Silver(I) Complexes Containing Triphenylphosphine and *N,N'*-Diphenylthiourea

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Thesis Title Silver(I) Complexes Containing Triphenylphosphine and *N,N'*-Diphenylthiourea
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ชื่อวิทยานิพนธ์ สารประกอบเชิงซ้อนของซิลเวอร์(I) ที่มีไตรฟีนิลฟอสฟีน
และไดฟีนิลไธโอยูเรีย
ผู้เขียน นางสาวเนตรนภา เอียดสงคราม
สาขาวิชา เคมีศึกษา
ปีการศึกษา 2552

บทคัดย่อ

สารประกอบเชิงซ้อน $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) เตรียมได้จากปฏิกิริยาระหว่างซิลเวอร์(I)เฮไลด์ (AgX, X = Cl, Br) กับลิแกนด์ไตรฟีนิลฟอสฟีน(PPh_3) และไดฟีนิลไธโอยูเรีย (dptu) ในอะซีโตไนไตรล์ ศึกษาโครงสร้างของสารประกอบเชิงซ้อนที่ได้โดยวิธีการวิเคราะห์ปริมาณธาตุที่เป็นองค์ประกอบ, วิธีทางสเปกโทรสโกปี เอกซเรย์ฟลูออเรสเซนซ์ อินฟราเรด และนิวเคลียร์แมกเนติกเรโซแนนซ์ และวิธีการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยวพบว่า สาร $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (1) และ $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (2) อยู่ในระบบผลึก orthorhombic, หมู่ปริภูมิ $P2_12_12_1$, พารามิเตอร์หน่วยเซลล์ของ(1) มีดังนี้ a = 13.98231(6), b = 16.7180(7), c = 19.6205(9) Å และ Z = 4, ผลึก (2) a = 14.0030(6), b = 16.7462(7), c = 19.8196(8) Å และ Z = 4 ตามลำดับ โครงสร้างของสารทั้งสองเป็นแบบมอนอเมอร์ และมีโครงสร้างผลึกเหมือนกัน รูปทรงเรขาคณิตของอะตอมซิลเวอร์เป็นแบบทรงสี่หน้าจากการโคออร์ดิเนตกับฟอสฟอรัส 1 อะตอมของลิแกนด์ไตรฟีนิลฟอสฟีน 2 โมเลกุล ซัลเฟอร์ 1 อะตอมของไดฟีนิลไธโอยูเรีย 1

โมเลกุล เฮไลด์ 1 อะตอม และมีอะซีโตไนไตรล์ซึ่งเป็นตัวทำละลาย 1 โมเลกุล อีกทั้งยังเกิดพันธะไฮโดรเจน NH···X ภายในโมเลกุล และพันธะไฮโดรเจน NH···N ระหว่างโมเลกุล

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ABSTRACT

The $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) complexes have been prepared by the reaction of silver halides (AgX, X = Cl, Br) with triphenylphosphine (PPh_3) and *N,N'*-diphenylthiourea (dptu) in acetonitrile. The structures of these complexes have been characterized by elemental analysis, XRF, IR and NMR spectroscopy and single crystal X-ray diffraction methods. The two complexes $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (1) and $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (2) crystalized in orthorhombic system, space group $P2_12_12_1$ with cell parameters a = 13.98231(6), b = 16.7180(7), c = 19.6205(9) Å, and $Z = 4$ for (1) and a = 14.0030(6), b = 16.7462(7), c = 19.8196(8) Å and Z = 4 for (2) respectively. Both are isomorphous and monomeric complexes with the silver atom is tetrahedrally coordinated by two P atoms of two PPh_3 molecules, one S atom of dptu molecules, one halide atom and accompanied by acetonitrile molecule of solvation. In addition the intramolecular NH···X and intermolecular NH···N hydrogen bonds were found in these complexes.

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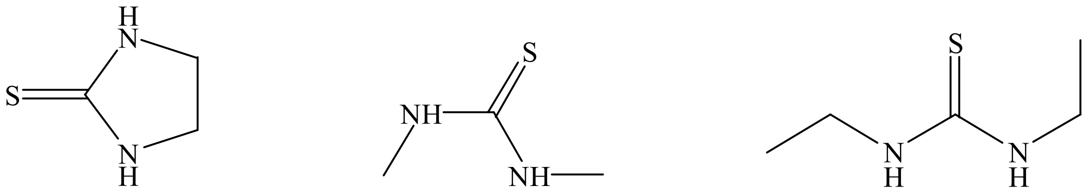
CHAPTER 1
INTRODUCTION

1.1 Introduction

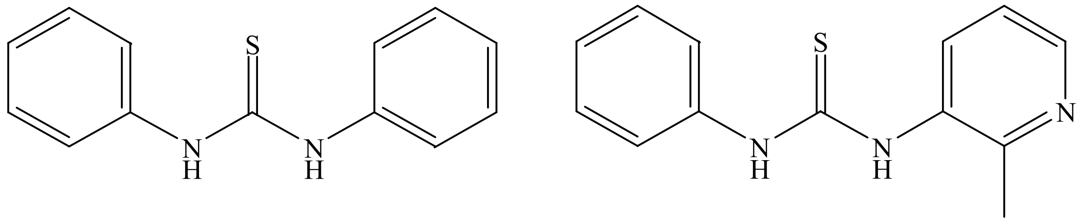
Silver, a chemical symbol Ag, atomic number 47, is chemically one of the heavy metals and one of the noble metals. Silver has a single s electron outside a complete d shell ([Kr] $4d^{10}$ $5s^1$). The common oxidation state is +1.

Triphenylphosphine 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.

Thiourea is an organic compound of carbon, nitrogen, sulfur and hydrogen, with the formula CSN_2H_4 or $(NH_2)_2CS$. It is similar to urea, except that the oxygen atom is replaced by a sulfur atom. The properties of urea and thiourea differ significantly because of the relative electronegativities of sulfur and oxygen. Thiourea is a versatile reagent in organic synthesis.



ethylenethiourea　*N,N'*-dimethylthiourea　*N,N'*-diethylthiourea



N,N'-diphenylthiourea　1-phenyl-3-(2-methylpyridyl)-2-thiourea

Fig.1 Some thiourea chemical structures.

"Thioureas" refers to a broad class of compounds with the general structure $(R^1R^2N)(R^3R^4N)C{=}S$. Thioureas are related to thioamides, e.g. $RC(S)NR_2$, where R is methyl, ethyl, etc.

Thioamide is a functional group with the general structure R-CS-NR'R″, where R, R', and R″ are organic groups. They are analogous to amides but they exhibit greater multiple bond character along the C-N bond, resulting in a larger rotational barrier. One of the best known thioamides is thioacetamide, which is used as a source of the sulfide ion and is a building block in heterocyclic chemistry.

Thiourea is a planar molecule. The C=S bond distance is 1.60±0.1 Å for a wide range of derivatives. This narrow range indicates that the C=S bond is insensitive to the nature of the substitutent. Thus, the thioamide, which is similar to an amide group, is difficult to perturb. Thiourea occurs in two tautomeric forms:

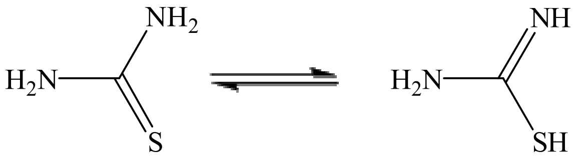


Fig. 2 The tautomerism structure of thiourea.

Lewis acid, a substance that can accept an electron pair to form a covalent bond (an electron-pair acceptor).

Lewis base, a substance that can supply an electron pair to form a covalent bond (an electron-pair donor).

Pearson's HSAB Classification System explaining the differential complexation behaviour of cations and ligands in terms of electron pair donating Lewis bases and electron pair accepting Lewis acids. Pearson classified Lewis acids and Lewis bases as hard, borderline or soft.

Table 1 Classification of Lewis acids.

Class (a)/Hard	Class (b)/Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	CH_3Hg^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	Tl^{3+}, $Tl(CH_3)_3$, RH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	RS^+, RSe^+, RTe^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I^+, Br^+, HO^+, RO^+
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	I_2, Br_2, INC, etc.
$Al(CH)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Trinitrobenzene, etc.
RPO_2^+, $ROPO_2^+$	Chloranil, Quinones, etc.
RSO_2^+, $ROSO_2^+$, SO_3	Tetracyanoethylene, etc.
I^{7+}, I^{5+}, Cl^{7+}	O, Cl, Br, I, R_3C
R_3C^+, RCO^+, CO_2, NC^+	M^o (metal atoms)
	Bulk metals
HX (hydrogen-bonding molecules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	

Table 2 Classification of Lewis bases

Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-
Borderline	
$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2	

(http://www.meta-synthesis.com/webbook /43_hsab/HSAB.html)

According to Pearson 's hard soft [Lewis] acid base (HSAB) principle:

" Hard [Lewis] acids prefer to bind to hard [Lewis] bases and soft [Lewis] acids prefer to bind to soft [Lewis] bases. "

This work studies complexes of silver(I) (soft acid) containing triphenylphosphine (soft base) and *N,N'*-diphenylthiourea (soft base) because silver(I) (in the +1 oxidation state) is found to adopt a wide variety of coordination geometries.

Table 3 The coordination geometry of silver(I) in complexes.

Geometry	Examples	Reference
Linear	$[Ag(etu)_2]ClO_4$	Sola *et al.*, 2004
Trigonal planar	$[Ag(Phflotu)(PPh_3)_2]NO_3$	Ferrari *et al.*, 2007
Distorted tetrahedral	$[Ag(PPh_3)_2(pytH)_2]NO_3$	Aslanidis *et al.*, 1997

That variety due to the lack of stereochemical preference which arises from a d^{10} configuration. Furthermore, the weak nature of the silver-ligand bond means, weak interactions and crystal packing force influence on its structure (Young and Hanton, 2007).

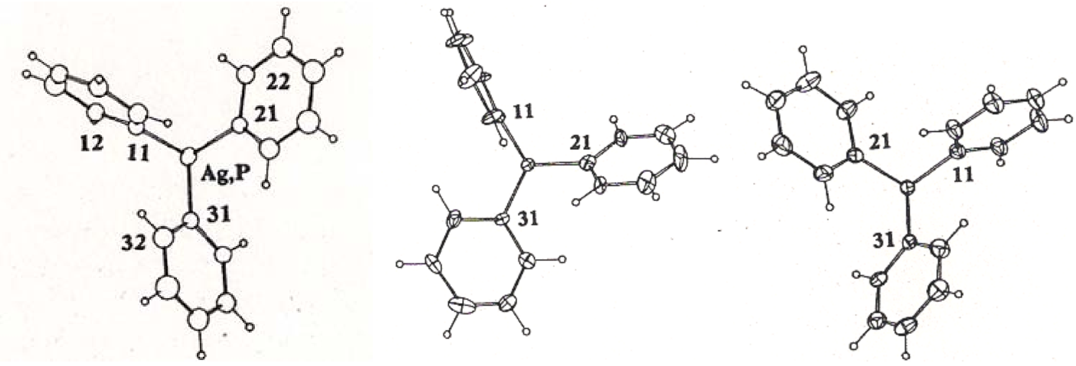
Table 4 The crystal structure of silver(I) complexes.

Feature of structure	Examples	Reference
Monomer	$[AgCl(\eta^1\text{-}S\text{-}HL^2)(PPh_3)]$	Lobana *et al.*, 2008
	$[Ag(N^3,\text{-}S\text{-}HL^4)(PPh_3)_2]NO_3$	Lobana *et al.*, 2008
Dimer	$[Ag_2(dmtu)_6]^{2+}$	Pakawatchai *et al.*, 1996
	$[Ag_2Cl_2(\mu\text{-}S\text{-}HL^1)_2(PPh_3)_2]$	Lobana *et al.*, 2008
Polymer	$\{[Ag(detu)]_2(AgSCN)]\}_\infty$	Bowmaker *et al.*, 2009

The ability of silver(I) complexes to adopt geometries with variable nuclearities and structural diversity make the study of silver(I) chemistry very attractive.

1.2 Literature reviews

Engelhardt *et al* (1987) studied 3:1 adducts of triphenylphosphine, PPh_3, with silver halides, AgX for chloride, bromide and iodide by single crystal X-ray structure determinations, the chloride as its diacetone solvate. Crystals of the chloride, $[(PPh_3)_3AgCl]\cdot 2(CH_3)_2CO$, are triclinic, $P\bar{1}$, 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 are residual R of 0.061 for N_o = 2428 independent observed reflections. Crystals of the bromide, $[(PPh_3)_3AgBr]$, are trigonal, $P3$, a = 19.366(6), c = 10.787(6) Å, Z = 3, R was 0.054 for N_o 2362. Crystals of the iodide, $[(PPh_3)_3AgI]$, are monoclinic, $P2_1/n$, 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. Ag—Cl, Br, I respectively are 2.533(4), 2.671(6)-2.691(4) and 2.858(1) Å. Ag—P for each of the three structures respectively lie in the ranges 2.558(5)-2.582(4), 2.528(3)-2.549(7) and 2.544(2)-2.780(3) Å.



X = Cl X = Br X = I

Fig. 3 The phosphine ligands of each of the chloride, bromide and iodide structures.

Pakawatchai *et al* (1996) 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.

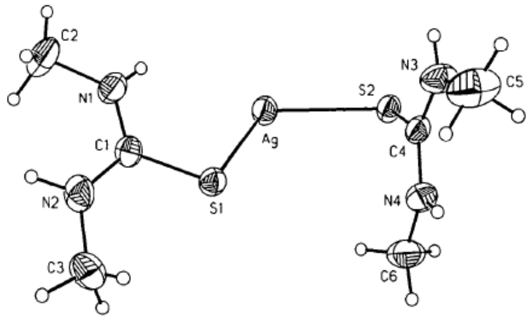


Fig. 4 A 30% displacement ellipsoid plot of the cationic unit in $[Ag(C_3H_8N_2S)_2]ClO_4$ with the atom-numbering scheme.

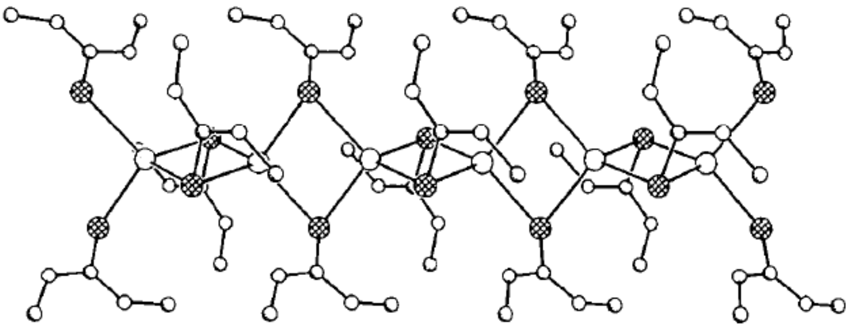


Fig. 5 The polynuclear chain structure of $[Ag(C_3H_8N_2S)_2]ClO_4$.

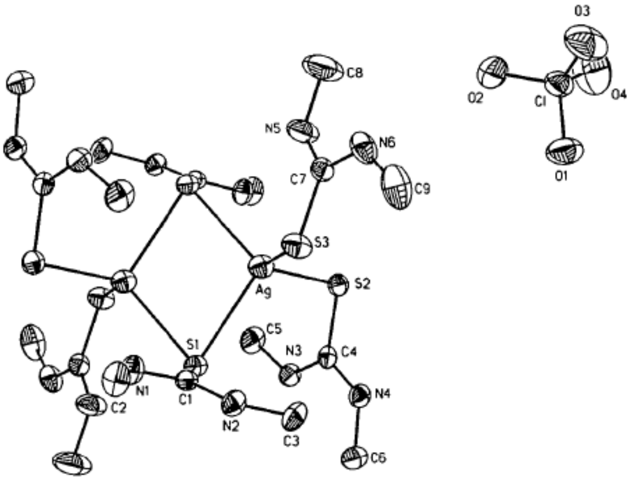


Fig. 6 A 30% displacement ellipsoid plot of $[Ag(C_3H_8N_2S)_3]C1O_4$ with the atomic numbering scheme for the atoms in one asymmetric unit.

Aslanidis *et al* (1997) studied mononuclear silver(I) nitrate complexes with various heterocyclic thiones (pytH = pyridine-2-thione, pymtH = pyrimidine-2-

thione, quin2tH = quinoline-2-thione, tzdtH = thiazolidine-2-thione, mbzimtH$_2$ = *N*-methyl-benzimidazoline-2-thione, pur6tH = purine-6-thione) and triphenylphosphine as ligands. The X-ray determination of the crystal structure of [Ag(PPh$_3$)$_2$(pytH)$_2$]NO$_3$ and [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ is also reported. The [Ag(PPh$_3$)$_2$(pytH)$_2$]NO$_3$ complex crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12.588(3), b = 18.234(5), c = 18.527(5) Å, β = 96.29(2)°, V = 4227 Å^3 and Z = 4, while crystals of [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ are triclinic, space group $P\bar{1}$, with 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. The coordination geometry about the silver atom is distorted tetrahedral in [Ag(PPh$_3$)$_2$(pytH)$_2$]NO$_3$, with one nitrate ion bridging two adjacent complex molecules via strong hydrogen bonds with the thione NH groups. The structure of [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$ consists of almost trigonal-planar AgP$_2$S units and strongly distorted nitrate ions hydrogen bonded to the protonated nitrogen atoms of the heterocyclic thione ligands. The electronic factors imposing the above difference in coordinating behavior are investigated by means of semi-empirical molecular orbital considerations.

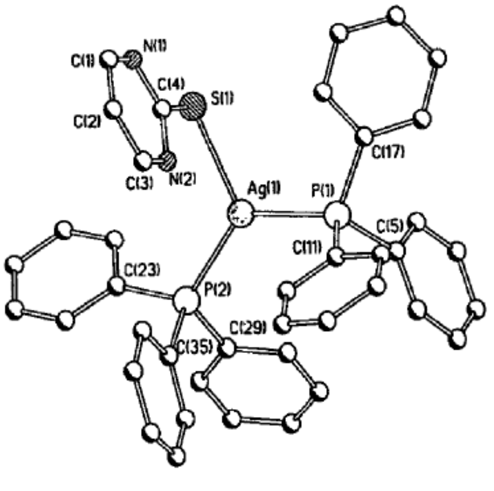


Fig. 7 ORTEP drawing with 50% thermal probability ellipsoids for the cationic unit of [Ag(PPh$_3$)$_2$(pymtH)]NO$_3$.

Fun *et al* (1998) studied 1:3 mononuclear complex silver(I) iodide with diethylthiourea (detu), namely [AgI(C$_2$H$_5$)$_2$N$_2$S)$_3$]. The metal atoms are approximately tetrahedrally coordinated to three S atoms and to one I atom.

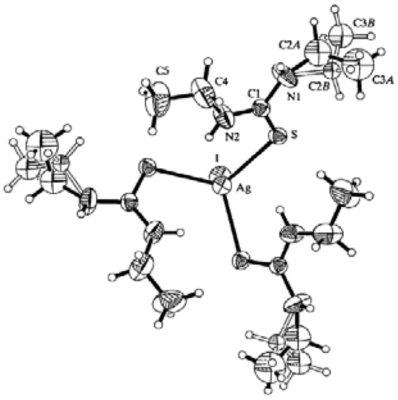
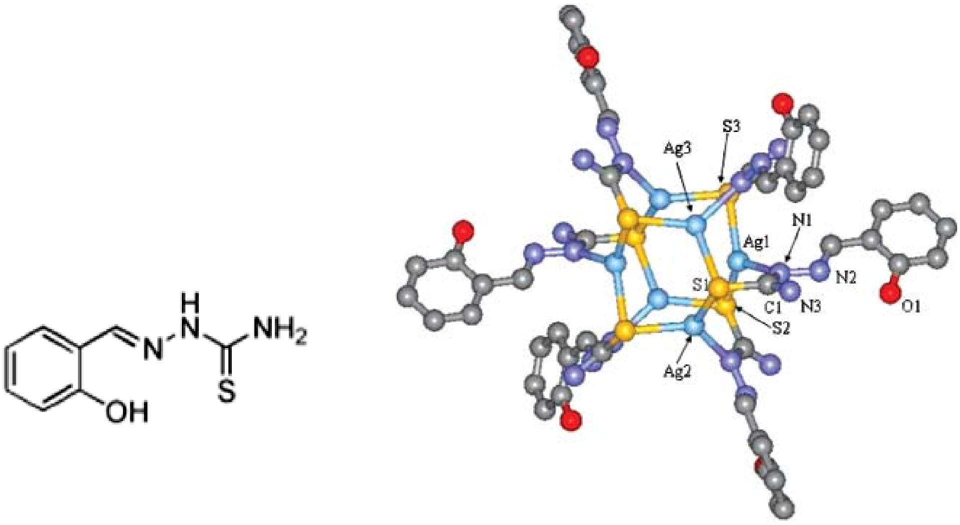


Fig. 8 A 30% displacement ellipsoid plot of $[AgI((C_2H_5)_2N_2S)_3]$ with the atomic numbering scheme.

Asfield *et al* (2004) studied the reaction of $[Ag(MeCN)_4]^+$ with thiosemicarbazone of salicylaldehyde (LH_2) gives hexanuclear clusters, $[Ag_6(LH)_6](4{\cdot}DMF{\cdot}Et_2O)$. The hexameric silver complex is situated on a crystallographic center of inversion, so the asymmetric unit contains three Ag atoms, three molecules of the ligand and three molecules of DMF.



a) b)

Fig. 9 a) The chemical structure of thiosemicarbazone of salicylaldehyde (LH_2)
b) The X-ray crystal structure of $[Ag_6(LH)_6]$. Hydrogen atoms and solvent molecules are omitted for clarity.

Ferrari *et al* (2007) studied the synthesis of $[(PPh_3)_2AgNO_3]$ with ligands obtained by condensation of phenylisothiocyanate with 2-aminopyridine, 2-aminomethylpyridine and 2-aminofluorene, namely 1-phenyl-3-(2-pyridyl)-2-

thiourea (Phpytu), 1-phenyl-3-(2-methylpyridyl)-2-thiourea (Phmepytu) and 1-phenyl-3-(2-fluorenyl)-2-thiourea (Phflotu) yeilding to three new [Ag(Phpytu)$_2$NO$_3$], [Ag(Phmepytu)(PPh$_3$)$_2$]NO$_3$ and [Ag(Phflotu)(PPh$_3$)$_2$]NO$_3$ complexes. The complexes were characterized by X-ray diffraction. The structures reveal remarkable differences in the silver coordination geometry in function of the nature and size of the ligand.

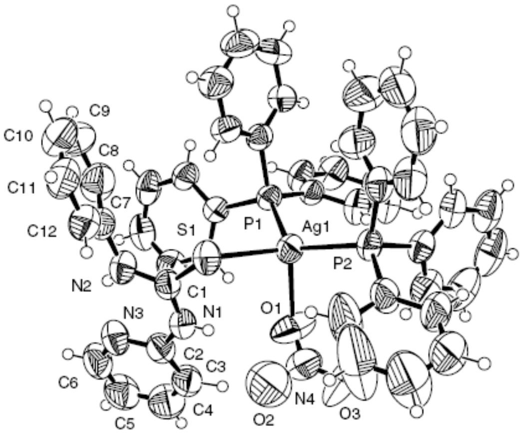


Fig. 10 ORTEP drawing of complex [Ag(Phpytu)$_2$NO$_3$] (thermal ellipsoids are drawn at the 50% probability level).

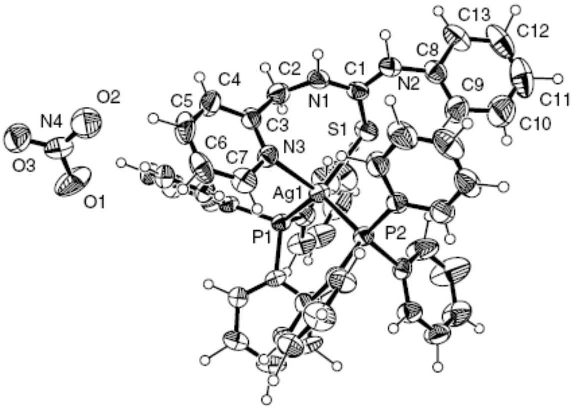


Fig. 11 ORTEP drawing of complex [Ag(Phmepytu)(PPh$_3$)$_2$]NO$_3$ (thermal ellipsoids are drawn at the 50% probability level).

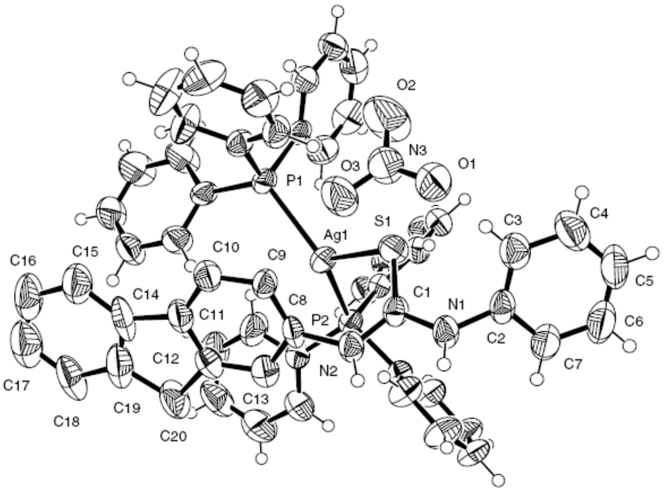


Fig. 12 ORTEP drawing of complex [Ag(Phflotu)$(PPh_3)_2$]NO_3 (Thermal ellipsoids are drawn at the 50% probability level, the fluorenyl moiety was drawing in its highest s.o.f.).

Jia *et al* (2007) studied $[Ag(etu)_3]_2SO_4$ (etu = ethylenethiourea) complex. In this complex crystallographically independent Ag ions are trigonally coordinated by three monodenate etu ligands.

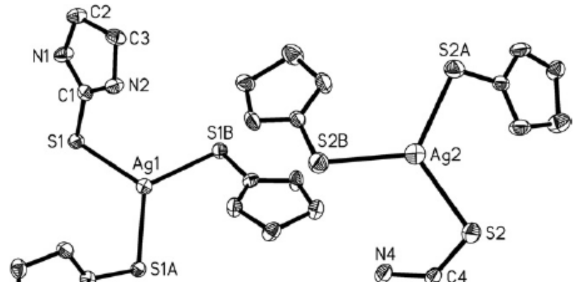


Fig. 13 Structures of the two crystallographically independent $[Ag(etu)_3]^+$ cations in the crystal structure of $[Ag(etu)_3]_2SO_4$ with the atom labelling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Lobana *et al* (2008) studied the reaction of several thiosemicarbazones ($R^1R^2C^2{=}N^3{-}N^2H{-}C({=}S)N^1H_2$) with silver salts, yielding a variety of complexes with different ligand coordination modes, nuclearities and stoichiometries. Reaction of silver(I) chloride with 2-benzoylpyridine thiosemicarbazone, HL^1, has formed a sulfur-bridged dimer, $[Ag_2Cl_2(\mu\text{-}S\text{–}HL^1)_2(PPh_3)_2]$ (2), while a similar reaction with 2-acetylpyridine thiosemicarbazone, HL^2, has formed a mononuclear complex $[AgCl(\eta^1\text{-}S\text{-}HL^2)_2(PPh_3)]$ (1), with an unusual Ag:ligand:PPh_3 stoichiometry of 1:2:1. Reaction of silver(I) nitrate/acetate with benzophenone thiosemicarbazone, HL^3, and acetone thiosemicarbazone, HL^4, have yielded mononuclear complexes, $[Ag(ONO_2)(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ (3), and $[Ag(N^3,S\text{–}HL^4)(PPh_3)_2]X$ (X = NO_3 (4), CH_3COO (5)). In complexes 1 and 3 and in dimeric complex 2, the ligands exhibit the usual η^1-S-bonding and μ-S-bridging coordination commonly observed for thiosemicarbazone ligands with tetrahedral coinage metal ions. In complexes 4 and 5, however, weak binding properties of nitrate or acetate anions to silver favored N_3,S-chelation with the methyl substituents at the C^2 carbon of the thiosemicarbazones.

