Copper(I) Halide Complexes with Triphenylphosphine and *N*,*N'*-Diphenylthiourea

Ladawan Duangmuengmai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemical Studies
Prince of Songkla University
2010

Thesis Title	Copper(I) Halide Complexes with Triphenylphosphine and *N,N’*-Diphenylthiourea
Author	Miss Ladawan Duangmuengmai
Major Program	Chemical Studies

Major Advisor:

……………………………………….
(Asst. Prof. Dr.Chaveng Pakawatchai)

Co-advisor:

……………………………………….
(Dr.Weena Aemaeg Tupchai)

Examining Committee:

…………………………..Chairperson
(Asst. Prof. Dr.Hirihattaya Phetmung)

……………………………………......
(Asst. Prof. Dr.Chaveng Pakawatchai)

…………………………………….....
(Dr.Weena Aemaeg Tupchai)

……………………………………......
(Asst. Prof. Dr.Cheawchan Utarapichart)

The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirement for the Master of Science Degree in Chemical Studies.

…..……………………………………......
(Assoc. Prof. Dr.Krerkchai Thongnoo)
Dean of Graduate School

ชื่อวิทยานิพนธ์ สารประกอบเชิงซ้อนของคอปเปอร์(I)เฮไลด์กับไตรฟีนิลฟอสฟีนและไดฟีนิลไธโอยูเรีย
ผู้เขียน นางสาวลดาวัลย์ ด้วงเมืองใหม่
สาขาวิชา เคมีศึกษา
ปีการศึกษา 2552

บทคัดย่อ

การศึกษาโครงสร้างผลึกสารประกอบเชิงซ้อนคอปเปอร์(I)เฮไลด์ กับลิแกนด์ไตรฟีนิลฟอสฟีน(PPh_3) และไดฟีนิลไธโอยูเรีย(dptu) คือ$[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$, $[Cu(PPh_3)_2(dptu)Br]\cdot H_2O$ และ $[Cu(PPh_3)_2(dptu)I]\cdot CH_3CN$ สารประกอบเหล่านี้เตรียมได้จากการทำปฏิกิริยาโดยตรงระหว่างเกลือคอปเปอร์(I)เฮไลด์ (CuX; X = Cl, Br, I) กับลิแกนด์ไดฟีนิลไธโอยูเรีย และไตรฟีนิลฟอสฟีนภายใต้สภาวะที่เหมาะ และทำการศึกษาวิเคราะห์โครงสร้าง โดยการวิเคราะห์ปริมาณธาตุที่เป็นองค์ประกอบ เอกซเรย์ฟลูออเรสเซนซ์สเปกโตรเมตรี นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโกปี และอินฟราเรดสเปกโตรสโกปี และหาโครงสร้างโดยใช้เทคนิคการเลี้ยวเบนรังสีเอกซ์บนผลึกเดี่ยว สารประกอบเชิงซ้อน $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$ และ $[Cu(PPh_3)_2(dptu)Br]\cdot H_2O$ ตกผลึกอยู่ในระบบไตรคลินิก หมู่ปริภูมิ $P\bar{1}$ มีเซลล์พารามิเตอร์ดังนี้ a = 11.0946(11), b = 12.8345(12), c = 18.5790(18) Å, α = 103.0339(2), β = 90.6470(2), γ = 111.292(2)^o และ a = 10.8100(11), b = 12.2861(13), c = 18.9086(19) Å, α = 73.330(2), β = 88.921(2), γ = 67.318(2)^o ตามลำดับ สารประกอบเชิงซ้อน $[Cu(PPh_3)_2(dptu)I]\cdot CH_3CN$ ตกผลึกอยู่ในระบบออร์โธรอมบิก หมู่ปริภูมิ $P2_12_12_1$ มีเซลล์พารามิเตอร์ดังนี้ a = 13.9088(7), b = 16.5452(8), c = 20.2573(10) Å ซึ่งโครงสร้างสารประกอบเชิงซ้อนที่ได้เป็นมอนอเมอร์ที่มีอะตอมคอปเปอร์เป็นแบบทรงสี่หน้าที่บิดเบี้ยว โคออร์ดิเนตกับลิแกนด์ไตรฟีนิลฟอสฟีนสองโมเลกุล ไดฟีนิลไธโอยูเรียหนึ่งโมเลกุลและเฮไลด์หนึ่งอะตอม

Thesis Title Copper(I) Halide Complexes with Triphenylphosphine and *N*,*N'*-Diphenylthiourea
Author Miss Ladawan Duangmuengmai
Major Program Chemical Studies
Academic Year 2009

ABSTRACT

The copper(I) halide complexes containing triphenylphosphine(PPh$_3$) and *N*,*N'*-diphenylthiourea(dptu), [Cu(PPh$_3$)$_2$(dptu)Cl]·2CH$_3$CN, [Cu(PPh$_3$)$_2$(dptu)Br]·H$_2$O and [Cu(PPh$_3$)$_2$(dptu)I]·CH$_3$CN have been prepared by direct reaction of copper(I) halide (CuX; X = Cl, Br, I) with triphenylphosphine and *N*,*N'*-diphenylthiourea under suitable conditions. The structures of these complexes have been characterized by elemental analysis, X-ray fluorescence spectrometry, Fourier transform nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy and single crystal X-ray diffraction methods. The complexes, [Cu(PPh$_3$)$_2$(dptu)Cl]·2CH$_3$CN and [Cu(PPh$_3$)$_2$(dptu)Br]·H$_2$O crystallized in triclinic system space group $P\bar{1}$ with cell parameters a = 11.0946(11), b = 12.8345(12), c = 18.5790(18) Å, α = 103.0339(2), β = 90.6470(2), γ = 111.292(2)^o and a = 10.8100(11), b = 12.2861(13), c = 18.9086(19) Å, α = 73.330(2), β = 88.921(2), γ = 67.318(2)^o respectively. The complex [Cu(PPh$_3$)$_2$(dptu)I]·CH$_3$CN crystallized in orthorhombic system space group $P2_12_12_1$ with cell parameters a = 13.9088(7), b = 16.5452(8), c = 20.2573(10) Å. Each complex is mononuclear which the copper atom is tetrahedrally coordinated by two PPh$_3$ molecules, one dptu molecule and one halogen atom.

ACKNOWLEDGEMENTS

I am extremely grateful my supervisor, Asst. Prof. Dr. Chaveng Pakawatchai of the Department of Chemistry, Faculty of Science, Prince of Songkla University for many helpful suggestions, expert guidance, kindness and a critical reading of the manuscript and also for the considerable assistance throughout my master degree.

I have great pleasure in thanking my co-supervisor, Dr. Weena Aemaeg Tupchai of the Department of Chemistry, Faculty of Science, Prince of Songkla University for her kindly, generous hospitality helpful suggestion on my research.

My sincere thank is expressed to Dr. Saowanit Saithong at Prince of Songkla University for her training on the technique of structure determination. I also would like to thank Asst. Prof. Dr. Hirihattaya Phetmung of the Department of chemistry, Faculty of Science, Thaksin University and Asst. Prof. Dr. Cheawchan Utarapichart of the Department of Chemistry, Faculty of Science, Prince of Songkla University for their helpful suggestions and comments during the thesis examination.

I would like to thank staff of the Department of Chemistry and also to many other people for their help and encouragement during my study.

Thank is also extended to the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, the Department of Chemistry and Graduate School, Prince of Songkla University for the financial support to enable me to carry out this study.

Finally, I am particularly indebted and grateful to my family and my friends for their kind help and encouragement throughout my life.

Ladawan Duangmuengmai

THE RELEVANCY OF THE RESEARCH WORK TO THAILAND

Copper(I) complexes have been widely studied because of providing suitable models for the representation of several enzymic sites as well as active intermediates in organic synthesis reactions.

The main propose of this work is to determine the crystal structures of copper(I) complexes containing N, S and P as donor atoms. The substituted thiourea ligand, *N.N'*-diphenylthiourea(dptu) is selected due to the interesting structures that might be formed coordinate bond with copper atom through both sulfur and nitrogen atoms 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 copper(I) halide (Cl, Br, I) with mixed ligands of PPh_3 and dptu. 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 photocatalytic isomerizations.

CONTENTS

Page

CONTENTS (continued)

Page

CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

LIST OF ILLUSTRATIONS (continued).

LIST OF ABBREVIATIONS AND SYMBOLS

° = degree
Å = Angstrom unit (1 Å = 10^{-10} metre)
A.R. = Analytical Reagent
°C = degree celsius
D_c = calculated density
D_m = measured density
EDXRF = Energy Dispersive X-ray Fluorescence
g = gram
g/cm^3 = gram per cubic centimetre
h = hour
K = Kelvin
keV = kilo electron volt
kg = kilogram
L.R. = Lab Reagent
ml = millilitre
mm = millimetre
mmol = millimole

CHAPTER 1

INTRODUCTION

1.1 Introduction

The element copper, symbol Cu, atomic number 29, is located in the periodic table between nickel and zinc in the first row of the transition elements and in the same group as others known as coinage metals, silver and gold. The electronic configuration of copper is $[1s^2 2s^2 2p^6 3s^2 3p^6]3d^{10}4s^1$ or $[\mathrm{Ar}]3d^{10}4s^1$. Copper has a single s electron outside the filled 3*d* 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 Cu 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 Cu are also much higher than those of the alkalis. These factors are responsible for the more noble character of copper, and the effect is to make the compounds more covalent and to give them higher lattice energies.

Copper is essential in all higher plants and animals. Copper is carried mostly in the bloodstream on a plasma protein called ceruloplasmin. When copper is first absorbed in the gut it is transported to the liver bound to albumin. Copper is found in a variety of enzymes, including the copper center of cytochrome c oxidase and the enzyme superoxide dismutase (containing copper and zinc). In addition to its enzymatic roles, copper is used for biological electron transport (Micheal *et al,*. 1996). The blue copper proteins that participate in electron transport include azurin and plastocyanin. The name “blue copper” comes from their intense blue color arising from a ligand-to-metal charge transfer (LMCT) absorption band around 600 nm.

Most molluscs and some arthropods such as the horseshoe crab use the copper-containing pigment hemocyanin rather than iron-containing hemoglobin for oxygen transport, so their blood is blue when oxygenated rather than red. In sufficient amounts, copper can be poisonous or even fatal to organisms.

The structure and stereochemistry of copper complexes have largely been influenced by the electronic configuration of the metal ion. Copper(I), a soft acceptor of a d^{10} configuration, is well coordinated with a soft donor prefers a tetrahedral orientation. Copper(II), a d^9 system, exhibit coordination number dependent structures: 4 coordination prefers square planar, the 5 coordinated system is square pyramid or trigonal bipyramidal and 6 coordinated complexes are distorted octahedral.

Ligands containing a thioamide structure have considerable coordination potential. The flexibility based on the tautomerism, thiol(-N=C(-SH)) ↔ thione (-NH-C(=S)), can afford various coordination modes. The ligands are potentially capable of forming coordinate bonds through both sulfur and nitrogen-metal bonds. *N*,*N'*-diphenylthiourea, the substituted thiourea in this work is in thione form. These possibilities will be reflected in the infrared spectra of the complexes. Bonding through sulfur will decrease the bond order of the carbon-sulfur link towards the value for a single bond while the carbon-nitrogen bond approaches the value for a double bond. Therefore, in such complexes, the C-S stretching frequency should decrease and that of C-N should increase. If a nitrogen-metal bond is formed just the opposite effect is to be expected. Furthermore, the N-H frequency should decrease if the metal coordinates through nitrogen, while remaining substantially unaffected if the bonding is through sulfur (Swaminathan and Irving, 1964 : 1291). Owing to their relevance in biological systems, heterocyclic thione have attracted considerable interest as ligands in metal complexes.

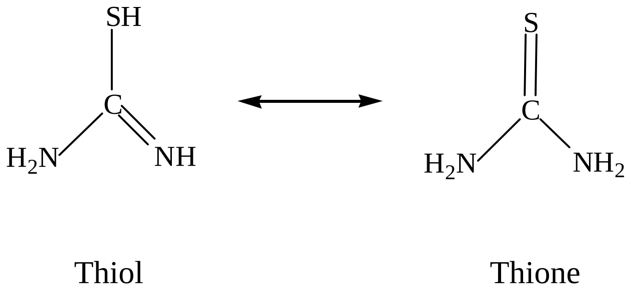
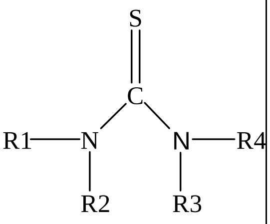
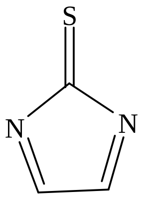


Figure 1 The tautomerism structure of thiourea.

Structures 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’’’*-tetramethylthiourea(tmtu), are shown in the table below :

Structures	Names	Remarks
	Thiourea(tu)	$R1=R2=R3=R4=H$
	acetylthiourea(atu)	$R1=R2=R3=H$ $R4=COCH_3$
	N-ethylthiourea(ettu)	$R1=R2=R3=H$ $R4=C_2H_5$
	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)	$R1=R4=H$ $R2=R3=C_2H_5$
	N-phenylthiourea(ptu)	$R1=R2=R3=H$ $R4=C_6H_5$
	N,*N’*-diphenylthiourea(dptu)	$R1=R3=H$ $R2=R4=C_6H_5$
	N,*N’*,*N’’*,*N’’’*-tetramethylthiourea(tmtu)	$R1=R2=R3=R4=CH_3$
	*N*-ethylenethiourea(etu)	-

Triphenylphosphine (PPh_3) is widely used in organic synthesis. The properties that guide its usage are its nucleophilicity and its reducing character. The nucleophilicity of PPh_3 is indicated by its reactivity toward electrophilic alkenes, such as Michael-acceptors, and alkyl halides. The structure of triphenylphosphine is shown in Figure 2.

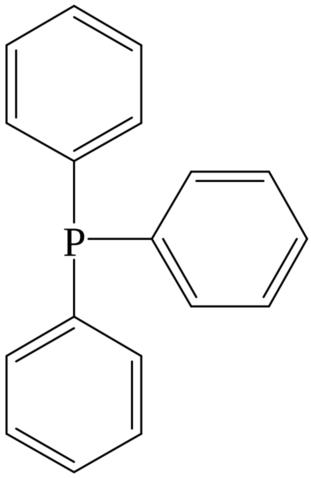


Figure 2 The structure of triphenylphosphine (PPh_3)

In this work, we prepared the single crystals of the series of Cu(I)X (X= Cl, Br and I) with triphenylphosphine (PPh_3) and *N,N'*-diphenylthiourea (dptu) 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

Dyason *et al.*, studied the crystal structure of the $(PPh_3)_2CuBr_2Cu(PPh_3)$ by single-crystal X-ray diffraction methods. $(PPh_3)_2CuBr_2Cu(PPh_3)$ complex crystallizes in monoclinic system, space group $P2_1/c$, a = 19.390(8), b = 9.912(5), c = 26.979(9) Å, $\beta = 112.33(3)^{\circ}$, D_c = 1.49 g/cm^3, R = 0.043 for N_o = 3444, Cu(trigonal)-P; Br are 2.191(3): 2.409(2), 2.364(2) Å, respectively, Cu(tetrahedral)-P;Br are 2.241(3), 2.550(2), 2.571(2) Å, respectively, (Dyason *et al.*, 1985).

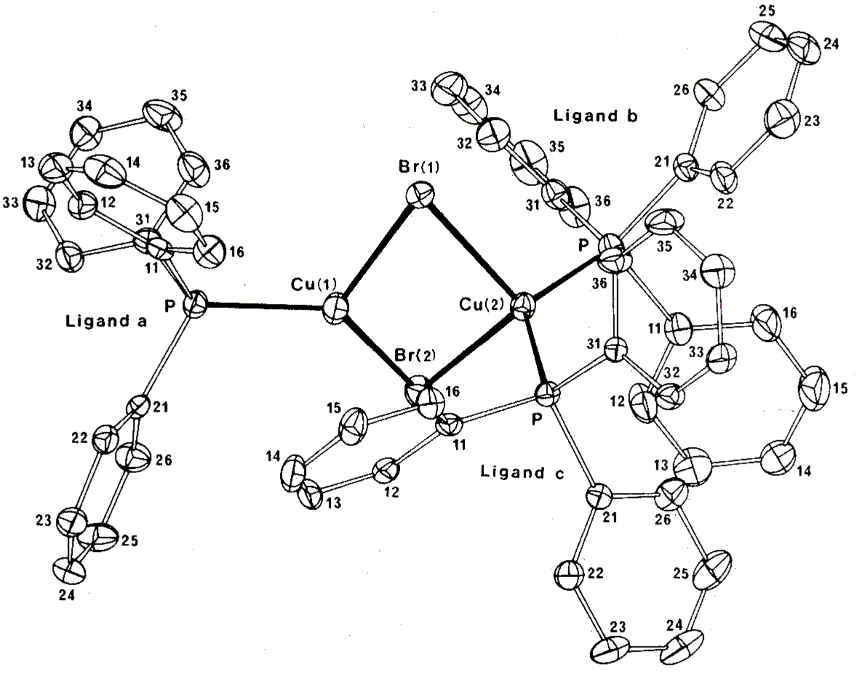


Figure 3 The structure of $(PPh_3)_2CuBr_2Cu(PPh_3)$.

