(C=N) + ν(C-N) + ν(C=S)	
1030-990	ν(C=S) + ν(C-N)	
900	ν(C=S)	
3000	ν(N-H)	Ferrari *et al.*, 1991
1500	ν(C-N)	
1400	ν(C=S) + ν(C-N)	
700	ν(C-N) + ν(N-H) + ν(C=S)	

Table 14 (continued).

Region (cm^{-1})	**Mode of vibration**	**References**
3000 1500 1300 1000 700	ν(N-H) ν(C-N) + δ(N-H) ν(C=S) + ν(C=N) + ν(C-H) ν(C-N) + ν(C-S) ν(C-S)	Singh *et al*., 1995
3052 1537 1027, 823 749	ν(N-H) ν(C-N) $\nu(NO_3)$ ν(C=S)	Ghassemzadeh *et al.,* 2004
3052 1537 1027, 823 749	ν(N-H) ν(C-N) $\nu(NO_3)$ ν(C=S)	Isab *et al.,* 2010

The infrared spectra of ligand ptu and three complexes are summarized in Table 15.

To support the crystal structures of three complexes, the five bands were considered :

Bands	Region	Mode of vibration
I	3000 cm^{-1}	ν(N-H)
II	1500 cm^{-1}	ν(C-N)
III	1400 cm^{-1}	ν(C=S) + ν(C-N) + δ(N-H)
IV	1100 cm^{-1}	ν(C-N) + ν(C=S)
V	700 cm^{-1}	ν(C-S)

Table 15 The infrared spectra of the ligand ptu and its complexes (cm^{-1}).

Compound	Mode of vibration				
	Band I	band II	band III	Band IV	Band V
ptu	3208	1494	1325	1070	757
$[AgCl(PPh_3)_2(ptu)]$ (1)	3067	1523	1433	1092	743
$[AgBr(PPh_3)_2(ptu)]$ (2)	3069	1518	1433	1093	742
$[Ag(PPh_3)_2(ptu)]NO_3$ (3)	3051	1570	1434	1095	742

In the spectra of the complexes, the N-H stretching frequency (band I) appears at 3067, 3069 and 3051 cm^{-1} lower than the free ligand (3208 cm^{-1}) is probably due to the hydrogen bonding in the complexes. This indicates that nitrogen to metal bonds are not present therefore the bonding in these complexes must be between the sulfur and metal atoms. The formation of S → Ag bonds is expected to increase the contribution of the highly polar structure to the substituted thiourea molecule, resulting in a greater double bond character for the nitrogen to carbon bond and a greater single bond character for the carbon to sulfur bond.

Complexes 1, 2 and 3 exhibit C-N stretching vibration at 1523, 1518, 1570 cm^{-1}, respectively. These values are blue shifted by about 14-76 cm^{-1} compared with free ligand at 1494 cm^{-1}. These increasing frequencies observed for the complexes can be explained as resulting from the greater double bond character of the carbon-to-nitrogen bonds on the complex formation.

The thioamide bands III found to the region 1433, 1433 and 1434 cm^{-1} which can be explained as NH vibration plus N-C-N plus C=S stretching vibration, $\nu(C{=}S) + \nu(C\text{-}N) + \delta(N\text{-}H)$. The shift of these bands to higher frequencies in spectra of complexes, shows the increase of the greater double bond character of the carbon-to-nitrogen bond on the complexes formation.

The absorption spectra of complexes 1, 2, 3 observed at 1092, 1093 and 1095 cm^{-1}, respectively can be assigned to thioamide band IV, whereas the peak of ptu appears at 1070 cm^{-1}. The shifts of these bands is due to the C-N stretching plus C-S stretching, however, C-S stretching dominates more than C-N stretching (upward shift of 20 cm^{-1}). This observation can be explained by the considerable change in nature of the C-N bond and the C=S bond on coordination of ligand through the sulfur atom.

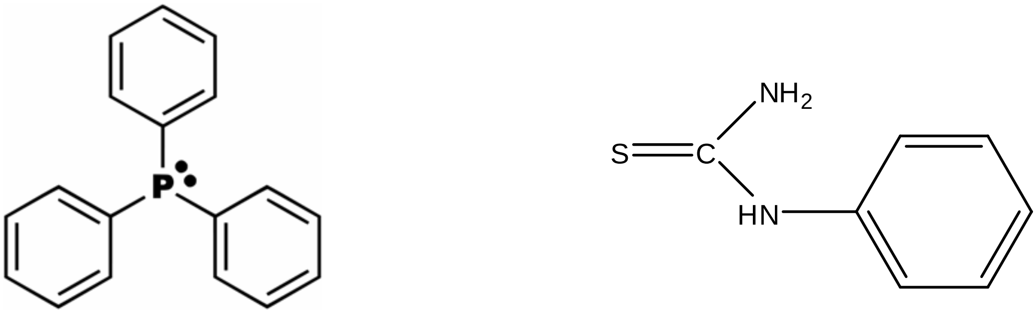
Finally, the bands V observed at about 700 cm^{-1} in the spectra of the complexes assigned to C=S stretching vibrations, [ν(C=S)]. The lower of frequency can be attributed to the reduced double bond character of the C=S bond.

The absorption bands in the spectra of the silver substituted thiourea complexes which have been assigned to the particular vibrations indicated the presence of sulfur to metal bonds in the silver complexes.

4.5 ^{1}H NMR and ^{13}C NMR Spectroscopy

NMR spectroscopy is used to determine structure of the ligands in the bound state and using complement X-ray crystallography. The ^{1}H NMR signal splitting depends on hydrogen atoms on neighboring carbon.

The ^{13}C NMR provides the number of different types of carbon atoms present and the environment of different types of carbons in the molecule.