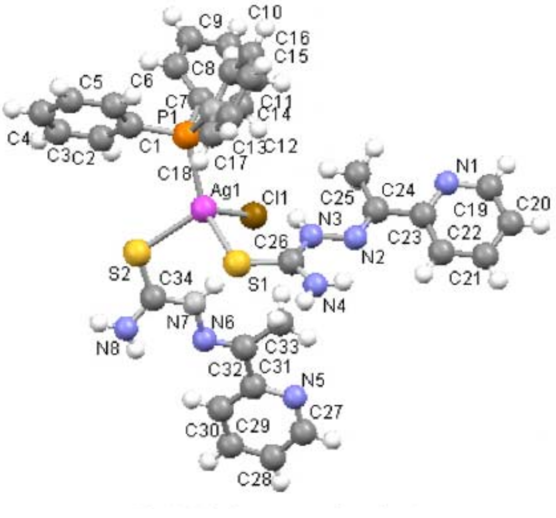


Fig. 14 Molecular structure of complex $[AgCl(\eta^1\text{-}S\text{–}HL^2)_2(PPh_3)]$ (1).

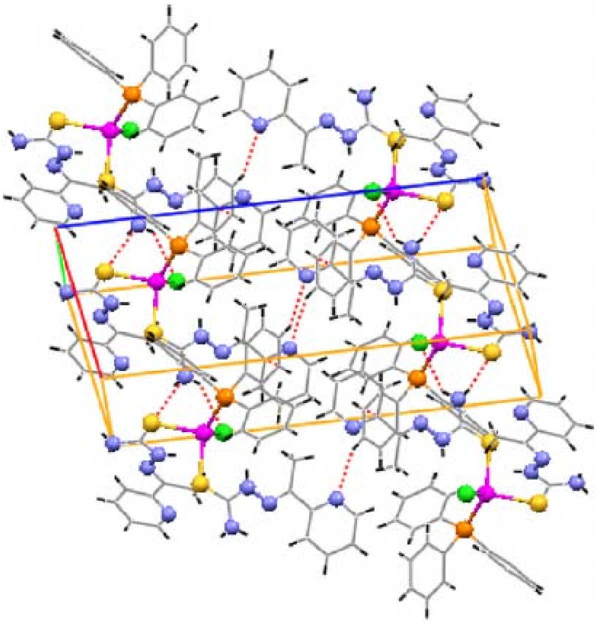


Fig. 15 Packing diagram of complex [AgCl(η^1-S–HL^2)$_2$(PPh$_3$)] (1).

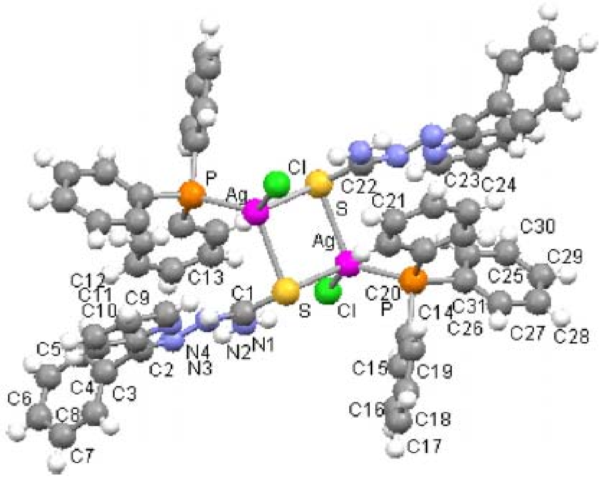


Fig. 16 Molecular structure of complex [Ag$_2$Cl$_2$(μ-S–HL^1)$_2$(PPh$_3$)$_2$] (2).

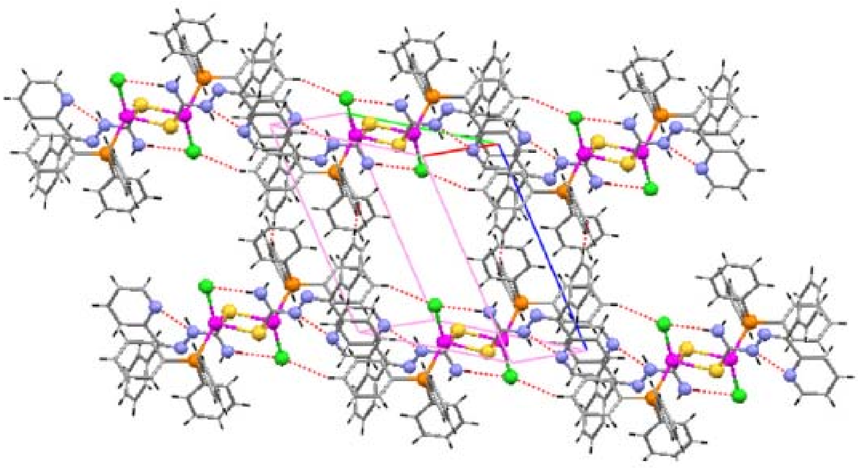


Fig. 17 Packing diagram of complex $[Ag_2Cl_2(\mu\text{-}S–HL^1)_2(PPh_3)_2]$ (2).

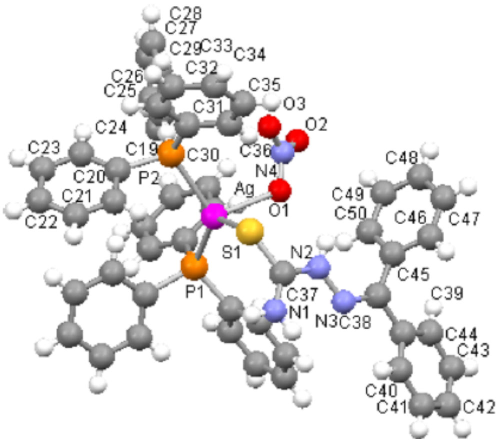


Fig. 18 Molecular structure of complex $[Ag(ONO_2)(\eta^1\text{-}S–HL^3)(PPh_3)_2]$ (3).

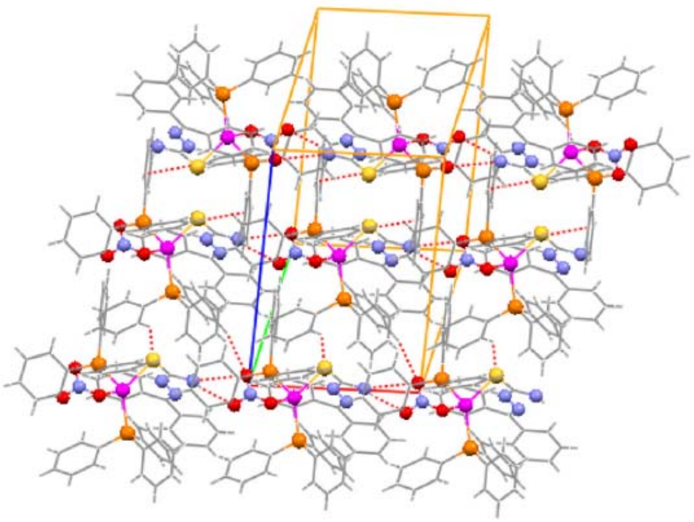


Fig. 19 Formation of a 2D network in the ab plane of complex $[Ag(ONO_2)(\eta^1\text{-}S–HL^3)(PPh_3)_2]$ (3).

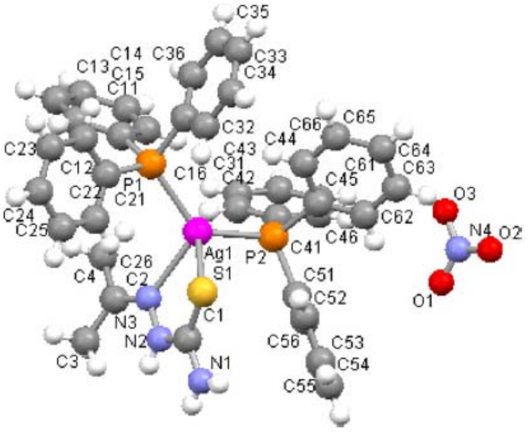


Fig. 20 Molecular structure of complex $[Ag(N^3,S–HL^4)(PPh_3)_2]NO_3$(4). (Complex 5 has a similar structure.)

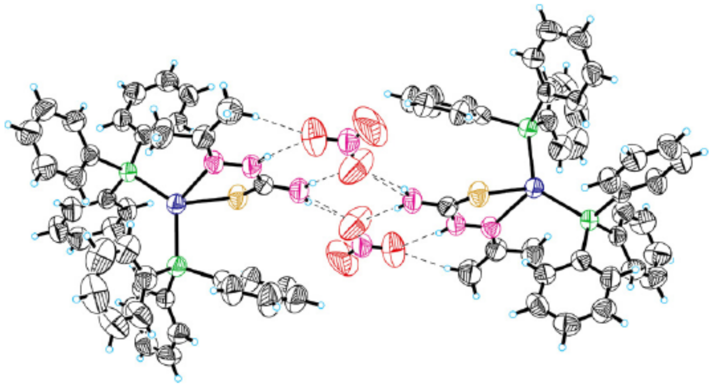


Fig. 21 Packing diagram of complex $[Ag(N^3,S–HL^4)(PPh_3)_2]NO_3$ (4).

Lobana *et al* (2008) studied the reactions of thiosemicarbazones $\{R^1R^2C^2=N^3\text{-}N^2(H)\text{-}C^1(=S)\text{-}N^1H_2\}$, a multidonor class of ligands, with silver(I) halides in the presence of PPh_3 have yielded a variety of compounds, viz. : (i) halogen-bridged dimers, $[Ag_2(\mu\text{-}X)_2(\eta^1\text{-S-Haptsc})_2(PPh_3)_2]$($R^1$= Ph, R^2 = Me, Haptsc, X = Cl (1); Br (2)), $[Ag_2(\mu\text{-}Br)_2(\eta^1\text{-S-Hbtsc})_2(PPh_3)_2]$ (R^1 = Ph, R^2 = H, Hbtsc (3)), $[Ag_2(\mu\text{-}Br)_2(\eta^1\text{-S-Hactsc})_2(PPh_3)_2]$ (R^1 = H, R^2 = Me, Hactsc (4)); (ii) sulfur-bridged dimers, $[Ag_2Br_2(\mu\text{-S-Hptsc})_2(PPh_3)_2]\cdot 2H_2O$ (R^1 = pyrrole, R^2 = H, Hptsc (5)), and $[Ag_2Cl_2(\mu\text{-S-Httsc})_2(PPh_3)_2]\cdot 2CH_3CN$ (R^1 = thiophene, R^2 = H, Httsc (6)), and (iii) monomers, $[AgX(\eta^1\text{-S-Hpytsc})(PPh_3)_2]\cdot CH_3CN$ (R^1 = pyridine, R^2 = H, Hpytsc, X = Br (7); Cl (8)). In contrast, silver(I) nitrate has formed only sulfur-bridged dimers, $[Ag_2(\eta^1\text{-N-}\mu\text{-S-Hftsc})_2(Ph_3P)_2](NO_3)_2$ (9) (R^1 = furan, R^2 = H, Hftsc), and $[Ag_2(\eta^1\text{-S-Hptsc})_2(\mu_2\text{-SHptsc})_2(Ph_3P)_2](NO_3)_2{\cdot}CHCl_3$ (10) (R^1 = pyrrole, R^2 = H, Hptsc) (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone, Hptsc = pyrrole-2-carbaldehyde thiosemicarbazone, Httsc = thiophene-2-carbaldehyde thiosemicarbazone, Hftsc = furan-2-carbaldehyde thiosemicarbazone, Hbtsc = benzaldehyde thiosemicarbazone, Hactsc = acetone thiosemicarbazone and Haptsc = acetophenone thiosemicarbazone). Complexes 1-10 are the first examples exhibiting new bonding modes (η^1-S, μ-S, and μ-S-η^1-N^3) in silver(I)-thiosemicarbazone chemistry. The substituents at C^2 carbon appear to have significant influence on the nature of bonding in the complexes. The intermolecular interactions such as, NH···X (X = S, Br, Cl, O), CH···π and CH···X (X = S, Cl) have led to the formation of one- and two-dimensional (1D and 2D) networks.

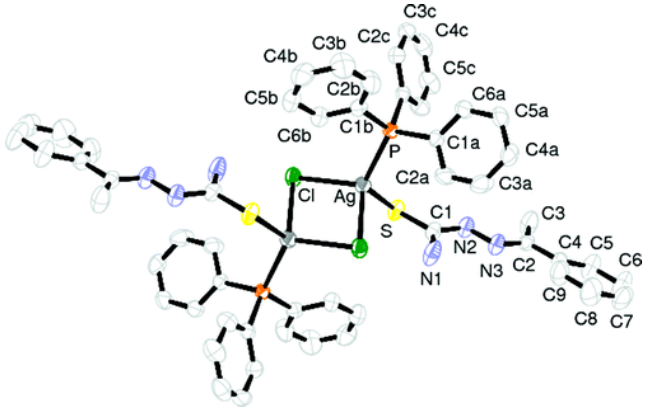


Fig. 22 Structure of $[Ag_2(\mu\text{-Cl})_2(\eta^1\text{-S-Haptsc})_2(PPh_3)_2]$ (1), with atomic numbering scheme. (Complexes 2-4 have similar molecular structures.)

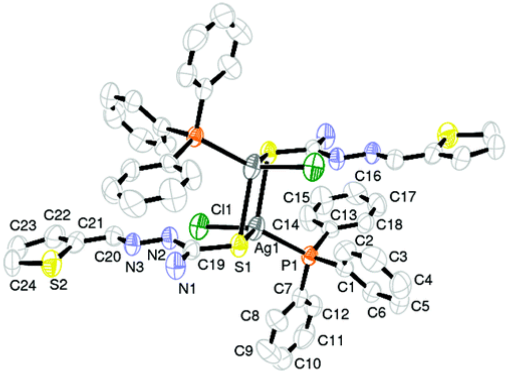


Fig. 23 Structure of $[Ag_2Br_2(\mu\text{-S-Httsc})_2(Ph_3P)_2]{\cdot}2CH_3CN$ (6) with atomic numbering scheme. (Complex 5 has similar molecular structure.)

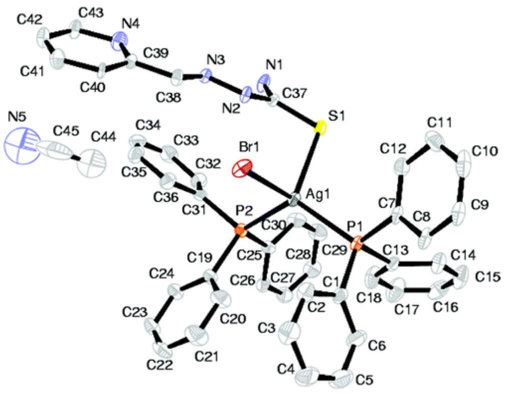


Fig. 24 Structure of [AgBr((η^1-S-Hpytsc)($Ph_3P)_2$]·CH_3CN (7) with atomic numbering scheme. (Compound 8 has similar structure.)

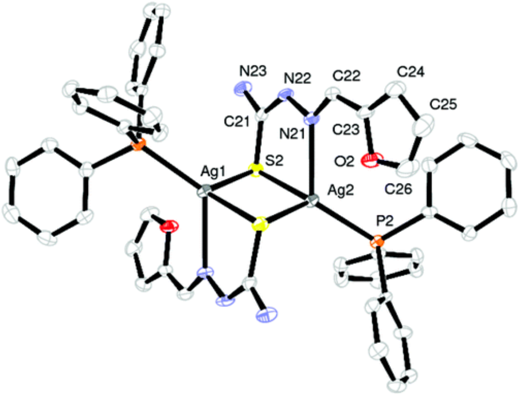


Fig. 25 Structure of [Ag_2(η^1-N^3-μ-S-Hftsc$)_2$($Ph_3P)_2$]($NO_3)_2$ (9) with atomic numbering scheme.

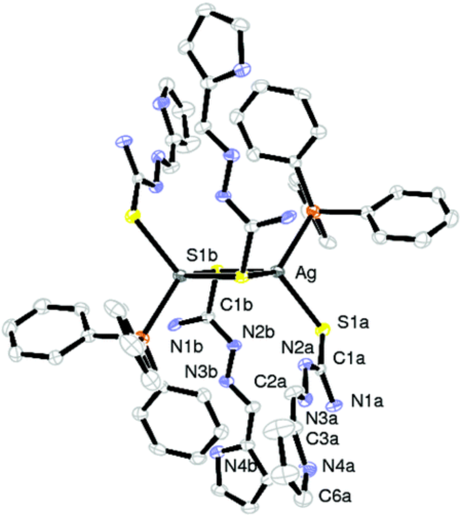


Fig. 26 Structure of [Ag_2(η^1-S-Hptsc$)_2$(μ_2-S-Hptsc$)_2$($Ph_3P)_2$]($NO_3)_2$ ···$CHCl_3$ (10) with partial atomic numbering scheme.

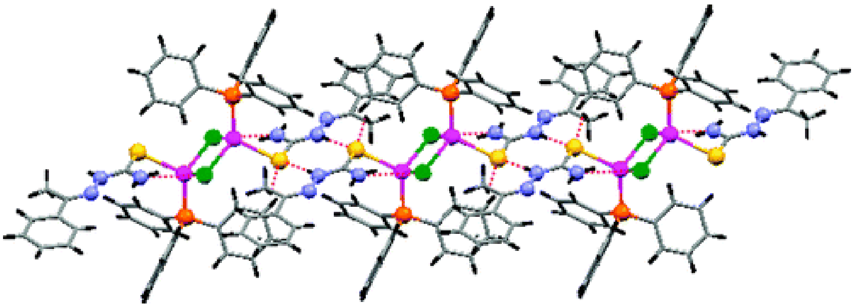


Fig. 27 Hydrogen-bonded 1D polymeric chains of $[Ag_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}Haptsc)_2(PPh_3)_2]$ (1).

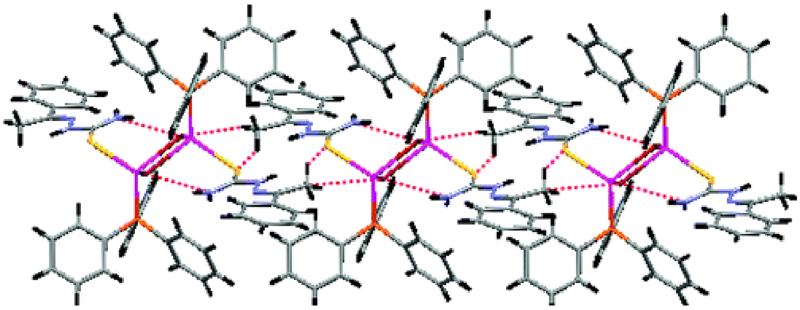


Fig. 28 Hydrogen-bonded 1D chains of $[Ag_2(\mu\text{-}Br)_2(\eta^1\text{-}S\text{-}Haptsc)_2(PPh_3)_2]$ (2).

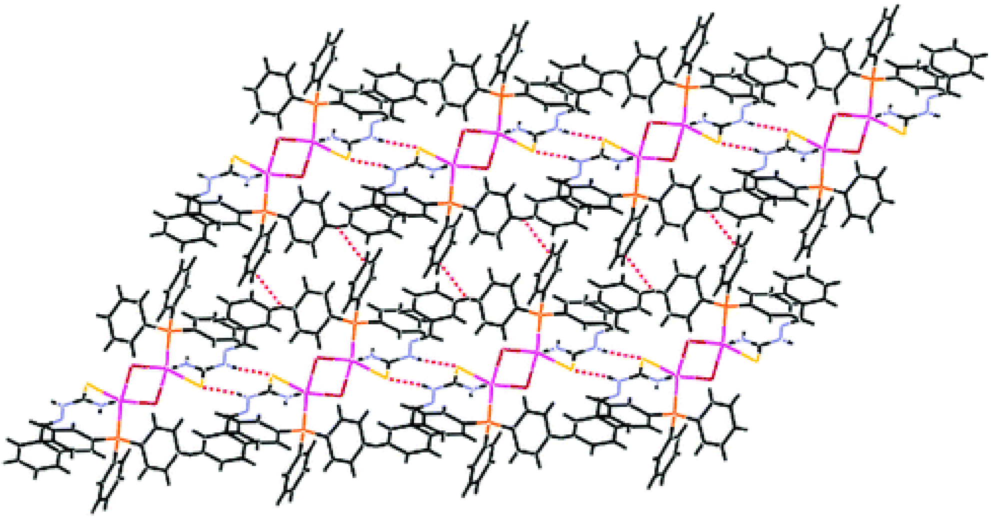


Fig. 29 Polymeric 2D network of bromo-bridged dimer $[Ag_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}Hbtsc)_2(PPh_3)_2]$ (3) (see supporting information for compound 4).

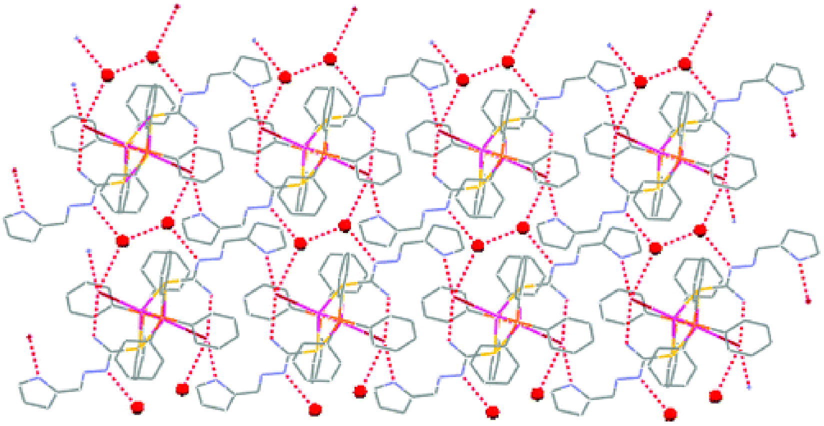


Fig. 30 Packing diagram of $[Ag_2Br_2(\mu\text{-S-Hptsc})_2(Ph_3P)_2]\cdot 2H_2O$ (5).

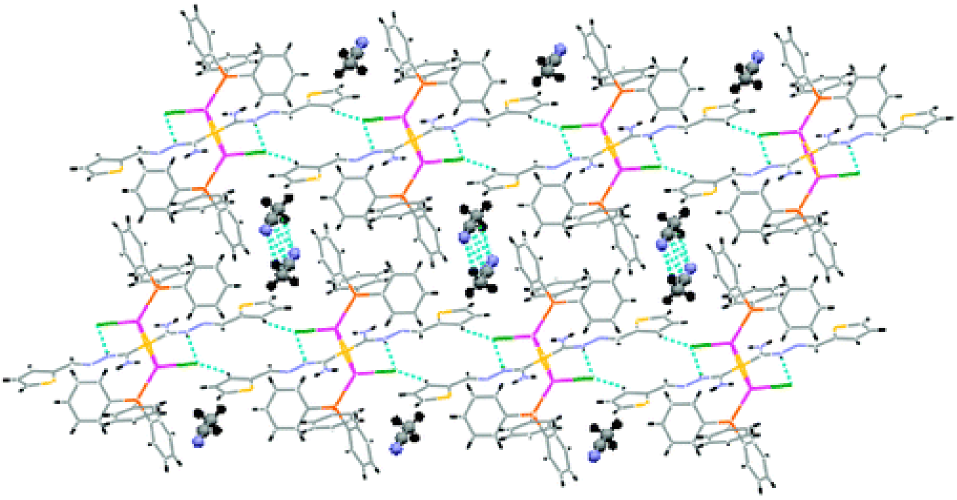


Fig. 31 Packing diagram of $[Ag_2Cl_2(\mu\text{-S-Httsc})_2(PPh_3)_2]$ (6) in sheet structure.

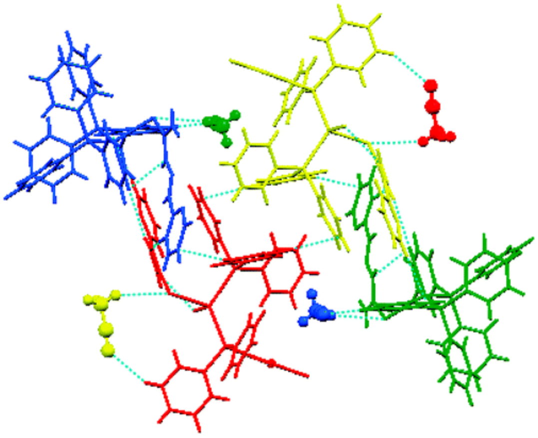


Fig. 32 Packing diagram of $[AgBr(\eta^1\text{-S-Hpytsc})(Ph_3P)_2]\cdot CH_3CN$(7) (see supporting information for compound 8).

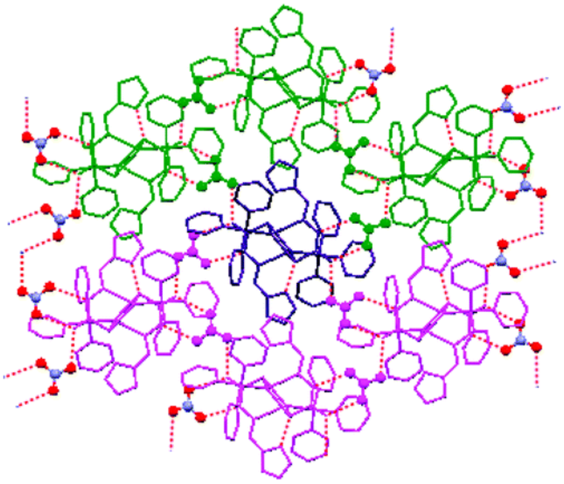


Fig. 33 Hydrogen-bonding contacts between nitrate groups and the dinuclear unit produces an extended 2D network in the *ab* plane in $[Ag_2(\mu_3\text{-N,S-Hftsc})_2(Ph_3P)_2](NO_3)_2$ (9).

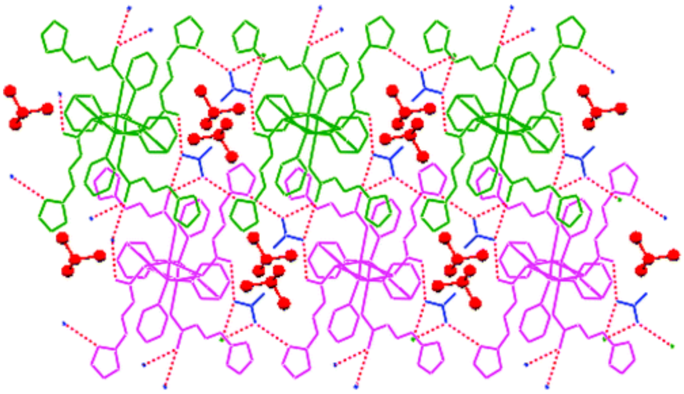


Fig. 34 Packing diagram of $[Ag_2(\eta^1\text{-S-Hptsc})_2(\mu\text{-S-Hptsc})_2(Ph_3P)_2](NO_3)_2 \cdot 2CHCl_3$ (10).

1.3 Objective

1.3.1 To study the method and find the optimum condition for synthesizing silver(I) complexes with the mixed ligand of triphenylphosphine and *N,N'*-diphenylthiourea by varying the mole ratios of reactants, solvents and temperature of reaction and etc.

1.3.2 To characterize the structures of the complexes by elemental analysis, XRF, IR and NMR spectroscopies and single crystal X-ray diffraction technique.

CHAPTER 2

Method of Study

2.1 Chemicals

2.1.1 Silver(I) chloride, silver(I) bromide, silver(I) iodide, triphenylphosphine and *N,N'*-diphenylthiourea were procured from Fluka Chemical, Buchs, Switzerland.

2.1.2 Acetonitrile and pyridine are A.R. grade.

2.1.3 *d*-Chloroform for NMR solvent.

2.2 Materials and instruments

2.2.1 Bee vax

2.2.2 UHU Epoxy adhesive

2.2.3 Fiber Glass, 0.1 - 0.4 mm (diameter)

2.2.4 Thermometer, Gallenkamp, England 0 - 360 °C

2.2.5 Hot plate stirrer with magnetic bar

2.2.5 Capillary melting point apparatus, Thomas Hoover, Unimelt 0 - 360 °C

2.2.6 CE Instruments Flash 1112 Series EA CHNS-O Analyzer

2.2.7 X-ray Fluorescence Spectrometer (PHILIPS PW2400)

2.2.8 Perkin Elmer GX-FTIR spectrometer

2.2.8 Fourier Transform NMR Spectrometer 500 MHz Model UNITY INOVA, Varian

2.2.9 Bruker SMART APEX CCD Diffractometer

2.3 Preparation of complexes

2.3.1 $[Ag(PPh_3)(py)I]_2$ complex was prepared by refluxing 1:2:1 mol ratio of silver(I) iodide (AgI) with triphenylphosphine (PPh_3) and *N,N'*-diphenylthiourea (dptu) in 10 mL pyridine at 60 °C for 7 h. Then the mixer was filtered and the filtrate was kept at room temperature, allowed to evaporate slowly and yielded block colorless crystals.