Karagiannidis *et al.*, synthesised and studied the reaction of bis(triphenylphosphine) copper(I) nitrate with 1,3-thiazolidine-2-thione(tzdtH) lead to the formation of mononuclear complex of the formula $[Cu(tzdtH)_2(PPh_3)_2].NO_3$. The complex was characterized by elemental analysis, infrared, UV-vis and NMR spectroscopy. The crystal structure of $[Cu(tzdtH)_2(PPh_3)_2].NO_3$ was determined by single-crystal X-ray diffraction methods. (Karagiannidis *et al.*, 1989).

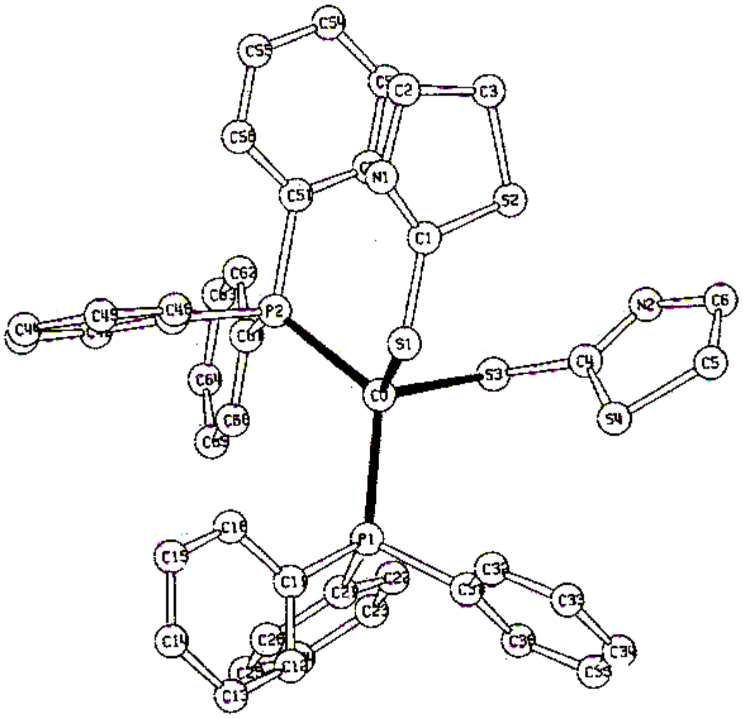


Figure 4 The structure of $[Cu(tzdtH)_2(PPh_3)_2].NO_3$.

Crystal data: monoclinic system, space group $P2_1/c$, a = 16.314(2), b = 9.981(2), c = 25.799(3) Å, β = 89.39(1)°, Z = 4, D_c = 1.456 g/cm^3, R = 0.0411, R_w = 0.0510.

Karagiannidis *et al.*, synthesized, characterized and studied electrochemistry of complex of copper(I) (triphenylphosphine)-bromide with pyridine-2-thione(py2SH) $[Cu(py2SH)(PPh_3)Br]_2$. The complex is binuclear, the stereochemistry of the Cu_2S_2 core is strictly planar. The equivalent copper atoms have pseudotetrahedral geometry. (Karagiannidis *et al.*, 1989).

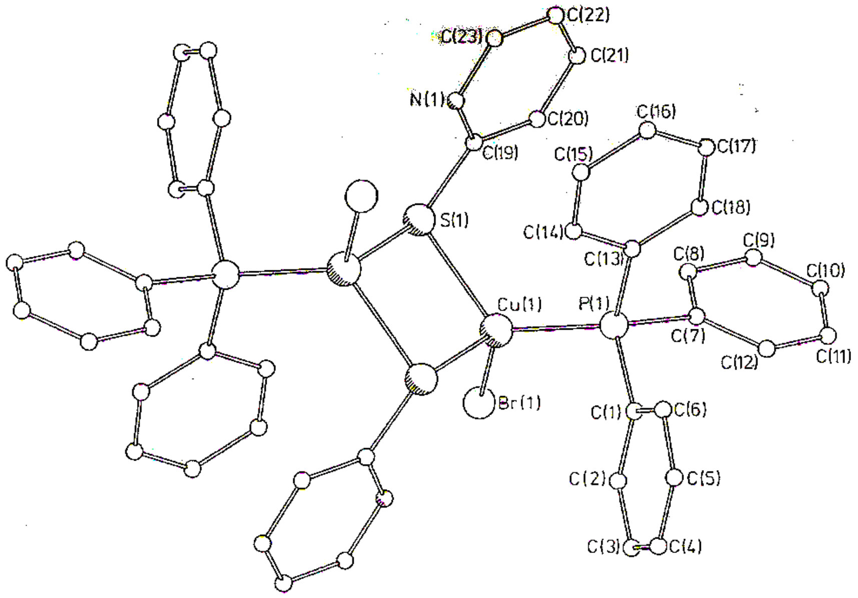


Figure 5 The structure of $[Cu(py2SH)(PPh_3)Br]_2$.

Crystal data: triclinic system, space group $P\bar{1}$, a = 9.586(4), b = 9.562(5), c = 13.573(5) Å, α = 77.56(3), β = 73.32(3), γ = 62.38(3)°, Z = 1, D_c = 1.63 g/cm^3, R = 0.0389.

Karagiannidis *et al.*, studied the copper(I) mixed ligand complexes with 1-methyl-1,3-imidazoline-2-thione(meimtH) and triphenylphosphine(PPh_3) of the general formla $[Cu(PPh_3)_2(meimtH)X]$ [X = Cl, Br, I)], and their characterization by various physico-chemical methods. The crystal structure of the complex $[Cu(PPh_3)_2(meimtH)Br]$ was solved by single-crystal X-ray diffraction method. The copper ion has a distorted tetrahedral geometry with bond lengths Cu-S = 2.375(1), Cu-Br = 2.509(0), Cu-P(1) = 2.268(1) and Cu-P(2) = 2.281(1)Å (Karagiannidis *et al.*, 1990).

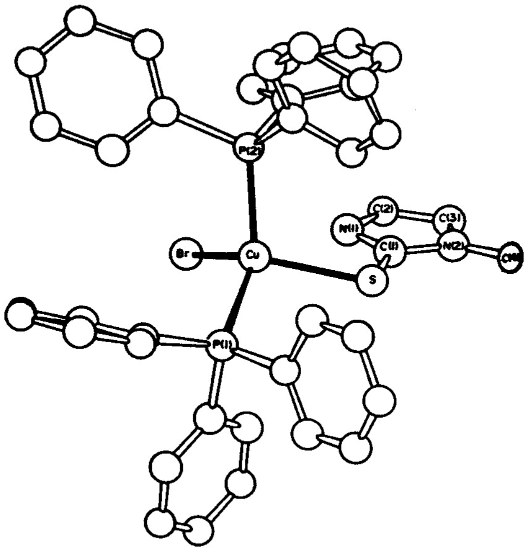


Figure 6 The structure of [Cu(PPh$_3$)$_2$(meimtH)Br].

Crystal data: triclinic system, space group $P\bar{1}$, a = 9.998(3), b = 10.212(2), c = 21.066(5) Å, α = 94.86(2), β = 91.70(2), γ = 119.16(2)$^{\circ}$, Z = 2, D_c = 1.394 g/cm^3, R = 0.0330, R_w = 0.0355.

Lecomte *et al.*, studied the reaction of copper(I) bromide with pyrimidine-2-thione(pymth) in the presence of triphenylphosphine(PPh$_3$) yielded mononuclear complex of the formula [Cu(PPh$_3$)$_2$(pymth)Br]. The complex was characterized by elemental analysis, IR, UV-vis and NMR spectroscopy. The crystal structure of [Cu(PPH$_3$)$_2$(pymth)Br] was determined by single-crystal X-ray diffraction methods. (Lecomte *et al.*,1989).

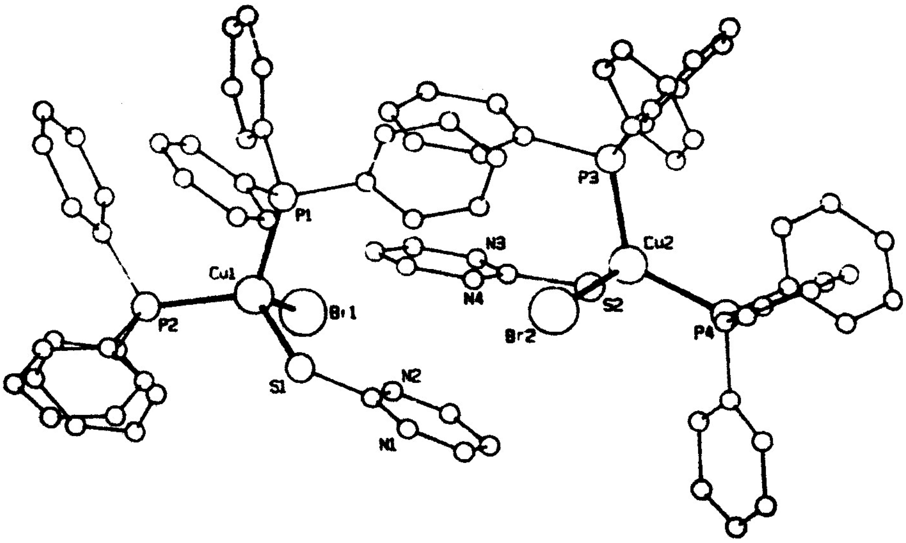


Figure 7 The structure of $[Cu(PPH_3)_2(pymth)Br]$.

Crystal data: monoclinic system, space group $P2_1/n$, a = 13.035(2), b = 43.660(9), c = 13.446(2) Å, β = 90.68(2)$^{\circ}$, Z = 8, D_c = 1.352 g/cm^3, R = 0.067, R_w = 0.069.

Skoulika *et al.*, studied the copper(I) chloride complex with benz-1,3-imidazoline-2-thione(bzimtH_2) and triphenylphosphine(PPh_3) as ligands and the cpmplex was characterized by elemental analysis, IR, UV-vis and NMR spectroscopies. Crystal structure of the complex $[Cu(PPh_3)_2(bzimtH_2)Cl]$ was determined by X-ray analysis. (Skoulika *et al.*, 1991).

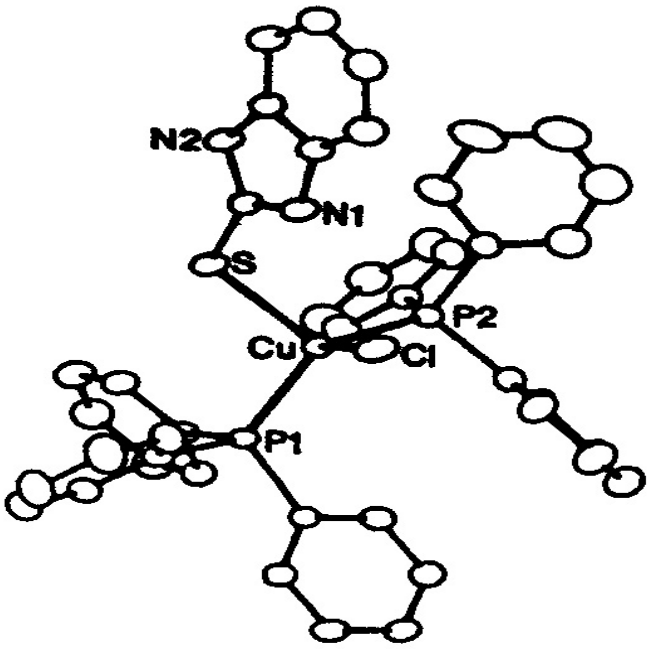


Figure 8 The structure of $[Cu(PPh_3)_2(bzimtH_2)Cl]$.

Crystal data: monoclinic system, space group $P2_1/c$, a = 13.147(2), b = 18.592(3), c = 17.259(3) Å, β = 97.45(2)°, Z = 4, D_c = 1.320 g/cm^3, R = 0.036, R_w = 0.036.

Aslanidis *et al.*, studied the reaction of $[Cu(PPh_3)I]_4$ with pyrimidine-2-thione(pymtH) in the presence of triphenylphosphine(PPh_3) to give mononuclear complex of the formula $[Cu(PPh_3)_2(pymtH)I]$. This complex was characterized by various physicochemical methods. The crystal structure of $[Cu(PPh_3)_2(pymtH)I]$ was determined by single-crystal X-ray diffraction methods. The molecule is mononuclear, with a distorted tetrahedral geometry and bond lengths Cu-S = 2.338(4), Cu-I = 2.674(2), Cu-P = 2.303(4) Å. (Aslanidis *et al.*, 1993).

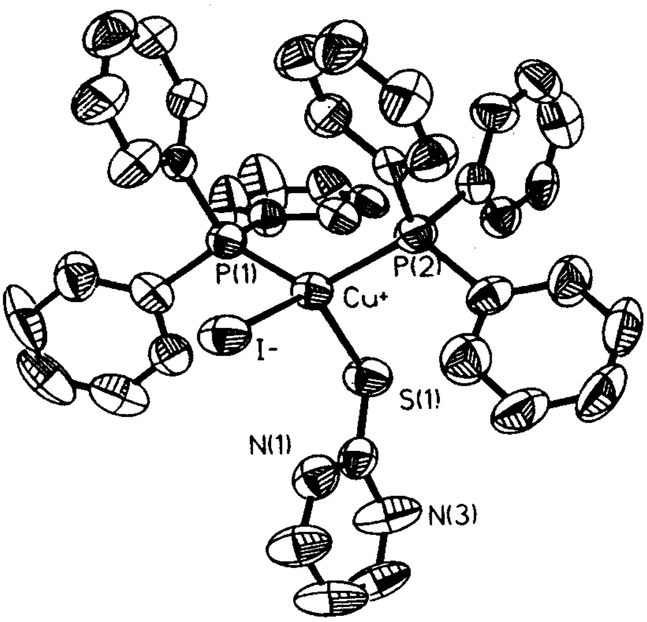


Figure 9 The molecular structure of [Cu(PPh$_3$)$_2$(pymtH)I].

Crystal data: monoclinic system, space group $P2_1/n$, a = 9.708(2), b = 19.838(4), c = 19.893(4) Å, β = 92.53(3)$^\circ$, Z = 4, D_c = 1.434 g/cm^3, R = 0.063, R_w = 0.070.

Jiangping and Kazuyuki, studied the reaction of copper(I) bromide with triphenylphosphine(PPh$_3$) in the presence of benz-1,3-thiazolidine-2-thione(bztzdtH) yielded the complex, [Cu(bztzdtH)(PPh$_3$)Br)]$_2$ and the complex was characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction methods. The molecule has a crystallographic center of symmetry that requires the Cu$_2$S moiety to be strictly planar. The copper atoms have a distorted tetrahedral geometry and the bztzdtH ligand is monodentate with sulfur atoms bridged to two copper atoms. (Jiangping and Kazuyuki, 1996).

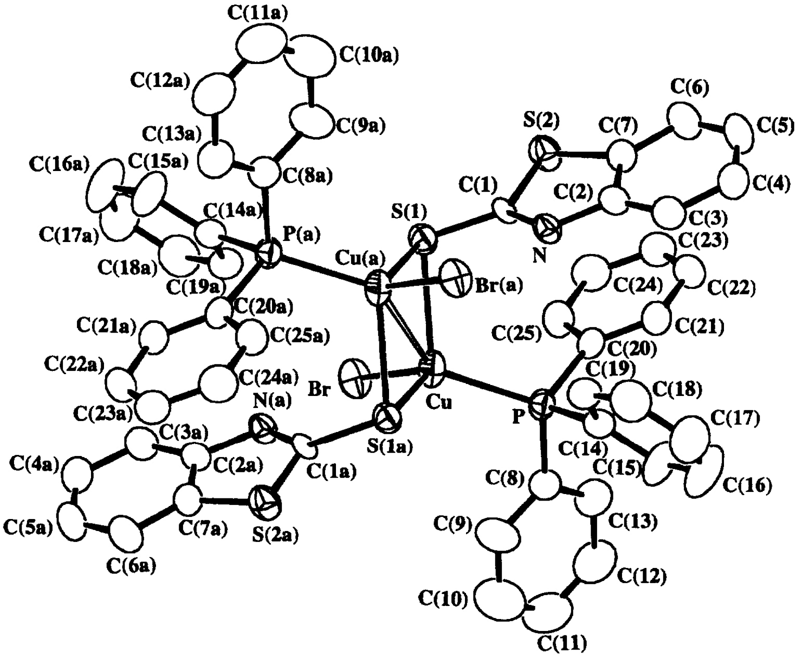


Figure 10 The molecular structure of $[Cu(bztzdtH)(PPh_3)Br)]_2$.

Crystal data: monoclinic system, space group *C*2/*c*, a = 25.991(14), b = 9.206(1), c = 19.943(3) Å, β = 100.02(1)°, Z = 4, D_c = 1.62 g/cm^3, R = 0.033.