(a) (b)

Figure 67. The chemical structure of (a) triphenylphosphine(PPh_3).
(b) *N*-phenylthiourea(ptu).

This study ^1H NMR of ligand phenylthiourea (ptu) shows a signals at 7.10-7.83 ppm due to equivalent ring protons (aromatic protons). Each of complexes (1), (2) and (3) shows a signals at a low field (7.19-7.43, 7.15-7.42, 7.11-7.89 ppm, respectively) in the solution state. Complexes (1), (2) and (3) show signals due to NH protons (10.19, 10.25, 10.75 ppm, respectively), while free ligand phenylthiourea shows a single resonance at 9.68 ppm.

The ^1H NMR spectra of the compounds in $CDCl_3$ solution also support the predominance of the thione tautomer by exhibiting a signal for the NH group at 10.19-10.75 ppm, is closely as compared to the value observed for NH group at 10-14 ppm in connection with the absence of the corresponding thiol (SH) proton. The broad nature of the signal implies the occurrence of hydrogen bonds. (Skoulika *et al.*, 1991).

Table 16 ^1H NMR spectra data of the ligand ptu and complexes.

Compound	δ N-H (ppm)
ptu	9.68(*s*, 1H > NH group) 7.08-7.39 (*m*, 5H > C_6H_5 group)
$[AgCl(PPh_3)_2(ptu)]$	10.25(*s*, 1H > NH group) 7.19-7.43 (*m*, 35H > C_6H_5 groups)
$[AgBr(PPh_3)_2(ptu)]$	10.19(*s*, 1H > NH group) 7.15-7.42 (*m*, 35H > C_6H_5 groups)
$[Ag(PPh_3)_2(ptu)]NO_3$	10.75(*s*, 1H > NH group) 7.11-7.89 (*m*, 35H > C_6H_5 groups)

The ^{31}C NMR spectra supply more convincing information about the monodentate behaviour of thiourea moiety in the complexes. The δ C=S signals appear at δ 179.15 ppm in complex (1), δ 179.05 ppm in complex (2) and δ 149.95 ppm in complex (3), which are upfield relative to the free ligand (δ 181.16 ppm). An upfield shift is attributed to lowering of C=S bond order upon coordination and a shift of N→C electron density producing a partial double bond character in the C-N bond.

Table 17 ^{13}C NMR spectra data of the ligand ptu and complexes.

Compound	δ C=S (ppm)
ptu	181.16
$[AgCl(PPh_3)_2(ptu)]$	179.15
$[AgBr(PPh_3)_2(ptu)]$	179.05
$[Ag(PPh_3)_2(ptu)]\ NO_3$	149.95

4.6 Crystallography

The X-ray diffraction analyses for complexes $[AgCl(PPh_3)_2(ptu)]$ $[AgBr(PPh_3)_2(ptu)]$ and $[Ag(PPh_3)_2(ptu)]NO_3$ were performed at room temperature on SMART APEX CCD diffractometer. The structures were solved and refined by using *WinGX1.7* (Farrugia, 2005) and *SHELX97* (Sheldrick, 2008) program.

4.6.1 The structure of [AgCl(PPh$_3$)$_2$(ptu)](1) and [AgBr(PPh$_3$)$_2$(ptu)](2)

The complex (1) is isomorphous and isostructural with complex (2), both complexes crystallize in triclinic system, space group $P\bar{1}$, $Z = 2$ with cell parameters $a = 10.5092(6)$, $b = 11.3943(6)$, $c = 17.2408(10)$ Å, $\alpha = 97.0180(10)$, $\beta = 103.9100(10)$, $\gamma = 103.2770(10)^{\circ}$ and $a = 10.6748(11)$, $b = 11.3434(12)$, $c = 17.2296(18)$ Å, $\alpha = 97.358(2)$, $\beta = 102.928(2)$, $\gamma = 102.580(2)^{\circ}$ for complex(1) and complex (2), respectively.

Each of these structures features a distorted tetrahedral silver(I) center with two phosphorus atoms of two triphenylphosphine molecules, one sulfur atom of phenylthiourea molecule and one chloride or bromide atom. The structures of these complexes are shown in Figure 54 and Figure 59. In both complexes, the angular deviations from the ideal tetrahedral value of 109.4° are comparable with several reported four coordinated silver(I) halide complex bearing a heterocyclic thioamide and two monodentate phosphines. In fact, the P(1)–Ag(1)–P(2) angles, to a value of 121.25° and 121.41° in complex(1) and complex(2), respectively compare with the previously observed values in a series of analogous complexes, e.g. in [AgCl(η^1-S-Hpytsc (Ph$_3$P)$_2$]•CH$_3$CN P(2)-Ag-P(1) = 120.03(2)°) (Lobana *et al.,* 2008) and in [AgBr(η^1-S-Hpytsc (Ph$_3$P)$_2$]•CH$_3$CN (P(2)-Ag-P(1) = 122.13(7)°) (Lobana *et al.,* 2008). A possible explanation for the large value is the steric interaction between the PPh$_3$ groups. This higher angle is counterbalanced by the bond angles X-Ag-S, X-Ag-P(2) and S-Ag-P(1), X = Cl and Br, whose values are lower than 109.4°.

The observed Ag-S distances of 2.7309(5) and 2.7114(6) Å in complex (1) and complex (2), respectively, are longer as compared to the value observed for [AgCl(η^1-S-Hpytsc (Ph$_3$P)$_2$]•CH$_3$CN (Ag-S = 2.6284(7)) (Lobana *et al.,* 2008) and in [AgBr(η^1-S-Hpytsc (Ph$_3$P)$_2$]•CH$_3$CN (Ag-S = 2.6405(19)) (Lobana *et al.,* 2008).