2.3.2 [$Ag(PPh_3)_3Cl$] complex was prepared by refluxing 1:2:1 mole ratio of silver(I) chloride (AgCl) with PPh_3 and dptu in 30 mL acetonitrile at 70 °C for 7 h. Then the mixer was filtered and the filtrate was kept at room temperature, allowed to evaporate slowly and yielded block colorless crystals.

2.3.3 The [$Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) complexes were prepared by refluxing 1:2:1 mole ratio of silver halide (AgX, X = Cl, Br) with PPh_3 and dptu in 30 mL acetonitrile at 70 °C for 7.5 h. Then the mixer was filtered and the filtrate was kept at room temperature, allowed to evaporate slowly and yielded block or prism colorless crystals.

2.4 Analytical and spectroscopic characterization

2.4.1 Elemental analysis reveals how much C H N and S are present in compounds to confirm the molecular formula of X-ray structure determined using CHNS-O Analyzer.

2.4.2 X-Ray fluorescence spectroscopy reveal the presence of Ag and X(X = Cl, Br) of silver salts and P of phosphine and S of thiourea ligands which are present in the complex composition by using X-ray Fluorescence Spectrometer.

2.4.3 Infrared spectroscopy was used to identify functional groups within compound using a Perkin Elmer GX FT-IR Spectrometer.

2.4.4 ^{1}H NMR and ^{13}C NMR spectroscopic techniques were used to determined amount and type of hydrogen and carbon atoms within complex using Fourier Transform NMR Spectrometer.

2.5 X-ray diffraction, crystal structure determination.

2.5.1 The single crystal of suitable size and shape was mounted on the end of a glass fiber.

2.5.2 The cell parameters were determined and the diffraction data were collected using Bruker SMART APEX CCD diffractometer.

2.5.3 The structure was solved by direct methods and refined using WinGX 1.7 (Farrugia, 2005) and SHELX (Sheldrick, 2008), ORTEP 3.2 (Farrugia, 2005) and Mercury 1.4.2 (Macrae *et al*., 2006) crystallographic program.

The elemental analysis, X-ray fluorescence and NMR spectroscopic techniques were carried out by Scientific Equipment Center, Prince of Songkla University.

CHAPTER 3

RESULTS

3.1 Preparation of complexes

The suitable conditions of synthesis silver(I) complexes containing triphenylphosphine and *N,N'*-diphenylthiourea have been determined and are shown in Table 5. Some of their physical properties together with reacting ligands are summarized in Table 6-7.

3.2 Elemental analysis

Relative amount of C, H, N, and S between calculated data (% calc.) and experimental data (% found) of the $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) complexes are shown in the Table 8.

3.3 X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectra of $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) complexes were focused on 4 elements; Ag, P, S and X (X = Cl, Br) as shown in Figure 35-42.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The present infrared absorption study of PPh_3, dptu and complexes of silver(I); $[Ag(PPh_3)(py)I]_2$, $[Ag(PPh_3)_3Cl]$ and $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (X = Cl, Br) are shown in Figures 43-48.

3.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

The present NMR chemical shift study of PPh_3, dptu and $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (X = Cl, Br) complexes are shown in Figures 49-56.

3.6 X-ray diffraction (XRD)

The X-ray crystallographic data and the structure of all complexes are shown in Table 9-18 and Figure 57-68 respectively.

Table 5 The suitable conditions for synthesizing complexes.

reactants	mole ratio	solvent	time (h.)	temp. (°C)	complexes	yield (%)
AgI:PPh$_3$:dptu	1:2:1	py	7	60	[Ag(PPh$_3$)(py)I]$_2$	73.34
AgCl:PPh$_3$:dptu	1:2:1	CH$_3$CN	7	70	[Ag(PPh$_3$)$_3$Cl]	30.77
AgCl:PPh$_3$:dptu	1:2:1	CH$_3$CN	7.5	70	[Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN	59.61
AgBr:PPh$_3$:dptu	1:2:1	CH$_3$CN	7.5	70	[Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN	72.69

Table 6 The physical properties of ligands and complexes.

compounds	morphology	colour	melting point (°C)
PPh$_3$	plate	white	79-81
dptu	powder	white	150-153
[Ag(PPh$_3$)(py)I]$_2$	block	colorless	>200
[Ag(PPh$_3$)$_3$Cl]	block	colorless	193-195
[Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN	block	colorless	123-125
[Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN	prism	colorless	121-123

Table 7 The solubility of complexes.

solvents	solubility of complexes			
	$[Ag(PPh_3)(py)I]_2$	$[Ag(PPh_3)_3Cl]$	$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$
H_2O	insoluble	insoluble	insoluble	insoluble
MeOH	partially soluble	soluble	partially soluble	soluble
EtOH	insoluble	partially soluble	partially soluble	partially soluble
CH_3CN	insoluble	partially soluble	partially soluble	partially soluble
CH_3COCH_3	partially soluble	partially soluble	soluble	soluble
$C_4H_{10}O$	insoluble	partially soluble	partially soluble	soluble
$CHCl_3$	soluble	soluble	soluble	soluble
CH_2Cl_2	soluble	soluble	soluble	soluble
n-C_6H_{12}	partial soluble	partial soluble	partially soluble	partially soluble
DMSO	insoluble	partial soluble	soluble	soluble

Table 8 The elemental analyses of the complexes

complexes	elemental analysis(%)							
	C		H		N		S	
	calc	found	calc	found	calc	found	calc	found
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	64.16	64.35	4.73	4.84	4.10	4.48	3.26	3.42
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$	62.39	62.05	4.62	4.65	4.28	3.89	3.27	3.19

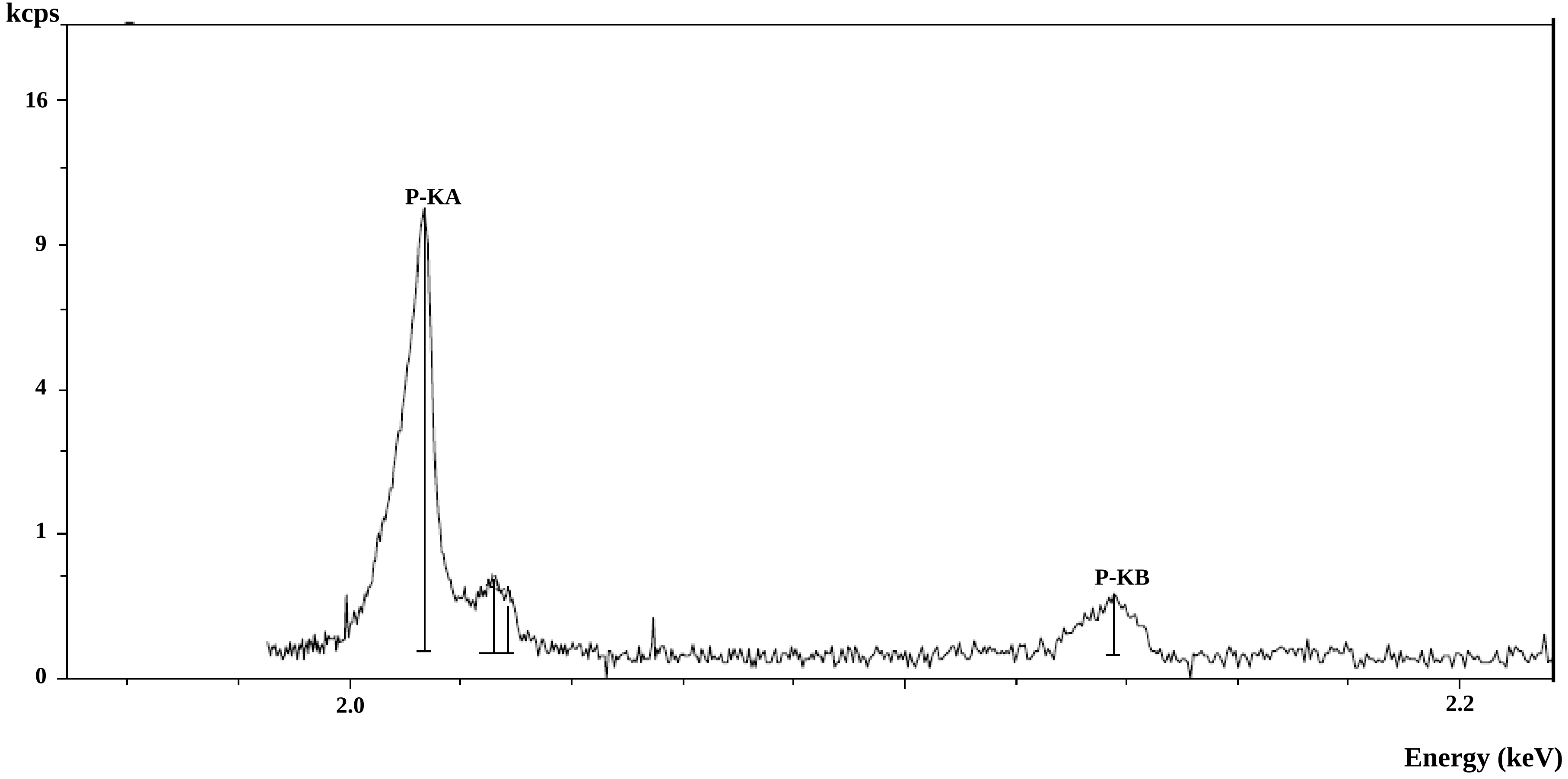


Fig. 35 The X-ray fluorescence spectrum of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (P atom)

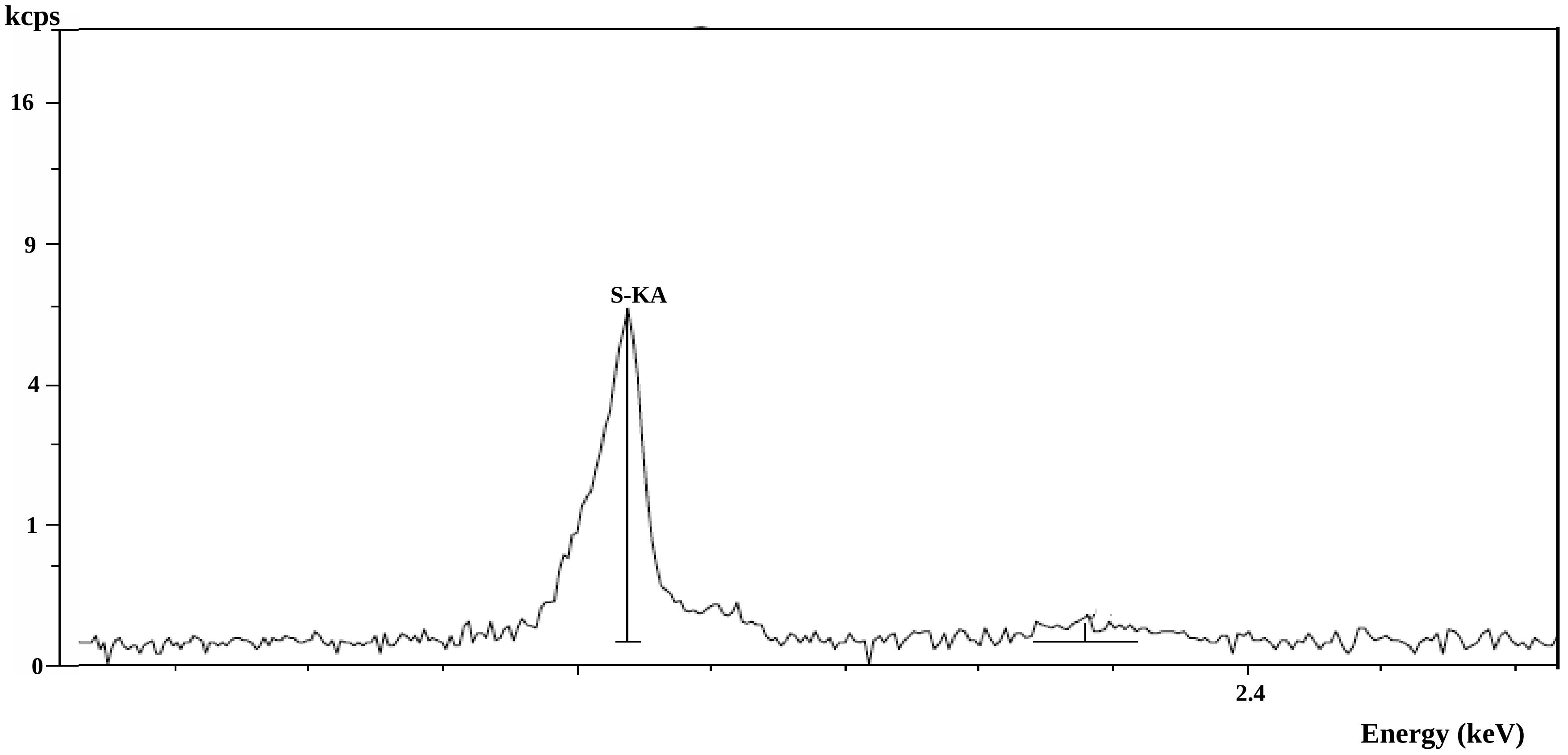


Fig. 36 The X-ray fluorescence spectrum of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (S atom)

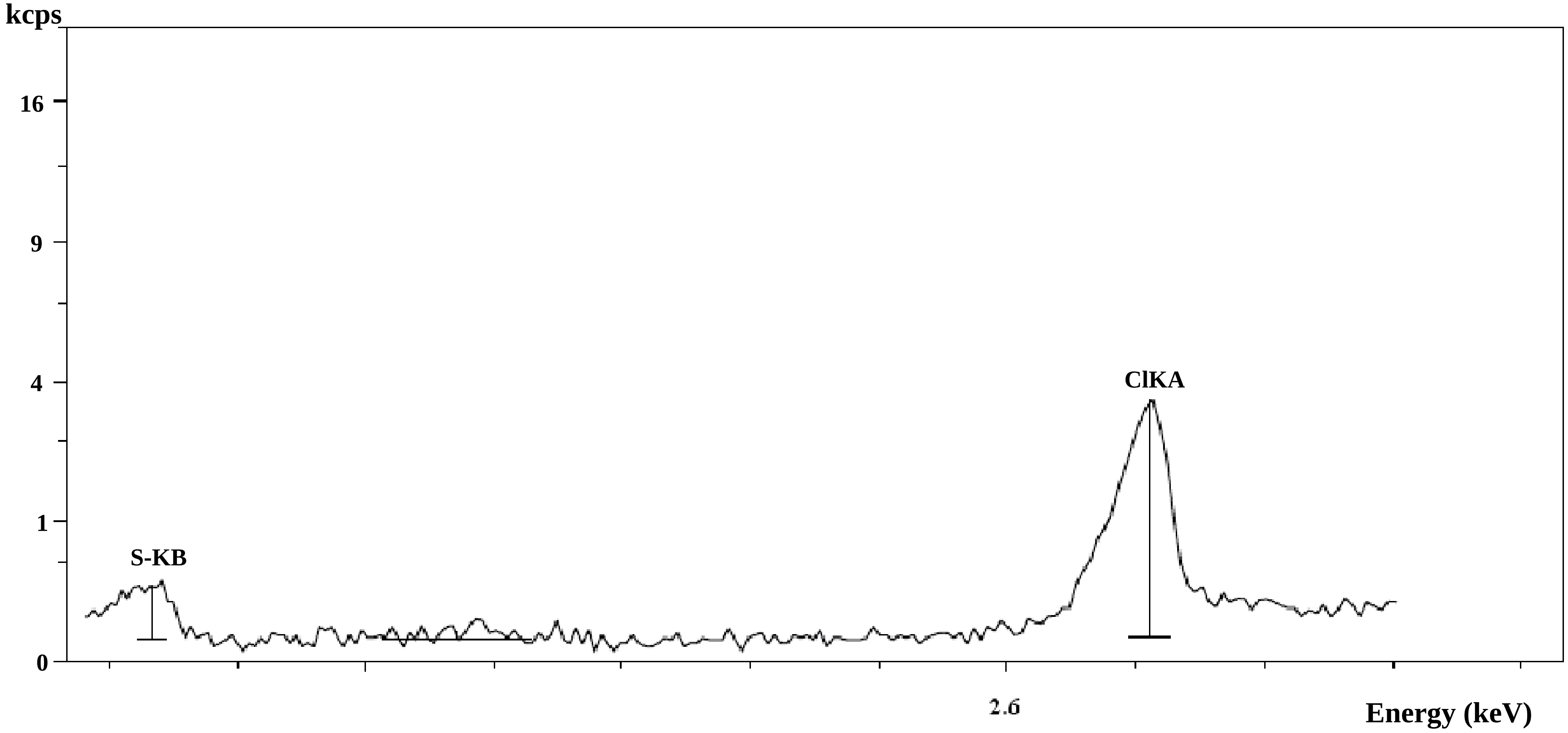


Fig. 37 The X-ray fluorescence spectrum of [Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN (Cl atom)

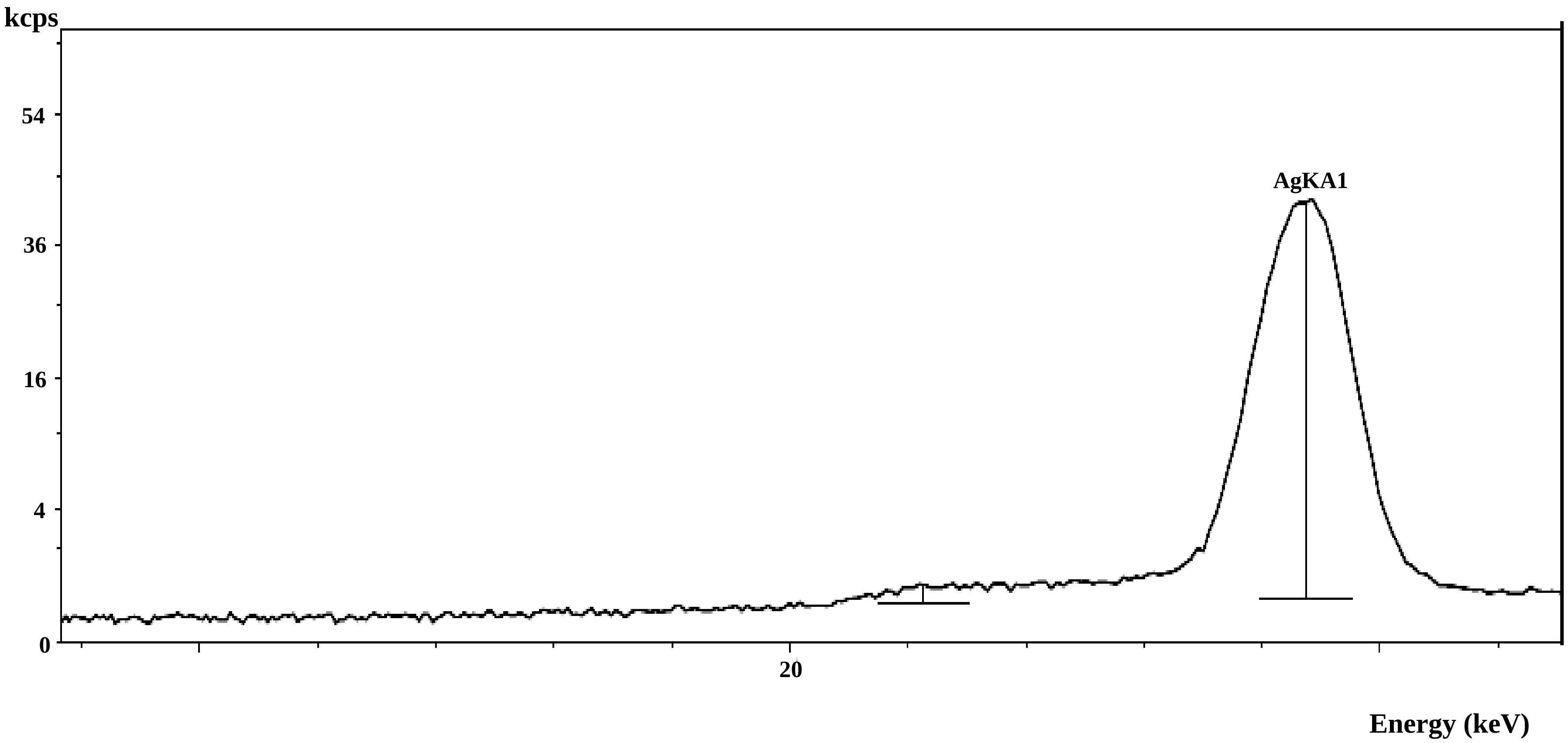


Fig. 38 The X-ray fluorescence spectrum of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (Ag atom)

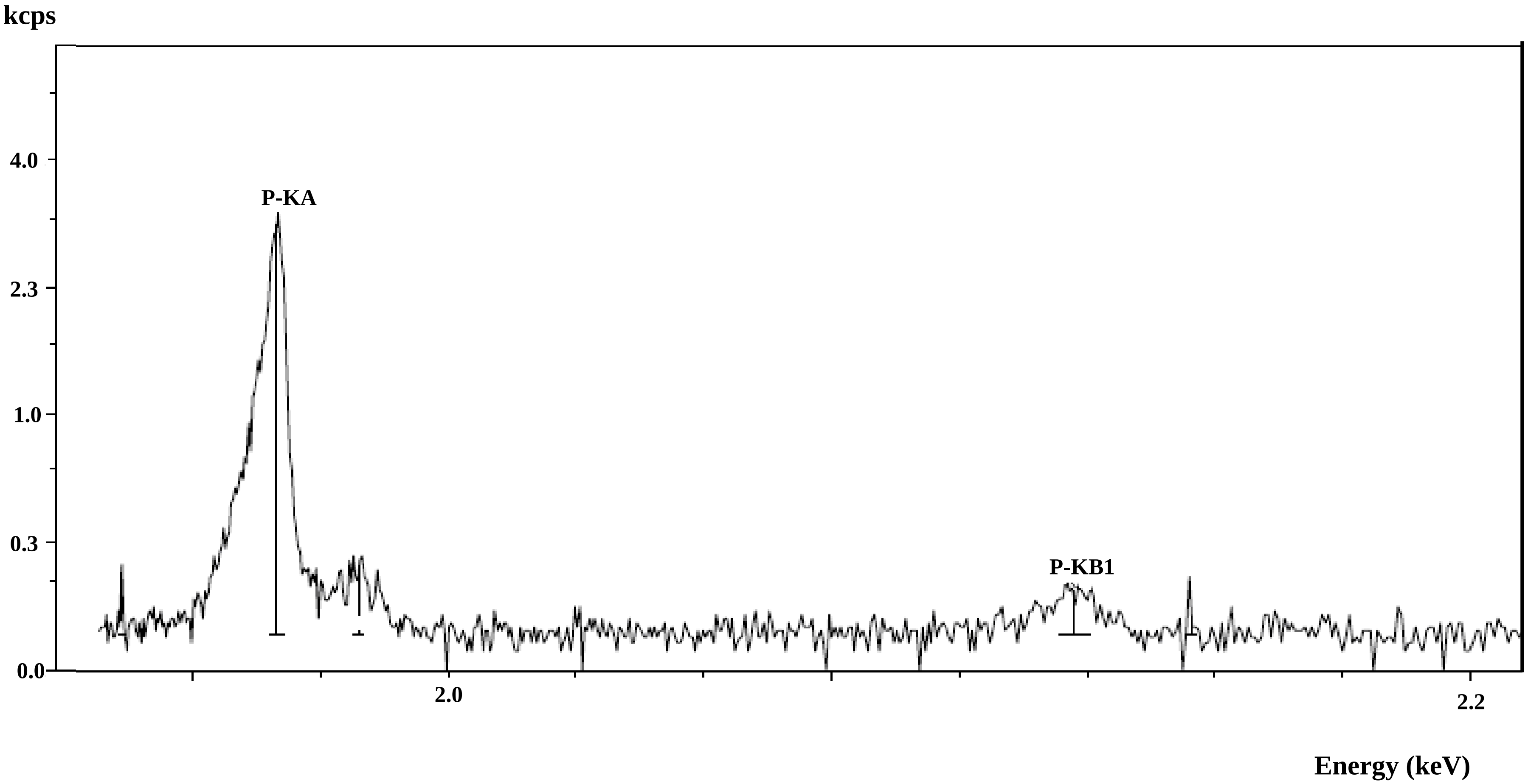


Fig. 39 The X-ray fluorescence spectrum of $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (P atom)

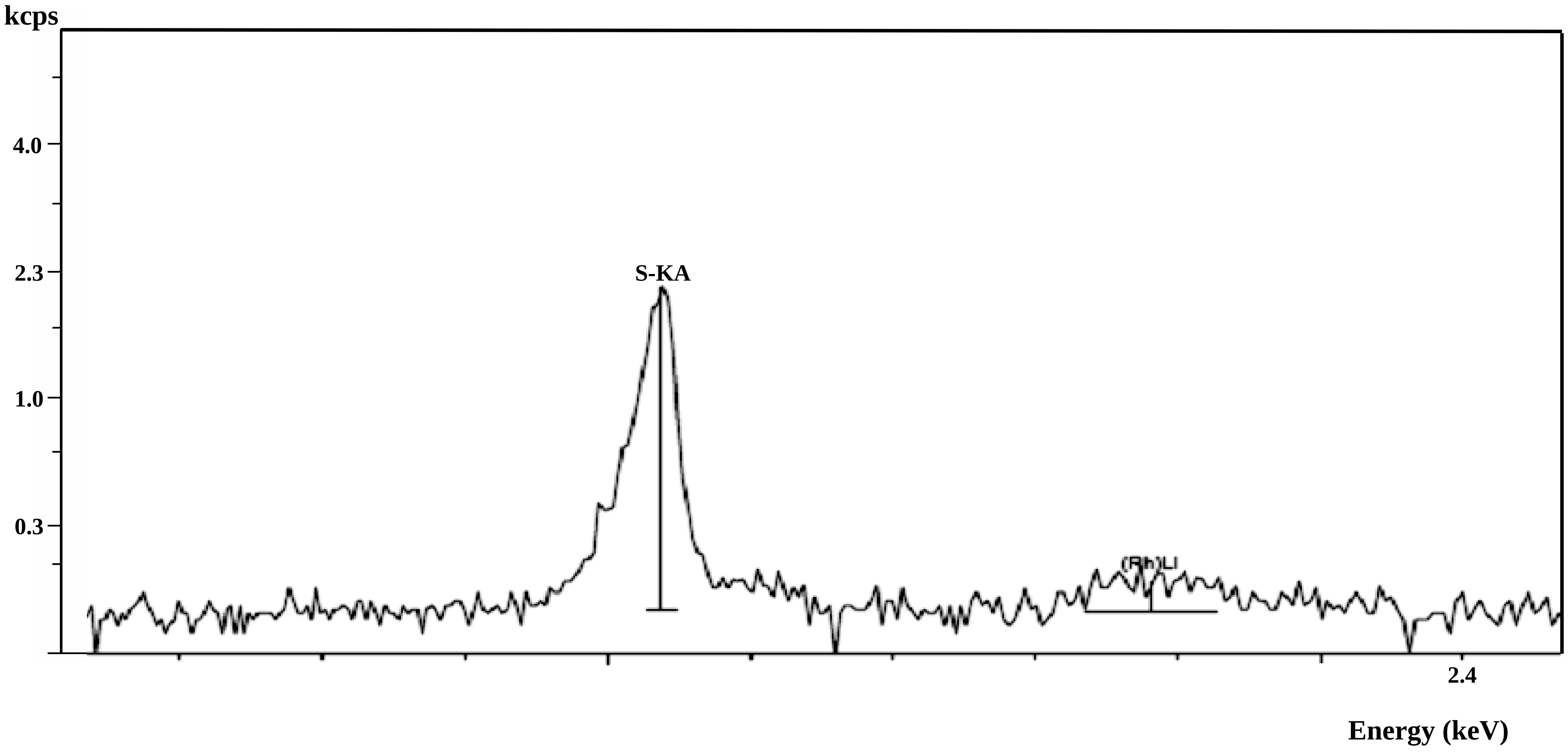


Fig. 40 The X-ray fluorescence spectrum of $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (S atom)