Aslanidis *et al*., studied the reaction of $[Cu(PPh_3)_3Cl]$ with 1,3-thiazolidine-2-thione(tzdtH) yielded mononuclear complex of the formula $[Cu(PPh_3)_2(tzdtH)Cl]$. The complex was characterized by single-crystal X-ray diffraction methods. The copper atom has pseudotetrahedral geometry with bond lengths Cu-S = 2.4181(5), Cu-Cl = 2.344(3), Cu-P(1) = 2.287(3) and Cu-P(2) = 2.298(2) Å. (Aslanidis *et al.*, 1998)

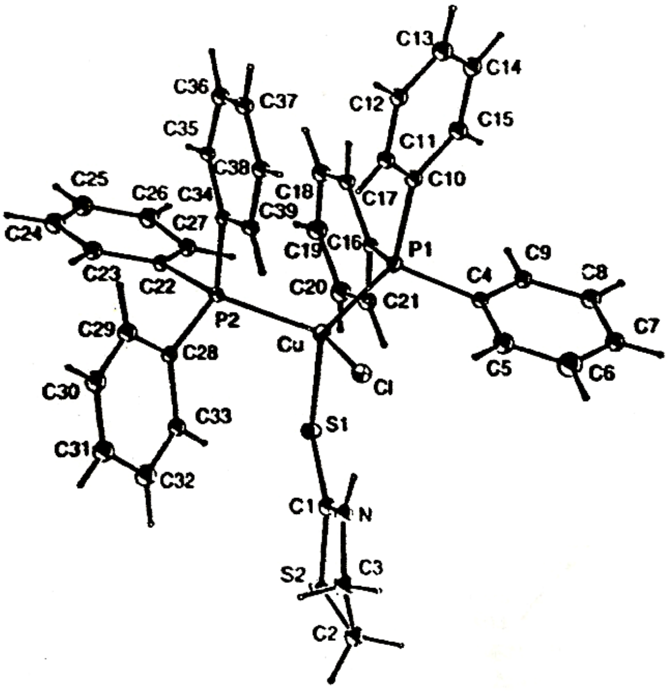


Figure 11 The molecular structure of [Cu(PPh$_3$)$_2$(tzdtH)Cl].

Crystal data: monoclinic system, space group $P2_1/c$, a = 14.31(2), b = 10.009(10), c = 24.52(2) Å, β = 93.53(7)$^\circ$, Z = 4, D_c = 1.395 g/cm^3, R = 0.0562, R_w = 0.1451.

Cox *et al.*, studied the reaction of [Cu(PPh$_3$)$_3$Cl] in acetonitrile/methanol solvent with benz-1,3-thiazolidine-2-thione(bztzdtH) yielded product of the formula [Cu(PPh$_3$)$_2$(bztzdtH)Cl]. The complex was characterized by IR, UV-vis and ^{1}H-NMR spectroscopic data and the structure was determined by single crystal X-ray diffraction methods. The copper(I) atom displays a distorted tetrahedral environment. In the molecule, the tetrahedral arrangement around the copper(I) atom is formed by two P atoms from two triphenylphosphines with Cu-P bond distance of 2.269(2) and 2.285(3) Å, one Cl atom (Cu-Cl = 2.400(2) Å) and one S atom from the thione ligand [Cu-S = 2.36(4)Å]. (Cox *et al.*, 1999)

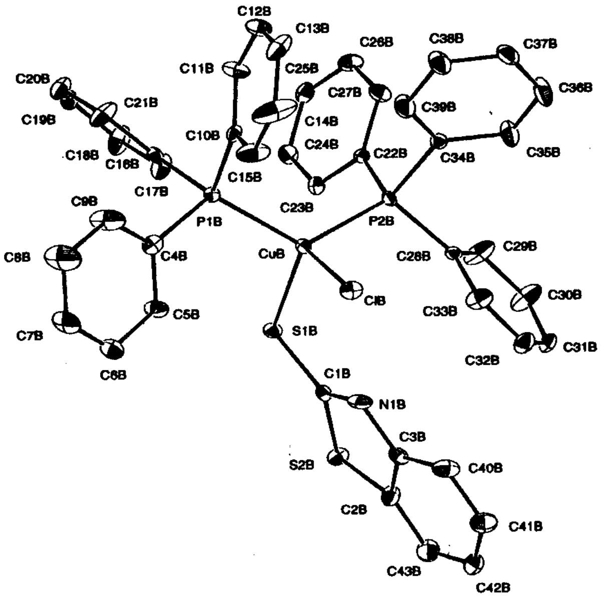


Figure 12 The molecular structure of $[Cu(PPh_3)_2(bztzdtH)Cl]$.

Crystal data: triclinic system, space group $P\bar{1}$, a = 9.998(5), b = 20.313(7), c = 20.874(7) Å, α = 82.93(6), β = 77.99(8), γ = 83.60(3)$^\circ$, Z = 2, R = 0.0399, R_w = 0.1140.

Lobana and Castineiras, synthesized and studied the reaction of copper(I) chloride with pyridine-2-thione(C_5H_5NS) and triphenylphosphine(PPh_3) yielded mononuclear complex of the formula $[CuCl(\eta^1\text{-}S\text{-}\mu\text{-}C_5H_5NS)_2(PPh_3)Cl]$. The complex was characterized using analytical data, IR and far-IR(4000-100 cm^{-1}), UV-vis spectra, NMR (^1H, ^{13}C) and X-ray crystallopgraphy. The strong intramolecular N-H···Cl hydrogen bonding appear to stabilise the monomer. (Lobana and Castineiras, 2002)

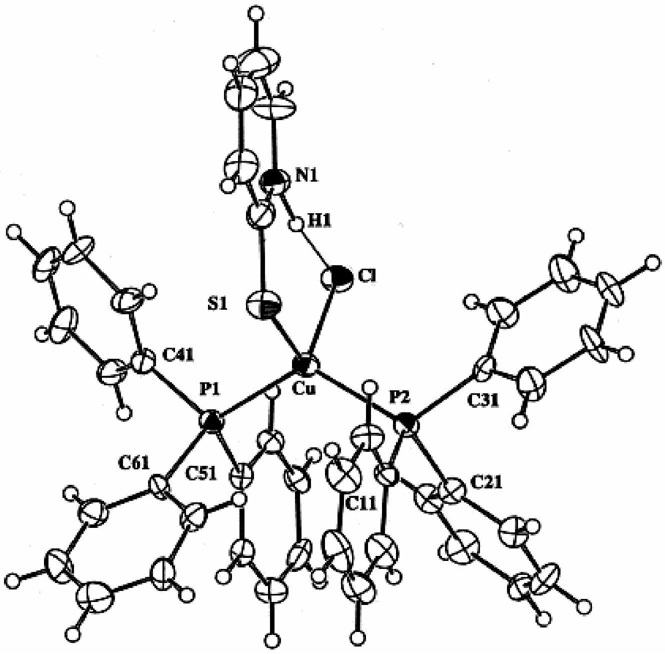


Figure 13 The structure of [CuCl(η^1-S-μ-$C_5H_5NS)_2(PPh_3)$Cl].

Crystal data: monoclinic system, space group $P2_1/c$, a = 14.4776(13), b = 10.1609(14), c = 24.5402(9) Å, β = 93.367(14)°, Z = 4, D_c = 1.354 g/cm^3, R = 0.0414, R_w = 0.0867.

Alexander *et al.*, synthesized copper(I) complexes of *N*-thioacylamido(thio) phosphates and triphenylphosphine(PPh_3). Copper is bound by two PPh_3 and SCNPX (X=O,S) fragment of chelating ligand in all cases. Triphenylphosphine molecules reversibly dissociate in solution and yielded mononuclear complexes of the formula, $(Ph_3P)_2$Cu[PhC(S)NP(S)(OPr-i$)_2$ and [$(Ph_3P)_2$Cu[Et_2NC(S)NP(S)(OPr-i$)_2$]. The complexes was characterized by elemental analysis, IR, NMR (^{1}H and ^{31}P) spectroscopy and X-ray crystallography. (Alexander *et al.*, 2006).

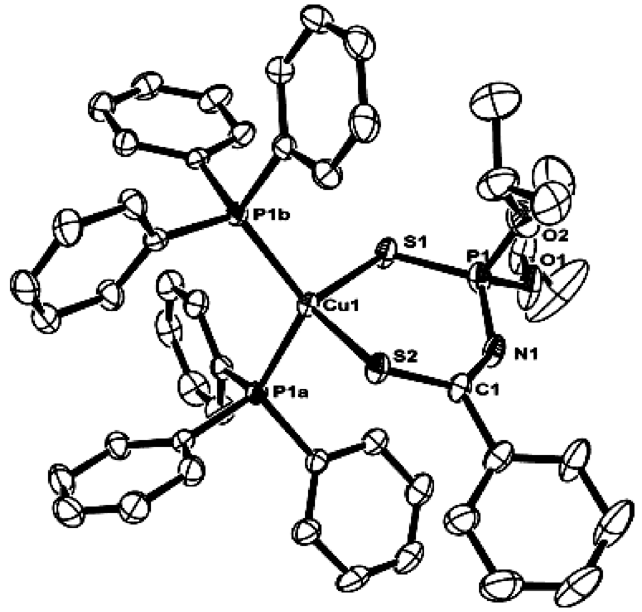


Figure 14 The structure of $[(Ph_3P)_2Cu[PhC(S)NP(S)(OPr\text{-}i)_2]$.

Crystal data: triclinic system, space group $P\bar{1}$, a = 12.092(2), b = 12.053(2), c = 18.899(4) Å, α = 98.25(2), β = 104.12(2) °, γ = 114.65(2)°, Z = 2, D_c = 1.29 g/cm^3, R = 0.039, R_w = 0.099.

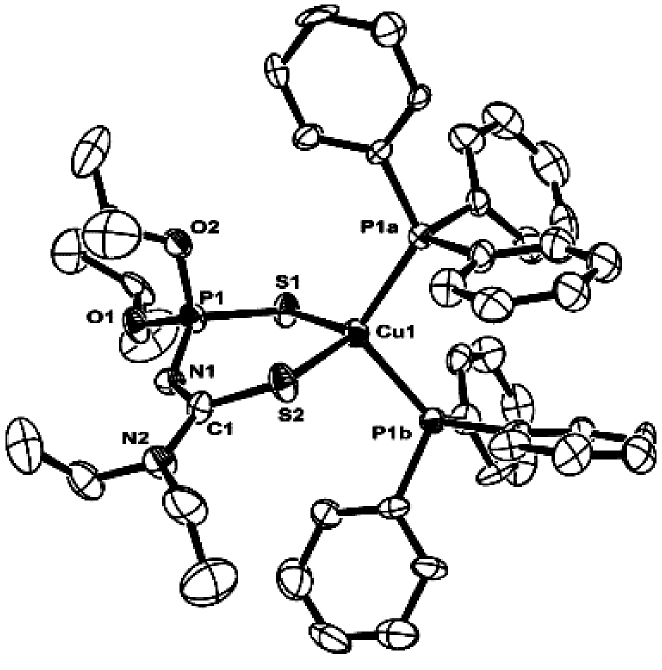


Figure 15 The structure of $[(Ph_3P)_2Cu[Et_2NC(S)NP(S)(OPr\text{-}i)_2]$.

Crystal data: monoclinic system, space group $P2_1/n$, a = 13.058(2), b = 20.931(2), c = 17.560(6) Å, β = 109.00(2)°, Z = 4, D_c = 1.32 g/cm^3, R = 0.040, R_w = 0.066.

Lobana *et al.*, studied the reaction of copper(I) chloride and copper(I) bromide with benzophenone thiosemicarbazone(Hbztsc) in the presence of triphenylphosphine (PPh$_3$) yielded monomeric tetrahedral complexes, [CuX(η^1-S-Hbztsc)(PPh$_3$)]·CH$_3$CN (X = Cl, Br). All complexes have been characterzed by elemental analyses, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and single crystallography. (Lobana *et al.*,2006)

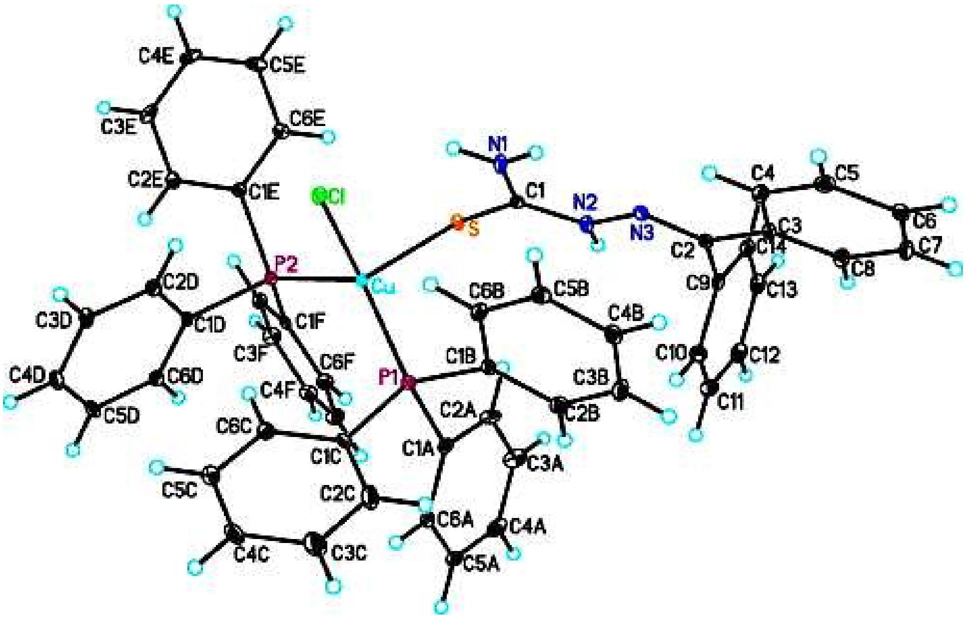


Figure 16 The structure of [CuCl(η^1-S-Hbztsc)(PPh$_3$)]·CH$_3$CN.

Crystal data: triclinic system, space group $P\bar{1}$, a = 12.3639(8), b = 13.9423(8), c = 14.8040(9) Å, α = 113.9130(10), β = 100.6420(10), γ = 94.9190(10)°, Z = 2, D_c = 1.354 g/cm^3, R = 0.0490, R_w = 0.1006.

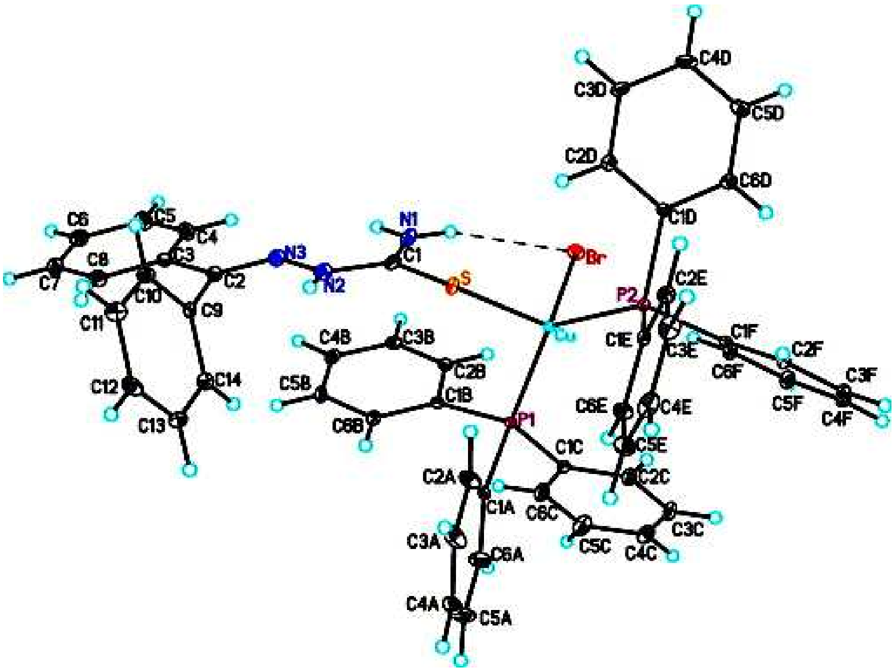


Figure 17 The structure of [CuBr(η^1-S-Hbztsc)(PPh$_3$)]·CH$_3$CN.

Crystal data: triclinic system, space group $P\bar{1}$, a = 10.356(7), b = 14.480(11), c = 17.684(13) Å, α = 66.206(12), β = 79.346(14), γ = 72.729(13)°, Z = 2, D_c = 1.386 g/cm^3, R = 0.0502, R_w = 0.114.

Lobana *et al.*, studied the reaction of copper(I) chloride with thiophene-2-carbaldehyde thiosemicarbazone(Httsc) in acetonitrile in the presence of triphenylphosphine (PPh$_3$) yielded a sulfur-bridged dimmer, [Cu$_2$Cl$_2$(μ$_2$-S-Httsc)$_2$(PPh$_3$)$_2$]· 2CH$_3$CN. The complex was characterized using elemental analysis, IR, ^{1}H and ^{31}P NMR spectroscopy and single crystal X-ray crystallography. Acetonitrile is engaged in hydrogen bonding with the chlorine atom {NCCH$_2$-H···Cl}, with is necessary for the stabilization of the bridging sulfur. The Cu···Cu contact of 2.7719(5)Å in complex is closed to twice the van der Waals radius of the Cu atom (2.80Å). (Lobana *et al.*, 2007).

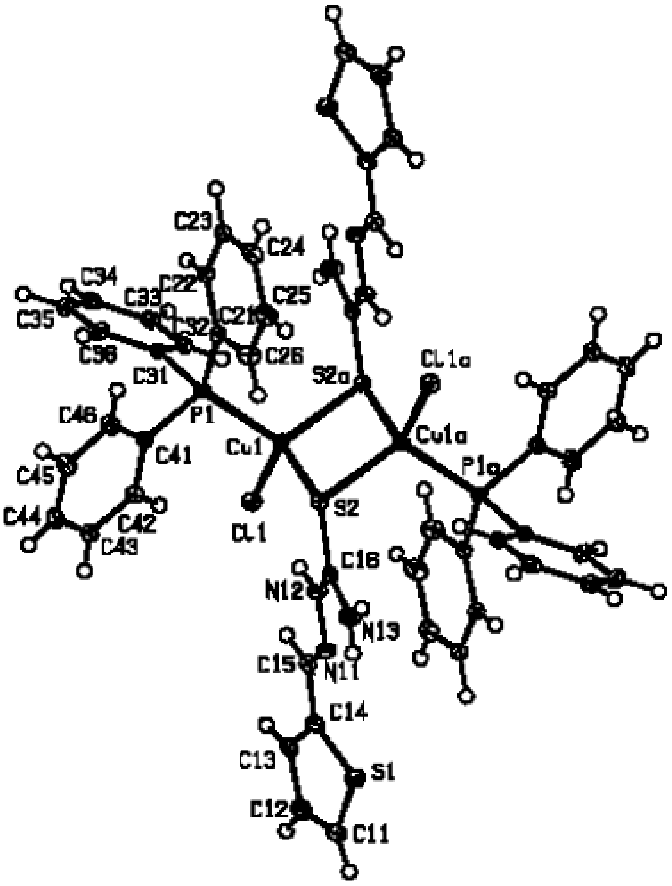


Figure 18 The structure of $[Cu_2Cl_2(\mu_2\text{-S-Httsc})_2(PPh_3)_2]\cdot 2CH_3CN$.