In both structures, the Ag-P(1) and Ag-P(2) distances of 2.4742(5) and 2.4869(5) Å in complex (1) and 2.4776(5) and 2.4886(6) Å in complex (2) respectively, are closed to the values of [AgCl(η^1-S-Hpytsc (Ph$_3$P)$_2$]•CH$_3$CN (Ag-P(1) = 2.4879(7), Ag-P(2) = 2.4409(7)) (Lobana *et al.,* 2008) and

[AgBr(η^1-S-Hpytsc ($Ph_3P)_2$]•CH_3CN (Ag-P(1) = 2.4605(19), Ag-P(2) = 2.4926(19)) (Lobana *et al.,* 2008). Moreover in both structures the presence of intramolecular hydrogen bonds between the chloride and the N(2)H(2A) hydrogen [N(2)H(2A)···Cl = 3.1087(2) Å] and between the bromide and the N(2)H(2A) hydrogen [N(2)H(2A)···Br = 3.2760(2) Å] could be responsible for the moderate narrowing of the S-Ag-Cl angle (95.813(18)°) and S-Ag-Br angle (98.662(14)°).

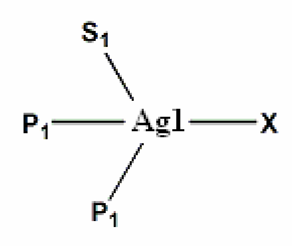
Table 18 Hydrogen bonding of [AgCl($PPh_3)_2$(ptu)] complex.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2A)...Cl(1)	0.858	2.253	3.1087(2)	175

Table 19 Hydrogen bonding of [AgBr($PPh_3)_2$(ptu)] complex.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2A)...Br(1)	0.862	2.415	3.2760(2)	177

Table 20. The selected bond lengths (Å) and angle (°) of the studied complexes (1) and (2).



Complexes	[AgCl(PPh$_3$)$_2$(ptu)]	[AgBr(PPh$_3$)$_2$(ptu)]
Ag1-X	2.5492(6)	2.6528(4)
Ag1-S1	2.7309(5)	2.7114(6)
Ag1-P1	2.4742(5)	2.4776(5)
Ag1-P2	2.4869(5)	2.4886(6)
P1-Ag1-P2	121.252(18)	121.417(18)
P1-Ag1-S1	95.992(17)	96.674(18)
P2-Ag1-S1	110.893(18)	110.766(18)
P1-Ag1-X	117.04(2)	115.325(15)
P2-Ag1-X	111.08(2)	110.383(15)
S1-Ag1-X	95.813(18)	98.662(14)

4.6.2 The structure of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$ complex (3).

The structure consists of the discrete mononuclear [Ag(ptu)(PPh$_3$)$_2$]$^+$cation and one NO$_3^-$ anion and is similar to that of [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ (Aslanidis *et al.,* 1997). A perspective view of the molecular structure of [Ag(ptu)(PPh$_3$)$_2$]NO$_3$ with atomic labeling is given in Figure 62. The cationic part contains silver(I) atom trigonally coordinated by two phosphorus atoms from two triphenylphosphine molecules and one sulfur atom from *N*–phenylthiourea molecule similar to that found in those silver oxyanion complexes containing mixed PPh$_3$/heterocyclic thione ligands (Aslanidis *et al.,* 1997; Ghassemzadeh *et al.,* 2004). The Ag—P bond lengths of 2.4645(5) and 2.4693(4) Å are similar to the values of 2.455(1) and 2.447(1) Å observed in [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ (Aslanidis *et al.,* 1997), however, these values are slightly different from the values of 2.458(2) and 2.507(2) Å in [Ag(TAMTTO)(PPh$_3$)$_2$]NO$_3$.1.5THF (Ghassemzadeh *et al.,* 2004) because of the massive and steric effect of TAMTTO heterocyclic ligands. The Ag—S bond length [2.5307(7)Å] is shorter than in those complexes [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ [2.573(1)Å] and [Ag(TAMTTO)(PPh$_3$)$_2$]NO$_3$.1.5THF [2.592(2) Å] (Aslanidis *et al.,* 1997; Ghassemzadeh *et al.,* 2004). The P(1)—Ag—P(2), P(1)—Ag—S(1) and P(2)—Ag—S(1) bond angles are 127.55(1)°, 113.02(1)° and 112.69(1)°, respectively. Due to the steric crowding of six phenyl ring from two bulky triphenylphosphine ligands and the π(CH)···Ag interaction between the centriod of phenyl ring (C2—C7) from the *N*–phenylthiourea and metal atom, the silver centre atom deviates from idealized trigonal planar with this atom lying *ca* 0.372 Å out of the P$_2$S plane. For the anion, although the oxygen atoms of the nitrate have no influence on coordination, they have great influence on the crystal packing of the complex. It is nearly planar with the bond angles around the nitrogen atom ranging from 119.01(1)-120.53(1)° and N(3)—O bond distances are 1.231(2) – 1.264(2) Å. Three N(H)···O hydrogen bonding interactions are observed between ligand amide group of [Ag(ptu)(PPh$_3$)$_2$]$^+$cation and nitrate oxygen atoms in the packing [N(1)—H(1A)···O(3)^{i} 2.877(2) Å, N(1)—H(1B)···O(3)^{ii} 2.921(2) Å, N(2)—H(2)···O(1)^{i} 2.823(2) Å ; symmetry code : (i) x-1,y,z, (ii) -x+1,-y+1,-z+2]. All interactions are depicted in Figure 66.