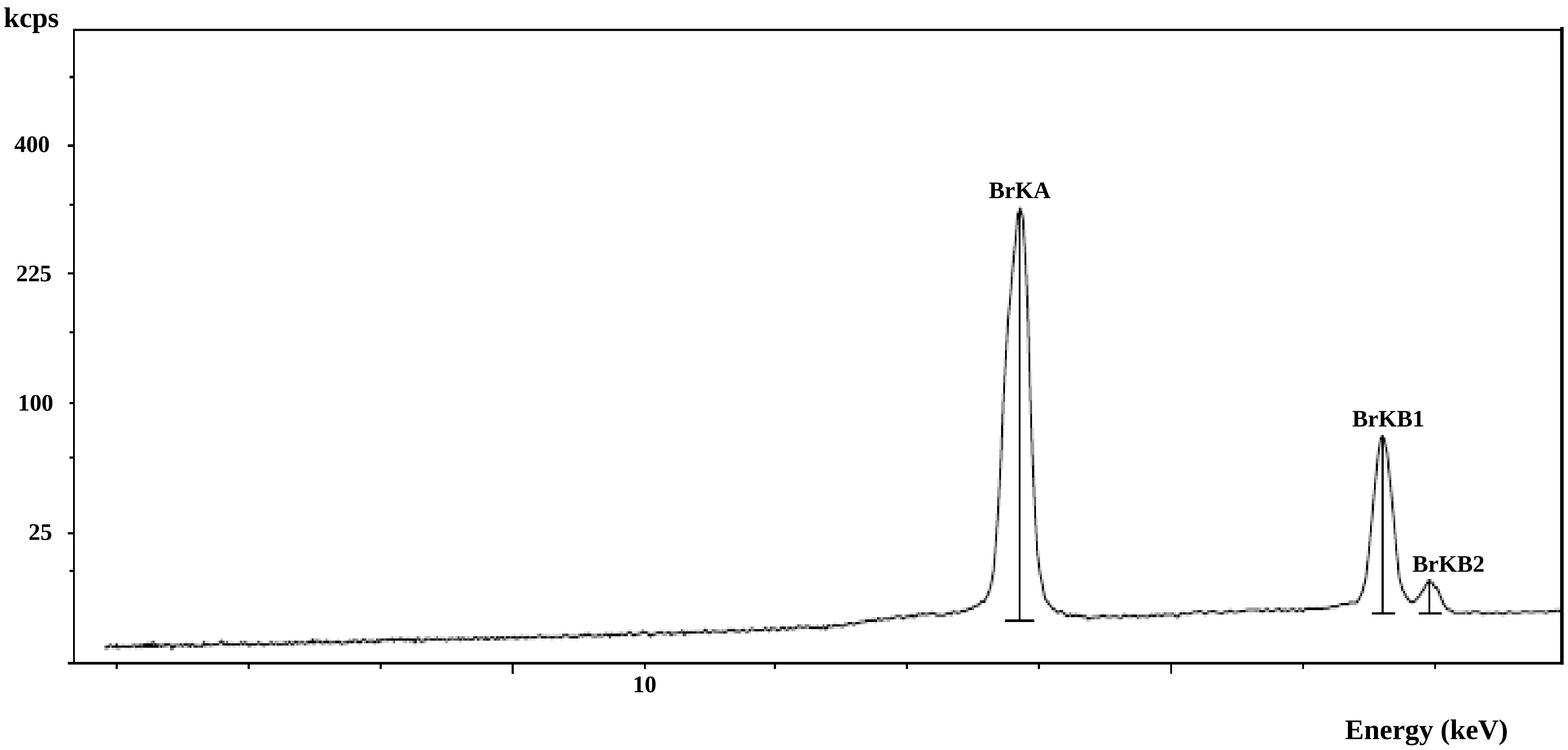


Fig. 41 The X-ray fluorescence spectrum of [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN (Br atom)

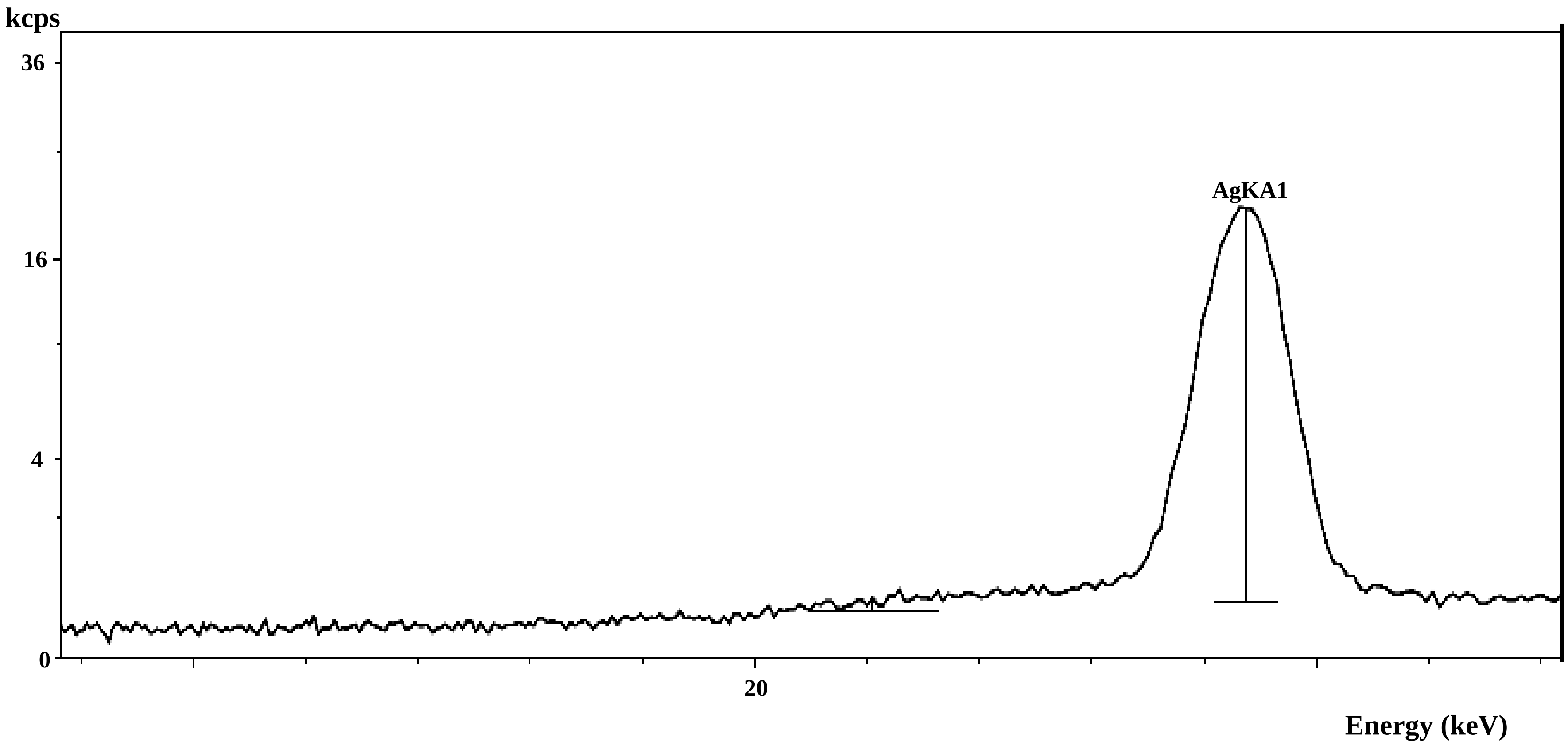


Fig. 42 The X-ray fluorescence spectrum of [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN (Ag atom)

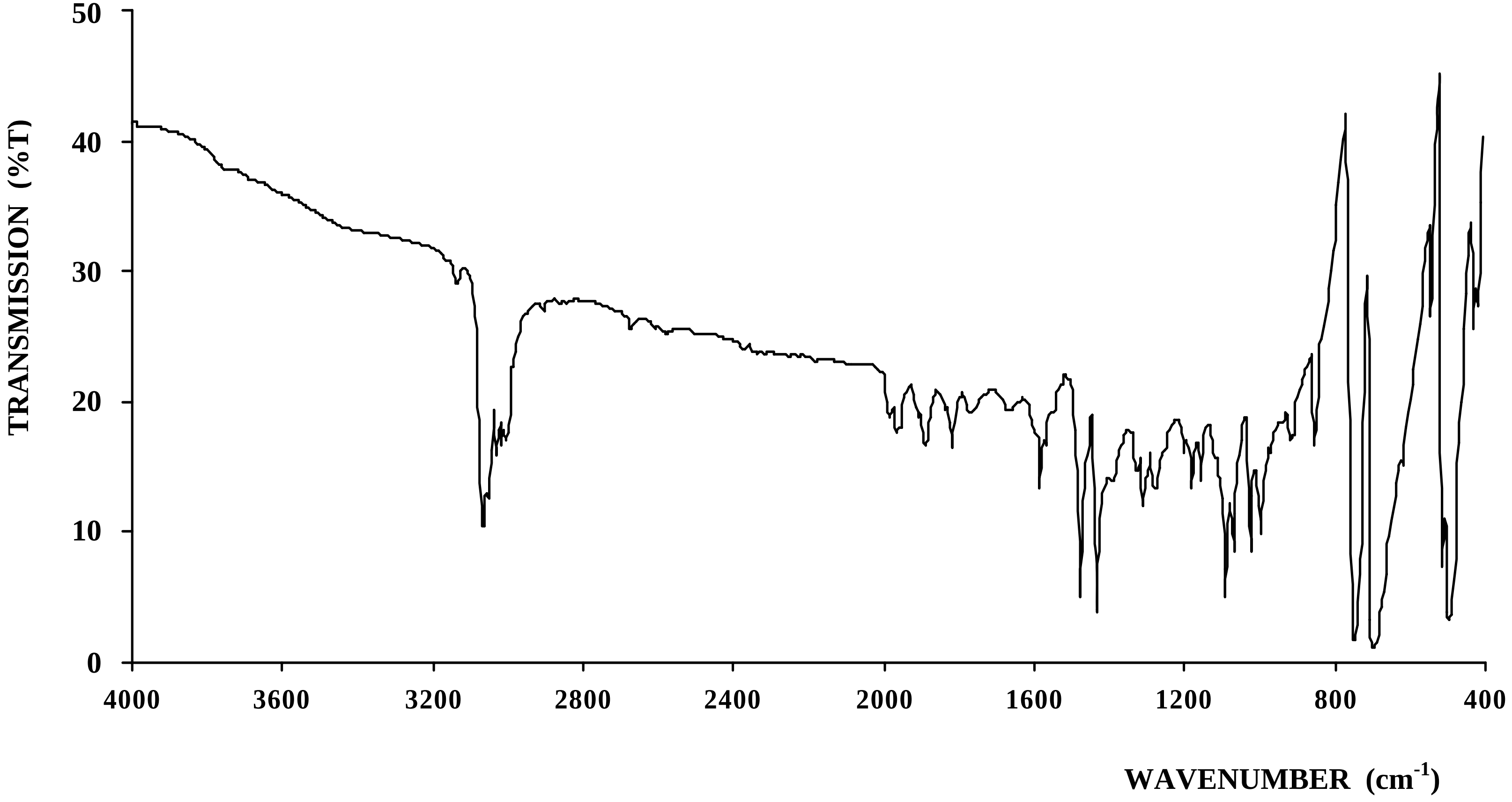


Fig. 43 The infrared spectrum of PPh_3

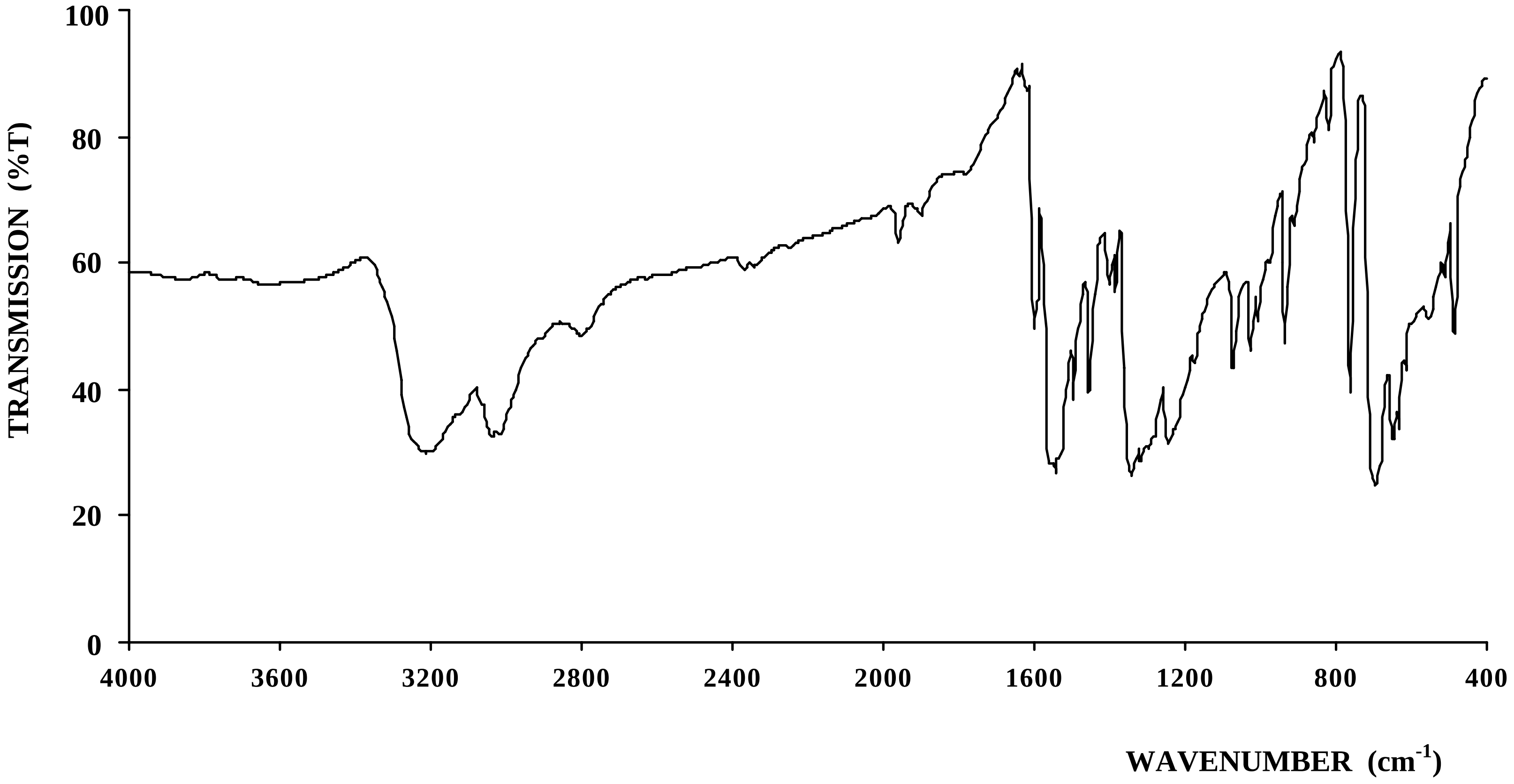


Fig. 44 The infrared spectrum of dptu

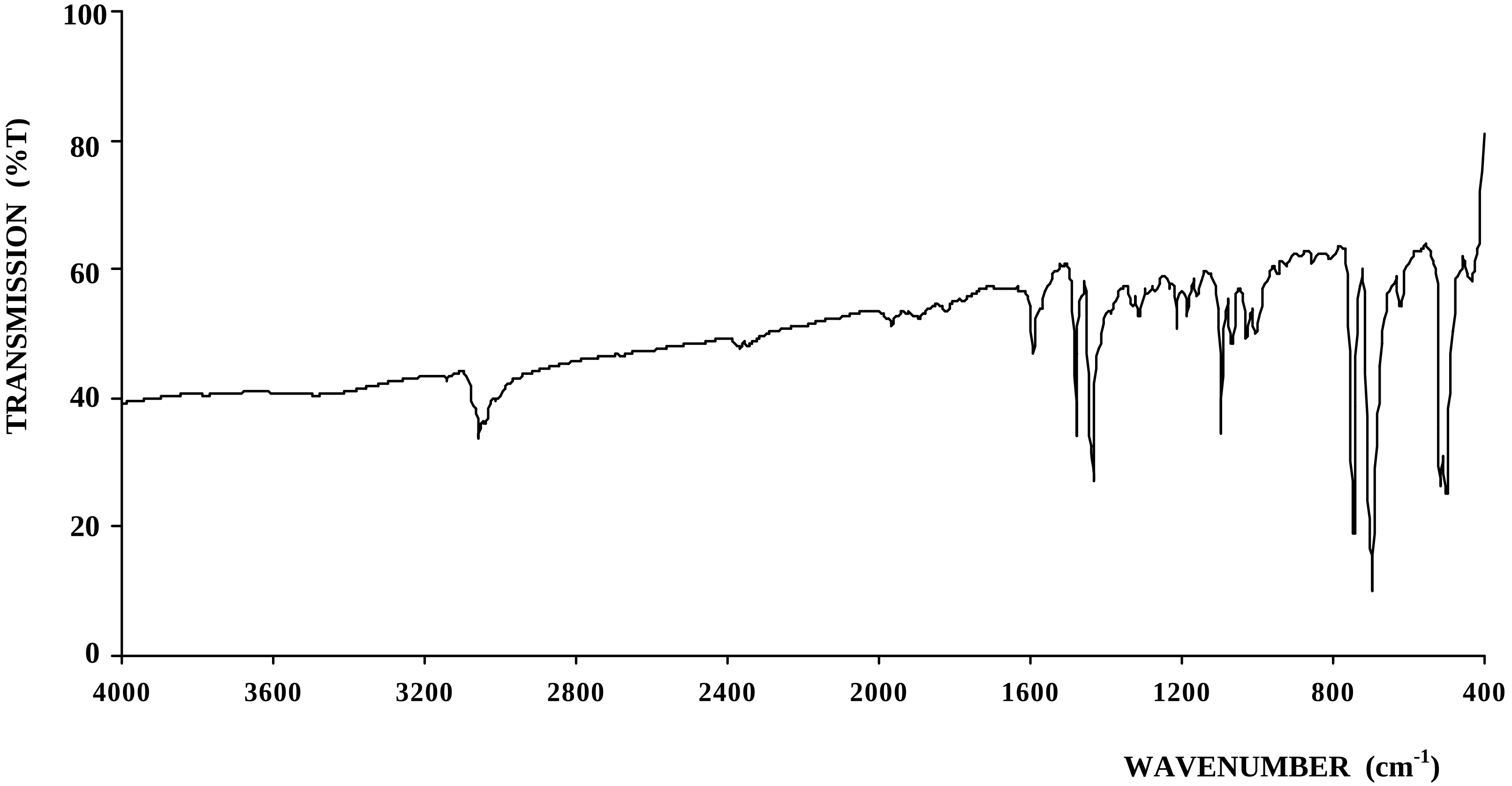


Fig. 45 The infrared spectrum of $[Ag(PPh_3)(py)I]_2$

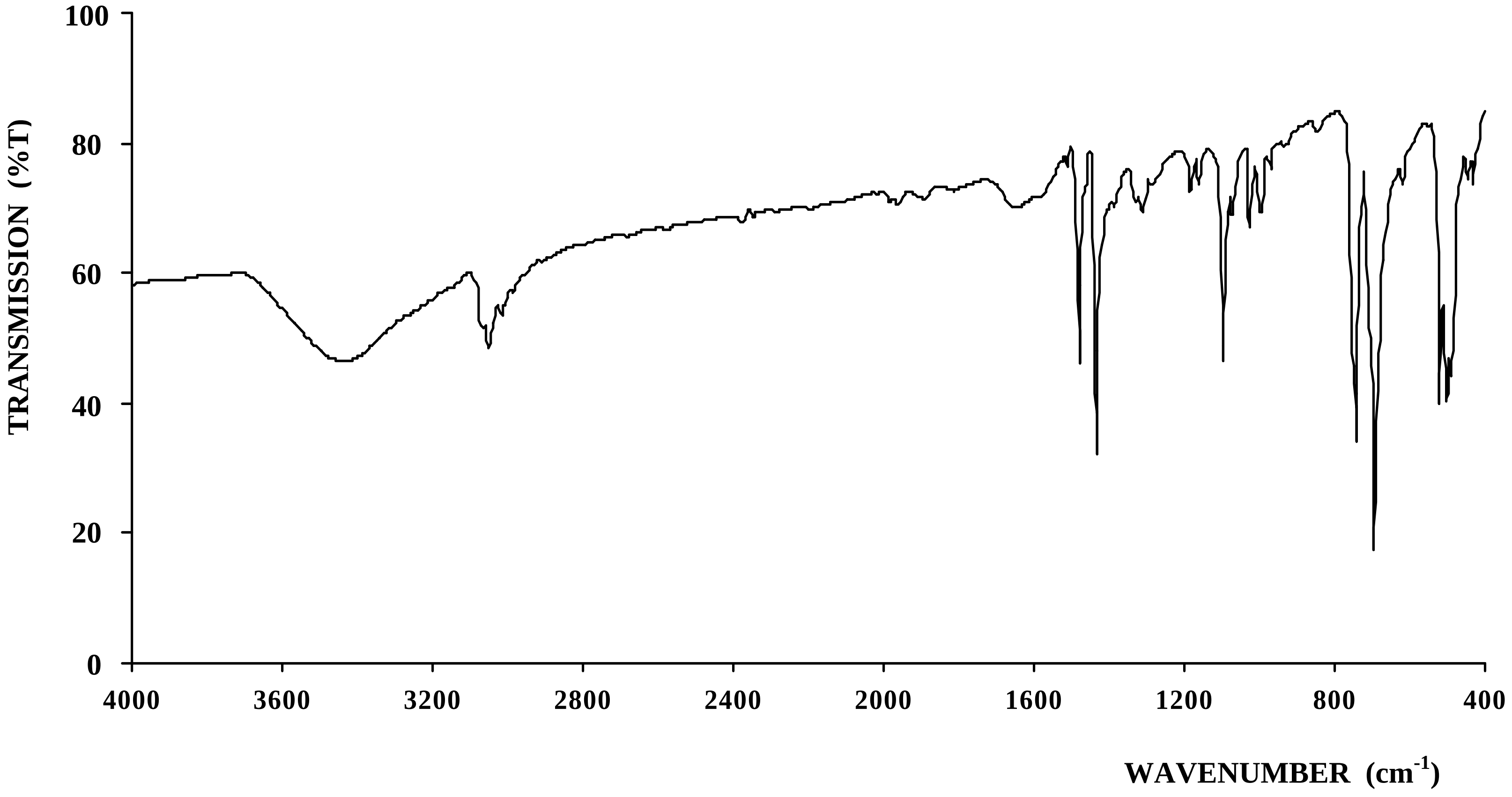


Fig. 46 The infrared spectrum of $[Ag(PPh_3)_3Cl]$

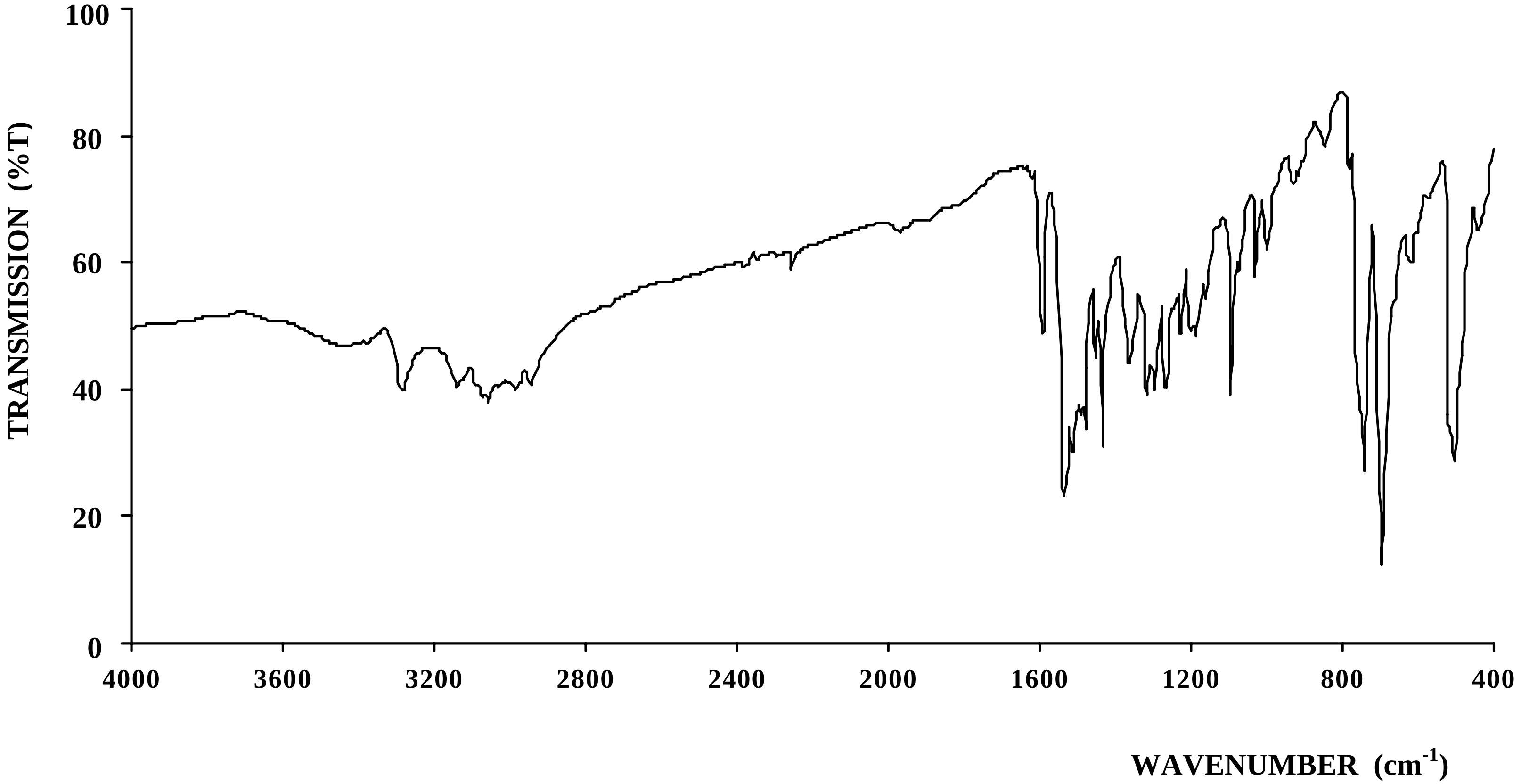


Fig. 47 The infrared spectrum of [Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN

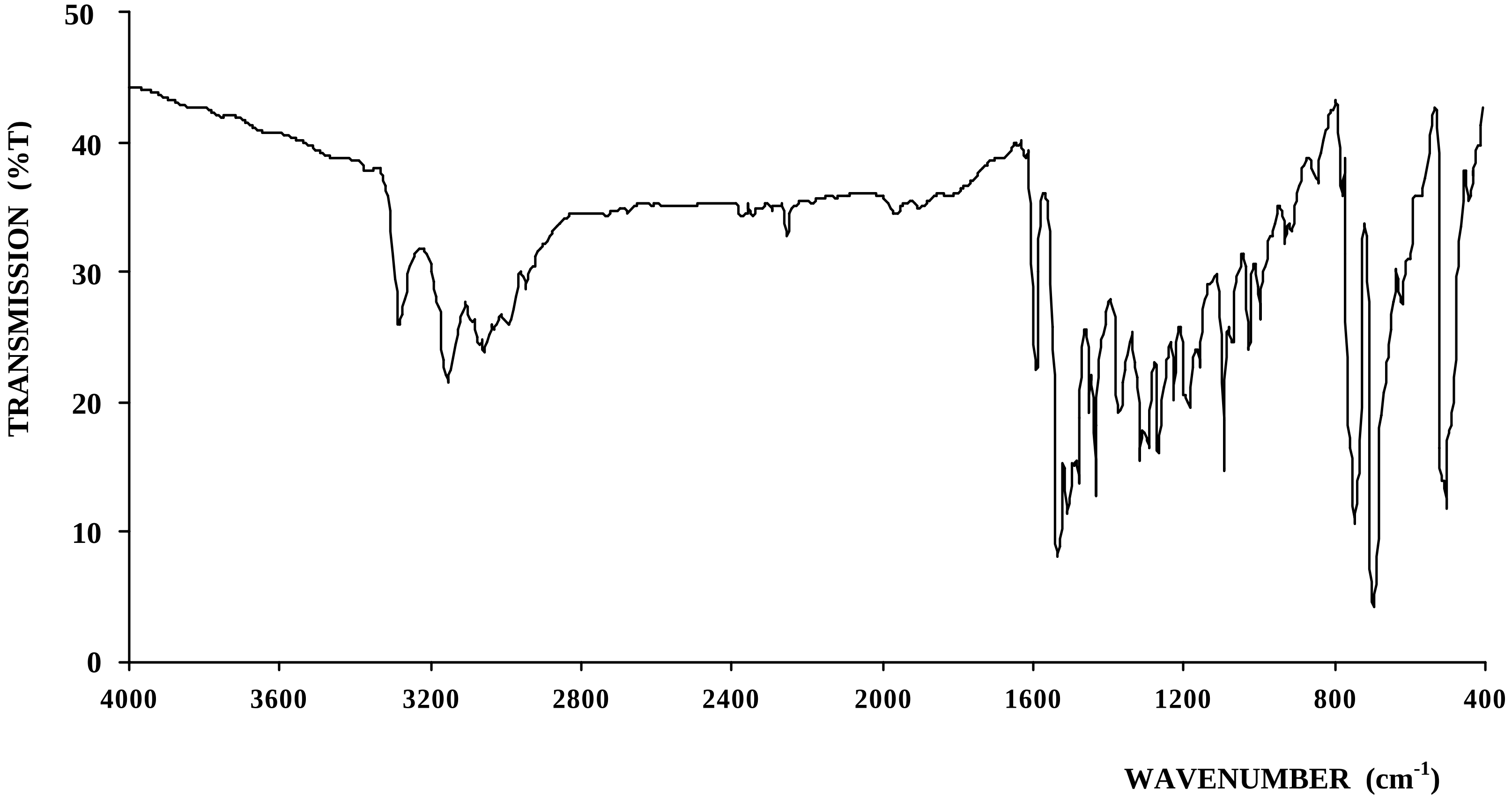


Fig. 48 The infrared spectrum of $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$