Crystal data: triclinic system, space group $P\bar{1}$, a = 9.2407(15), b = 11.1336(17), c = 14.125(2) Å, α = 74.720(9), β = 71.123(9), γ = 78.615(9)$^{\circ}$, Z = 1, D_c = 1.482 g/cm^3, R = 0.0363, R_w = 0.0719.

Lobana *et al.*, studied the reaction of cyclopentanone thiosemicarbazone(Hcptsc) with copper(I) bromide and triphenylphosephine(PPh_3) in 1:1:1 molar ratio in acetonitrile. An asymmetric dimer, $[(Ph_3P)Cu(\mu\text{-Br})(\mu_3\text{-S,N–Hcptsc})CuBr(PPh_3)]$ was formed. The complex was characterized using elemental analysis, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and single crystal X-ray crystallography. (Lobana *et al.*, 2008).

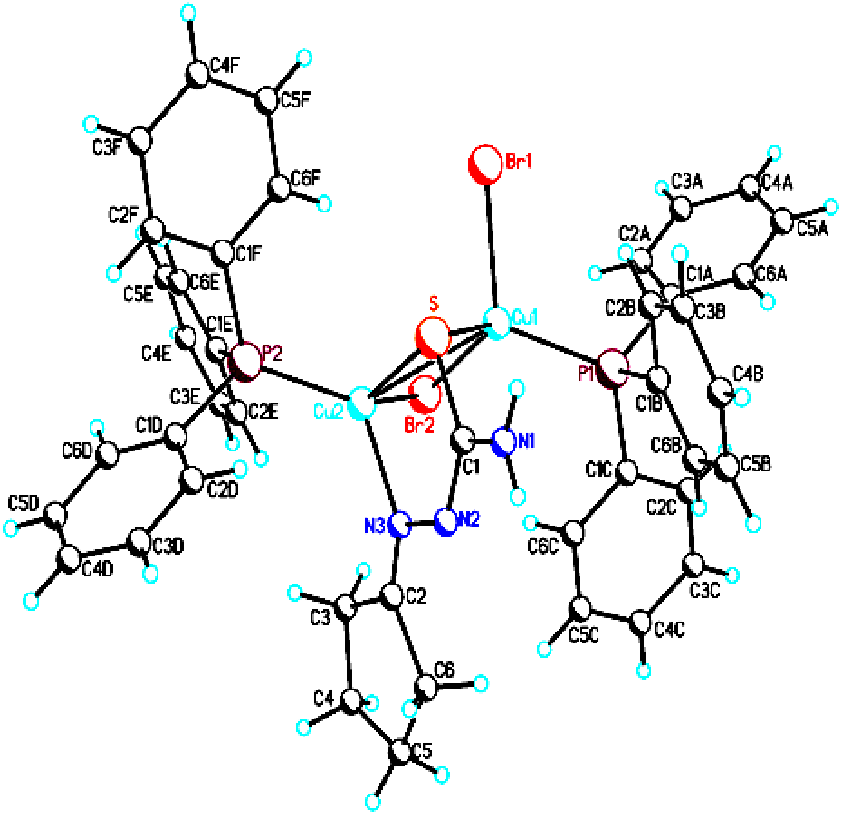


Figure 19 The structure of [$(Ph_3P)Cu(\mu\text{-}Br)(\mu_3\text{-}S,N\text{–}Hcptsc)CuBr(PPh_3)$].

Crystal data: triclinic system, space group $P\bar{1}$, a = 10.356(7), b = 14.480(11), c = 17.684(13) Å, α = 66.206(12), β = 79.346(14), γ = 72.729(13)$^\circ$, Z = 2, D_c = 1.386 g/cm^3, R = 0.0502, R_w = 0.114.

Belicchi-Ferrari *et al.***,** synthesized and studied complex of bis(triphenylphosphine)copper(I) nitrate with N^1-ethyl methylpyruvate thiosemicarbarzone. The complex of the formula $[Cu(PPh_3)_2(Et\text{-}Hmpt](NO_3)_2$ was characterized by elemental analysis, IR, ^{1}H NMR, EPR spectroscopy and X-ray crystallography. The copper(I) ion is coordinated to two triphenylphosphine and an N^1-ethyl methylpyruvate thiosemicarbarzone molecule in its neutral form. The thiosemicarbazone binds to the metal through the sulfur and the iminic nitrogen and form a five-term chelation ring. The structure is shown in Figure 20 (Belicchi-Ferrari *et al.*, 2009).

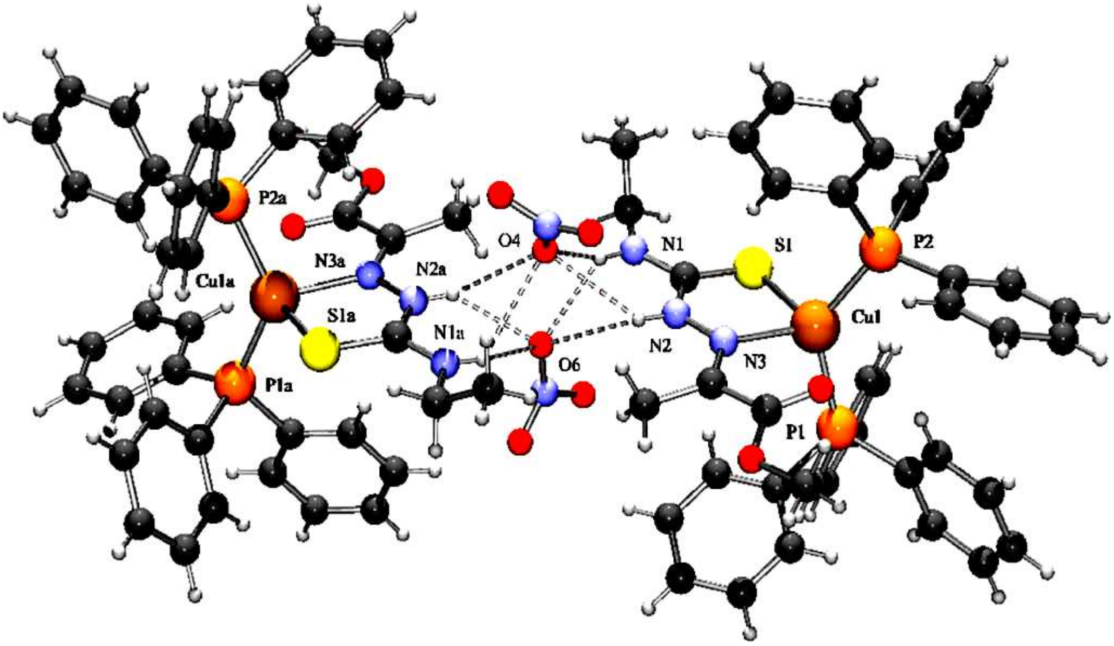


Figure 20 The structure of $[Cu(PPh_3)_2(Et\text{-}Hmpt](NO_3)_2]$.

Crystal data: orthorhombic system, space group $Pca2_1$, a = 19.057(4), b = 18.376(3), c = 24.365(8) Å, Z = 4, D_c = 1.329 g/cm^3, R = 0.0678, R_w = 0.1811.

Lobana *et al***.** studied the reaction of copper(I) chloride complex with thophene-2-carbaldehyde-N^1-methyl thiosemicarbalzone. The complex was characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, spectroscopy and X-ray crystallography. The molecule is dinuclear, with two bridging chlorine atom, one P atom and S atoms formed tetra-coordination around copper atom. The central core $Cu(\mu\text{-}Cl)_2Cu$ forms parallelograms and PPh_3/HttscMe ligands occupy trans positions across this core the structure is shown in Figure 21 (Lobana *et al***.**, 2009).

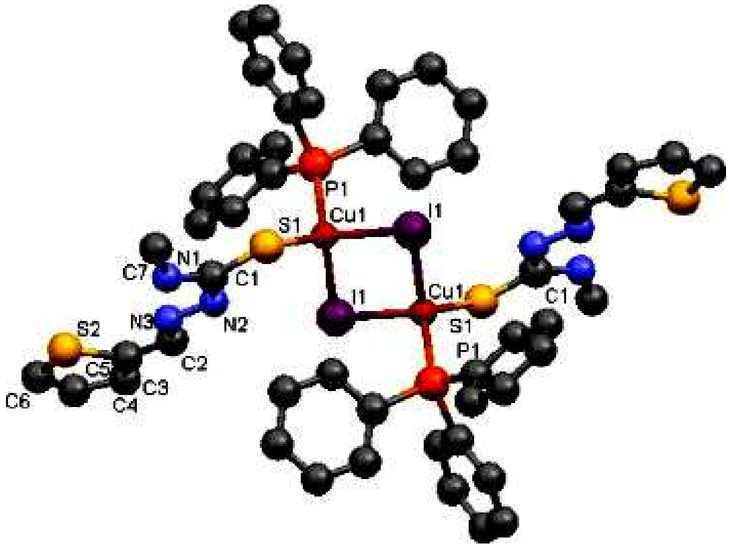


Figure 21 The structure of $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscMe)_2(PPh_3)_2]$.

Crystal data: triclinic system, space group $P\bar{1}$, a = 11.0530(10), b = 11.1610(10), c = 12.1320(10) Å, α = 107.540(10), β = 91.470(10), γ = 113.100(10)$^\circ$, Z = 1, D_c = 1.438 g/cm^3, R = 0.0412, R_w = 0.1056.

1.3 Objectives

1. To study the method and find the optimum condition for synthesizing Cu(I) complexes with mixed ligands of triphenylphospine and diphenylthiourea 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 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) Ultrasonic cleaner model AS 7240 AT, Auto science
6) X-ray fluorescence spectrometer model PW 2400, Philips
7) Fourier transform infrared spectrometer, model 783, Perkin – Elmer
8) Fourier transform NMR spectrometer 500 MHz, model UNITY INOVA, Varian
9) Bruker SMART APEX CCD diffractometer
10) UHU epoxy adhesive
11) Fiber glass, 0.4-0.7 mm. (in diameter)
12) Bee wax

2.2 Chemicals

Products of Fluka Chemical, Buchs, Switzerland

1) *N,N'*-Diphenylthiourea, $C_{13}H_{12}N_2S$, purum
2) Triphenylphosphine, $C_{18}H_{18}P$, purum
3) Copper(I) bromide, CuBr, L.R. grade
4) Copper(I) chloride, CuCl, L.R. grade

Products of Lab-Scan Analytical Science

1) Acetonitrile, CH_3CN, A.R. grade

Products of Aldrich Chemical Company, Inc

1) Copper(I) iodide, CuI, L.R. grade

2.3 Preparation of complexes

2.3.1 Preparation of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$ complex

Triphenylphosphine (0.53g, 2.02 mmol) was dissolved in 30 cm^3 of acetonitrile at 40 °C and then CuCl (0.1g, 1.01 mmol) was added. The mixture was sonicated for 15 minutes during that time a greenish precipitate was formed. *N,N'*-diphenylthiourea (0.23g, 1.01 mmol) was added and the new reaction mixture was sonicated for 30 minute where upon the precipitate gradually disappeared. 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.

2.3.2 Preparation of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$ complex

Triphenylphosphine (0.37g, 1.40 mmol) was dissolved in 30 cm^3 of acetonitrile at 40 °C and then CuBr (0.10g, 0.70 mmol) was added. The mixture was sonicated for 15 minutes during that time a greenish precipitate was formed. *N,N'*-diphenylthiourea (0.16g, 0.70 mmol) was added and the new reaction mixture was sonicated for 30 minute where upon the precipitate gradually disappeared. 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.

2.3.3 Preparation of $[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$ complex

Triphenylphosphine (0.28g, 1.06 mmol) was dissolved in 30 cm^3 of acetonitrile at 70-75 °C and then CuI (0.1g, 0.53 mmol) was added. The mixture was stirred for 2 hours. After that formation of a complete clear solution, *N,N'*-

diphenylthiourea (0.12g, 0.53 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 of 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

Cu, S, P and halides (Cl, Br and I) qualitative analyses of $[Cu(dptu)(PPh_3)_2Cl]\cdot 2CH_3CN$, $[Cu(dptu)(PPh_3)_2Br]\cdot H_2O$ and $[Cu(dptu)(PPh_3)_2I]\cdot CH_3CN$ 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)

^1H and ^{13}C-NMR spectra were recorded in DMSO-d_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 [Cu(dptu)(PPh$_3$)$_2$Cl]·2CH$_3$CN, [Cu(dptu)(PPh$_3$)$_2$Br]·H$_2$O and [Cu(dptu)(PPh$_3$)$_2$I]·CH$_3$CN were collected using SMART APEX CCD at Prince of Songkla University.

The structures of the synthesized crystals were determined by following steps in Figure 22. (Clegg, 1998)

Figure 22 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.

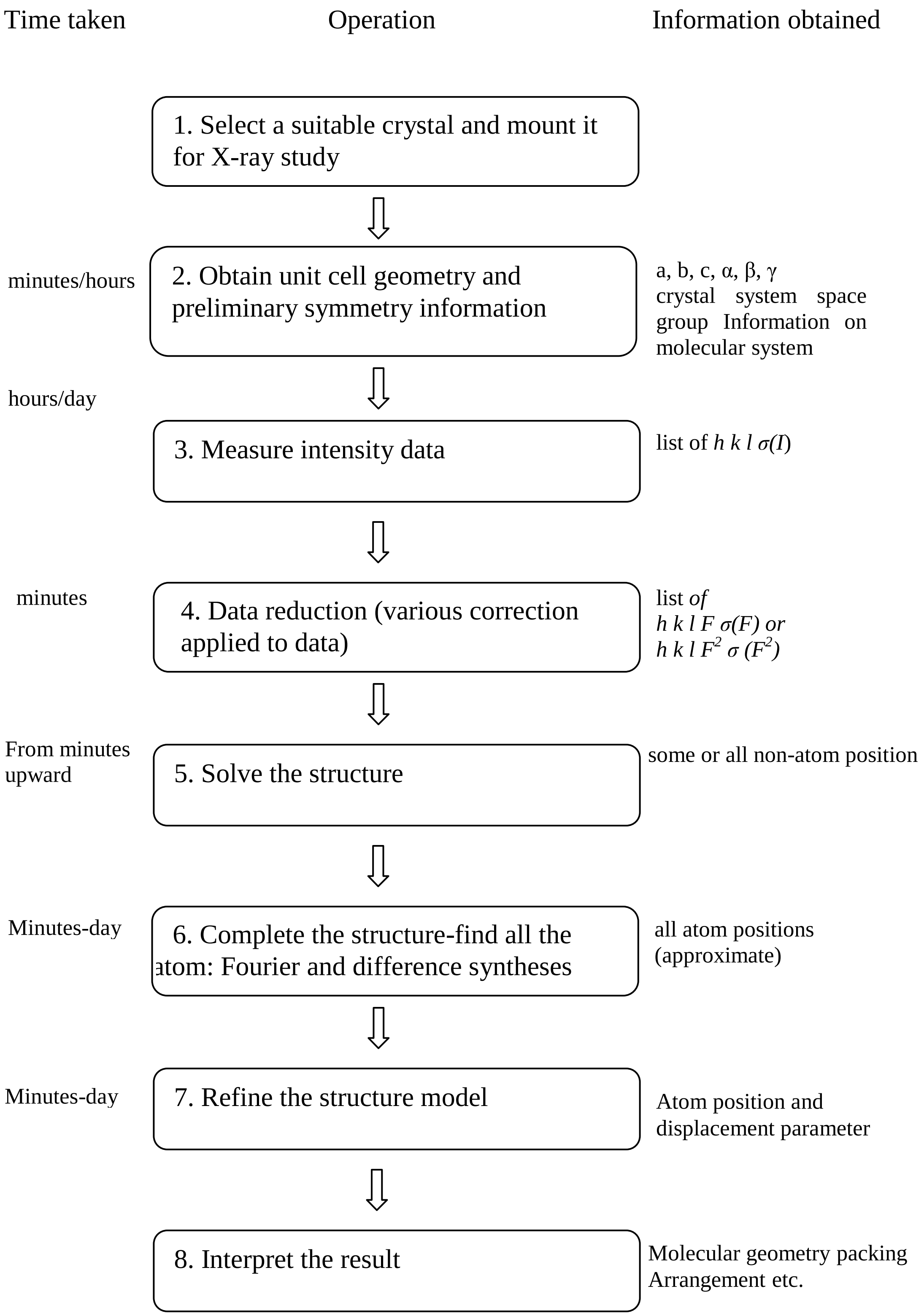


Figure 22 A flowchart for the step involved in a crystal structure determination (Clegg, 1998)

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.