Table 21 Hydrogen bonding $[Ag(PPh_3)_2(ptu)]NO_3$ of complex (3).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1—H1A···O3^{i}	0.86	2.02	2.877 (2)	180
N1—H1B···O3^{ii}	0.86	2.17	2.921 (2)	145
N2—H2···O1^{i}	0.86	1.97	2.823 (2)	171

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

CHAPTER 5

CONCLUSION

In this work, silver(I) complexes with triphenylphosphine(PPh_3) and *N*-phenylthiourea(ptu) have been prepared and characterized by elemental analysis, XRF, IR, NMR and X-ray diffraction methods. They are neutral complexes, $[AgCl(PPh_3)_2(ptu)]$ (1) and $[AgBr(PPh_3)_2(ptu)]$ (2) and one ionic complex $[Ag(PPh_3)_2(ptu)]NO_3$ (3).

The crystal structures of $[AgCl(PPh_3)_2(ptu)]$ (1) and $[AgBr(PPh_3)_2(ptu)]$ (2) are isomorphous. Both complexes crystallize in the triclinic system, space group $P\bar{1}$ with cell parameters a = 10.5092(6), b = 11.3943(6), c = 17.2408(10) Å, α = 97.0180(10), β = 103.9100(10), γ = 103.2770(10)^{o} and a = 10.6748(11), b = 11.3434(12), c = 17.2296(18) Å, α = 97.358(2), β = 102.928(2), γ = 102.580(2)° for complex (1) and complex (2), respectively. Both structures are neutral monomers with the silver atom is distorted tetrahedrally coordinated by two phosphorus atoms of two triphenylphosphine molecules, one sulfur atom of phenylthiourea molule and one chloride or bromide atom.

The complex of $[Ag(PPh_3)_2(ptu)]NO_3$ crystallizes in monoclinic system, space group $P2_1/c$ with cell parameters a = 13.6113(5), b = 10.6431(4) and c = 26.4365(10) Å, β = 96.0680(10). The structure is an ionic consisting of the independent $[Ag(ptu)(PPh_3)_2]^+$ cation and one NO_3^- anion. The cationic part contains silver(I) atom trigonally coordinated by two phosphorus atoms from two triphenylphosphine molecules and one sulfur atom from *N*–phenylthiourea molecule.

In the molecule, the O atom is hydrogen bonded to the *N*–phenylthiourea NH atom. There are hydrogen bonding between three oxygen atoms of the nitrate ion and the NH-group of the ligand.

The experimental results show different structure types of complexes which prepared by silver(I) salts with triphenylphosphine(PPh$_3$) and *N*-phenylthiourea(ptu). The reactions among these reactants generated a variety of complexes which have unpredictable stoichiometry and stereochemistry. The silver(I) coordination is distorted trigonal planar or distorted tetrahedral in such a manner as to minimize steric interactions either monomer.

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APPENDIX

APPENDIX A

Calculation of unit cell volume

The equations of calculation of the unit cell volume depend on crystal system :

Crystal system	Equation
Cubic	$V = a^3$
Tetragonal	$V = a^2c$
Orthorhombic	$V = abc$
Hexagonal	$V = 0.866a^2c$
Monoclinic	$V = abc\ \sin\beta$
Triclinic	$V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cdot \cos\beta \cdot \cos\gamma)^{1/2}$

Calculation of number of molecules per unit cell (Z)

$$Z = \frac{D \times V \times N}{\mathrm{Fw}}$$

D = Density of crystal (g/cm^3)

V = Volume of unit cell (cm^3)

N = Avogadro number (6.02×10^{23} mol^{-1})

Fw = Formula weight

APPENDIX B

Table 24 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters (Å^2 x 10^3) of [AgCl(PPh$_3$)$_2$(ptu)]

Atom	x	y	z	U(eq)
Ag(1)	7714(1)	9719(1)	2451(1)	37(1)
Cl(1)	10026(1)	9608(1)	2275(1)	54(1)
S(1)	6826(1)	10423(1)	1004(1)	40(1)
P(1)	7646(1)	11586(1)	3321(1)	33(1)
P(2)	6296(1)	7656(1)	2473(1)	33(1)
N(1)	6269(2)	9028(2)	-441(1)	57(1)
N(2)	8143(2)	8902(2)	503(1)	46(1)
C(1)	7089(2)	9371(2)	305(1)	36(1)
C(2)	8432(2)	7963(2)	-8(1)	39(1)
C(3)	7971(3)	6758(2)	41(2)	52(1)
C(4)	8318(3)	5861(2)	-410(2)	65(1)
C(5)	9150(3)	6174(3)	-893(2)	64(1)
C(6)	9618(3)	7376(3)	-943(2)	66(1)
C(7)	9255(3)	8281(2)	-506(2)	55(1)
C(11)	8914(2)	13020(2)	3395(1)	39(1)
C(12)	8939(3)	14120(2)	3855(2)	57(1)
C(13)	10006(4)	15156(2)	3951(2)	72(1)
C(14)	11031(3)	15090(3)	3603(2)	71(1)
C(15)	11015(3)	14016(3)	3149(2)	67(1)
C(16)	9960(2)	12971(2)	3043(2)	50(1)
C(21)	5960(2)	11808(2)	2948(1)	36(1)
C(22)	5677(2)	12848(2)	2703(2)	52(1)
C(23)	4333(3)	12891(3)	2430(2)	65(1)

Table 24 (continued).