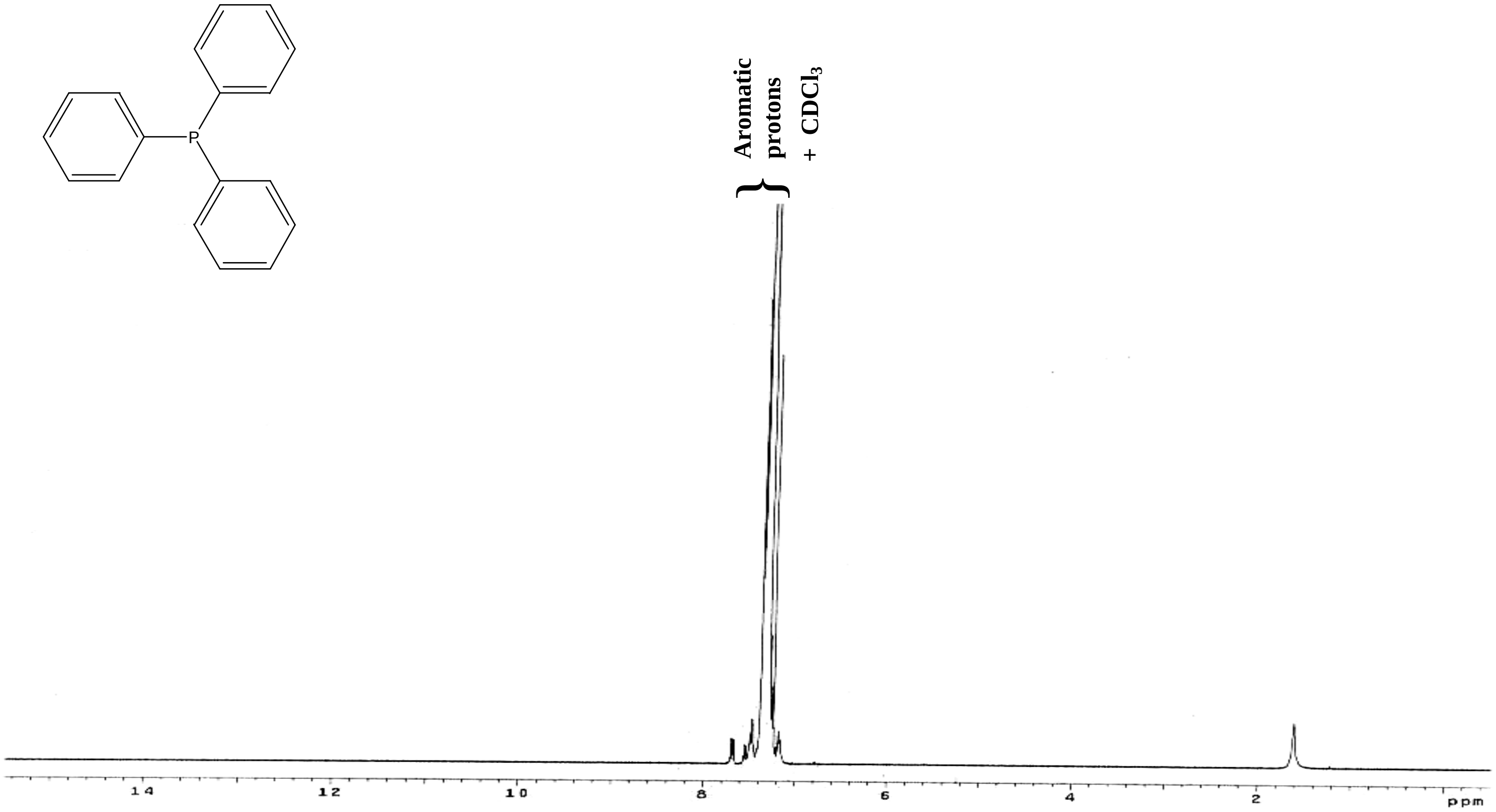


Fig. 49 The ^{1}H NMR spectrum of PPh_3

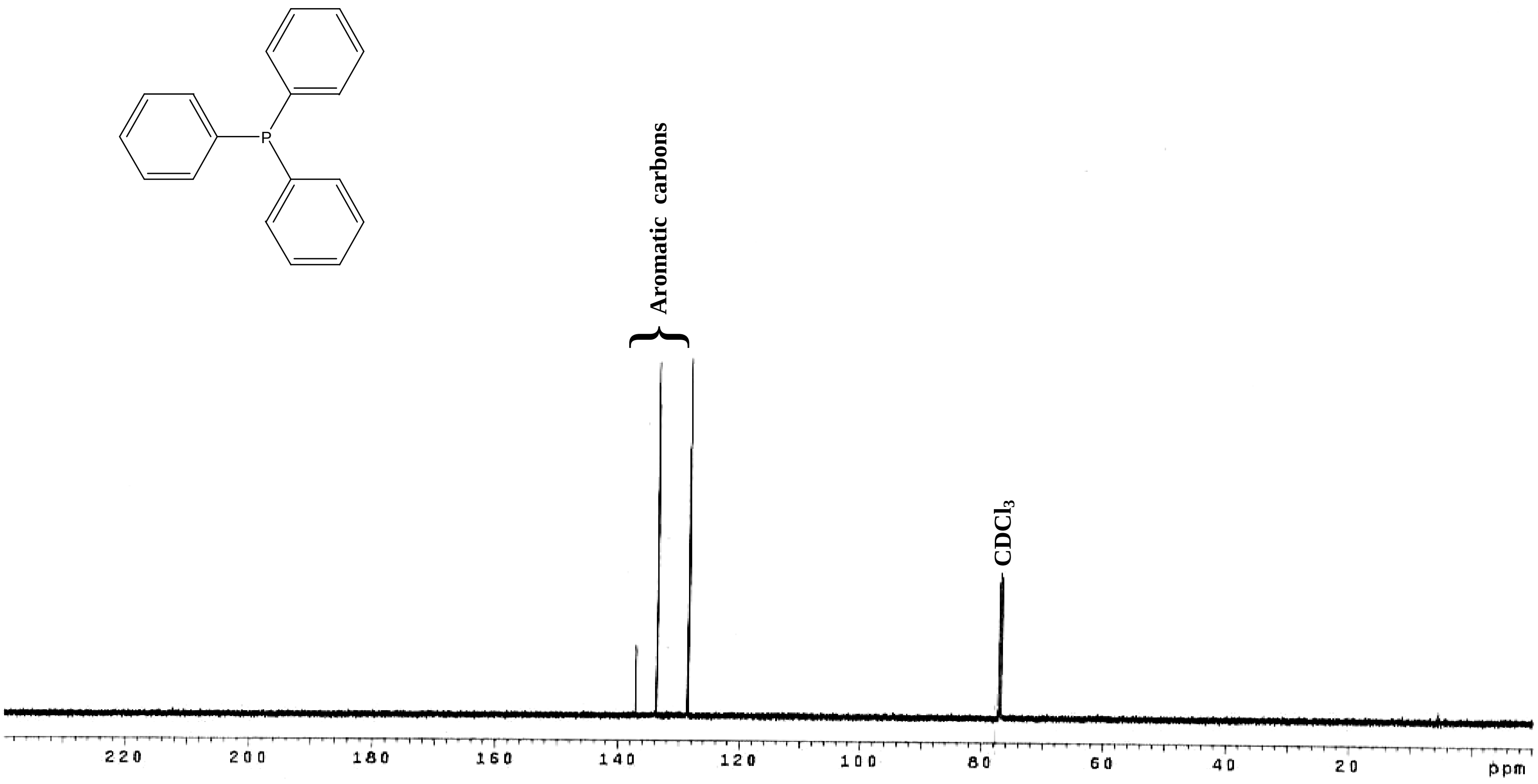


Fig. 50 The ^{13}C NMR spectrum of PPh_3

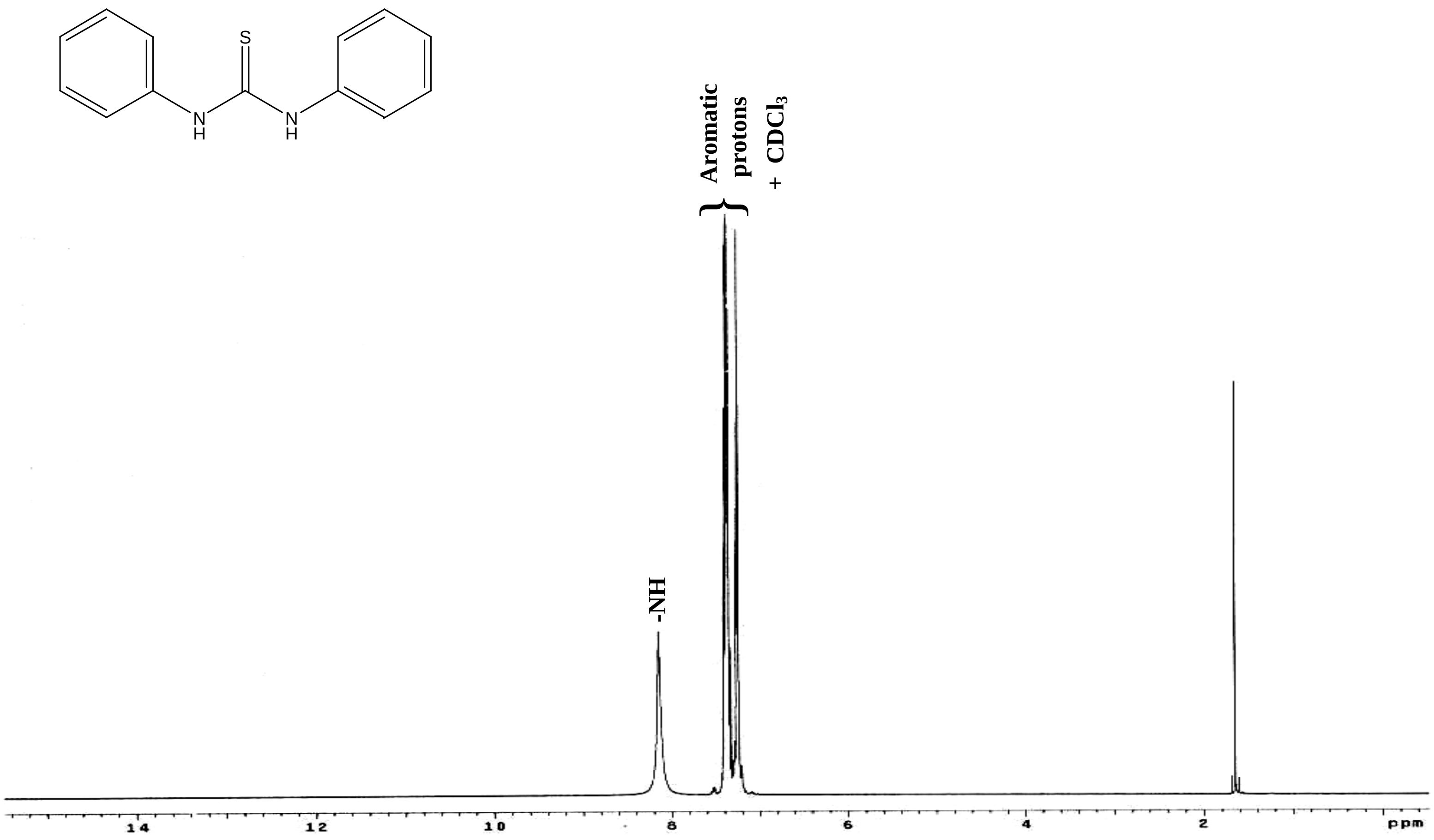


Fig. 51 The ^{1}H NMR spectrum of dptu

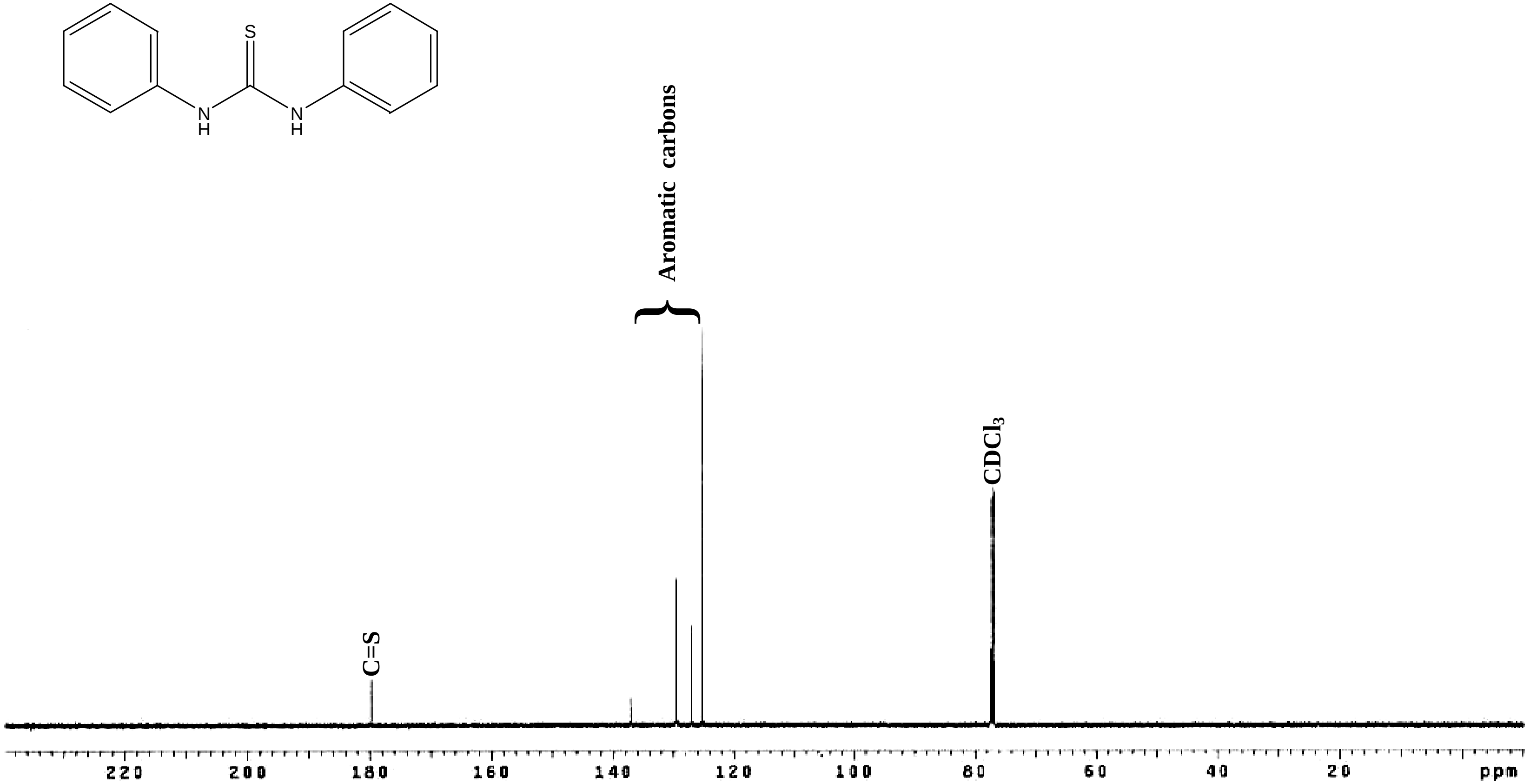


Fig. 52 The ^{13}C NMR spectrum of dptu

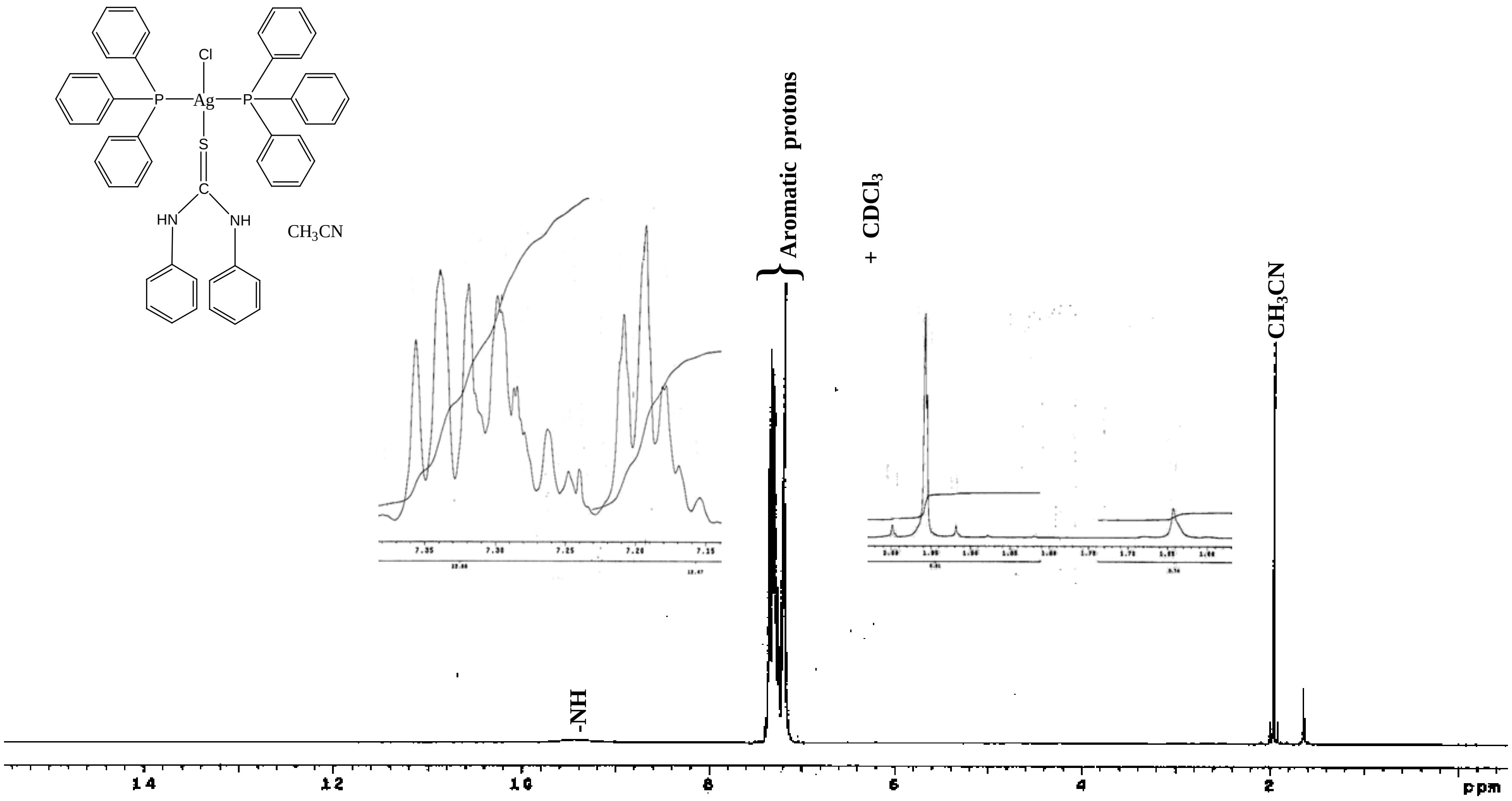


Fig. 53 The ^{1}H NMR spectrum of [Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN

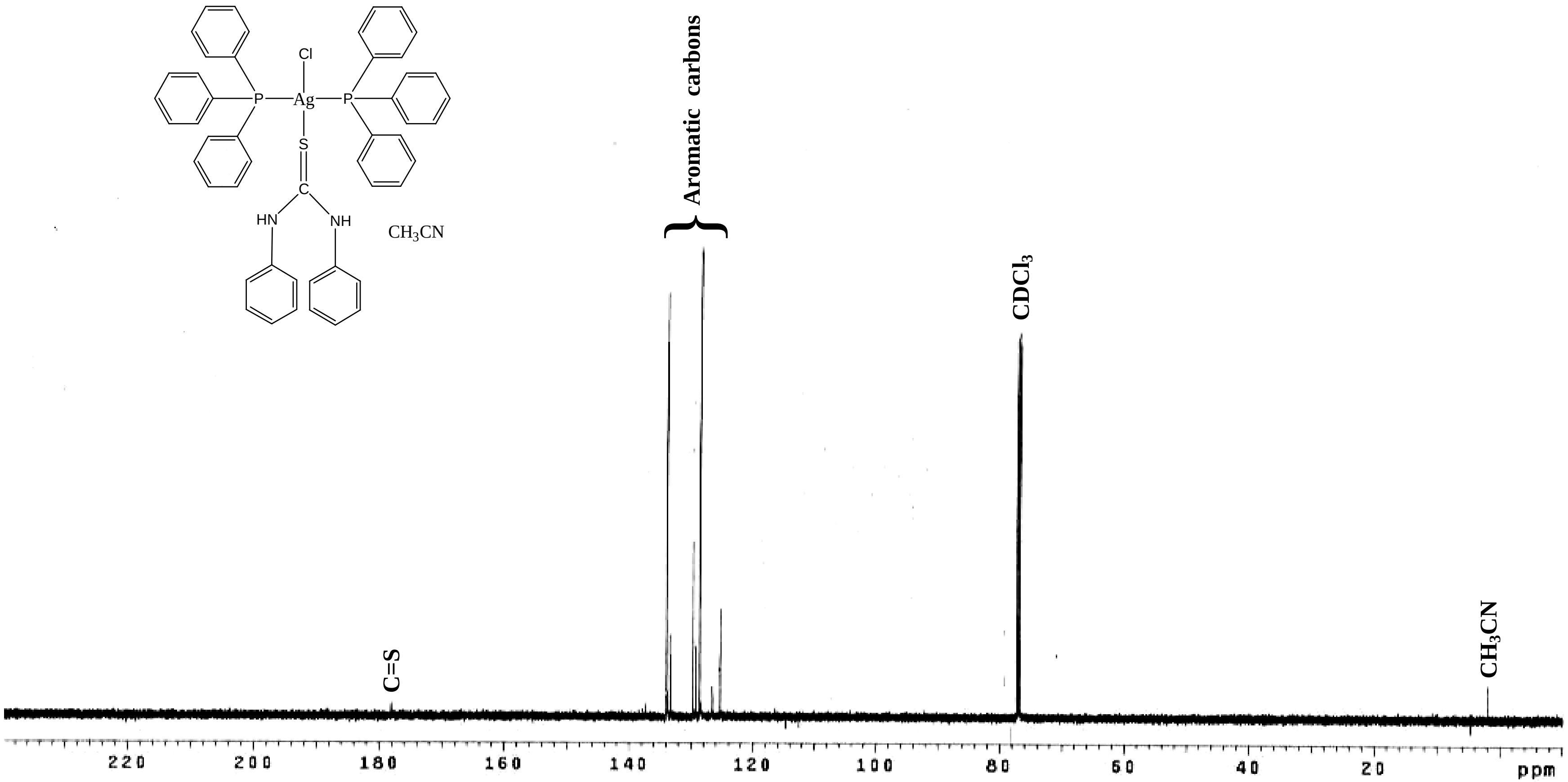


Fig. 54 The ^{13}C NMR spectrum of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$

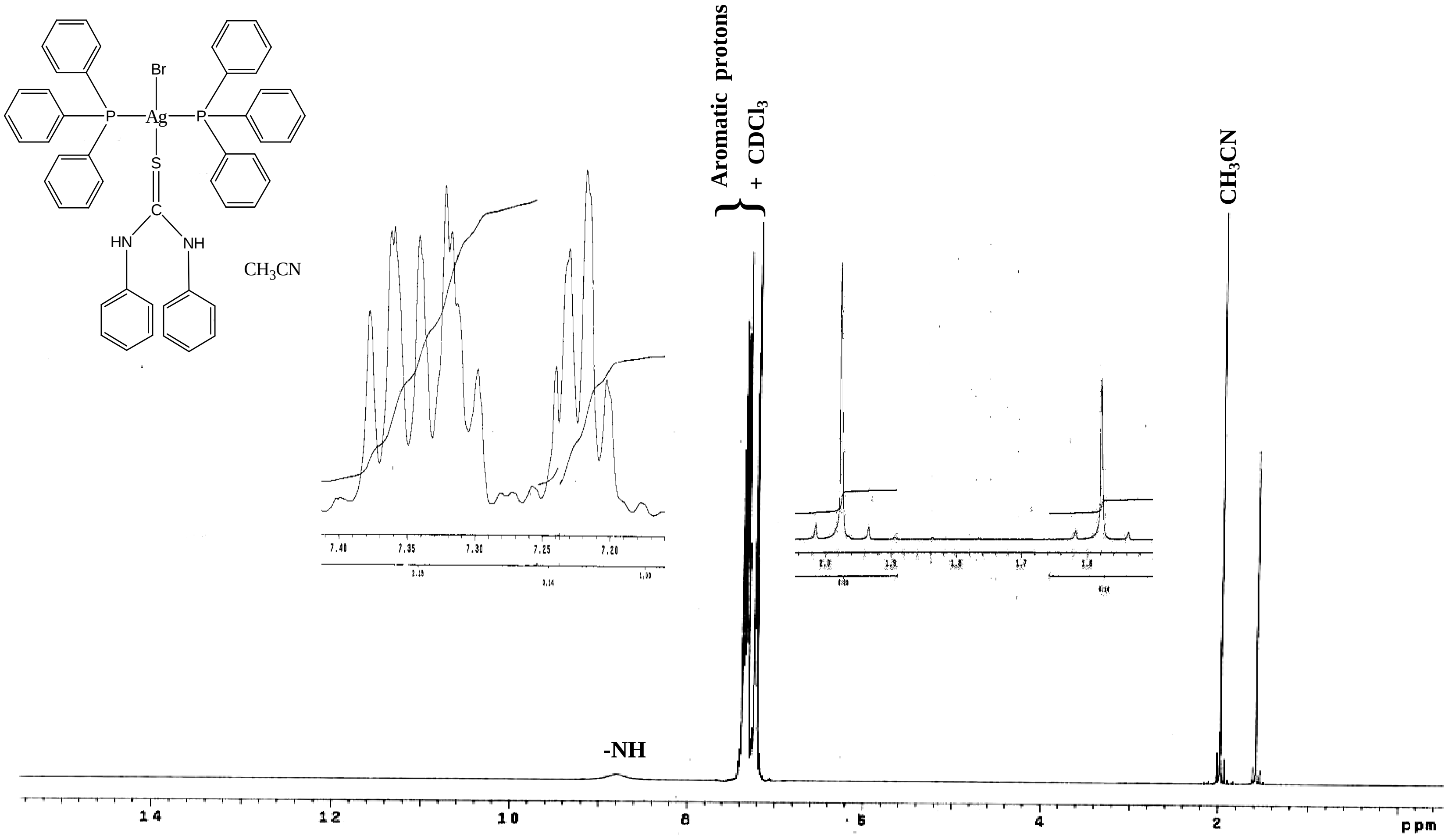


Fig. 55 The ^{1}H NMR spectrum of $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$

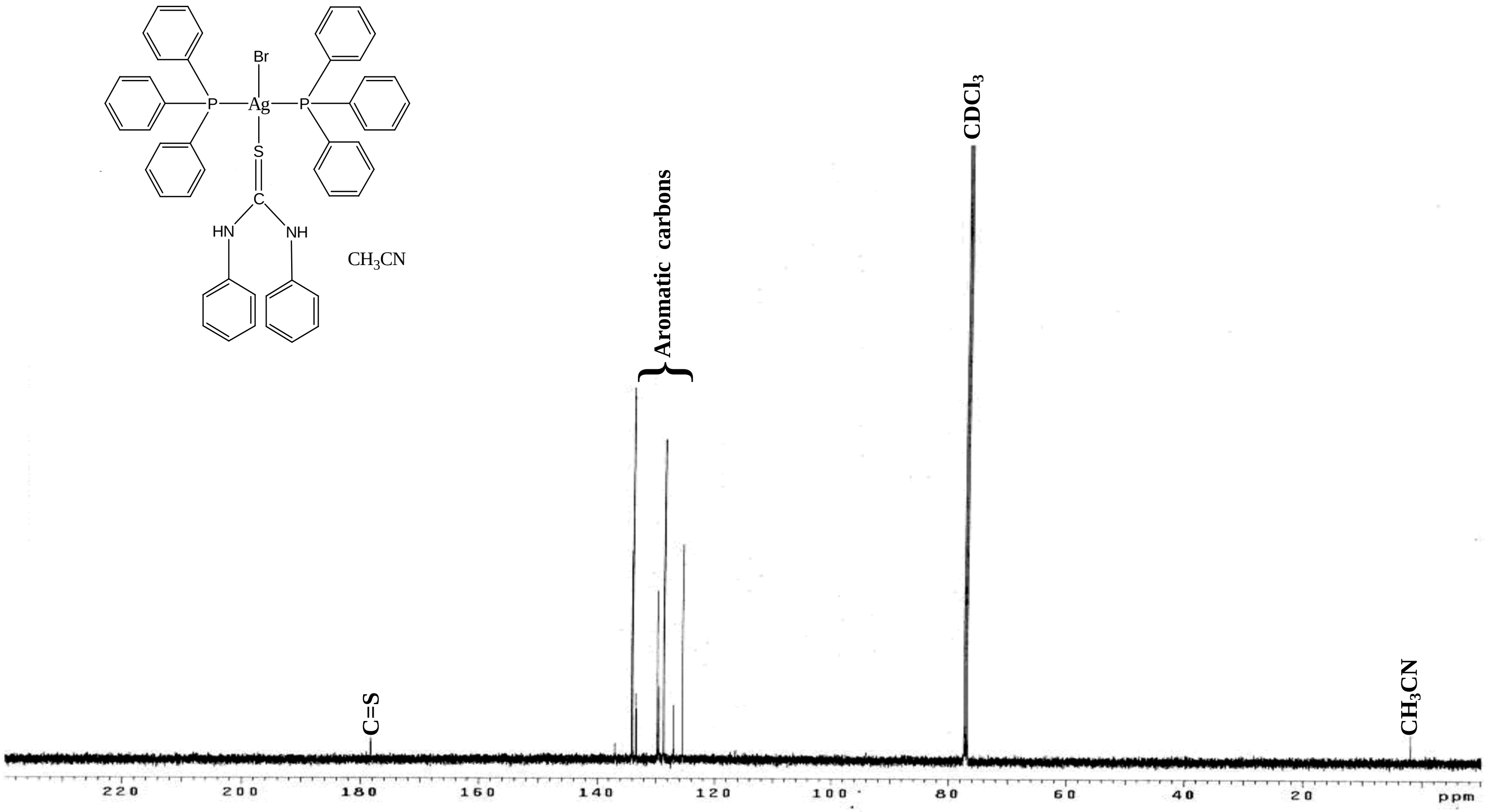


Fig. 56 The ^{13}C NMR spectrum of [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN

Table 9 Crystal data of $[Ag(PPh_3)(py)I]_2$.