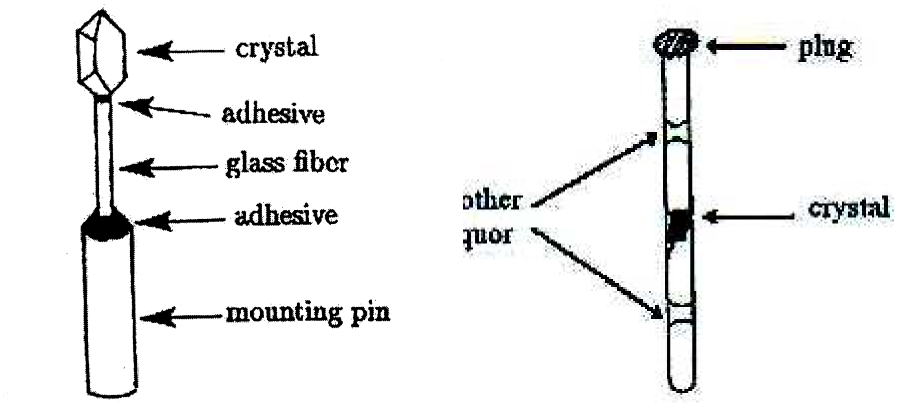
(4) Scan crystal with the Apex CCD, i.e. make a few quick exposures and check the images visually on spot shape, spacing and distribution.

2.5.2 Crystal Mounting

For single-crystal 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 23a). 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 23b). 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 23 Crystal mounting.

2.5.3 Optical Alignment

The mounted crystal was attached to a goniometer head (Figure 24). 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 (omega) 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 omega.

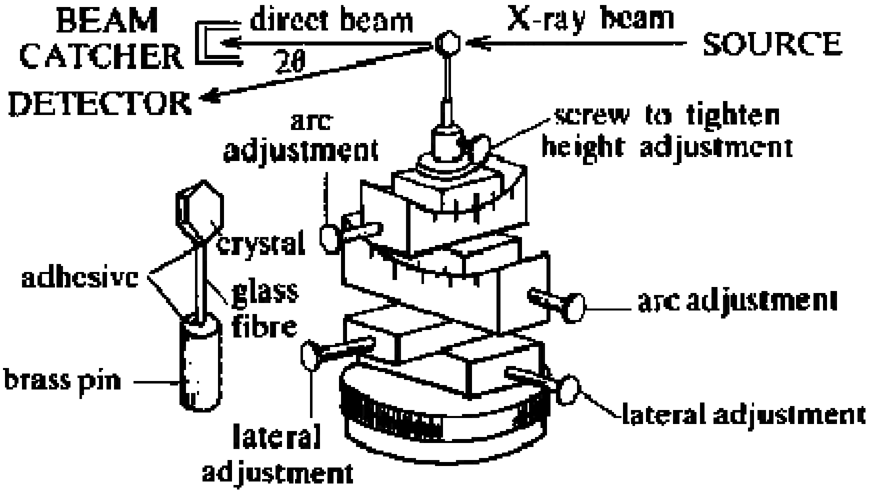


Figure 24 The goniometer head.

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. A diffractometer will often give a unit cell and orientation for a crystal in less than an hour ; a few minutes are usually enough with an area detector.

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.), σ (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 [$I(hkl) \alpha \left| F(hkl) \right|^2$]. The measured intensity is affected by various factors, eg. Lorenz-polarixation factors, absorption problems etc., however, for which corrections must be applied. The conversion of intensities I to ‘observed structure amplitudes’ $\left| F_o \right|$ (o = observed) or F^2_{o} and, correspondingly, of s.u.’s $\sigma(I)$ to σ (F_o) or σ (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 $h, k, l,$ $\left| F_o \right|$, $\sigma(F_o)$ [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, 2008).

A simplified flow chart is shown in Figure 25.

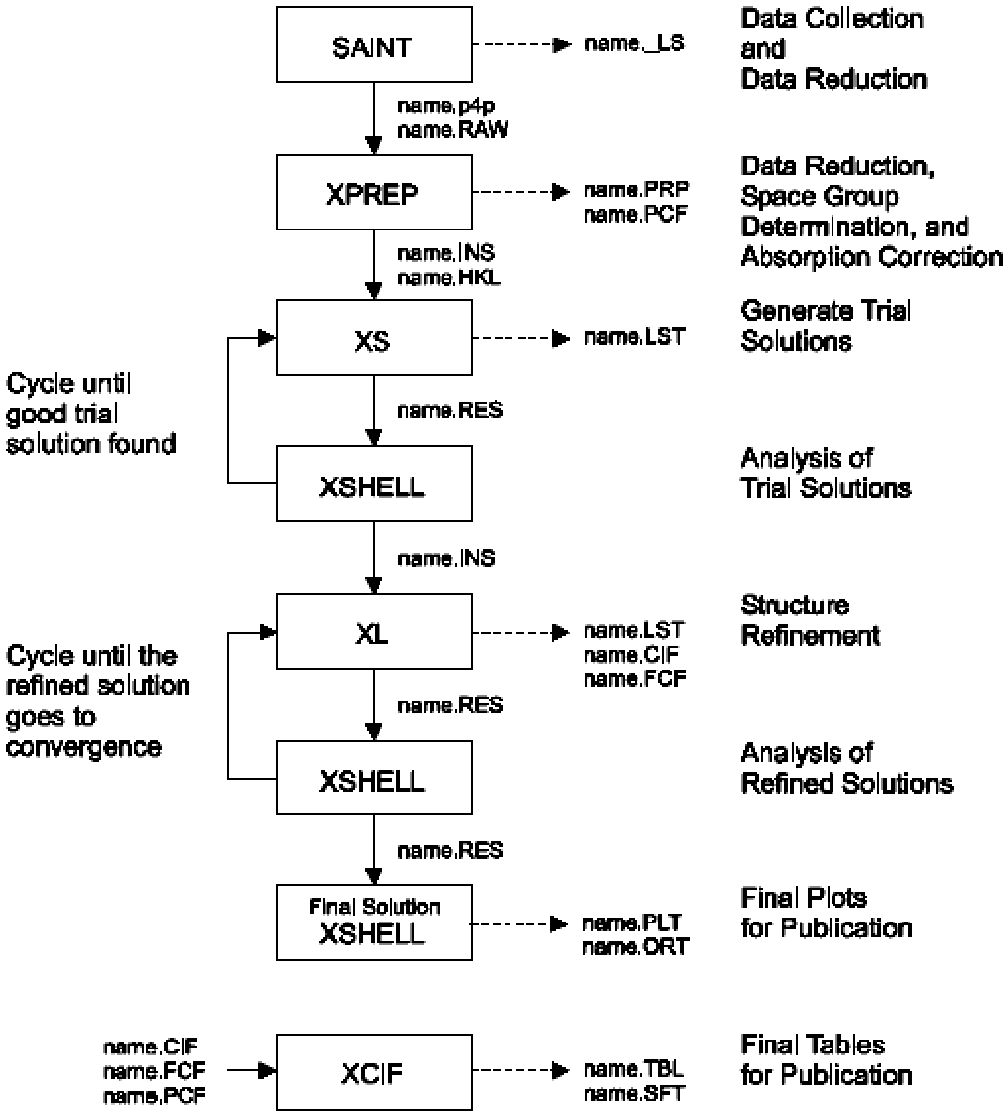


Figure 25 A flowchart of structure determination and refinement.

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

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

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

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 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 Table 2.

Table 1 The condition of preparation compounds.

Reactants	Mole ratio	Solvent	Temp* (°C)	Complex
CuCl : PPh_3 : dptu	1:2:1	acetonitrile	40	$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$
CuBr : PPh_3 : dptu	1:2:1	acetonitrile	40	$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$
CuI : PPh_3 : dptu	1:2:1	acetonitrile	70-75	$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$

Temp* = temperature

Table 2 The physical properties of ligands and complexes.

Compound	Physical properties			
	Apperance	Colour	Melting point (°C)	Solubility
Ligand dptu	Powder	White	150-153	Soluble*
Ligand PPh_3	Powder	White	79-81	Soluble**
$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$	Prism	Colorless	124-126	Soluble***
$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$	Prism	Colorless	147-149	Soluble***
$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$	Prism	Colorless	159-161	Soluble***

Soluble* = soluble in ethanol, acetone and acetonitrile

Soluble** = soluble in ethanol, acetone, acetonitrile and water

Soluble*** = soluble in chloroform, dichloromethane, DMSO, acetone and acetonitrile

3.2 Elemetal analysis

Table 3 The partial elemental analyses of the complexes.

Complex	%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	%S Found (Calcd.)
$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$	68.12 68.16	5.14 5.18	6.13 6.00	3.57 3.43
$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$	64.87 64.37	4.74 4.85	3.18 3.06	3.48 3.51
$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$	62.06 62.23	4.65 4.61	4.12 4.27	3.12 3.26

3.3 X-ray Fluorescence Spectrometry

The X-ray fluorescence spectra of the compounds are shown in Figure 26-34.

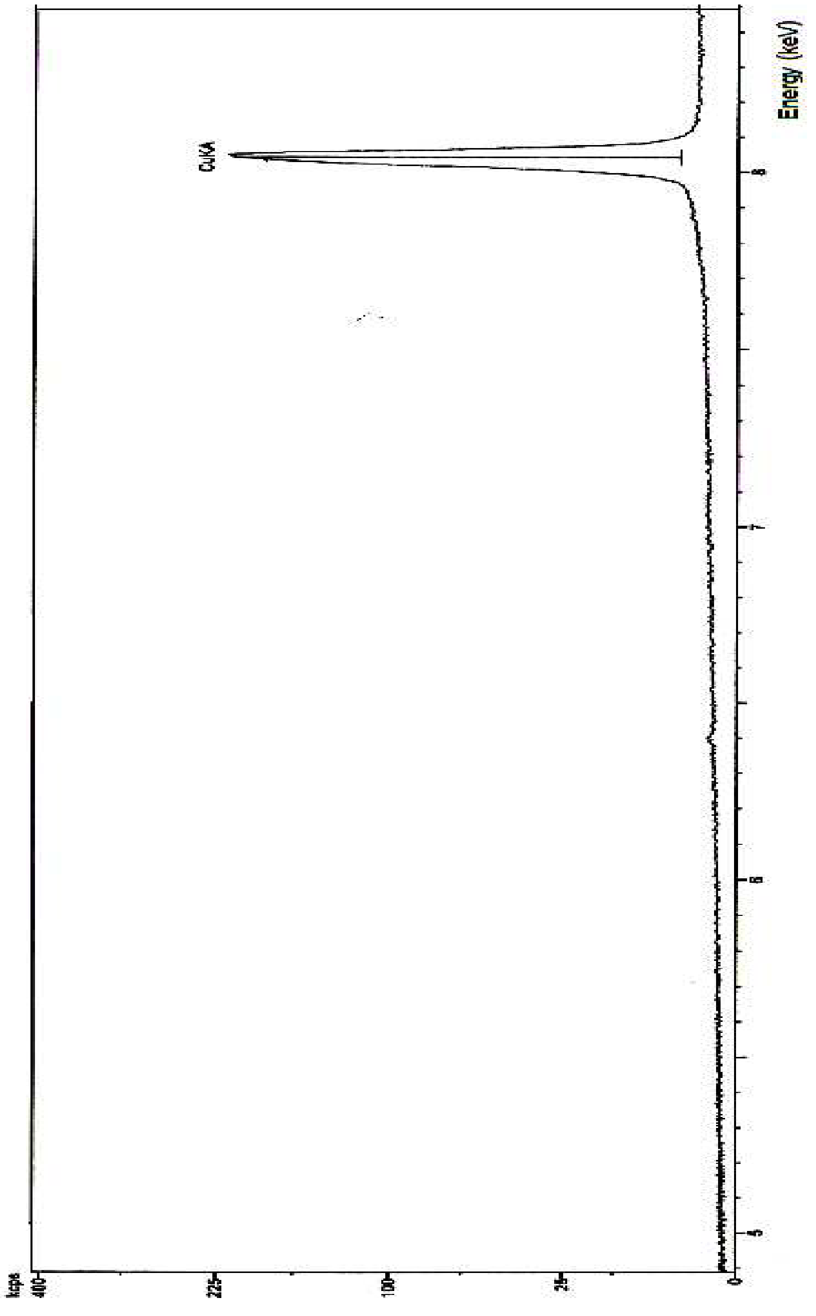


Figure 26 The Cu(K_α) spectrum of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$.

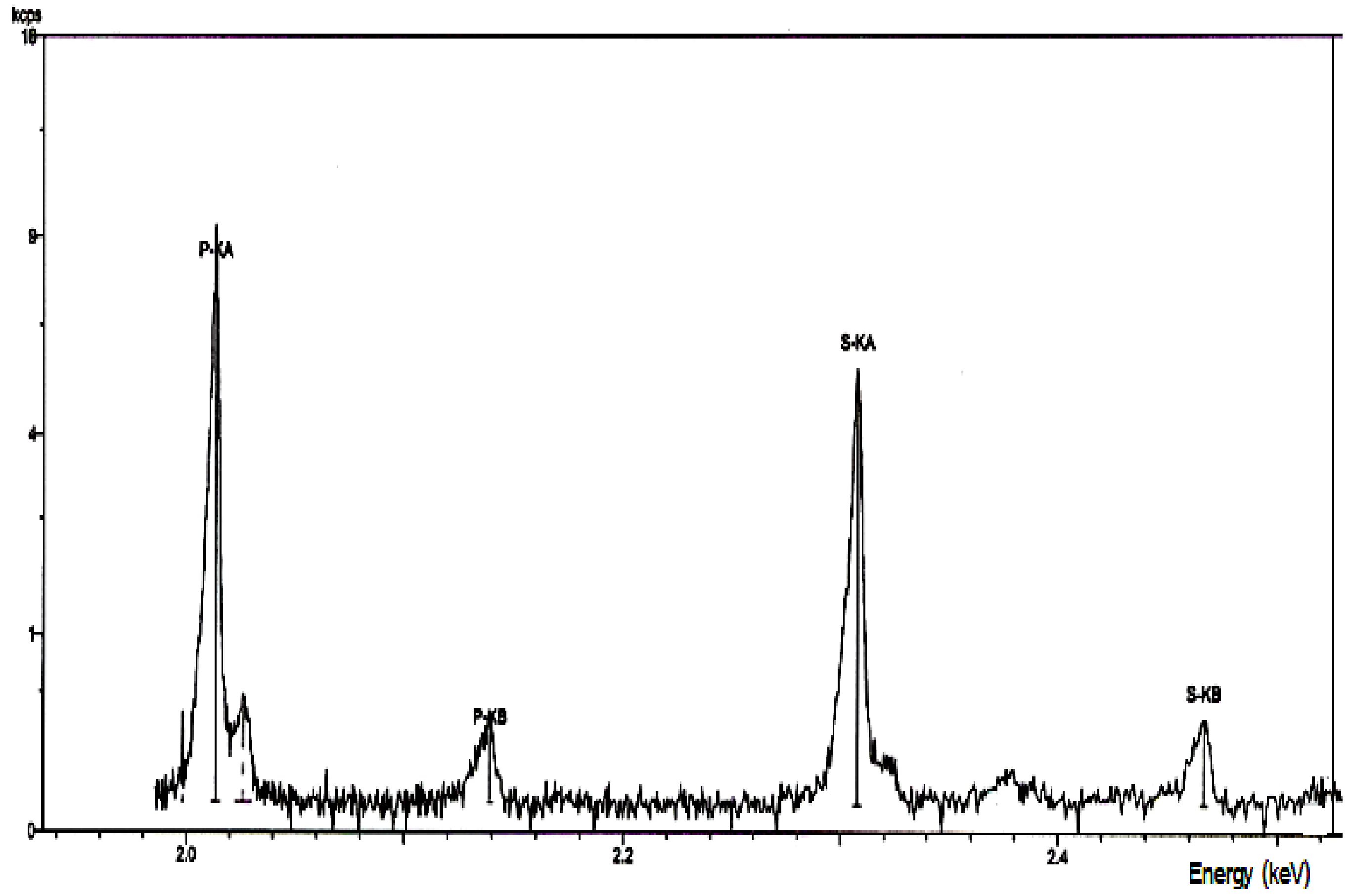


Figure 27 The S(K_α), S(K_β), P(K_α) and P(K_β) spectrum of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$.