Atom	x	y	z	U(eq)
C(24)	3283(3)	11919(3)	2403(2)	57(1)
C(25)	3548(3)	10861(3)	2609(2)	62(1)
C(26)	4866(2)	10803(2)	2871(2)	56(1)
C(31)	7809(2)	11555(2)	4398(1)	38(1)
C(32)	9010(3)	11371(2)	4852(1)	51(1)
C(33)	9189(3)	11283(3)	5665(2)	67(1)
C(34)	8186(4)	11367(3)	6025(2)	75(1)
C(35)	7005(4)	11559(3)	5587(2)	75(1)
C(36)	6807(3)	11656(2)	4775(1)	56(1)
C(41)	6617(2)	6314(2)	1941(1)	37(1)
C(42)	5624(2)	5421(2)	1346(1)	48(1)
C(43)	5948(3)	4411(2)	980(2)	58(1)
C(44)	7236(3)	4283(2)	1212(2)	60(1)
C(45)	8225(3)	5161(3)	1801(2)	60(1)
C(46)	7928(2)	6182(2)	2155(2)	51(1)
C(51)	6399(2)	7301(2)	3488(1)	40(1)
C(52)	6747(3)	8235(2)	4140(2)	64(1)
C(53)	6821(4)	8015(3)	4918(2)	87(1)
C(54)	6571(4)	6858(4)	5051(2)	90(1)
C(55)	6207(5)	5903(4)	4411(2)	115(2)
C(56)	6112(4)	6111(3)	3627(2)	86(1)
C(61)	4492(2)	7495(2)	2023(1)	37(1)
C(62)	3491(2)	7094(2)	2398(2)	51(1)
C(63)	2155(3)	7080(3)	2038(2)	66(1)
C(64)	1801(3)	7441(3)	1310(2)	66(1)
C(65)	2781(3)	7824(2)	919(2)	64(1)
C(66)	4121(2)	7860(2)	1279(2)	53(1)

Table 25 Non – hydrogen atom thermal parameters ($Å^2$ x 10^3) of [AgCl(PPh_3)$_2$(ptu)].

Atom	U11	U22	U33	U23	U13	U12
Ag(1)	37(1)	36(1)	38(1)	3(1)	14(1)	9(1)
Cl(1)	32(1)	86(1)	46(1)	8(1)	9(1)	21(1)
S(1)	49(1)	42(1)	32(1)	6(1)	10(1)	22(1)
P(1)	36(1)	30(1)	30(1)	2(1)	9(1)	7(1)
P(2)	33(1)	30(1)	38(1)	6(1)	12(1)	9(1)
N(1)	60(1)	76(2)	36(1)	-5(1)	0(1)	41(1)
N(2)	50(1)	57(1)	31(1)	-2(1)	6(1)	28(1)
C(1)	40(1)	40(1)	32(1)	9(1)	12(1)	14(1)
C(2)	37(1)	49(1)	31(1)	2(1)	7(1)	18(1)
C(3)	53(1)	55(1)	55(1)	12(1)	24(1)	16(1)
C(4)	73(2)	45(1)	80(2)	5(1)	28(2)	19(1)
C(5)	61(2)	67(2)	65(2)	-11(1)	19(1)	27(1)
C(6)	60(2)	81(2)	58(2)	-3(1)	34(1)	13(1)
C(7)	66(2)	52(1)	49(1)	5(1)	26(1)	9(1)
C(11)	42(1)	34(1)	32(1)	3(1)	4(1)	2(1)
C(12)	74(2)	41(1)	48(1)	-4(1)	18(1)	4(1)
C(13)	104(2)	37(1)	51(2)	-5(1)	8(2)	-7(1)
C(14)	69(2)	59(2)	62(2)	15(1)	4(1)	-17(1)
C(15)	53(2)	65(2)	76(2)	21(2)	18(1)	0(1)
C(16)	46(1)	47(1)	54(1)	12(1)	16(1)	8(1)
C(21)	40(1)	36(1)	31(1)	3(1)	11(1)	12(1)
C(22)	50(1)	41(1)	64(2)	15(1)	14(1)	11(1)
C(23)	62(2)	58(2)	83(2)	24(1)	17(1)	30(1)
C(24)	43(1)	74(2)	56(1)	7(1)	9(1)	25(1)
C(25)	42(1)	59(2)	77(2)	9(1)	13(1)	6(1)
C(26)	44(1)	42(1)	78(2)	14(1)	12(1)	9(1)

Table 25 (continued).

Atom	U11	U22	U33	U23	U13	U12
C(31)	51(1)	31(1)	32(1)	2(1)	11(1)	11(1)
C(32)	58(1)	50(1)	44(1)	7(1)	7(1)	16(1)
C(33)	87(2)	61(2)	43(1)	9(1)	-5(1)	25(2)
C(34)	125(3)	66(2)	36(1)	13(1)	19(2)	29(2)
C(35)	105(3)	86(2)	50(2)	15(2)	42(2)	33(2)
C(36)	68(2)	65(2)	42(1)	12(1)	22(1)	26(1)
C(41)	41(1)	34(1)	39(1)	8(1)	15(1)	13(1)
C(42)	44(1)	40(1)	56(1)	2(1)	13(1)	11(1)
C(43)	68(2)	40(1)	60(2)	-5(1	16(1)	10(1)
C(44)	80(2)	50(1)	64(2)	9(1)	30(1)	35(1)
C(45)	59(2)	68(2)	64(2)	9(1)	21(1)	37(1)
C(46)	45(1)	55(1)	51(1)	2(1)	10(1)	20(1)
C(51)	42(1)	40(1)	42(1)	12(1)	15(1)	14(1)
C(52)	89(2)	45(1)	45(1)	5(1)	15(1)	1(1)
C(53)	118(3)	82(2)	42(2)	4(1)	19(2)	-2(2)
C(54)	125(3)	112(3)	54(2)	39(2)	36(2)	49(2)
C(55)	224(5)	81(2)	94(3)	58(2)	91(3)	76(3)
C(56)	166(4)	49(2)	71(2)	24(1)	63(2)	42(2)
C(61)	34(1)	30(1)	47(1)	4(1)	12(1)	9(1)
C(62)	42(1)	63(2)	48(1)	4(1)	18(1)	11(1)
C(63)	38(1)	82(2)	73(2)	-9(2)	22(1)	8(1)
C(64)	39(1)	60(2)	87(2)	-7(1)	2(1)	19(1)
C(65)	54(2)	54(2)	75(2)	19(1)	-3(1)	15(1)
C(66)	43(1)	53(1)	63(2)	22(1)	11(1)	9(1)

Table 26 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters (Å^{2}x 10^3) of [AgBr $(PPh_3)_2$(ptu)].