Empirical formula	$C_{46}H_{40}Ag_2I_2N_2P_2$
Formula weight	1152.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimentions	a = 27.1395(13) Å
	b = 14.5510(7) Å
	c = 11.3199(6) Å
Volume	4454.3(4) $Å^3$
Z	4
Calculated density	1.718 g/cm^3
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0368$, $wR2 = 0.0816$
R indices (all data)	$R1 = 0.0536$, $wR2 = 0.0887$
$F(000)$	2240
Reflections collected	26199
Unique	5397
R(int)	0.0417

Table 10 Selected bond lengths [Å] and angles [°] of $[Ag(PPh_3)(py)I]_2$.

N(1)-Ag(1)	2.338(3)
P(1)-Ag(1)	2.4399(8)
Ag(1)-I(1)	2.8536(4)
Ag(1)-I(2)	2.8778(4)
Ag(1)-Ag(1)#1	2.9566(5)
I(1)-Ag(1)#1	2.8536(4)
I(2)-Ag(1)#1	2.8778(4)
C(1)-N(1)	1.318(4)
C(1)-C(2)	1.377(5)
C(1)-H(1)	0.9300

Table 10 (continued)

C(2)-C(3)	1.379(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.348(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.360(6)
C(4)-H(4)	0.9300
C(5)-N(1)	1.333(4)
C(5)-H(5)	0.9300
C(6)-C(11)	1.386(4)
C(6)-C(7)	1.392(5)
C(6)-P(1)	1.826(3)
C(7)-C(8)	1.381(5)
C(7)-H(12)	0.9300
C(8)-C(9)	1.366(5)
C(8)-H(13)	0.9300
C(9)-C(10)	1.369(5)
C(9)-H(14)	0.9300
C(10)-C(11)	1.386(5)
C(10)-H(15)	0.9300
C(11)-H(16)	0.9300
C(12)-C(13)	1.385(4)
C(12)-C(17)	1.390(4)
C(12)-P(1)	1.821(3)
C(13)-C(14)	1.381(5)
C(13)-H(22)	0.9300
C(14)-C(15)	1.366(5)
C(14)-H(23)	0.9300
C(15)-C(16)	1.378(5)
C(15)-H(24)	0.9300

Table 10 (continued)

C(16)-C(17)	1.377(5)
C(16)-H(25)	0.9300
C(17)-H(26)	0.9300
C(18)-C(23)	1.379(4)
C(18)-C(19)	1.394(4)
C(18)-P(1)	1.828(3)
C(19)-C(20)	1.390(5)
C(19)-H(32)	0.9300
C(20)-C(21)	1.367(6)
C(20)-H(33)	0.9300
C(21)-C(22)	1.363(6)
C(21)-H(34)	0.9300
C(22)-C(23)	1.374(5)
C(22)-H(35)	0.9300
C(23)-H(36)	0.9300
N(1)-Ag(1)-Ag(1)#1	108.99(7)
P(1)-Ag(1)-Ag(1)#1	133.37(2)
I(1)-Ag(1)-Ag(1)#1	58.798(6)
I(2)-Ag(1)-Ag(1)#1	59.089(6)
Ag(1)#1-I(1)-Ag(1)	62.403(12)
Ag(1)-I(2)-Ag(1)#1	61.821(12)
N(1)-Ag(1)-P(1)	117.62(8)
N(1)-Ag(1)-I(1)	100.13(7)
P(1)-Ag(1)-I(1)	111.621(19)
N(1)-Ag(1)-I(2)	99.20(7)
P(1)-Ag(1)-I(2)	109.879(19)
I(1)-Ag(1)-I(2)	117.888(11)
C(1)-N(1)-Ag(1)	121.9(2)
C(5)-N(1)-Ag(1)	120.3(3)

Table 10 (continued)

C(12)-P(1)-Ag(1)	114.73(9)
C(6)-P(1)-Ag(1)	115.37(10)
C(18)-P(1)-Ag(1)	113.53(9)
C(12)-P(1)-C(6)	104.57(13)
C(12)-P(1)-C(18)	102.92(14)
C(6)-P(1)-C(18)	104.34(14)
C(1)-N(1)-C(5)	117.8(3)
N(1)-C(1)-C(2)	122.9(4)
N(1)-C(1)-H(1)	118.6
C(2)-C(1)-H(1)	118.6
C(1)-C(2)-C(3)	117.4(4)
C(1)-C(2)-H(2)	121.3
C(3)-C(2)-H(2)	121.3
C(4)-C(3)-C(2)	120.4(4)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	118.1(4)
C(3)-C(4)-H(4)	120.9
C(5)-C(4)-H(4)	120.9
N(1)-C(5)-C(4)	123.4(4)
N(1)-C(5)-H(5)	118.3
C(4)-C(5)-H(5)	118.3
C(11)-C(6)-C(7)	119.1(3)
C(11)-C(6)-P(1)	123.2(2)
C(7)-C(6)-P(1)	117.7(2)
C(8)-C(7)-C(6)	119.5(4)
C(8)-C(7)-H(12)	120.3
C(6)-C(7)-H(12)	120.3
C(9)-C(8)-C(7)	121.0(4)
C(9)-C(8)-H(13)	119.5

Table 10 (continued)

C(7)-C(8)-H(13)	119.5
C(8)-C(9)-C(10)	120.1(4)
C(8)-C(9)-H(14)	119.9
C(10)-C(9)-H(14)	119.9
C(9)-C(10)-C(11)	119.9(3)
C(9)-C(10)-H(15)	120.1
C(11)-C(10)-H(15)	120.1
C(6)-C(11)-C(10)	120.4(3)
C(6)-C(11)-H(16)	119.8
C(10)-C(11)-H(16)	119.8
C(13)-C(12)-C(17)	118.4(3)
C(13)-C(12)-P(1)	124.0(2)
C(17)-C(12)-P(1)	117.6(2)
C(14)-C(13)-C(12)	120.6(3)
C(14)-C(13)-H(22)	119.7
C(12)-C(13)-H(22)	119.7
C(15)-C(14)-C(13)	120.3(3)
C(15)-C(14)-H(23)	119.9
C(13)-C(14)-H(23)	119.9
C(14)-C(15)-C(16)	120.2(4)
C(14)-C(15)-H(24)	119.9
C(16)-C(15)-H(24)	119.9
C(17)-C(16)-C(15)	119.8(4)
C(17)-C(16)-H(25)	120.1
C(15)-C(16)-H(25)	120.1
C(16)-C(17)-C(12)	120.8(3)
C(16)-C(17)-H(26)	119.6
C(12)-C(17)-H(26)	119.6
C(23)-C(18)-C(19)	118.4(3)
C(23)-C(18)-P(1)	123.9(2)

Table 10 (continued)

C(19)-C(18)-P(1)	117.6(3)
C(20)-C(19)-C(18)	119.9(4)
C(20)-C(19)-H(32)	120.1
C(18)-C(19)-H(32)	120.1
C(21)-C(20)-C(19)	120.4(4)
C(21)-C(20)-H(33)	119.8
C(19)-C(20)-H(33)	119.8
C(22)-C(21)-C(20)	119.9(4)
C(22)-C(21)-H(34)	120.1
C(20)-C(21)-H(34)	120.1
C(21)-C(22)-C(23)	120.5(4)
C(21)-C(22)-H(35)	119.7
C(23)-C(22)-H(35)	119.7
C(22)-C(23)-C(18)	120.9(4)
C(22)-C(23)-H(36)	119.5
C(18)-C(23)-H(36)	119.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 .

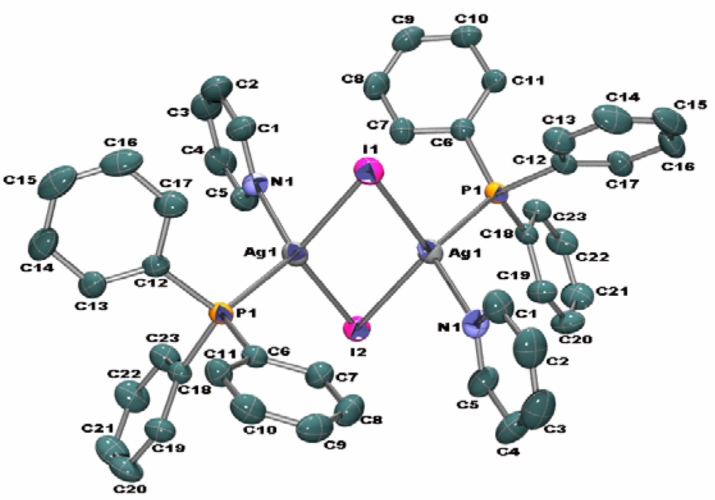


Fig. 57 The structure of $[Ag(PPh_3)(py)I]_2$.

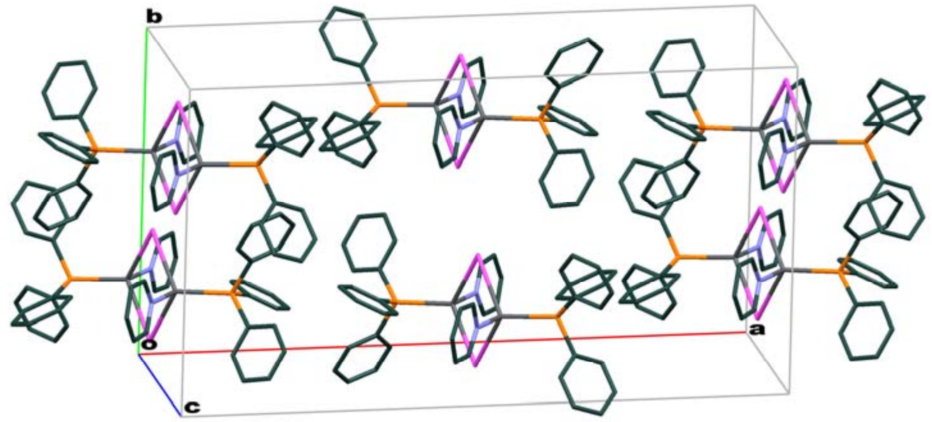


Fig. 58 Unit cell contents of $[Ag(PPh_3)(py)I]_2$.

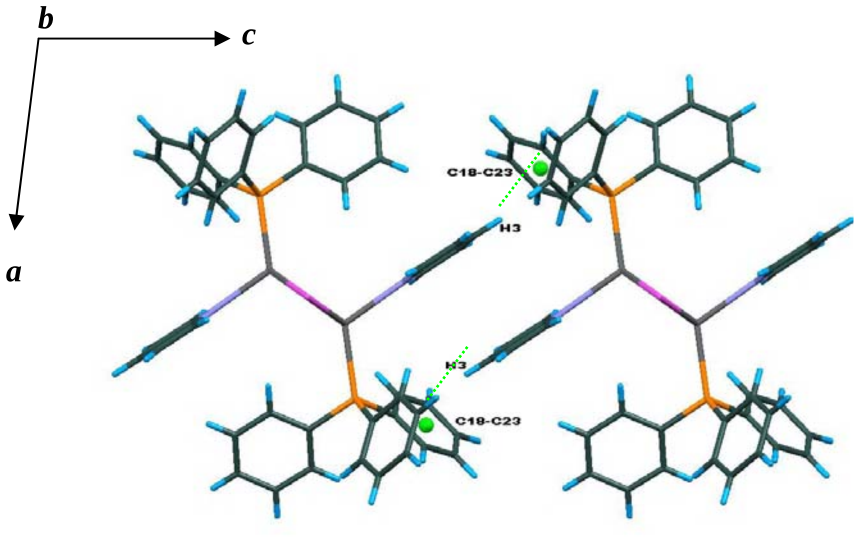


Fig. 59 Short contacts of $[Ag(PPh_3)(py)I]_2$ plotted down *b* axis.

Table 11 Crystal data of [$Ag(PPh_3)_3Cl$].

Empirical formula	$C_{54}H_{45}AgClP_3$
Formula weight	930.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic,
Space group	$P2_1/n$
Unit cell dimensions	a = 10.2196(4) Å
	b = 33.7415(14) Å
	c = 13.3841(6) Å
	β = 90.2250(10) °
Volume	4615.1(3) $Å^3$
Z	4
Calculated density	1.339 Mg/m^3
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0450, $wR2$ = 0.0923
R indices (all data)	$R1$ = 0.0571, $wR2$ = 0.0970
F(000)	1912
Unique	11180
R(int)	0.045

Table 12 Selected bond lengths [Å] and angles [°] of [$Ag(PPh_3)_3Cl$].

P(1)-Ag(1)	2.5214(6)
P(2)-Ag(1)	2.5527(7)
P(3)-Ag(1)	2.5573(6)
Cl(1)-Ag(1)	2.5510(7)
C(1)-C(6)	1.380(4)
C(1)-C(2)	1.385(4)
C(1)-P(1)	1.829(3)
C(2)-C(3)	1.387(4)
C(3)-C(4)	1.360(5)

Table 12 (Continued)

C(4)-C(5)	1.367(5)
C(5)-C(6)	1.390(4)
C(7)-C(12)	1.383(4)
C(7)-C(8)	1.394(4)
C(7)-P(1)	1.826(3)
C(8)-C(9)	1.375(4)
C(9)-C(10)	1.371(5)
C(10)-C(11)	1.368(5)
C(11)-C(12)	1.387(4)
C(13)-C(18)	1.378(4)
C(13)-C(14)	1.387(4)
C(13)-P(1)	1.828(3)
C(14)-C(15)	1.381(4)
C(15)-C(16)	1.357(5)
C(16)-C(17)	1.370(5)
C(17)-C(18)	1.389(4)
C(19)-C(24)	1.360(4)
C(19)-C(20)	1.373(4)
C(19)-P(2)	1.828(3)
C(20)-C(21)	1.374(5
C(21)-C(22)	1.345(6)
C(22)-C(23)	1.346(6)
C(23)-C(24)	1.397(5)
C(25)-C(30)	1.376(4)
C(25)-C(26)	1.395(4)
C(25)-P(2)	1.820(3)
C(26)-C(27)	1.371(4)
C(27)-C(28)	1.366(4)
C(28)-C(29)	1.370(5)
C(29)-C(30)	1.379(4)

Table 12 (Continued)

C(31)-C(32)	1.386(4)
C(31)-C(36)	1.390(4)
C(31)-P(2)	1.830(3)
C(32)-C(33)	1.392(4)
C(33)-C(34)	1.360(5)
C(34)-C(35)	1.369(5)
C(35)-C(36)	1.377(5)
C(37)-C(38)	1.369(4)
C(37)-C(42)	1.389(4)
C(37)-P(3)	1.829(2)
C(38)-C(39)	1.372(4)
C(39)-C(40)	1.354(4)
C(40)-C(41)	1.353(5)
C(41)-C(42)	1.391(4)
C(43)-C(44)	1.377(4)
C(43)-C(48)	1.391(4)
C(43)-P(3)	1.825(2)
C(44)-C(45)	1.391(4)
C(45)-C(46)	1.367(5)
C(46)-C(47)	1.366(5)
C(47)-C(48)	1.385(4)
C(49)-C(50)	1.384(3)
C(49)-C(54)	1.400(3)
C(49)-P(3)	1.821(2)
C(50)-C(51)	1.388(4)
C(51)-C(52)	1.369(4)
C(52)-C(53)	1.379(4)
C(53)-C(54)	1.381(4)
P(1)-Ag(1)-Cl(1)	102.75(2)
P(1)-Ag(1)-P(2)	114.60(2)

Table 12 (Continued)

Cl(1)-Ag(1)-P(2)	109.70(2)
P(1)-Ag(1)-P(3)	117.11(2)
Cl(1)-Ag(1)-P(3)	96.63(2)
P(2)-Ag(1)-P(3)	113.51(2)
C(49)-P(3)-Ag(1)	117.46(8)
C(43)-P(3)-Ag(1)	116.66(8)
C(37)-P(3)-Ag(1)	110.38(8)
C(6)-C(1)-C(2)	118.7(3)
C(6)-C(1)-P(1)	124.5(2)
C(2)-C(1)-P(1)	116.7(2)
C(1)-C(2)-C(3)	119.9(3)
C(4)-C(3)-C(2)	120.8(3)
C(3)-C(4)-C(5)	120.1(3)
C(4)-C(5)-C(6)	119.9(3)
C(1)-C(6)-C(5)	120.6(3)
C(12)-C(7)-C(8)	118.8(3)
C(12)-C(7)-P(1)	118.9(2)
C(8)-C(7)-P(1)	122.2(2)
C(9)-C(8)-C(7)	120.5(3)
C(10)-C(9)-C(8)	120.2(3)
C(11)-C(10)-C(9)	120.1(3)
C(10)-C(11)-C(12)	120.4(3)
C(7)-C(12)-C(11)	120.0(3)
C(18)-C(13)-C(14)	118.0(3)
C(18)-C(13)-P(1)	117.2(2)
C(14)-C(13)-P(1)	124.4(2)
C(15)-C(14)-C(13)	120.8(3)
C(16)-C(15)-C(14)	120.2(3)
C(15)-C(16)-C(17)	120.5(3)
C(16)-C(17)-C(18)	119.4(3)

Table 12 (Continued)

C(13)-C(18)-C(17)	121.1(3)
C(24)-C(19)-C(20)	117.8(3)
C(24)-C(19)-P(2)	125.0(2)
C(20)-C(19)-P(2)	117.2(2)
C(19)-C(20)-C(21)	121.7(3)
C(22)-C(21)-C(20)	120.1(4)
C(21)-C(22)-C(23)	119.5(4)
C(22)-C(23)-C(24)	121.1(4)
C(19)-C(24)-C(23)	119.8(4)
C(30)-C(25)-C(26)	118.1(2)
C(30)-C(25)-P(2)	119.4(2)
C(26)-C(25)-P(2)	122.5(2)
C(27)-C(26)-C(25)	121.0(3)
C(28)-C(27)-C(26)	119.9(3)
C(27)-C(28)-C(29)	120.0(3)
C(28)-C(29)-C(30)	120.4(3)
C(25)-C(30)-C(29)	120.6(3)
C(32)-C(31)-C(36)	118.3(3)
C(32)-C(31)-P(2)	123.6(2)
C(36)-C(31)-P(2)	117.9(2)
C(31)-C(32)-C(33)	120.6(3)
C(34)-C(33)-C(32)	120.0(4)
C(33)-C(34)-C(35)	120.2(3)
C(34)-C(35)-C(36)	120.6(3)
C(35)-C(36)-C(31)	120.3(3)
C(38)-C(37)-C(42)	117.4(2)
C(38)-C(37)-P(3)	117.82(19)
C(42)-C(37)-P(3)	124.7(2)
C(37)-C(38)-C(39)	121.6(3)
C(40)-C(39)-C(38)	121.1(3)

Table 12 (Continued)

C(41)-C(40)-C(39)	118.7(3)
C(40)-C(41)-C(42)	121.3(3)
C(37)-C(42)-C(41)	119.9(3)
C(44)-C(43)-C(48)	118.6(2)
C(44)-C(43)-P(3)	124.6(2)
C(48)-C(43)-P(3)	116.6(2)
C(43)-C(44)-C(45)	120.1(3)
C(46)-C(45)-C(44)	120.1(3)
C(47)-C(46)-C(45)	121.0(3)
C(46)-C(47)-C(48)	118.9(3)
C(47)-C(48)-C(43)	121.2(3)
C(50)-C(49)-C(54)	118.4(2)
C(50)-C(49)-P(3)	123.44(19)
C(54)-C(49)-P(3)	118.17(19)
C(49)-C(50)-C(51)	120.5(3)
C(52)-C(51)-C(50)	120.8(3)
C(51)-C(52)-C(53)	119.4(3)
C(52)-C(53)-C(54)	120.6(3)
C(53)-C(54)-C(49)	120.4(3)
C(7)-P(1)-C(13)	105.88(12)
C(7)-P(1)-C(1)	101.10(12)
C(13)-P(1)-C(1)	105.07(12)
C(7)-P(1)-Ag(1)	115.66(8)
C(13)-P(1)-Ag(1)	111.60(8)
C(1)-P(1)-Ag(1)	116.29(8)
C(25)-P(2)-C(19)	101.40(12)
C(25)-P(2)-C(31)	103.80(12)
C(19)-P(2)-C(31)	104.03(12)
C(25)-P(2)-Ag(1)	116.34(8)
C(19)-P(2)-Ag(1)	114.56(9)

Table 12 (Continued)

C(31)-P(2)-Ag(1)	114.96(9)
C(49)-P(3)-C(43)	102.28(11)
C(49)-P(3)-C(37)	102.95(11)
C(43)-P(3)-C(37)	105.60(11)

Symmetry transformations used to generate equivalent atoms:

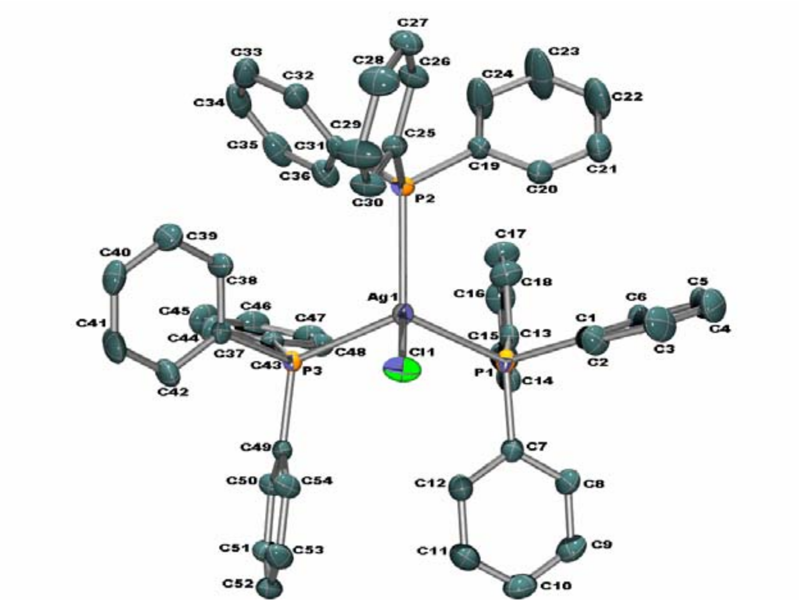


Fig. 60 The structure of $[Ag(PPh_3)_3Cl]$.

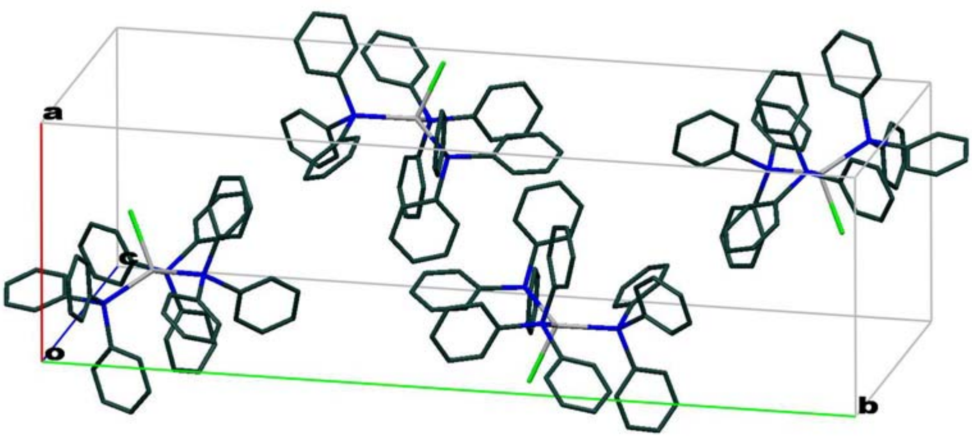


Fig. 61 Unit cell contents of $[Ag(PPh_3)_3Cl]$.

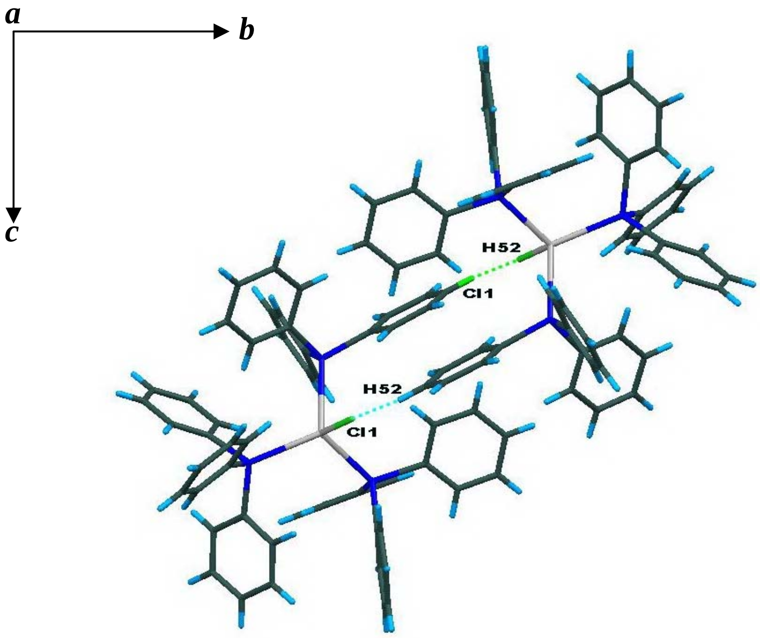


Fig. 62 Short contacts of [Ag(PPh$_3$)$_3$Cl] plotted down *a* axis.