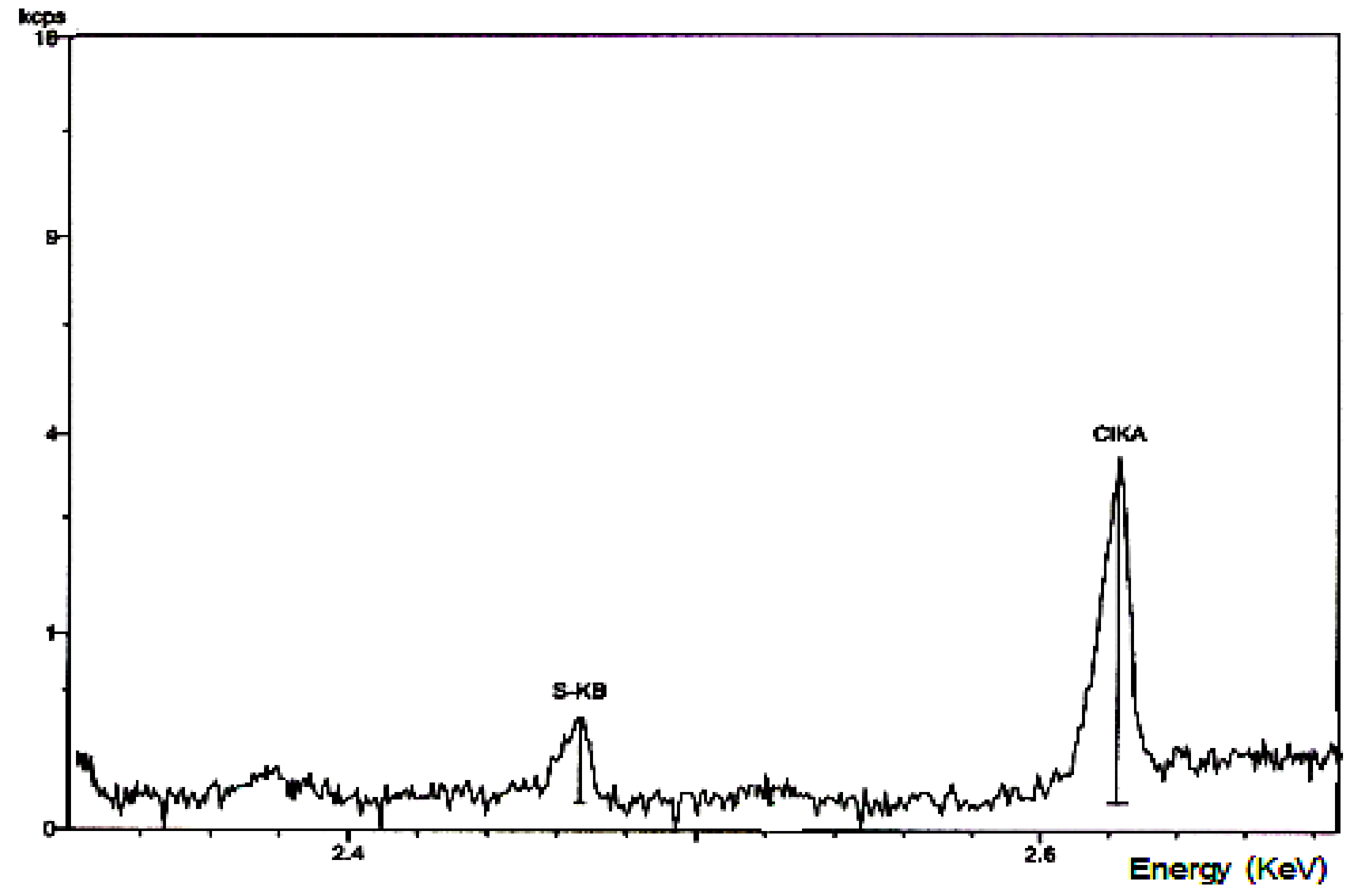


Figure 28 The Cl(K_α) spectrum of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$.

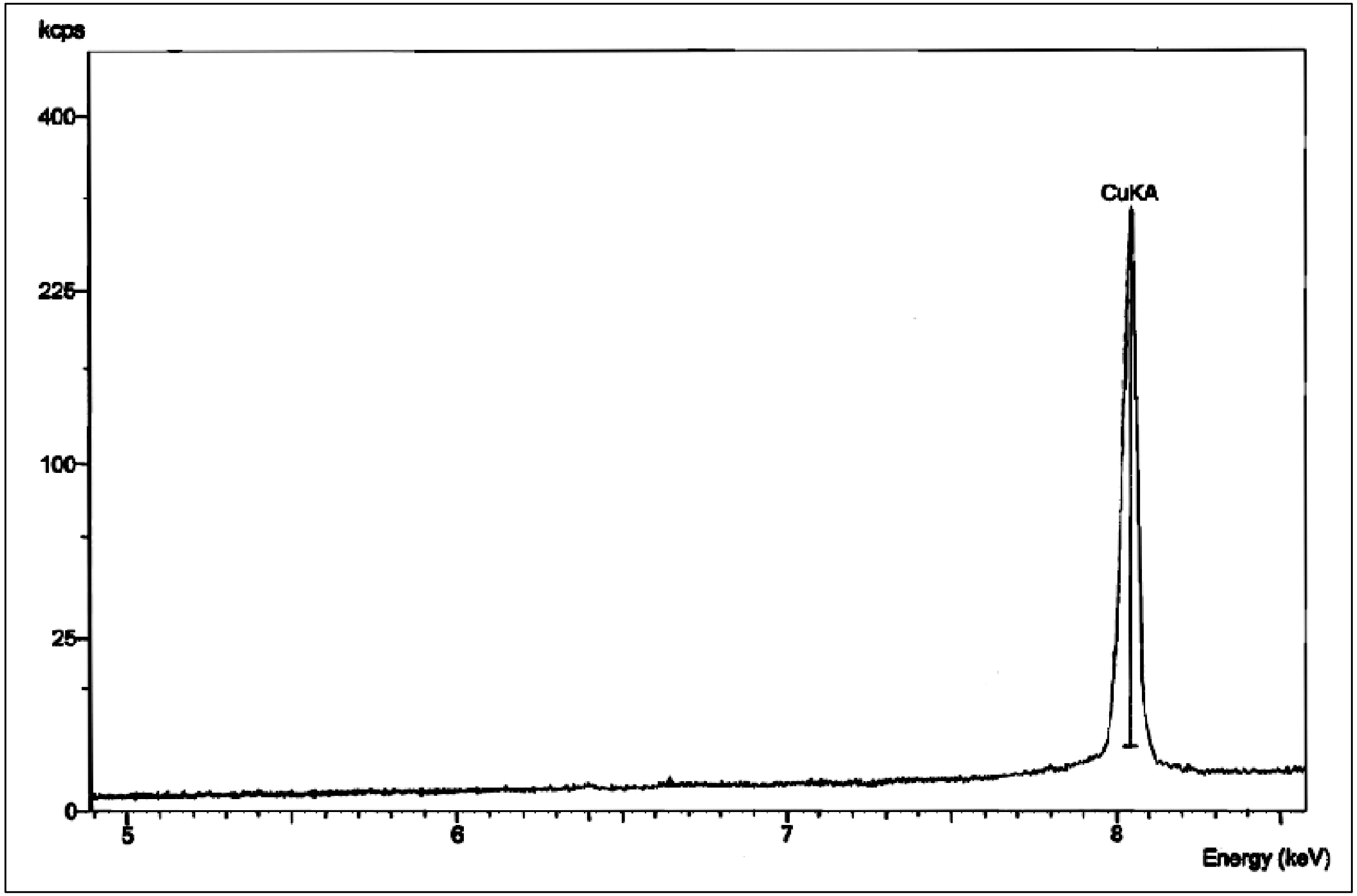


Figure 29 The Cu(K_α) spectrum of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

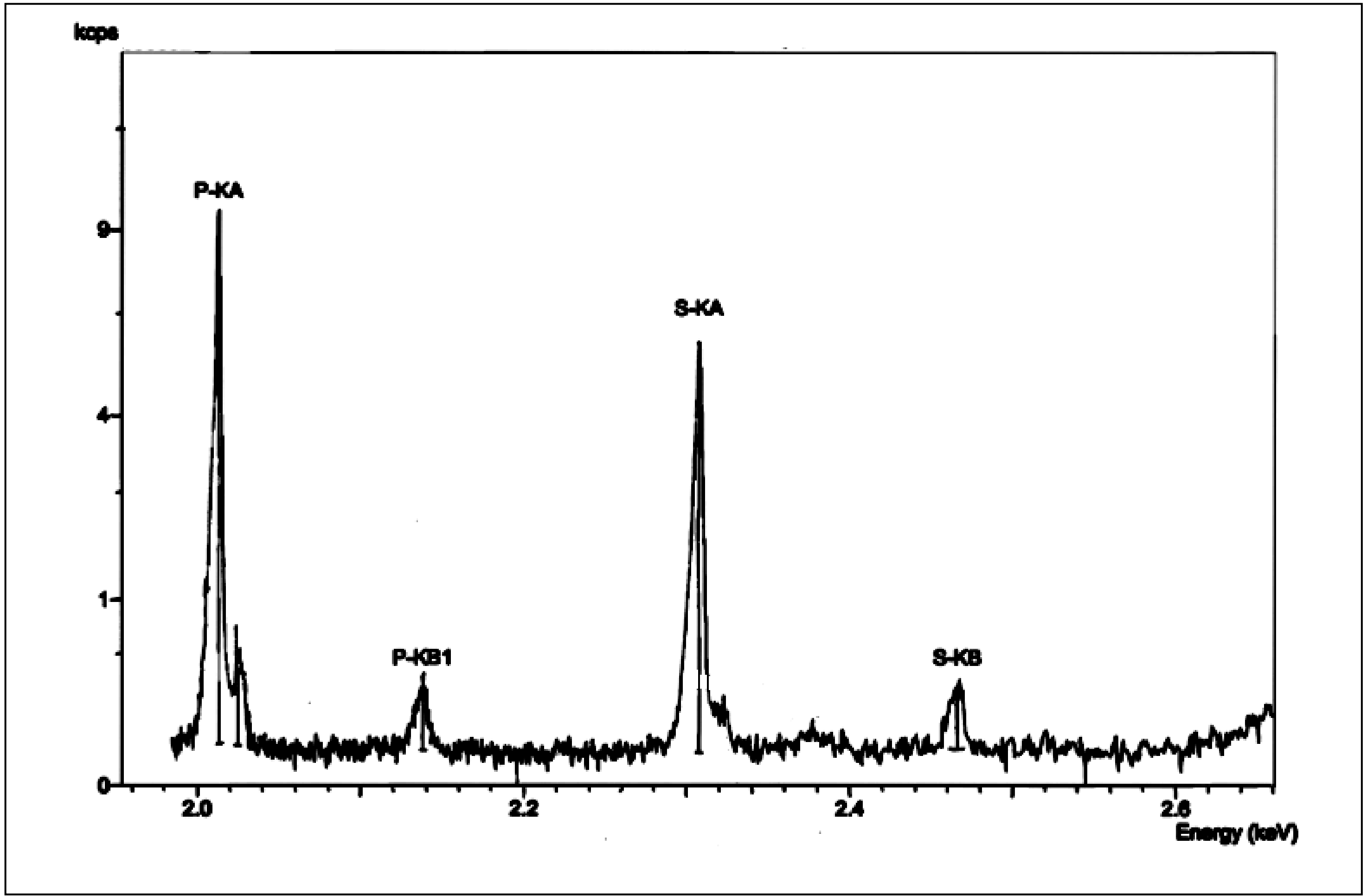


Figure 30 The S(K_α), S(K_β), P(K_α) and P(K_β) spectrum of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

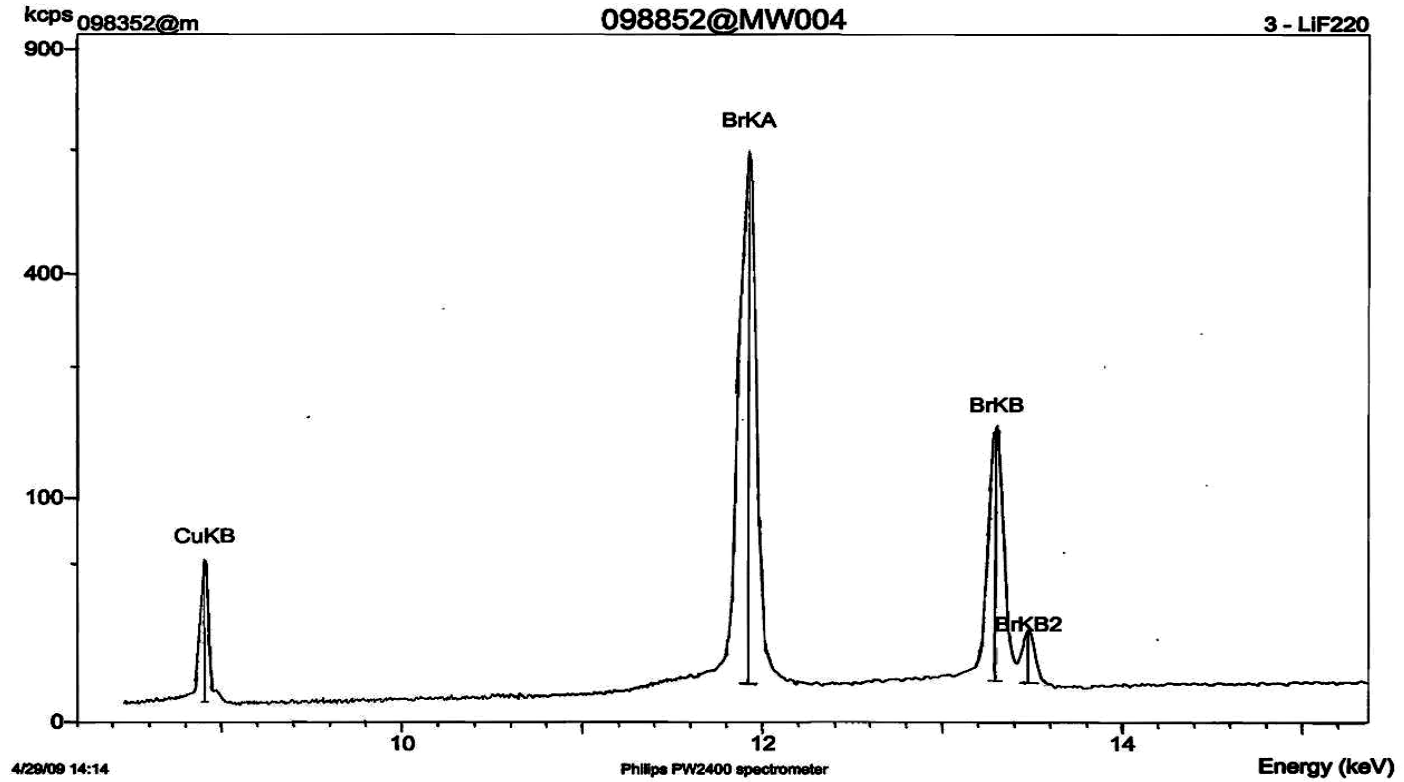


Figure 31 The Br(K_{α}) spectrum of [CuBr(PPh$_3$)$_2$(dptu)]·H$_2$O.

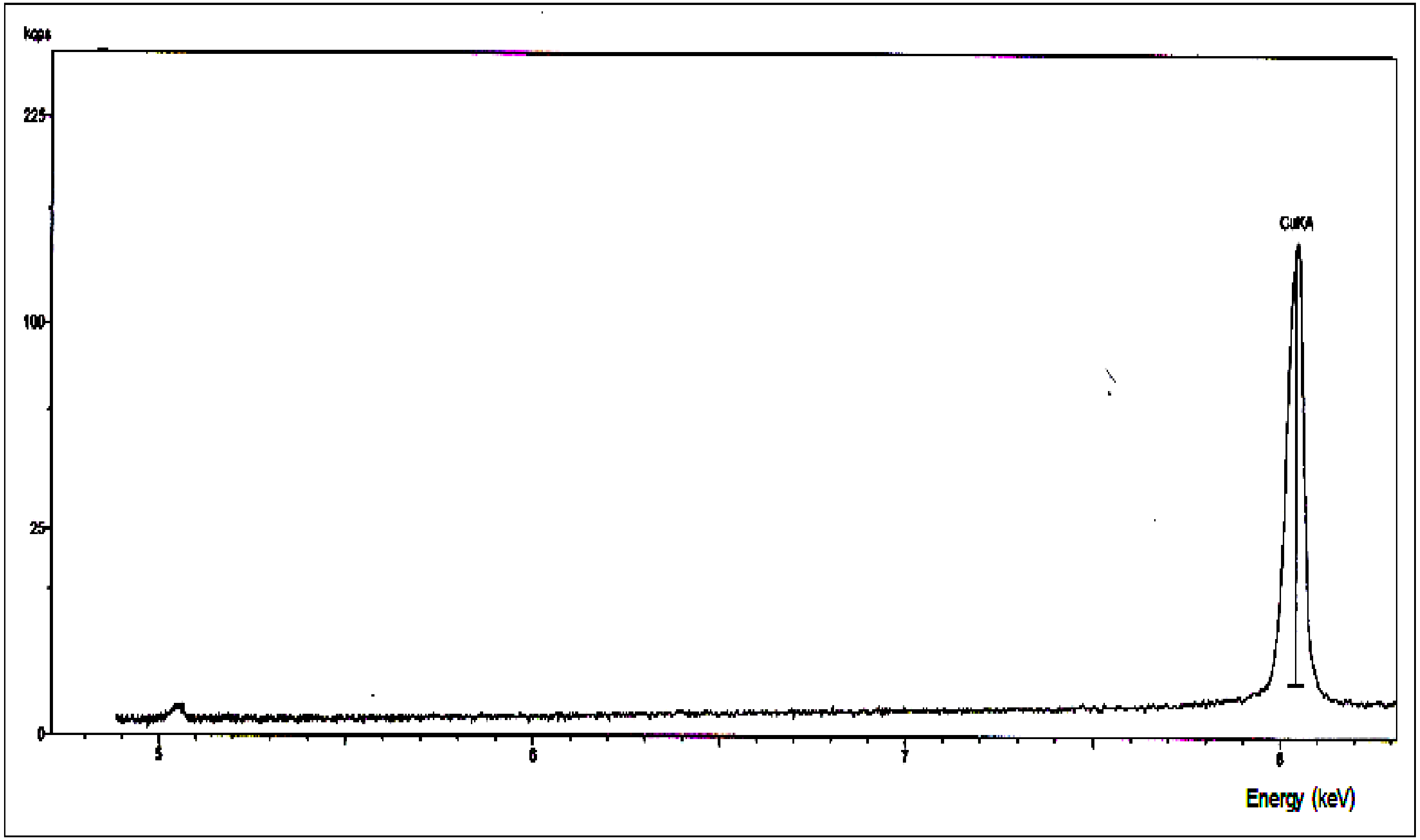


Figure 32 The Cu(K_α) spectrum of $[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$.