Atom	x	y	z	U(eq)
Ag(1)	7591(1)	9745(1)	2423(1)	40(1)
Br(1)	10005(1)	9603(1)	2334(1)	59(1)
S(1)	6776(1)	10427(1)	981(1)	43(1)
P(1)	7502(1)	11629(1)	3289(1)	36(1)
P(2)	6208(1)	7686(1)	2450(1)	37(1)
N(1)	6257(2)	9007(2)	-449(1)	62(1)
N(2)	8105(2)	8912(2)	476(1)	51(1)
C(1)	7058(2)	9371(2)	284(1)	40(1)
C(2)	8427(2)	7974(2)	-24(1)	43(1)
C(3)	7967(3)	6768(2)	16(2)	60(1)
C(4)	8343(3)	5867(2)	-427(2)	74(1)
C(5)	9190(3)	6184(3)	-898(2)	69(1)
C(6)	9653(3)	7382(3)	-937(2)	72(1)
C(7)	9268(3)	8290(2)	-505(2)	62(1)
C(11)	8739(2)	13065(2)	3379(1)	44(1)
C(12)	8722(3)	14154(2)	3842(2)	65(1)
C(13)	9764(4)	15191(2)	3956(2)	84(1)
C(14)	10797(3)	15140(3)	3624(2)	86(1)
C(15)	10817(3)	14080(3)	3169(2)	79(1)
C(16)	9785(2)	13025(2)	3036(2)	57(1)
C(21)	5858(2)	11867(2)	2925(1)	38(1)
C(22)	5582(2)	12907(2)	2678(2)	54(1)
C(23)	4262(3)	12955(3)	2408(2)	68(1)
C(24)	3241(2)	11990(3)	2387(2)	63(1)
C(25)	3506(2)	10926(3)	2594(2)	68(1)
C(26)	4798(2)	10863(2)	2851(2)	58(1)

Table 26 (continued).

Atom	x	y	z	U(eq)
C(31)	7636(2)	11572(2)	4360(1)	43(1)
C(32)	8803(3)	11384(2)	4802(1)	58(1)
C(33)	8966(3)	11290(3)	5619(2)	74(1)
C(34)	7958(4)	11362(3)	5975(2)	85(1)
C(35)	6813(4)	11551(3)	5547(2)	87(1)
C(36)	6637(3)	11664(3)	4738(2)	65(1)
C(41)	6545(2)	6338(2)	1915(1)	40(1)
C(42)	5591(2)	5451(2)	1318(1)	51(1)
C(43)	5931(3)	4440(2)	954(2)	63(1)
C(44)	7187(3)	4301(2)	1186(2)	66(1)
C(45)	8134(3)	5174(3)	1777(2)	65(1)
C(46)	7827(2)	6199(2)	2134(2)	55(1)
C(51)	6334(2)	7324(2)	3466(1)	44(1)
C(52)	6830(3)	8245(3)	4125(2)	76(1)
C(53)	6959(4)	8005(3)	4910(2)	104(1)
C(54)	6597(4)	6847(4)	5024(2)	95(1)
C(55)	6068(5)	5904(3)	4373(2)	106(1)
C(56)	5938(4)	6141(3)	3592(2)	83(1)
C(61)	4441(2)	7520(2)	2017(1)	41(1)
C(62)	3450(2)	7107(2)	2388(2)	57(1)
C(63)	2140(3)	7078(3)	2029(2)	73(1)
C(64)	1801(3)	7441(3)	1301(2)	68(1)
C(65)	2760(3)	7834(2)	918(2)	68(1)
C(66)	4080(2)	7885(2)	1272(2)	57(1)

Table 27 Non – hydrogen atom thermal parameters (Å^2 x 10^3) of [AgBr(PPh$_3$)$_2$(ptu)].

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	38(1)	40(1)	41(1)	3(1)	14(1)	9(1)
Br(1)	34(1)	89(1)	54(1)	11(1)	8(1)	21(1)
S(1)	52(1)	45(1)	34(1)	6(1)	10(1)	23(1)
P(1)	39(1)	34(1)	32(1)	2(1)	9(1)	6(1)
P(2)	38(1)	33(1)	41(1)	6(1)	13(1)	9(1)
N(1)	65(1)	83(2)	38(1)	-7(1)	-1(1)	43(1)
N(2)	53(1)	64(1)	35(1)	-3(1)	4(1)	29(1)
C(1)	45(1)	43(1)	35(1)	9(1)	13(1)	14(1)
C(2)	40(1)	53(1)	36(1)	2(1)	8(1)	19(1)
C(3)	63(2)	61(2)	64(2)	13(1)	32(1)	18(1)
C(4)	87(2)	50(2)	91(2)	5(1)	37(2)	23(1)
C(5)	67(2)	73(2)	70(2)	-9(1)	22(1)	32(1)
C(6)	66(2)	89(2)	64(2)	-5(1)	37(1)	15(2)
C(7)	72(2)	58(2)	57(2)	3(1)	30(1)	7(1)
C(11)	46(1)	40(1)	36(1)	5(1)	3(1)	0(1)
C(12)	79(2)	47(1)	53(1)	-6(1)	15(1)	-3(1)
C(13)	117(3)	44(1)	60(2)	-7(1)	5(2)	-16(2)
C(14)	76(2)	73(2)	76(2)	21(2)	-4(2)	-29(2)
C(15)	53(2)	79(2)	94(2)	28(2)	15(2)	-8(1)
C(16)	51(1)	56(1)	64(2)	17(1)	17(1)	6(1)
C(21)	42(1)	37(1)	34(1)	2(1)	10(1)	10(1)
C(22)	57(1)	43(1)	61(1)	11(1)	11(1)	11(1)
C(23)	67(2)	60(2)	80(2)	19(1)	10(1)	29(1)
C(24)	45(1)	78(2)	63(2)	4(1)	10(1)	21(1)
C(25)	41(1)	65(2)	93(2)	12(1)	15(1)	5(1)
C(26)	43(1)	45(1)	81(2)	14(1)	12(1)	7(1)