Table 13 Crystal data of [Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN.

Empirical formula	$AgClC_{51}H_{45}N_3P_2S$
Formula weight	937.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimentions	a = 13.9823 (6) Å
	b = 16.7180 (7) Å
	c = 19.6205 (9) Å
Volume	4586.4 (3) Å^3
Z	4
Calculated density	1.357 g/cm^3
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0430, $wR2$ = 0.0944
R indices (all data)	$R1$ = 0.0532, $wR2$ = 0.0990
$F(000)$	1928

Table 13 (continued)

Reflections collected	63458
Unique	11084
R(int)	0.0516

Table 14 Selected bond lengths [Å] and angles [°] of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$.

Cl(1)-Ag(1)	2.5736(9)
S(1)-Ag(1)	2.6432(9)
P(1)-Ag(1)	2.4793(8)
P(2)-Ag(1)	2.5245(8)
C(1)-N(2)	1.338(4)
C(1)-N(1)	1.340(5)
C(1)-S(1)	1.687(4)
C(2)-C(7)	1.376(6)
C(2)-C(3)	1.381(6)
C(2)-N(1)	1.425(5)
C(3)-C(4)	1.387(6)
C(4)-C(5)	1.363(7)
C(5)-C(6)	1.363(7)
C(6)-C(7)	1.377(6)
C(8)-C(9)	1.358(6)
C(8)-C(13)	1.370(6)
C(8)-N(2)	1.431(5)
C(9)-C(10)	1.389(7)
C(10)-C(11)	1.368(8)
C(11)-C(12)	1.353(9)
C(12)-C(13)	1.368(7)
C(14A)-C(15A)	1.379(5)
C(14A)-C(19A)	1.393(5)

Table 14 (continued)

C(14A)-P(1)	1.832(4)
C(15A)-C(16A)	1.389(6)
C(16A)-C(17A)	1.373(6)
C(17A)-C(18A)	1.372(7)
C(18A)-C(19A)	1.385(6)
C(20A)-C(25A)	1.383(5)
C(20A)-C(21A)	1.385(5)
C(20A)-P(1)	1.830(3)
C(21A)-C(22A)	1.390(6)
C(22A)-C(23A)	1.365(7)
C(23A)-C(24A)	1.364(7)
C(24A)-C(25A)	1.380(6)
C(26A)-C(31A)	1.390(4)
C(26A)-C(27A)	1.396(5)
C(26A)-P(1)	1.825(3)
C(27A)-C(28A)	1.380(5)
C(28A)-C(29A)	1.381(5)
C(29A)-C(30A)	1.364(6)
C(30A)-C(31A)	1.388(5)
C(32B)-C(37B)	1.364(6)
C(32B)-C(33B)	1.365(5)
C(32B)-P(2)	1.826(3)
C(33B)-C(34B)	1.380(6)
C(34B)-C(35B)	1.351(8)
C(35B)-C(36B)	1.353(8)
C(36B)-C(37B)	1.386(6)
C(38B)-C(43B)	1.377(5)
C(38B)-C(39B)	1.387(5)
C(38B)-P(2)	1.833(3)
C(39B)-C(40B)	1.386(6)

Table 14 (continued)

C(40B)-C(41B)	1.363(7)
C(41B)-C(42B)	1.362(7)
C(42B)-C(43B)	1.398(6)
C(44B)-C(45B)	1.359(6)
C(44B)-C(49B)	1.369(6)
C(44B)-P(2)	1.834(3)
C(45B)-C(46B)	1.388(6)
C(46B)-C(47B)	1.337(7)
C(47B)-C(48B)	1.353(7)
C(48B)-C(49B)	1.377(7)
C(50)-N(3)	1.117(11)
C(50)-C(51)	1.458(12)
C(1)-S(1)-Ag(1)	110.17(12)
P(1)-Ag(1)-P(2)	122.27(3)
P(1)-Ag(1)-Cl(1)	113.07(3)
P(2)-Ag(1)-Cl(1)	107.80(3)
P(1)-Ag(1)-S(1)	111.05(3)
P(2)-Ag(1)-S(1)	94.01(3)
Cl(1)-Ag(1)-S(1)	106.14(3)
C(14A)-P(1)-Ag(1)	116.65(11)
C(20A)-P(1)-Ag(1)	112.77(10)
C(26A)-P(1)-Ag(1)	116.23(10)
C(32B)-P(2)-Ag(1)	114.58(11)
C(38B)-P(2)-Ag(1)	118.93(12)
C(44B)-P(2)-Ag(1)	110.75(12)
N(2)-C(1)-N(1)	116.9(3)
N(2)-C(1)-S(1)	121.2(3)
N(1)-C(1)-S(1)	121.8(3)
C(7)-C(2)-C(3)	119.3(4)
C(7)-C(2)-N(1)	119.1(4)

Table 14 (continued)

C(3)-C(2)-N(1)	121.5(4)
C(2)-C(3)-C(4)	119.3(4)
C(5)-C(4)-C(3)	121.0(5)
C(6)-C(5)-C(4)	119.4(4)
C(5)-C(6)-C(7)	120.7(4)
C(2)-C(7)-C(6)	120.2(4)
C(9)-C(8)-C(13)	119.9(4)
C(9)-C(8)-N(2)	121.4(4)
C(13)-C(8)-N(2)	118.5(4)
C(8)-C(9)-C(10)	119.6(5)
C(11)-C(10)-C(9)	120.0(5)
C(12)-C(11)-C(10)	119.8(5)
C(11)-C(12)-C(13)	120.4(5)
C(12)-C(13)-C(8)	120.3(5)
C(15A)-C(14A)-C(19A)	119.1(3)
C(15A)-C(14A)-P(1)	119.1(3)
C(19A)-C(14A)-P(1)	121.8(3)
C(14A)-C(15A)-C(16A)	119.9(4)
C(17A)-C(16A)-C(15A)	120.7(4)
C(18A)-C(17A)-C(16A)	119.7(4)
C(17A)-C(18A)-C(19A)	120.2(4)
C(18A)-C(19A)-C(14A)	120.3(4)
C(25A)-C(20A)-C(21A)	118.7(3)
C(25A)-C(20A)-P(1)	117.7(3)
C(21A)-C(20A)-P(1)	123.6(3)
C(20A)-C(21A)-C(22A)	120.1(4)
C(23A)-C(22A)-C(21A)	120.1(4)
C(24A)-C(23A)-C(22A)	120.3(4)
C(23A)-C(24A)-C(25A)	120.1(4)
C(24A)-C(25A)-C(20A)	120.6(4)

Table 14 (continued)

C(31A)-C(26A)-C(27A)	118.1(3)
C(31A)-C(26A)-P(1)	124.2(3)
C(27A)-C(26A)-P(1)	117.6(2)
C(28A)-C(27A)-C(26A)	120.8(3)
C(27A)-C(28A)-C(29A)	120.0(3)
C(30A)-C(29A)-C(28A)	120.2(3)
C(29A)-C(30A)-C(31A)	120.3(3)
C(30A)-C(31A)-C(26A)	120.6(3)
C(37B)-C(32B)-C(33B)	118.8(4)
C(37B)-C(32B)-P(2)	119.1(3)
C(33B)-C(32B)-P(2)	122.0(3)
C(32B)-C(33B)-C(34B)	120.2(5)
C(35B)-C(34B)-C(33B)	120.4(5)
C(34B)-C(35B)-C(36B)	120.1(4)
C(35B)-C(36B)-C(37B)	119.7(5)
C(32B)-C(37B)-C(36B)	120.7(5)
C(43B)-C(38B)-C(39B)	118.9(3)
C(43B)-C(38B)-P(2)	117.7(3)
C(39B)-C(38B)-P(2)	123.3(3)
C(40B)-C(39B)-C(38B)	120.4(4)
C(41B)-C(40B)-C(39B)	120.0(5)
C(42B)-C(41B)-C(40B)	120.5(4)
C(41B)-C(42B)-C(43B)	120.1(4)
C(38B)-C(43B)-C(42B)	120.1(4)
C(45B)-C(44B)-C(49B)	117.1(4)
C(45B)-C(44B)-P(2)	118.0(3)
C(49B)-C(44B)-P(2)	124.9(3)
C(44B)-C(45B)-C(46B)	121.6(4)
C(47B)-C(46B)-C(45B)	120.2(5)
C(46B)-C(47B)-C(48B)	119.4(4)

Table 14 (continued)

C(47B)-C(48B)-C(49B)	120.6(5)
C(44B)-C(49B)-C(48B)	121.1(4)
N(3)-C(50)-C(51)	177.1(9)
C(1)-N(1)-C(2)	126.5(3)
C(1)-N(2)-C(8)	126.6(3)
C(26A)-P(1)-C(20A)	102.36(14)
C(26A)-P(1)-C(14A)	101.13(15)
C(20A)-P(1)-C(14A)	106.00(15
C(32B)-P(2)-C(38B)	101.68(15)
C(32B)-P(2)-C(44B)	103.24(16)
C(38B)-P(2)-C(44B)	106.10(15)

Table 15 Hydrogen bonds for [Ag(PPh_3)$_2$(dptu)Cl]·CH_3CN [Å and °].

D—H…A	d(D—H)	d(H…A)	d(D…A)	<(DHA)
N(1)—H(1)...Cl(1)	0.81(4)	2.47(4)	3.252(3)	162(4)
N(2)—H...N(3)#1	0.72(4)	2.40(4)	3.053(7)	153(4)

Symmetry transformations used to generate equivalent atoms: #1 x-1/2, -y+1/2, -z.

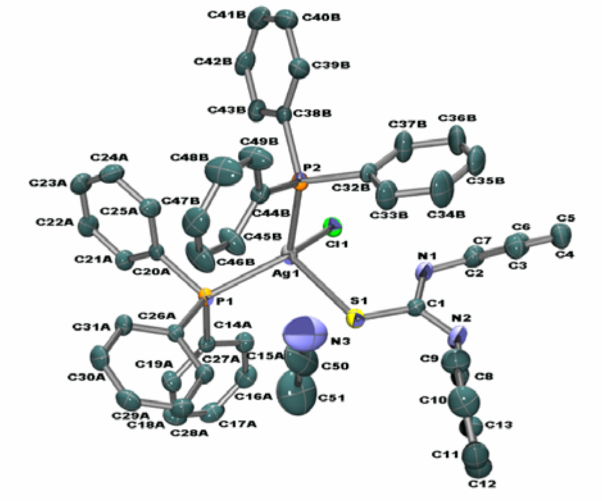


Fig. 63 The structure of [Ag(PPh_3)$_2$(dptu)Cl]·CH_3CN.

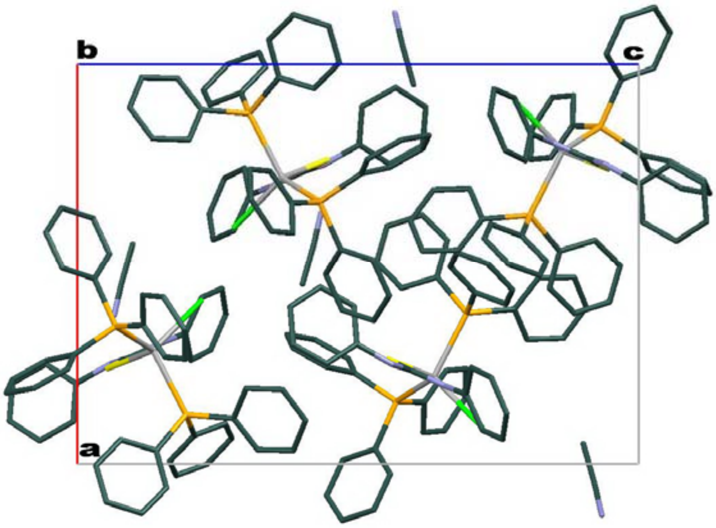


Fig. 64 Unit cell contents of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ plotted down *b* axis.

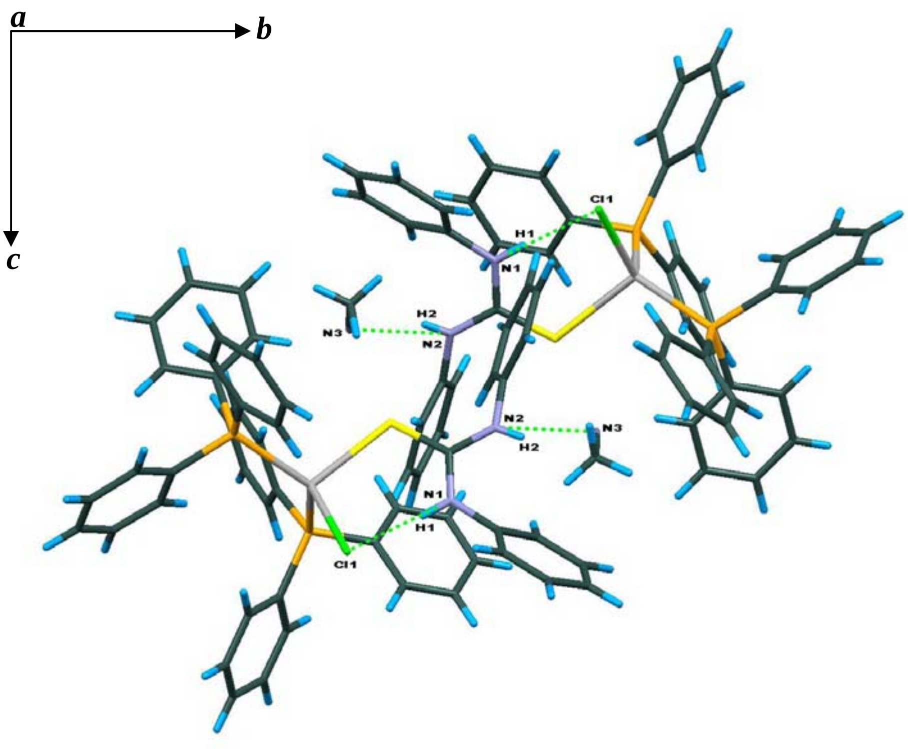


Fig. 65 Hydrogen bonds of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ plotted down *a* axis.

Table 16 Crystal data and structure refinement for $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$.

Empirical formula	$AgBrC_{51}H_{45}N_3P_2S$
Formula weight	981.68
Temperature	566(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 14.0030(6) Å
	b = 16.7462(7) Å
	c = 19.8196(8) Å
Z	4
Volume	4647.6(3) Å^3
Calculated density	1.403 g/cm^3
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0425, $wR2$ = 0.0661
R indices (all data)	$R1$ = 0.0639, $wR2$ = 0.0717
$F(000)$	2000
Reflections collected	48090
Unique	11237
R(int)	0.0645

Table 17 Bond lengths [Å] and angles [°] for $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$.

Br(1)-Ag(1)	2.6809(4)
S(1)-Ag(1)	2.6412(10)
P(1)-Ag(1)	2.4818(9)
P(2)-Ag(1)	2.5203(8)
C(1)-N(2)	1.335(4)
C(1)-N(1)	1.336(5)
C(1)-S(1)	1.687(4)
C(2)-C(7)	1.349(6)
C(2)-C(3)	1.358(5)

Table 17 (continued)

C(2)-N(1)	1.425(5)
C(3)-C(4)	1.368(6)
C(4)-C(5)	1.337(7)
C(5)-C(6)	1.360(7)
C(6)-C(7)	1.402(6)
C(8)-C(13)	1.363(5)
C(8)-C(9)	1.379(5)
C(8)-N(2)	1.425(5)
C(9)-C(10)	1.378(5)
C(10)-C(11)	1.355(6)
C(11)-C(12)	1.364(6)
C(12)-C(13)	1.381(5)
C(14A)-C(19A)	1.386(5)
C(14A)-C(15A)	1.388(5)
C(14A)-P(1)	1.826(3)
C(15A)-C(16A)	1.388(5)
C(16A)-C(17A)	1.372(6)
C(17A)-C(18A)	1.372(6)
C(18A)-C(19A)	1.377(5)
C(20A)-C(21A)	1.389(5)
C(20A)-C(25A)	1.400(4)
C(20A)-P(1)	1.823(3)
C(21A)-C(22A)	1.383(5)
C(22A)-C(23A)	1.369(5)
C(23A)-C(24A)	1.371(5)
C(24A)-C(25A)	1.371(5)
C(26A)-C(31A)	1.379(5)
C(26A)-C(27A)	1.385(5)
C(26A)-P(1)	1.828(3)
C(27A)-C(28A)	1.390(5)

Table 17 (continued)

C(28A)-C(29A)	1.360(6)
C(29A)-C(30A)	1.368(6)
C(30A)-C(31A)	1.383(5)
C(32B)-C(37B)	1.341(5)
C(32B)-C(33B)	1.365(5)
C(32B)-P(2)	1.837(3)
C(33B)-C(34B)	1.385(6)
C(34B)-C(35B)	1.340(6)
C(35B)-C(36B)	1.320(6)
C(36B)-C(37B)	1.389(6)
C(38B)-C(43B)	1.375(5)
C(38B)-C(39B)	1.380(5)
C(38B)-P(2)	1.836(4)
C(39B)-C(40B)	1.380(5)
C(40B)-C(41B)	1.360(6)
C(41B)-C(42B)	1.360(6)
C(42B)-C(43B)	1.392(5)
C(46B)-C(47B)	1.346(7)
C(47B)-C(48B)	1.349(7)
C(48B)-C(49B)	1.393(6)
C(50)-N(3)	1.097(8)
C(50)-C(51)	1.441(9)
C(44B)-C(45B)	1.356(5)
C(44B)-C(49B)	1.363(5)
C(44B)-P(2)	1.825(3)
C(45B)-C(46B)	1.370(6)
P(1)-Ag(1)-P(2)	122.73(3)
P(1)-Ag(1)-S(1)	110.90(3)
P(2)-Ag(1)-S(1)	94.97(3)
P(1)-Ag(1)-Br(1)	110.95(2)

Table 17 (continued)

P(2)-Ag(1)-Br(1)	107.19(2)
S(1)-Ag(1)-Br(1)	108.52(2)
C(14A)-P(1)-Ag(1)	117.33(12)
C(20A)-P(1)-Ag(1)	116.08(10)
C(26A)-P(1)-Ag(1)	112.95(11)
C(32B)-P(2)-Ag(1)	110.50(12)
C(38B)-P(2)-Ag(1)	119.41(12)
C(44B)-P(2)-Ag(1)	114.49(11)
C(1)-S(1)-Ag(1)	110.48(13)
N(2)-C(1)-N(1)	117.2(3)
N(2)-C(1)-S(1)	121.9(3)
N(1)-C(1)-S(1)	120.9(3)
C(7)-C(2)-C(3)	120.1(4)
C(7)-C(2)-N(1)	120.4(4)
C(3)-C(2)-N(1)	119.4(4)
C(2)-C(3)-C(4)	120.4(5)
C(5)-C(4)-C(3)	120.6(5)
C(4)-C(5)-C(6)	120.0(5)
C(5)-C(6)-C(7)	119.8(5)
C(2)-C(7)-C(6)	119.2(5)
C(13)-C(8)-C(9)	118.7(4)
C(13)-C(8)-N(2)	122.6(4)
C(9)-C(8)-N(2)	118.7(4)
C(10)-C(9)-C(8)	120.0(4)
C(11)-C(10)-C(9)	121.1(4)
C(10)-C(11)-C(12)	118.9(4)
C(11)-C(12)-C(13)	120.6(4)
C(8)-C(13)-C(12)	120.6(4)
C(19A)-C(14A)-C(15A)	118.5(3)
C(19A)-C(14A)-P(1)	122.5(3)

Table 17 (continued)

C(15A)-C(14A)-P(1)	118.9(3)
C(16A)-C(15A)-C(14A)	120.3(4)
C(17A)-C(16A)-C(15A)	120.2(4)
C(18A)-C(17A)-C(16A)	119.9(4)
C(17A)-C(18A)-C(19A)	120.3(4)
C(18A)-C(19A)-C(14A)	120.7(4)
C(21A)-C(20A)-C(25A)	117.9(3)
C(21A)-C(20A)-P(1)	124.5(3)
C(25A)-C(20A)-P(1)	117.5(2)
C(22A)-C(21A)-C(20A)	120.5(3)
C(23A)-C(22A)-C(21A)	120.4(4)
C(22A)-C(23A)-C(24A)	120.1(3)
C(25A)-C(24A)-C(23A)	120.2(3)
C(24A)-C(25A)-C(20A)	121.0(3)
C(31A)-C(26A)-C(27A)	118.5(3)
C(31A)-C(26A)-P(1)	124.0(3)
C(27A)-C(26A)-P(1)	117.4(3)
C(26A)-C(27A)-C(28A)	120.4(4)
C(29A)-C(28A)-C(27A)	120.1(4)
C(28A)-C(29A)-C(30A)	120.3(4)
C(29A)-C(30A)-C(31A)	120.1(4)
C(26A)-C(31A)-C(30A)	120.7(4)
C(37B)-C(32B)-C(33B)	117.0(4)
C(37B)-C(32B)-P(2)	117.9(3)
C(33B)-C(32B)-P(2)	125.1(3)
C(32B)-C(33B)-C(34B)	121.2(4)
C(35B)-C(34B)-C(33B)	120.1(4)
C(36B)-C(35B)-C(34B)	119.4(4)
C(35B)-C(36B)-C(37B)	120.8(5)
C(32B)-C(37B)-C(36B)	121.5(4)

Table 17 (continued)

C(43B)-C(38B)-C(39B)	118.6(3)
C(43B)-C(38B)-P(2)	118.0(3)
C(39B)-C(38B)-P(2)	123.4(3)
C(40B)-C(39B)-C(38B)	120.3(4)
C(41B)-C(40B)-C(39B)	120.6(4)
C(40B)-C(41B)-C(42B)	120.1(4)
C(41B)-C(42B)-C(43B)	119.8(4)
C(38B)-C(43B)-C(42B)	120.6(4)
C(45B)-C(44B)-C(49B)	118.0(4)
C(45B)-C(44B)-P(2)	123.0(3)
C(49B)-C(44B)-P(2)	118.8(3)
C(44B)-C(45B)-C(46B)	121.4(5)
C(47B)-C(46B)-C(45B)	120.7(5)
C(46B)-C(47B)-C(48B)	119.2(4)
C(47B)-C(48B)-C(49B)	120.3(5)
C(44B)-C(49B)-C(48B)	120.4(4)
N(3)-C(50)-C(51)	176.7(10)
C(1)-N(1)-C(2)	127.7(4)
C(1)-N(2)-C(8)	127.3(3)
C(20A)-P(1)-C(14A)	100.81(15)
C(20A)-P(1)-C(26A)	101.94(15)
C(14A)-P(1)-C(26A)	105.86(15)
C(44B)-P(2)-C(38B)	101.41(15)
C(44B)-P(2)-C(32B)	103.21(16)
C(38B)-P(2)-C(32B)	106.22(16)

Table 18 Hydrogen bonds for [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(3)#1	0.69(3)	2.40(3)	3.057(7)	163(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z

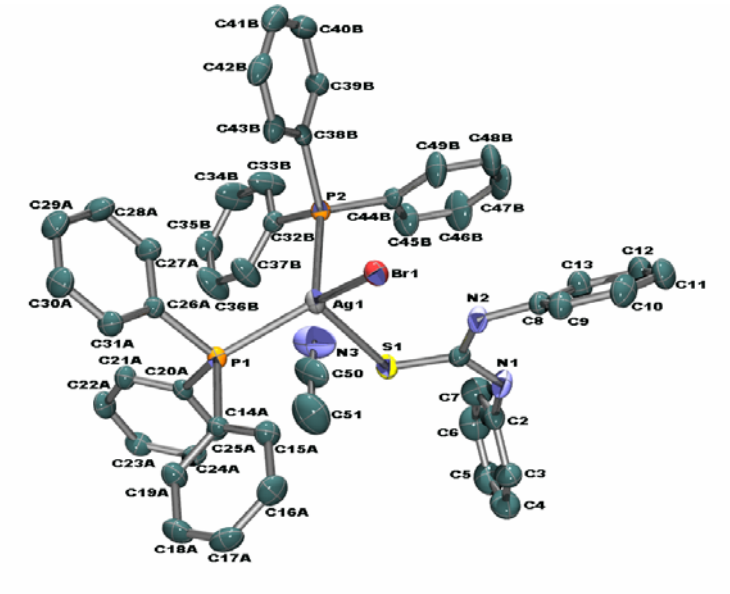


Fig. 66 The structure of [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN.

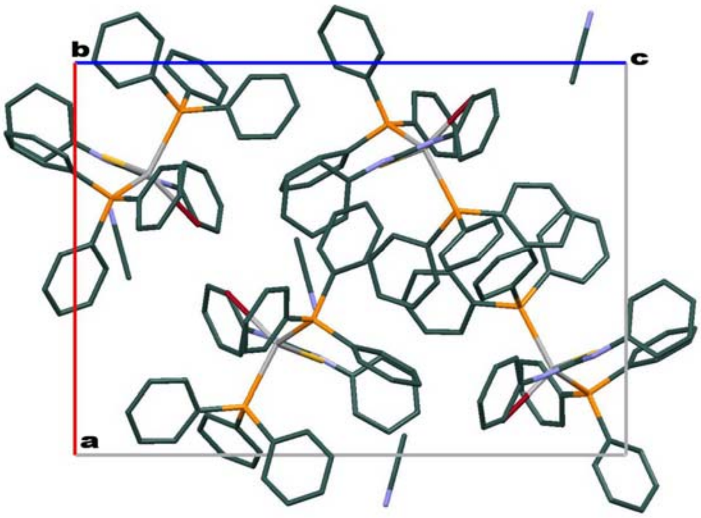


Fig. 67 Unit cell contents of [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN plotted down *b* axis.

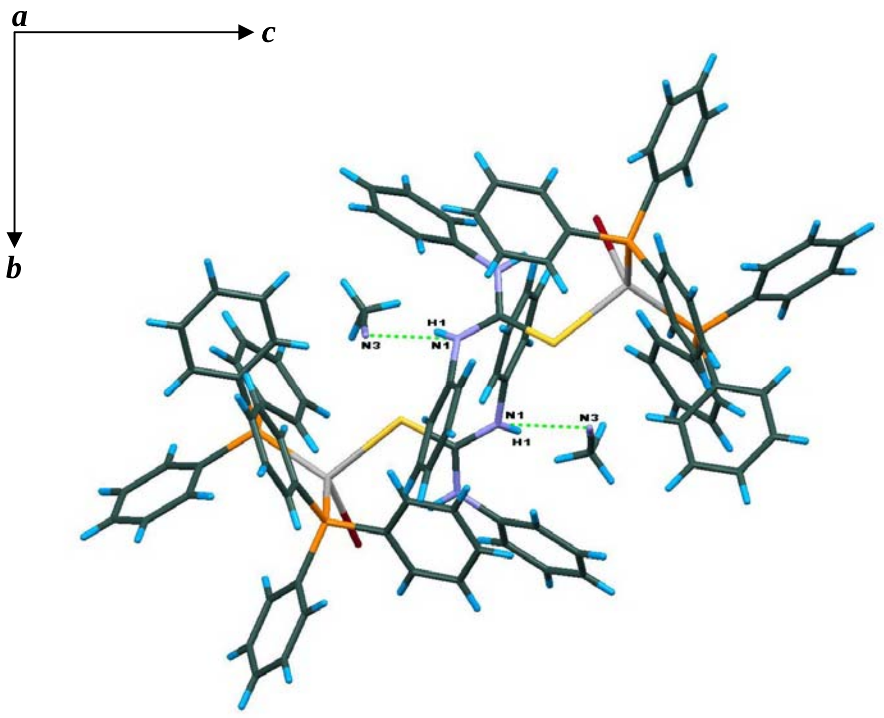


Fig. 68 Hydrogen bonds of [Ag(PPh_3)$_2$(dptu)Br]·CH_3CN plotted down *a* axis.

CHAPTER 4

DISCUSSION

4.1 Preparation of complexes

The synthesis of silver(I) complexes containing triphenylphosphine and *N,N'*-diphenylthiourea by varying mole ratio of reactants, solvents and temperature of reaction yielded four complexes. Two of them are known complexes, $[Ag(PPh_3)(py)I]_2$ (Gotsis *et al.*, 1989 and Effendy *et al.*, 1991) and $[Ag(PPh_3)_3Cl]$ (Cassel *et al.*, 1981). However the new complexes $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl (1), Br (2)) will be discussed.