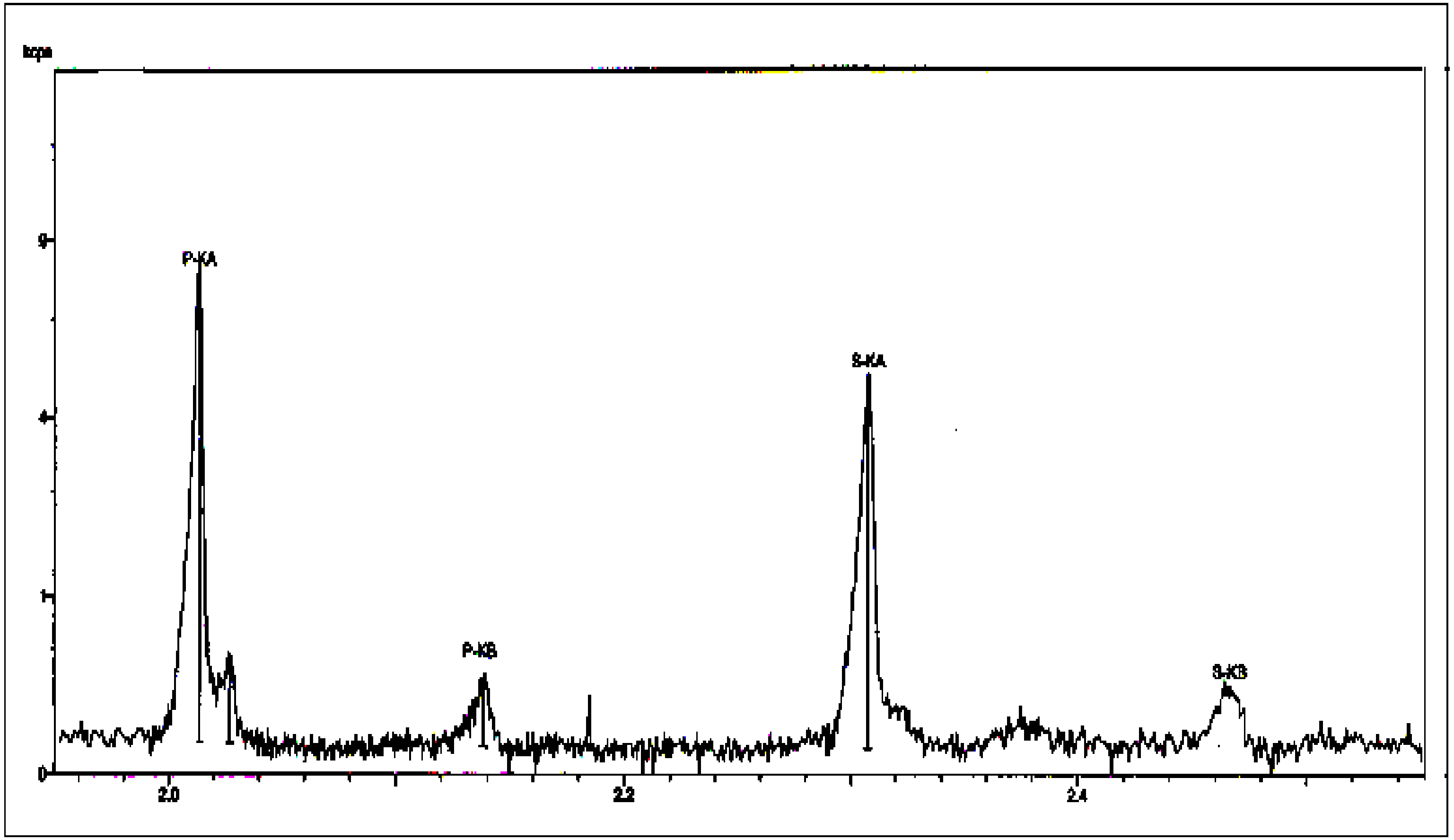


Figure 33 The S(K_α), S(K_β), P(K_α) and P(K_β) spectrum of [CuI(PPh_3)$_2$(dptu)]·CH_3CN.

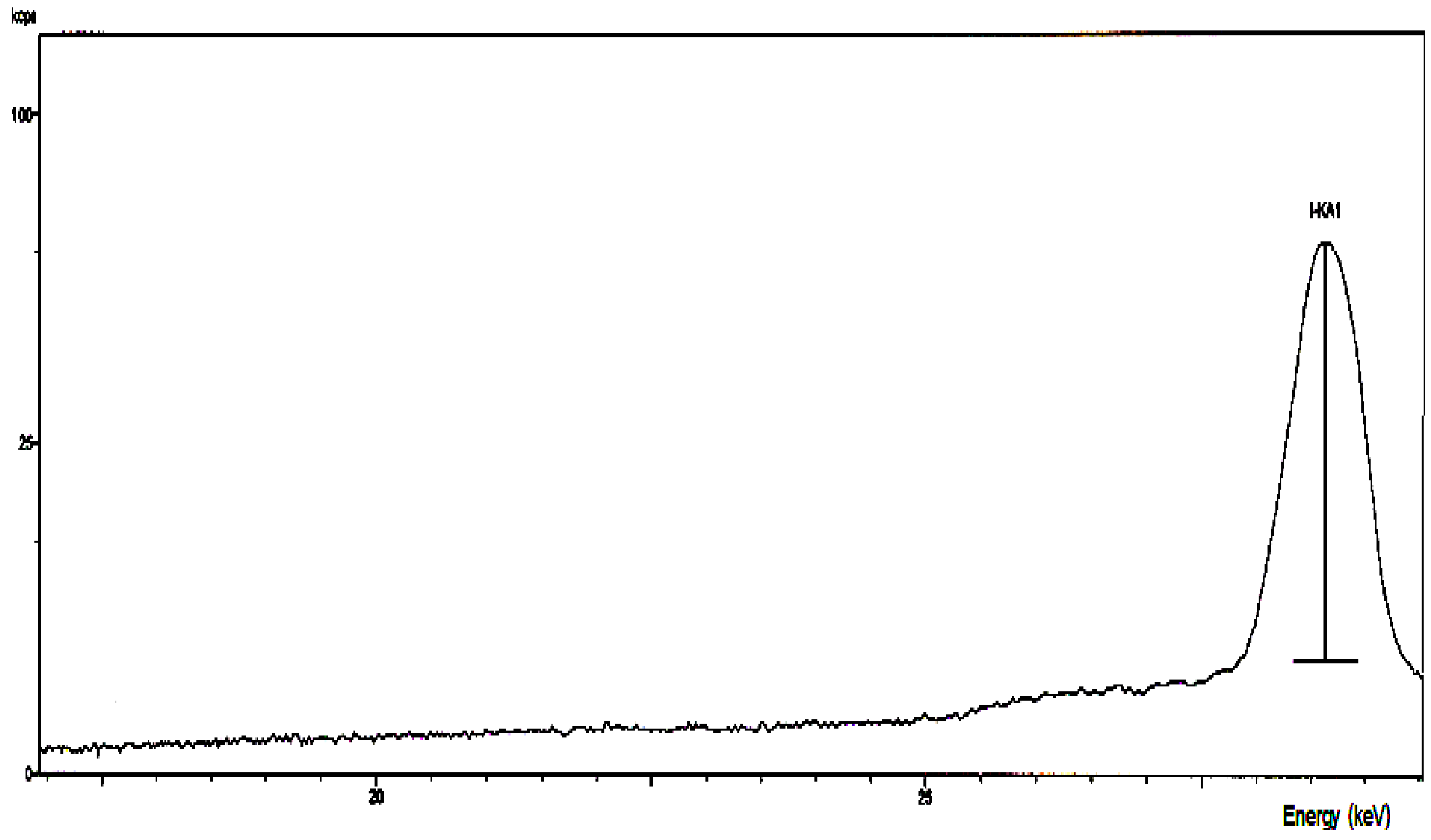


Figure 34 The I(K_{α}) spectrum of [CuI$(PPh_3)_2$(dptu)]·CH_3CN.

3.4 Infrared Spectroscopy

The infrared spectrum of the ligands and compounds are shown in Figure 35-39.

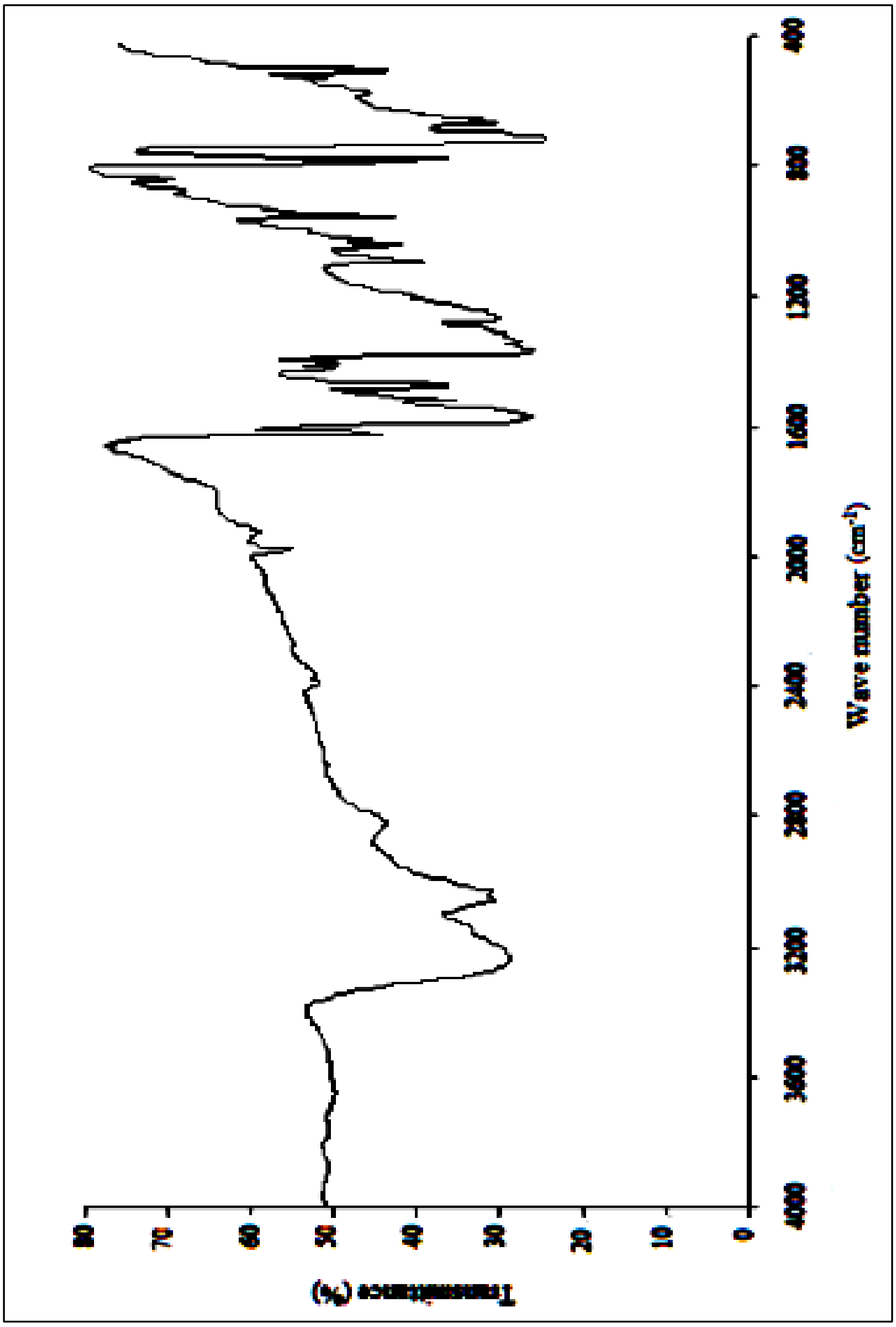


Figure 35 The infrared spectrum of Triphenylphosphine(PPh$_3$).

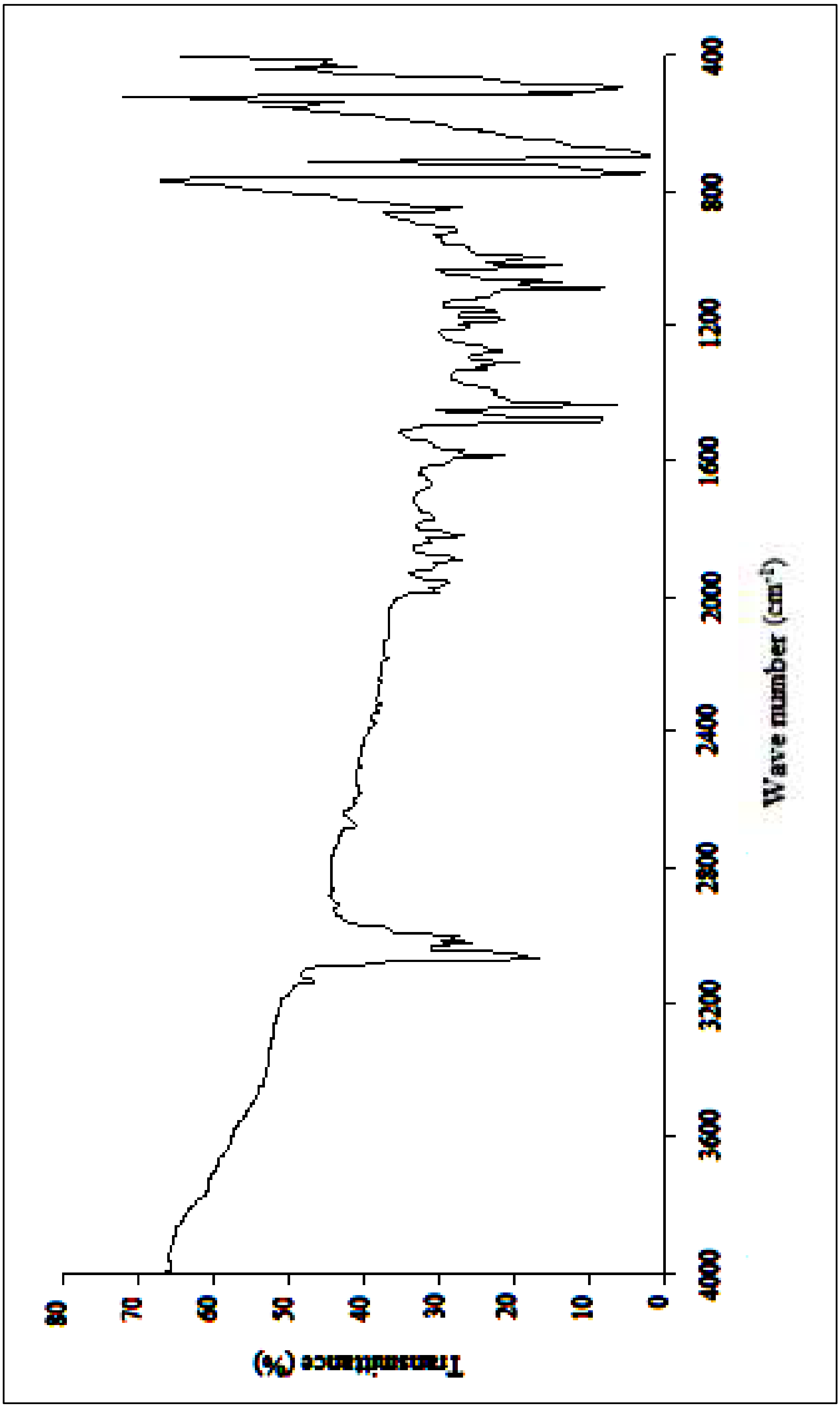


Figure 36 The infrared spectrum of *N*,*N*’-diphenylthiourea (dptu).