Table 27 (continued)

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(31)	58(1)	35(1)	35(1)	3(1)	11(1)	11(1)
C(32)	68(2)	54(1)	46(1)	7(1)	6(1)	16(1)
C(33)	95(2)	65(2)	49(2)	10(1)	-7(2)	21(2)
C(34)	140(3)	78(2)	40(1)	14(1)	23(2)	34(2)
C(35)	123(3)	104(2)	52(2)	19(2)	45(2)	45(2)
C(36)	85(2)	77(2)	47(1)	15(1)	28(1)	33(2)
C(41)	47(1)	38(1)	42(1)	8(1)	18(1)	15(1)
C(42)	52(1)	44(1)	57(1)	5(1)	16(1)	13(1)
C(43)	79(2)	45(1)	61(2)	-3(1)	18(1)	14(1)
C(44)	92(2)	53(1)	66(2)	9(1)	31(2)	38(1)
C(45)	70(2)	73(2)	68(2)	13(1)	25(1)	42(1)
C(46)	50(1)	59(1)	57(1)	2(1)	11(1)	21(1)
C(51)	49(1)	42(1)	47(1)	12(1)	19(1)	18(1)
C(52)	110(2)	52(2)	48(1)	8(1)	10(2)	-1(2)
C(53)	150(4)	89(2)	46(2)	8(2)	11(2)	-10(2)
C(54)	135(3)	108(3)	57(2)	38(2)	34(2)	42(2)
C(55)	193(4)	74(2)	89(2)	46(2)	76(3)	56(3)
C(56)	148(3)	49(2)	65(2)	16(1)	51(2)	27(2)
C(61)	38(1)	33(1)	52(1)	2(1)	14(1)	9(1)
C(62)	47(1)	69(2)	51(1)	1(1)	20(1)	8(1)
C(63)	43(1)	87(2)	80(2)	-12(2)	27(1)	7(1)
C(64)	41(1)	65(2)	89(2)	-10(1)	4(1)	18(1)
C(65)	57(2)	56(2)	82(2)	18(1)	-3(1)	16(1)
C(66)	45(1)	55(1)	70(2)	24(1)	12(1)	9(1)

Table 28 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters (Å^{2}x 10^3) of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$.

Atom	x	y	z	U(eq)
Ag(1)	3095(1)	8054(1)	8753(1)	13(1)
S(1)	2737(1)	6546(1)	9451(1)	17(1)
P(1)	4856(1)	8115(1)	8613(1)	13(1)
P(2)	1882(1)	9782(1)	8637(1)	14(1)
N(1)	1087(2)	5414(2)	9621(1)	21(1)
N(2)	1355(2)	5411(2)	8790(1)	20(1)
N(3)	9155(2)	3540(2)	8900(1)	20(1)
O(1)	9803(2)	3662(2)	8598(1)	29(1)
O(2)	8383(2)	2969(2)	8768(1)	34(1)
O(3)	9298(2)	4032(2)	9336(1)	32(1)
C(1)	1665(2)	5755(2)	9268(1)	17(1)
C(2)	1764(2)	5756(3)	8335(1)	16(1)
C(3)	2722(2)	5442(3)	8251(1)	20(1)
C(4)	3069(2)	5774(3)	7792(1)	25(1)
C(5)	2461(2)	6389(3)	7421(1)	24(1)
C(6)	1498(2)	6677(3)	7500(1)	23(1)
C(7)	1148(2)	6360(3)	7959(1)	21(1)
C(11)	5654(2)	6845(2)	8871(1)	14(1)
C(12)	6684(2)	6939(2)	8881(1)	16(1)
C(13)	7289(2)	5970(3)	9073(1)	17(1)
C(14)	6880(2)	4904(3)	9270(1)	18(1)
C(15)	5866(2)	4824(2)	9281(1)	18(1)
C(16)	5250(2)	5783(2)	9080(1)	15(1)
C(21)	5537(2)	9457(2)	8902(1)	14(1)
C(22)	5901(2)	10437(2)	8629(1)	16(1)
C(23)	6448(2)	11397(3)	8883(1)	18(1)

Table 28 (continued).

Atom	x	y	z	U(eq)
C(24)	6642(2)	11375(3)	9408(1)	20(1)
C(25)	6259(2)	10414(3)	9684(1)	21(1)
C(26)	5705(2)	9465(3)	9433(1)	19(1)
C(31)	5023(2)	8193(2)	7937(1)	14(1)
C(32)	5745(2)	7526(3)	7715(1)	18(1)
C(33)	5803(2)	7596(3)	7195(1)	21(1)
C(34)	5139(2)	8332(3)	6891(1)	21(1)
C(35)	4418(2)	9001(3)	7107(1)	21(1)
C(36)	4356(2)	8931(3)	7628(1)	18(1)
C(41)	664(2)	9497(2)	8841(1)	17(1)
C(42)	-199(2)	10000(3)	8598(1)	26(1)
C(43)	-1095(2)	9812(3)	8796(1)	31(1)
C(44)	-1136(2)	9117(3)	9234(1)	27(1)
C(45)	-277(2)	8597(3)	9475(1)	29(1)
C(46)	620(2)	8779(3)	9278(1)	24(1)
C(51)	2393(2)	11009(2)	9069(1)	15(1)
C(52)	3391(2)	11297(3)	9058(1)	18(1)
C(53)	3827(2)	12249(3)	9358(1)	22(1)
C(54)	3279(2)	12924(3)	9676(1)	24(1)
C(55)	2288(2)	12637(3)	9694(1)	24(1)
C(56)	1842(2)	11688(3)	9391(1)	21(1)
C(61)	1683(2)	10641(2)	8037(1)	15(1)
C(62)	1452(2)	11920(3)	8020(1)	20(1)
C(63)	1368(2)	12559(3)	7558(1)	23(1)
C(64)	1511(2)	11929(3)	7113(1)	23(1)
C(65)	1730(2)	10657(3)	7127(1)	24(1)
C(66)	1817(2)	10020(3)	7587(1)	19(1)