The suitable condition for prepare silver(I) complexes containing triphenylphosphine (PPh_3) and *N,N'*-diphenylthiourea (dptu) is the reflux 1:2:1 mole ratio of AgX:PPh_3:dptu in acetonitrile at 70 °C for 7.5 h.

The $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ complex appearance is block colorless, 59.61 % yielded, melting point 123-125 °C while the $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ complex appearance is prism colorless, 72.69 % yielded, melting point 121-123 °C and soluble in acetone, chloroform, dichloromethane and DMSO.

4.2 Analytical and spectroscopic characterization

Elemental analysis reveals relative amounts of C, H, N and S between calculated and experimental data are not significantly different.

XRF spectra of complexes with the Kα spectrum of Ag and X (X = Cl, Br), P and S are represented for silver(I) halide, triphenylphosphine and *N,N'*-diphenylthiourea respectively.

The structures of complexes have been determined by using IR and NMR spectroscopies and X-ray diffraction.

The solid state FT-IR spectra of complexes recorded in the range 4000-400 cm^{-1}. The IR spectra of the studied complexes confirmed the presence of the triphenylphosphine and thiourea ligands via their ν(N-H), ν(C-H), ν(C=C), δ(N-H), ν(C-N), δ(C-H) and ν(C=S) vibration modes which assign by referred to related complexes (Cox *et al*., 2000, Ferrari *et al*., 2007, Kalzoglou *et al*., 2007, Lobana *et al*., 2008, Mcfarlane *et al* ., 1998) as shown in Table 19. Relative absorption frequencies of complexes and free dptu ligand are investigated as shown in Table 20. The useful informations regarding the mode of thione ligand coordination are from the disappearance of the S-H stretching band around 2560 cm^{-1} (Aslanidis *et al*., 2005), the presence of ν(N-H) band in the 3137-3282 cm^{-1} region and from the ν(C=S) vibration which undergoes downward shift (by 10-15 cm^{-1}) upon coordination, indicating M-S bond formation. However, all the expected strong phosphine bands, which remain practically unshifted upon coordination.

Relative absorption frequencies of complexes and dptu indicating M-S bond formation are described by peaks as follows.

The ν(N-H) peak is shifted to low energy region, 71 cm^{-1} in (1) and 56 cm^{-1} in (2), due to hydrogen bonding interaction in the complexes.

compound	ν(N-H) (cm^{-1})
dptu	3208
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (1)	3137
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (2)	3152

Table 19 IR spectra of related complexes.

peaks	absorption frequencies (cm^{-1}) of compounds			
	$[Ag(PPh_3)LBr]$ (Cox *et al.*, 2000)	$[AgBr(dppbz)(py2SH)]$ (Kalzoglou *et al.*, 2007)	$[Ag(Phmepytu)(PPh_3)_2]NO_3$ (Ferrari *et al.*, 2007)	$[AgCl(\eta^1\text{-S-Hpytsc})(PPh_3)_2]\cdot CH_3CN$ (Lobana *et al.*, 2008)
ν(N-H)	3160	3155	-	3125
$\nu(C\text{-}H)_{Ph}$	3050	3047	3052	3068, 3051
$\nu(C{=}C)_{Ph}$	1510	1614	1590, 1555	1630, 1537
ν(C-N)	1320	1436	1477	1070, 1029
δ(N-H)+ $\delta(C\text{-}H)_{Ph}$	-	1095-986	745, 695	-
ν(C=S)	1000, 750	1135, 751	1140	822

Remark : - mean not assign

Table 20 IR spectra of free dptu ligand and complexes.

peaks	absorption frequencies (cm^{-1}) of compounds		
	dptu	$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$
ν(N-H)	3208	3282, 3137	3279, 3152
ν(C-H)$_{Ph}$	3035	3053	3053
ν(C=C)$_{Ph}$	1599, 1590	1590, 1560	1590, 1560
δ(N-H)	1541	1533	1531
ν(C-N) + δ(C-H)$_{Ph}$	1494 - 1339	1509 - 1362	1507 - 1370
ν(C=S)	1242, 757	1225, 742	1224, 742

The ν(C-N) peak is shifted to high energy region, 15 cm^{-1} in (1) and 13 cm^{-1} in (2), due to complex formation, increasing double bond character of C-N in complexes.

compound	ν(C-N) (cm^{-1})
dptu	1494
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (1)	1509
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (2)	1507

The two peaks of ν(C=S) are shifted to low energy region, 17 and 15 cm^{-1} in (1) and 18 and 15 cm^{-1} in (2), in complex formation due to a significant weakening of the C=S double bond.

compound	ν(C=S) (cm^{-1})
dptu	1242, 757
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ (1)	1225, 742
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ (2)	1224, 742

The observed NMR spectra of complexes are as follows: $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$; ^1H NMR data (δ, $CDCl_3$): CH_3CN, 1.96(s); $-CH_{Ph}$, 7.18-7.36(m); -NH, 9.44(br, s) ppm. ^{13}C NMR (δ, $CDCl_3$): CH_3CN, 1.64(s); C_{Ph}, 125.24(s, C_p, PPh_3); 126.53(s, C_p, dptu); 128.55(d, C_m, PPh_3); 129.16(s, C_i, PPh_3); 129.62(d, C_m, dptu); 133.23(d, C_o, dptu); 133.89(d, C_o, PPh_3); 137.24(s, C_i, dptu); C=S, 178.04(s) ppm and $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$; ^1H NMR data (δ, $CDCl_3$): CH_3CN, 1.97(s); $-CH_{Ph}$, 7.20-7.38(m); -NH, 8.79(br, s) ppm. ^{13}C NMR (δ, $CDCl_3$): CH_3CN, 1.64(s); C_{Ph}, 125.40(s, C_p, PPh_3); 126.95(s, C_p, dptu); 128.59(d, C_m, PPh_3); 129.40(s, C_i, PPh_3); 129.66(d, C_m, dptu); 133.28(d, C_o, dptu); 133.94(d, C_o, PPh_3); 136.91(s, C_i, dptu); C=S, 178.13(s) ppm.

The ^1H NMR spectra of the complexes, recorded in deuterated chloroform, are dominated by the presence of complex multiplets in the 7.18-7.38 ppm region due to phenyl resonances (Kalzoglou *et al.*, 2007), as well as, in the case of complexes 1 and 2, signals attributable to the aromatic proton of *N,N'*-

diphenylthiourea unit. Upon coordination, the multiplets assigned undergo splitting due to a small upfield shift of the ortho-positioned protons. The relative chemical shifts of complexes and free ligands are shown in Table 21.

Table 21 The relative chemical shift of free ligands and complexes

compounds	chemical shifts (ppm) of NMR spectra			
	^{1}H NMR		^{13}C NMR	
	-CH$_{Ph}$	-NH	C$_{Ph}$	C=S
PPh$_3$	7.24 - 7.38	-	128.43 - 137.16	-
dptu	7.24 - 7.41	8.14	125.21 - 137.04	179.69
[Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN	7.18 - 7.36	9.44	125.24 - 137.24	178.04
[Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN	7.20 - 7.38	8.79	125.40 - 136.91	178.13

Relative chemical shifts of complexes and ligands indicating Ag-S bond formation are described by peaks as follows.

The small upfield shift of -CH$_{Ph}$ proton signals due to ortho-positioned protons upon coordination.

compound	chemical shift (ppm)
PPh$_3$	7.24-7.38
dptu	7.24-7.41
[Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN	7.18-7.36
[Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN	7.20-7.38

The downfield shift of -NH proton signals due to hydrogen bonding interaction in the complexes.

compound	chemical shift (ppm)
dptu	8.14
[Ag(PPh$_3$)$_2$(dptu)Cl]·CH$_3$CN	9.44
[Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN	8.79

The small upfield shift of C_{Ph} carbon signals due to shielding effected upon coordination.

compound	chemical shift (ppm)
PPh_3	128.43-137.16
dptu	125.21-137.04
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	125.24-137.24
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$	125.40-136.91

The upfield shift of C=S carbon signals due to shielding effected upon coordination.

compound	chemical shift (ppm)
dptu	179.69
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	178.04
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$	178.13

4.3 X-ray diffraction, crystal structure determination.

X-ray diffraction studies show the general molecular formula of complexes is $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br). Details regarding the crystal data collection and refinement for the complexes are reported in chapter 3. Complexes 1 and 2 are isomorphous and crystallized in orthorhombic system space group $P2_12_12_1$ with four monomer units in the unit cell as well as four lattice CH_3CN molecules. The solvent molecule of CH_3CN appear in the crystal lattice was confirmed by the elemental analysis. The silver atom is tetrahedrally coordinated by two phosphorous atoms from two triphenylphosphine molecules, one sulfur atom from *N,N'*-diphenylthiourea molecule and one halogen atom.

All the bond lengths around silver(I) atom in this $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br) complexes compared with $[Ag(ONO_2)(PPh_3)_2(\eta^1\text{-S-HL})]$ (Lobana *et al.*, 2008) and $[Ag(dppb)(py2SH)]_2(NO_3)\cdot H_2O$ (Aslanidis *et al.*, 2004) are shown in Table 22.

Table 22 A comparison of important bond lengths (Å) for studied complexes with other related complexes.

complexes	bond lengths (Å)			
	Ag-X	Ag-P(1)	Ag-P(2)	Ag-S
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	2.5736(9)	2.4793(8)	2.5245(8)	2.6432(9)
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$	2.6809(4)	2.4818(9)	2.5203(8)	2.6412(1)
$[Ag(ONO_2)(PPh_3)_2(\eta^1\text{-S-HL})]$	2.557(3)	2.468(9)	2.495(6)	2.562(7)
$[Ag(dppb)(py2SH)]_2(NO_3)\cdot H_2O$	-	2.514(2)	2.480(1)	2.638(2) 2.699(2)

The Ag—P bond distances 2.4793(8) and 2.524598) Å in (1), 2.4818(9) and 2.5203(8) Å in (2), lie within the limits of 2.45-2.60 Å found for a number of tetracoordinated silver complexes with two or more triphenylphosphine ligands, i.e. monomeric $AgCl(PPh_3)_3$ (Cassel, 1981), $[Ag(PPh_3)_2(bzoxtH)_2]NO_3$ (Mcfarlane *et al.*, 1998).

The bond angles around silver(I) atom observed in the ranges 94.01(3)-122.73(3)° of both complexes are closed to 95.84-123.88° of the $[Ag(PPh_3)_2(bzoxtH)_2]NO_3$ (McFarlane *et al.*, 1998) and 94.01-129.28° of the $[Ag(PPh_3)_3(tsac)]$ (Dennehy *et al.*, 2007). The deviation from perfect tetrahedral coordination is illustrated by the P(1)-Ag(1)-P(2) angles of 122.27(3)° in (1) and 122.73(3)° in (2), can be accounted for the steric hindrance induced by the two phosphine molecules, consequently compressing the P(2)-Ag(1)-S(1) to 94.01(3) in (1) and 94.97(3)° in (2) respectively.

In addition, the complex molecules exhibit intramolecular NH···X and intermolecular NH···N hydrogen bonds as shown in the Table 24. The presence hydrogen bonds effects to the distortion of silver(I) atom geometry and the greater stability of complexes at room temperature.

The existence of a hydrogen bond between the NH group of the ligand and an nitrogen atom of the solvate acetonitrile [N(2)···N(3), 3.053(7) Å of (1) and N(1)···N(3), 3.057(7) Å of (2)] contributes to the angular distortion about the silver atom (Ghassemzadeh *et al.*, 2004).

Table 23 The hydrogen bonds contribute to the angular distortion about the silver atom.

complexes	hydrogen bonds (Å)		some bond angles (°) of silver(I) atom geometry	
	NH···X	NH···N	P(1)-Ag(1)-X(1)	X(1)-Ag(1)-S(1)
$[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$	3.252(3)	3.053(7)	113.07(3)	106.14(3)
$[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$	-	3.057(7)	110.95(2)	108.52(2)

The angular distortion about the silver atom of complexes, especially to the P(1)-Ag(1)-X(1) and X(1)-Ag(1)-S(1) which contain halogen atom, accepter atom of the hydrogen bond. The strong NH···Cl and NH···N hydrogen bonds of $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ effected to P(1)-Ag(1)-Cl(1) and Cl(1)-Ag(1)-S(1) than the weak hydrogen bonds of $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ to P(1)-Ag(1)-Br(1) and Br(1)-Ag(1)-S(1) due to the inductive of stronger hydrogen bond containing high electronegative chlorine than bromine.

The IR and NMR spectroscopies and X-ray data of determining structure are supported with each other that can conclude the accurate structure.

CHAPTER 5

CONCLUSIONS

The complexes of AgX (X = Cl, Br) with PPh_3 and dptu in the mole ratio 1:2:1 have been synthesized and characterized.

The $[Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$ complex is colorless block crystals, 59.61 % yield, melting point 123-125 °C while the $[Ag(PPh_3)_2(dptu)Br]\cdot CH_3CN$ complex is prism-shaped colorless, 72.69 % yield, melting point 121-123 °C and soluble in acetone, chloroform, dichloromethane and DMSO.

X-ray diffraction studies show the general molecular formula of complexes is $[Ag(PPh_3)_2(dptu)X]\cdot CH_3CN$ (X = Cl, Br). Both complexes are isomorphous crystallize in orthorhombic system, space group $P2_12_12_1$. The silver atom is tetrahedrally coordinated by two phosphorous atoms from two triphenylphosphine molecules, one sulfur atom from *N*,*N'*-diphenylthiourea molecule and one halogen atom. In addition the complex molecules exhibit intramolecular NH···X and intermolecular NH···N hydrogen bonding interactions. The hydrogen bonding and the sterically bulky PPh_3 ligand affects the distortion of Ag(I) atom geometry and the stability of complexes.

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APPENDIX

Table 24 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ag(PPh_3)(py)I$]_2$.

Atom	x	y	z	U(eq)
C(1)	5350(1)	1672(3)	4344(3)	70(1)
C(2)	5629(2)	1662(3)	3383(4)	91(1)
C(3)	5733(2)	2497(4)	2882(4)	97(2)
C(4)	5570(2)	3285(4)	3339(4)	92(1)
C(5)	5297(1)	3229(3)	4289(4)	75(1)
C(6)	3424(1)	2752(2)	7124(3)	47(1)
C(7)	3623(1)	2552(2)	8269(3)	61(1)
C(8)	3355(2)	2756(3)	9219(3)	76(1)
C(9)	2900(2)	3162(3)	9053(4)	75(1)
C(10)	2703(1)	3374(2)	7932(4)	68(1)
C(11)	2964(1)	3170(2)	6964(3)	57(1)
C(12)	3525(1)	1366(2)	5338(3)	45(1)
C(13)	3058(1)	1055(2)	5554(3)	59(1)
C(14)	2871(1)	256(2)	5034(4)	75(1)
C(15)	3144(2)	-239(3)	4301(4)	86(1)
C(16)	3612(2)	48(3)	4088(4)	84(1)
C(17)	3802(1)	843(2)	4608(3)	66(1)
C(18)	3588(1)	3262(2)	4724(3)	48(1)
C(19)	3833(1)	4103(2)	4711(4)	71(1)
C(20)	3714(2)	4725(3)	3799(5)	89(1)
C(21)	3359(2)	4514(3)	2911(4)	89(1)
C(22)	3117(1)	3695(3)	2926(3)	77(1)
C(23)	3227(1)	3075(3)	3826(3)	59(1)
N(1)	5184(1)	2437(2)	4793(3)	60(1)
P(1)	3789(1)	2448(1)	5897(1)	44(1)

Table 24 (continued)

Atom	x	y	z	U(eq)
Ag(1)	4682(1)	2423(1)	6373(1)	56(1)
I(1)	5000	745(1)	7500	60(1)
I(2)	5000	4120(1)	7500	66(1)

Table 25 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [$Ag(PPh_3)_3Cl$].

Atom	x	y	z	U(eq)
C(1)	2749(3)	563(1)	312(2)	39(1)
C(2)	4102(3)	538(1)	303(2)	54(1)
C(3)	4754(4)	487(1)	-594(3)	75(1)
C(4)	4082(4)	464(1)	-1471(3)	77(1)
C(5)	2748(4)	492(1)	-1477(2)	71(1)
C(6)	2079(3)	541(1)	-583(2)	53(1)
C(7)	1973(2)	100(1)	1964(2)	40(1)
C(8)	1571(3)	-212(1)	1354(2)	54(1)
C(9)	1601(4)	-595(1)	1701(3)	70(1)
C(10)	2036(4)	-674(1)	2651(3)	74(1)
C(11)	2462(4)	-372(1)	3252(3)	73(1)
C(12)	2435(3)	16(1)	2913(2)	55(1)
C(13)	266(2)	735(1)	1263(2)	39(1)
C(14)	-786(3)	492(1)	1487(2)	51(1)
C(15)	-2056(3)	624(1)	1367(3)	65(1)
C(16)	-2290(3)	997(1)	1030(3)	71(1)
C(17)	-1273(3)	1244(1)	790(3)	75(1)
C(18)	5(3)	1111(1)	913(3)	61(1)
C(19)	2720(3)	1856(1)	693(2)	42(1)
C(20)	3155(3)	1577(1)	26(2)	57(1)

Table 25 (continued)

Atom	x	y	z	U(eq)
C(21)	2789(5)	1585(1)	-962(3)	80(1)
C(22)	2010(5)	1876(2)	-1305(3)	102(2)
C(23)	1600(6)	2161(2)	-674(3)	135(2)
C(24)	1928(4)	2149(1)	341(3)	96(2)
C(25)	4917(2)	1997(1)	1928(2)	40(1)
C(26)	5261(3)	2313(1)	1310(2)	51(1)
C(27)	6521(3)	2452(1)	1284(2)	59(1)
C(28)	7461(3)	2280(1)	1869(3)	69(1)
C(29)	7145(3)	1969(1)	2479(3)	77(1)
C(30)	5880(3)	1828(1)	2509(2)	56(1)
C(31)	2356(3)	2193(1)	2652(2)	41(1)
C(32)	2905(3)	2552(1)	2933(2)	52(1)
C(33)	2190(4)	2824(1)	3490(2)	69(1)
C(34)	942(4)	2738(1)	3766(2)	75(1)
C(35)	391(3)	2383(1)	3503(2)	72(1)
C(36)	1087(3)	2110(1)	2956(2)	55(1)
C(37)	3246(2)	1418(1)	5302(2)	35(1)
C(38)	3634(3)	1775(1)	4920(2)	50(1)
C(39)	4478(3)	2019(1)	5431(2)	62(1)
C(40)	4978(3)	1911(1)	6329(2)	55(1)
C(41)	4609(4)	1560(1)	6727(2)	68(1)
C(42)	3737(3)	1311(1)	6232(2)	62(1)
C(43)	531(2)	1277(1)	4739(2)	36(1)
C(44)	149(3)	1502(1)	5547(2)	53(1)
C(45)	-1165(4)	1596(1)	5677(3)	72(1)
C(46)	-2083(3)	1458(1)	5018(3)	72(1)
C(47)	-1732(3)	1233(1)	4214(3)	62(1)
C(48)	-420(3)	1149(1)	4067(2)	47(1)

Table 25 (continued)

Atom	x	y	z	U(eq)
C(49)	2220(2)	632(1)	5181(2)	34(1)
C(50)	1113(3)	456(1)	5574(2)	44(1)
C(51)	1193(3)	90(1)	6042(2)	53(1)
C(52)	2371(3)	-99(1)	6148(2)	51(1)
C(53)	3484(3)	74(1)	5767(2)	53(1)
C(54)	3416(3)	433(1)	5275(2)	46(1)
P(1)	1974(1)	614(1)	1535(1)	35(1)
P(2)	3255(1)	1805(1)	1991(1)	36(1)
P(3)	2198(1)	1104(1)	4523(1)	32(1)
Cl(1)	5243(1)	810(1)	3058(1)	55(1)
Ag(1)	2994(1)	1109(1)	2713(1)	35(1)

Table 26 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [$Ag(PPh_3)_2(dptu)Cl]\cdot CH_3CN$.

Atom	x	y	z	U(eq)
C(1)	7346(3)	2139(2)	924(2)	43(1)
C(2)	6735(3)	2873(2)	1926(2)	46(1)
C(3)	7406(3)	3469(3)	2022(2)	62(1)
C(4)	7151(4)	4155(2)	2376(2)	70(1)
C(5)	6259(4)	4237(3)	2647(2)	74(1)
C(6)	5614(4)	3632(3)	2576(2)	71(1)
C(7)	5844(3)	2952(3)	2215(2)	58(1)
C(8)	7990(3)	2957(2)	-21(2)	49(1)
C(9)	8944(4)	2816(3)	-72(3)	74(1)
C(10)	9421(4)	3010(4)	-671(3)	88(2)
C(11)	8928(5)	3333(3)	-1207(3)	87(2)
C(12)	7977(5)	3465(3)	-1152(2)	84(2)

Table 26 (continued)

Atom	x	y	z	U(eq)
C(13)	7505(4)	3284(3)	-560(2)	65(1)
C(14A)	5371(2)	-997(2)	306(2)	39(1)
C(15A)	4745(3)	-443(2)	575(2)	50(1)
C(16A)	3849(3)	-339(3)	283(2)	65(1)
C(17A)	3583(3)	-772(3)	-280(2)	65(1)
C(18A)	4206(3)	-1317(3)	-557(2)	63(1)
C(19A)	5097(3)	-1435(2)	-266(2)	54(1)
C(20A)	6536(2)	-2028(2)	1179(2)	37(1)
C(21A)	5782(3)	-2564(2)	1163(2)	50(1)
C(22A)	5829(4)	-3269(3)	1537(2)	63(1)
C(23A)	6629(4)	-3445(3)	1906(2)	68(1)
C(24A)	7377(4)	-2921(3)	1925(2)	69(1)
C(25A)	7332(3)	-2213(2)	1567(2)	54(1)
C(26A)	7269(2)	-1385(2)	-60(2)	36(1)
C(27A)	7423(3)	-804(2)	-559(2)	46(1)
C(28A)	7897(3)	-990(2)	-1155(2)	52(1)
C(29A)	8230(3)	-1757(3)	-1261(2)	55(1)
C(30A)	8109(3)	-2328(2)	-772(2)	55(1)
C(31A)	7630(3)	-2148(2)	-172(2)	45(1)
C(32B)	9289(2)	1026(2)	2085(2)	40(1)
C(33B)	9935(4)	1357(3)	1645(3)	71(1)
C(34B)	10289(5)	2115(3)	1763(4)	98(2)
C(35B)	10005(4)	2535(3)	2316(3)	81(2)
C(36B)	9356(5)	2221(3)	2751(3)	84(2)
C(37B)	8995(4)	1462(2)	2634(3)	74(1)
C(38B)	8866(3)	-415(2)	2786(2)	40(1)
C(39B)	9646(3)	-304(2)	3212(2)	56(1)
C(40B)	9667(4)	-656(3)	3851(2)	70(1)

Table 26 (continued)

Atom	x	y	z	U(eq)
C(41B)	8919(4)	-1115(3)	4065(2)	72(1)
C(42B)	8142(4)	-1226(2)	3657(2)	64(1)
C(43B)	8112(3)	-876(2)	3010(2)	50(1)
C(44B)	9668(2)	-461(2)	1406(2)	42(1)
C(45B)	9397(3)	-719(3)	778(2)	68(1)
C(46B)	10042(4)	-1074(4)	333(3)	86(2)
C(47B)	10953(4)	-1176(3)	519(3)	73(1)
C(48B)	11238(4)	-938(4)	1146(3)	97(2)
C(49B)	10602(4)	-583(4)	1588(2)	83(2)
C(50)	10501(7)	642(5)	-786(4)	124(3)
C(51)	9498(6)	655(5)	-987(5)	161(4)
N(1)	6951(3)	2169(2)	1546(2)	49(1)
N(2)	7488(3)	2837(2)	606(2)	57(1)
N(3)	11280(6)	643(5)	-659(4)	159(3)
P(1)	6563(1)	-1100(1)	684(1)	35(1)
P(2)	8770(1)	39(1)	1938(1)	36(1)
S(1)	7614(1)	1263(1)	543(1)	51(1)
Cl(1)	5926(1)	602(1)	2203(1)	48(1)
Ag(1)	7163(1)	55(1)	1351(1)	43(1)

Table 27 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ag(PPh$_3$)$_2$(dptu)Br]·CH$_3$CN.

Atom	x	y	z	U(eq)
C(1)	2642(3)	7136(2)	906(2)	44(1)
C(2)	2005(3)	7951(2)	-36(2)	52(1)
C(3)	2493(3)	8261(2)	-567(2)	68(1)
C(4)	2029(5)	8441(3)	-1155(2)	88(2)

Table 27 (continued)

Atom	x	y	z	U(eq)
C(5)	1092(5)	8306(3)	-1218(3)	92(2)
C(6)	590(4)	7996(3)	-693(3)	96(2)
C(7)	1060(4)	7805(3)	-90(2)	81(1)
C(8)	3204(3)	7870(2)	1914(2)	48(1)
C(9)	4084(3)	7950(2)	2220(2)	55(1)
C(10)	4292(4)	8628(3)	2586(2)	70(1)
C(11)	3645(4)	9225(3)	2652(2)	74(1)
C(12)	2770(4)	9142(2)	2358(2)	71(1)
C(13)	2548(3)	8464(2)	1994(2)	62(1)
C(14A)	4628(2)	4002(2)	302(2)	38(1)
C(15A)	5257(3)	4560(2)	567(2)	50(1)
C(16A)	6148(3)	4673(2)	275(2)	65(1)
C(17A)	6409(3)	4239(3)	-282(2)	65(1)
C(18A)	5790(3)	3689(3)	-549(2)	65(1)
C(19A)	4907(3)	3569(2)	-261(2)	55(1)
C(20A)	2742(2)	3610(2)	-56(2)	36(1)
C(21A)	2381(2)	2848(2)	-165(2)	45(1)
C(22A)	1898(3)	2670(2)	-755(2)	54(1)
C(23A)	1784(3)	3239(2)	-1245(2)	55(1)
C(24A)	2117(3)	3999(2)	-1141(2)	51(1)
C(25A)	2587(2)	4187(2)	-556(2)	47(1)
C(26A)	3473(2)	2976(2)	1166(2)	37(1)
C(27A)	2682(3)	2799(2)	1559(2)	56(1)
C(28A)	2641(4)	2089(3)	1919(2)	71(1)
C(29A)	3385(4)	1567(3)	1897(2)	72(1)
C(30A)	4178(4)	1739(3)	1521(2)	67(1)
C(31A)	4222(3)	2442(2)	1156(2)	51(1)
C(32B)	332(2)	4535(2)	1397(2)	43(1)

Table 27 (Continued)

Atom	x	y	z	U(eq)
C(33B)	-598(3)	4413(4)	1575(2)	93(2)
C(34B)	-1236(3)	4054(4)	1136(3)	103(2)
C(35B)	-949(4)	3826(3)	520(3)	77(1)
C(36B)	-47(4)	3923(3)	345(3)	95(2)
C(37B)	597(3)	4286(3)	782(2)	72(1)
C(38B)	1136(3)	4581(2)	2765(2)	41(1)
C(39B)	363(3)	4695(2)	3187(2)	57(1)
C(40B)	349(4)	4351(3)	3819(2)	71(1)
C(41B)	1092(4)	3896(3)	4036(2)	74(1)
C(42B)	1865(3)	3783(2)	3632(2)	66(1)
C(43B)	1888(3)	4126(2)	2992(2)	51(1)
C(44B)	712(2)	6017(2)	2071(2)	42(1)
C(45B)	80(3)	6363(3)	1643(2)	77(1)
C(46B)	-282(4)	7109(3)	1765(3)	99(2)
C(47B)	0(4)	7530(3)	2308(3)	86(2)
C(48B)	647(4)	7209(3)	2734(3)	85(2)
C(49B)	1022(4)	6453(2)	2609(2)	74(1)
C(50)	-507(6)	5648(4)	-788(3)	121(3)
C(51)	487(5)	5657(4)	-976(4)	151(3)
N(1)	2486(3)	7827(2)	589(2)	59(1)
N(2)	3020(3)	7171(2)	1524(2)	51(1)
N(3)	-1262(5)	5678(4)	-641(3)	165(3)
P(1)	3443(1)	3902(1)	678(1)	36(1)
P(2)	1231(1)	5033(1)	1924(1)	38(1)
S(1)	2392(1)	6257(1)	529(1)	53(1)
Br(1)	4122(1)	5558(1)	2235(1)	47(1)
Ag(1)	2826(1)	5054(1)	1334(1)	43(1)