Table 29 Non – hydrogen atom thermal parameters ($Å^2$ x 10^3) of [Ag(PPh$_3$)$_2$(ptu)]NO$_3$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	13(1)	14(1)	15(1)	0(1)	3(1)	-1(1)
S(1)	17(1)	20(1)	13(1)	2(1)	1(1)	-5(1)
P(1)	12(1)	12(1)	13(1)	1(1)	2(1)	0(1)
P(2)	13(1)	14(1)	15(1)	0(1)	3(1)	0(1)
N(1)	19(1)	26(1)	17(1)	0(1)	5(1)	-7(1)
N(2)	16(1)	25(1)	18(1)	-1(1)	4(1)	-8(1)
N(3)	16(1)	19(1)	26(1)	-1(1)	6(1)	-1(1)
O(1)	23(1)	38(1)	28(1)	-8(1)	12(1)	-11(1)
O(2)	22(1)	36(1)	45(1)	-16(1)	11(1)	-15(1)
O(3)	24(1)	50(2)	24(1)	-11(1)	9(1)	-12(1)
C(1)	17(1)	16(1)	17(1)	2(1)	3(1)	0(1)
C(2)	17(1)	18(1)	14(1)	-2(1)	3(1)	-6(1)
C(3)	19(1)	23(1)	18(1)	-2(1)	1(1)	-2(1)
C(4)	21(1)	32(2)	22(1)	-6(1)	9(1)	-2(1)
C(5)	33(2)	25(2)	16(1)	-4(1)	8(1)	-8(1)
C(6)	30(2)	20(1)	18(1)	-1(1)	-3(1)	-3(1)
C(7)	17(1)	25(2)	21(1)	-3(1)	1(1)	-2(1)
C(11)	16(1)	13(1)	13(1)	-1(1)	1(1)	0(1)
C(12)	17(1)	16(1)	15(1)	1(1)	4(1)	-1(1)
C(13)	14(1)	22(1)	13(1)	-2(1)	1(1)	2(1)
C(14)	23(1)	16(1)	14(1)	-1(1)	-1(1)	5(1)
C(15)	24(1)	12(1)	16(1)	1(1)	1(1)	-2(1)
C(16)	16(1)	16(1)	14(1)	-1(1)	2(1)	-2(1)
C(21)	11(1)	14(1)	16(1)	-1(1)	2(1)	2(1)
C(22)	17(1)	19(1)	13(1)	0(1)	3(1)	-2(1)
C(23)	18(1)	18(1)	19(1)	1(1)	5(1)	-3(1)

Table 29 (continued).

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(24)	19(1)	17(1)	22(1)	-5(1)	-1(1)	-1(1)
C(25)	29(2)	21(1)	13(1)	-1(1)	-1(1)	2(1)
C(26)	24(1)	17(1)	16(1)	3(1)	4(1)	1(1)
C(31)	14(1)	14(1)	13(1)	0(1)	1(1)	-3(1)
C(32)	19(1)	19(1)	17(1)	0(1)	1(1)	4(1)
C(33)	23(1)	24(1)	18(1)	-3(1)	6(1)	3(1)
C(34)	27(2)	22(1)	14(1)	-1(1)	2(1)	-3(1)
C(35)	23(1)	20(1)	18(1)	3(1)	-2(1)	2(1)
C(36)	16(1)	19(1)	19(1)	0(1)	2(1)	2(1)
C(41)	16(1)	15(1)	20(1)	-1(1)	5(1)	-1(1)
C(42)	19(1)	30(2)	30(2)	9(1)	4(1)	1(1)
C(43)	14(1)	38(2)	42(2)	7(2)	4(1)	3(1)
C(44)	18(1)	28(2)	37(2)	-2(1)	13(1)	-4(1)
C(45)	28(2)	32(2)	29(2)	7(1)	13(1)	1(1)
C(46)	19(1)	28(2)	27(2)	6(1)	7(1)	4(1)
C(51)	17(1)	14(1)	14(1)	2(1)	1(1)	1(1)
C(52)	20(1)	17(1)	17(1)	0(1)	4(1)	0(1)
C(53)	22(1)	21(1)	22(1)	2(1)	1(1)	-6(1)
C(54)	34(2)	18(1)	18(1)	-2(1)	-2(1)	-3(1)
C(55)	29(2)	22(1)	20(1)	-4(1)	6(1)	4(1)
C(56)	20(1)	23(1)	19(1)	-2(1)	4(1)	2(1)
C(61)	12(1)	18(1)	16(1)	2(1)	3(1)	-1(1)
C(62)	21(1)	21(1)	18(1)	0(1)	3(1)	1(1)
C(63)	24(2)	20(1)	25(2)	6(1)	1(1)	0(1)
C(64)	18(1)	34(2)	18(1)	8(1)	2(1)	-4(1)
C(65)	21(1)	35(2)	16(1)	-3(1)	4(1)	-3(1)
C(66)	17(1)	21(1)	20(1)	-2(1)	3(1)	-1(1)

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