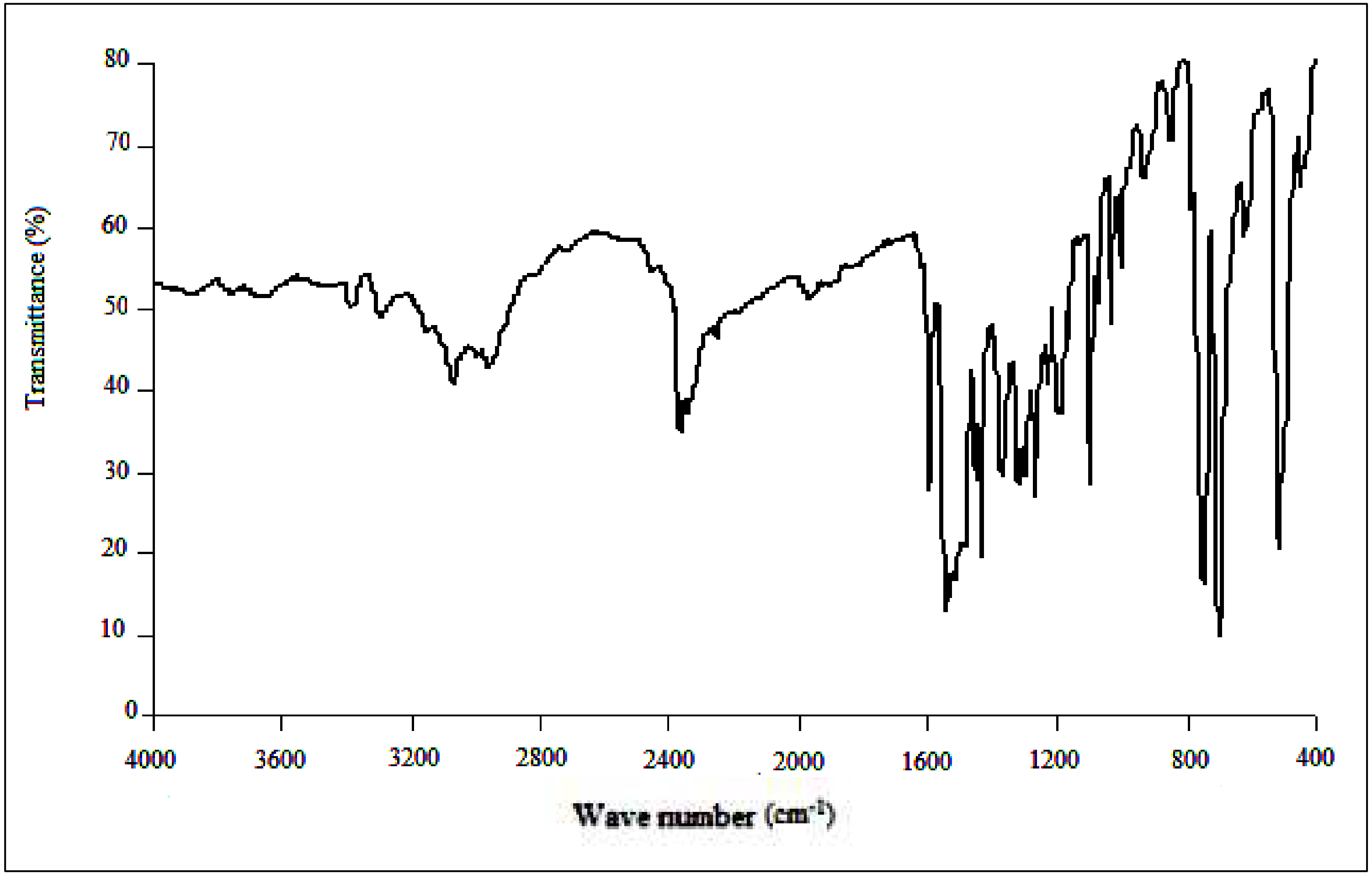


Figure 37 The infrared spectrum of [CuCl(PPh$_3$)$_2$(dptu)]·2CH$_3$CN.

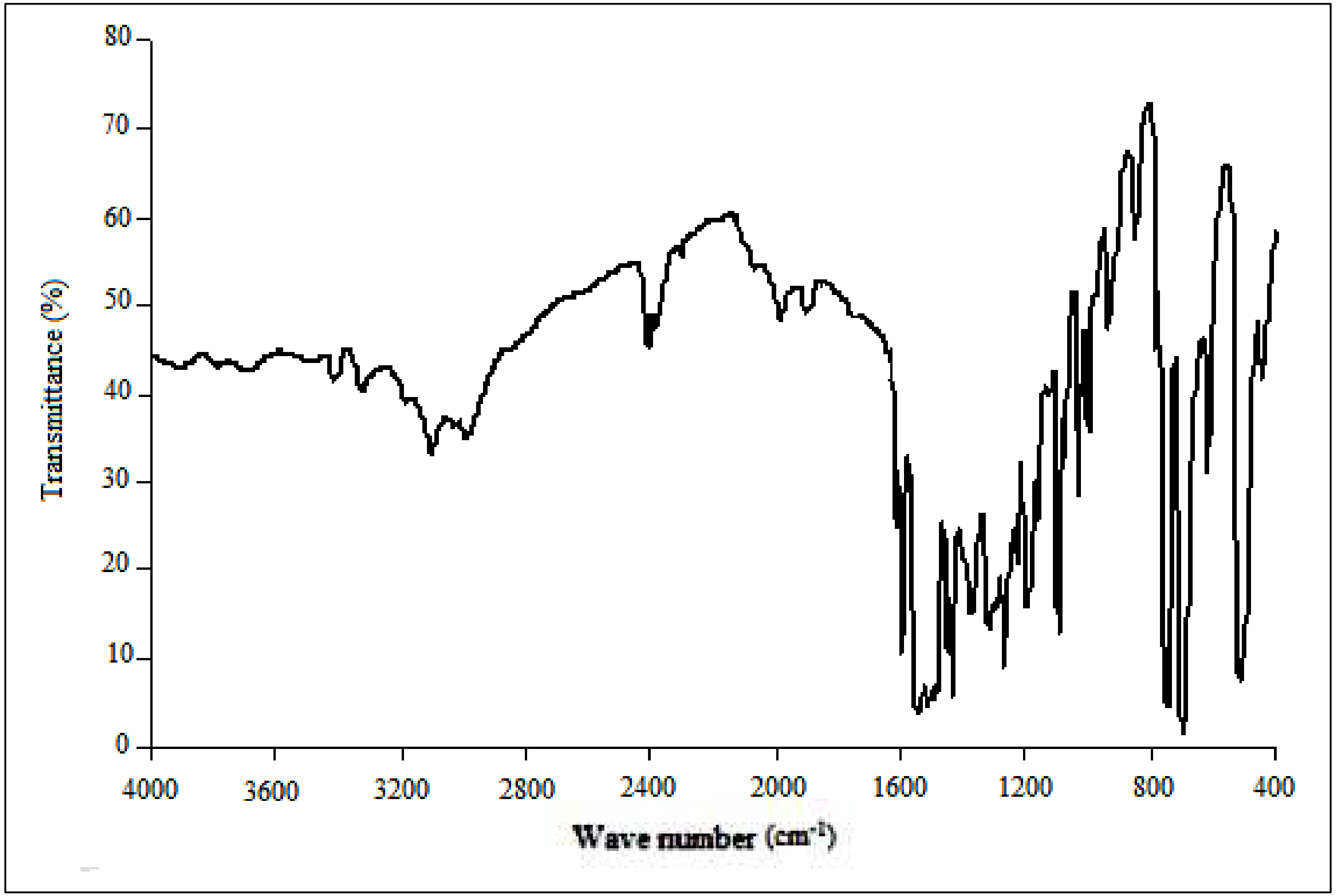


Figure 38 The infrared spectrum of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

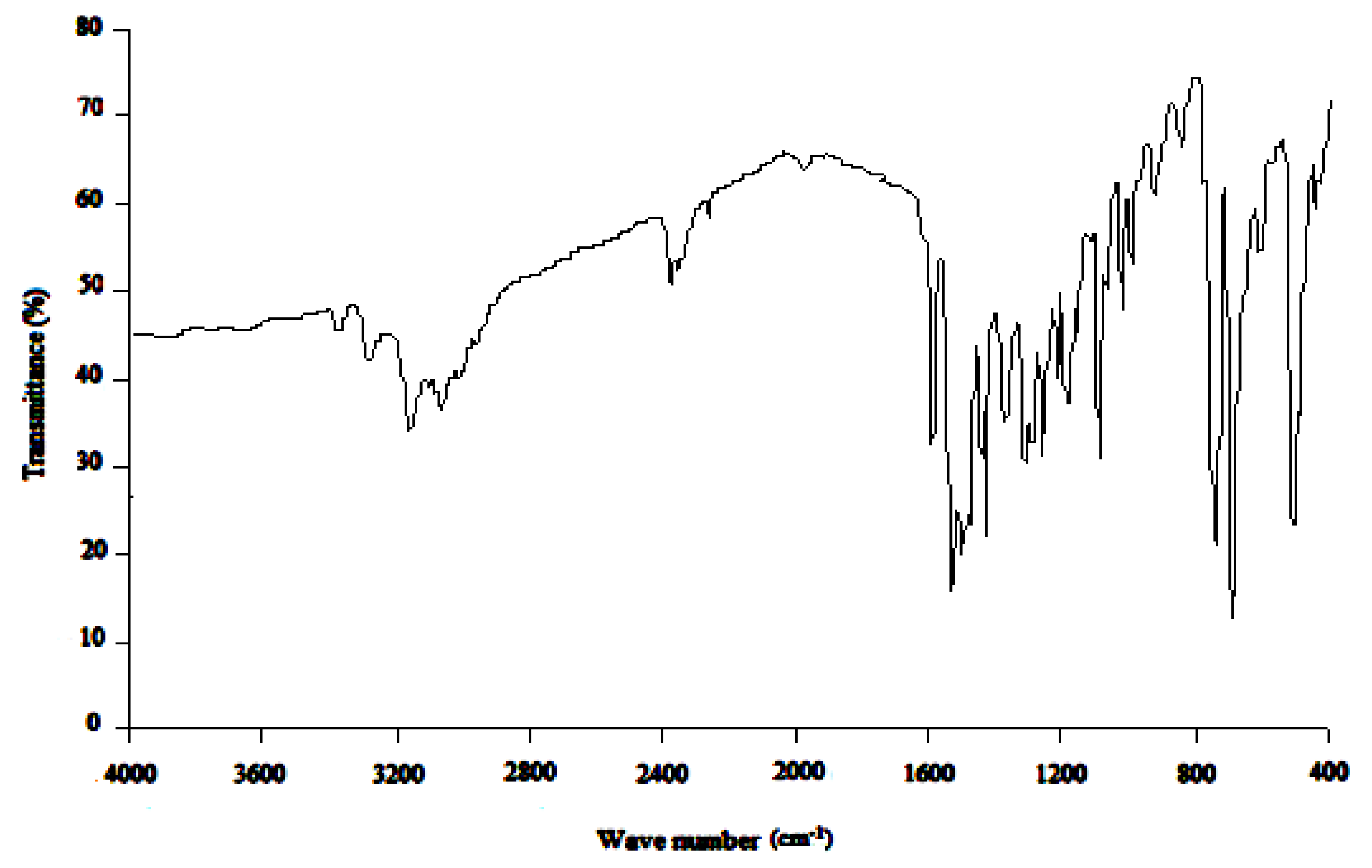


Figure 39 The infrared spectrum of $[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$.

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 the shown in Figures 40-49.

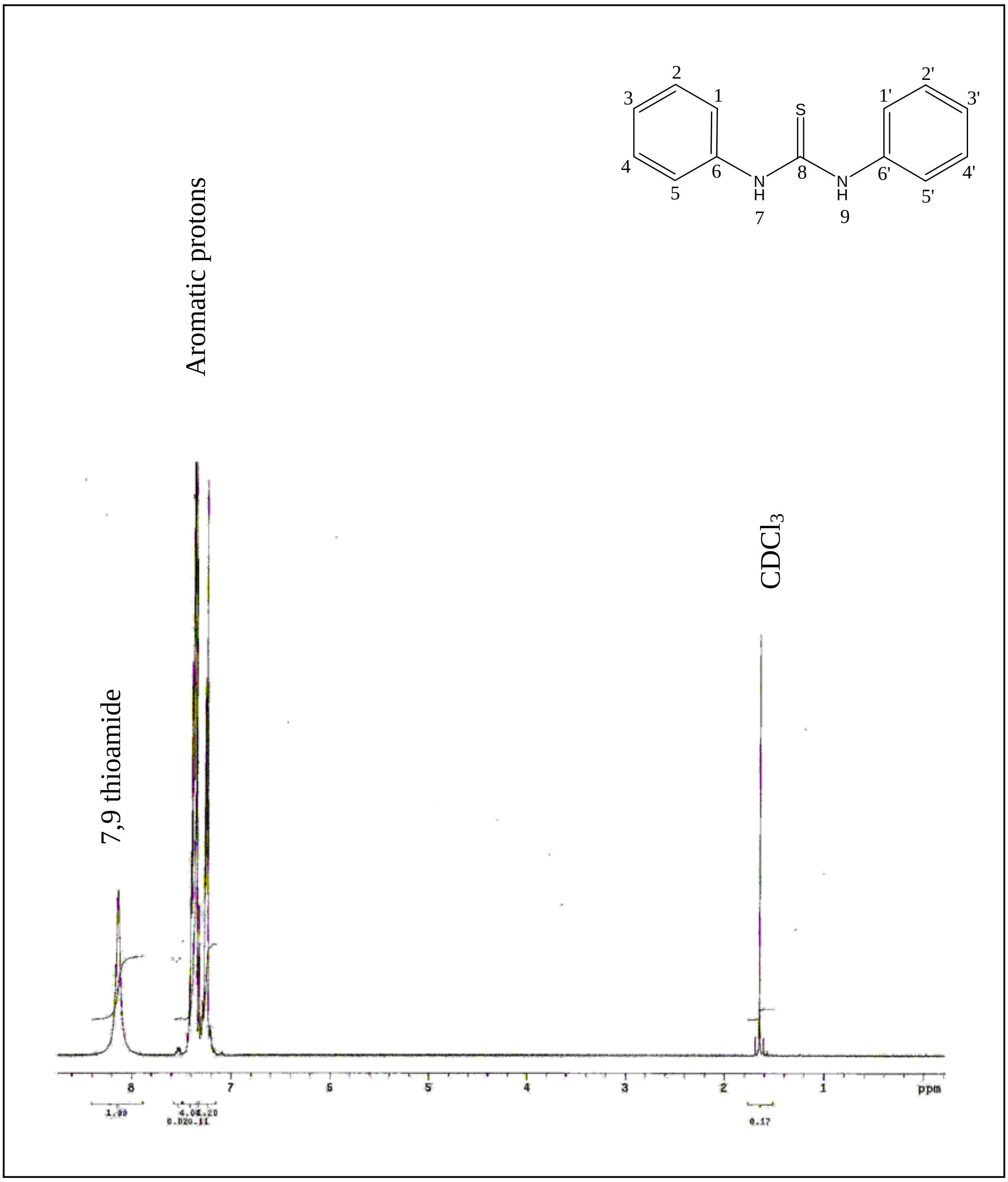


Figure 40 ^{1}H NMR spectrum of *N,N'*-diphenylthiourea (dptu).

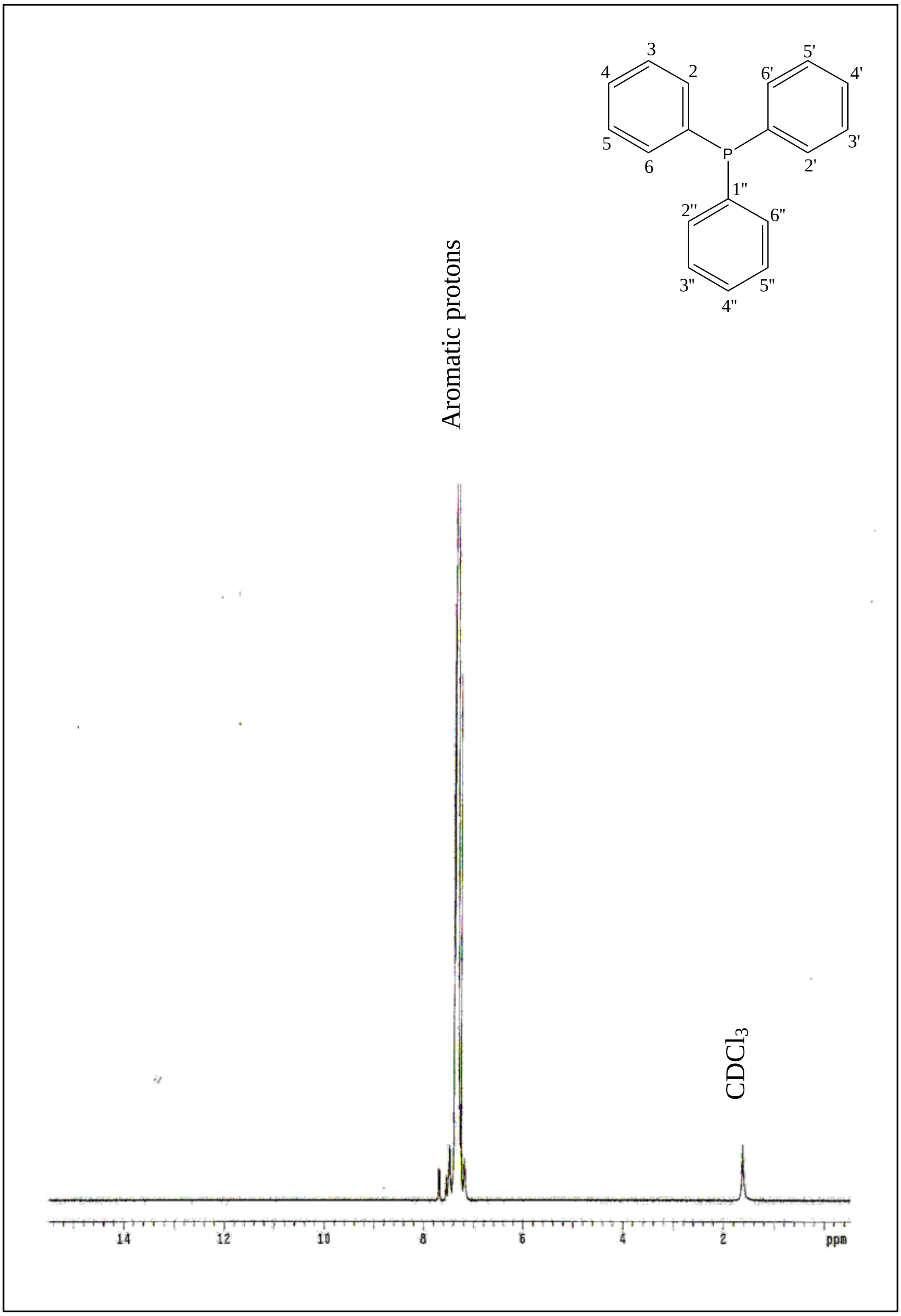


Figure 41 ^{1}H NMR spectrum of Triphenylphosphine (PPh$_3$).

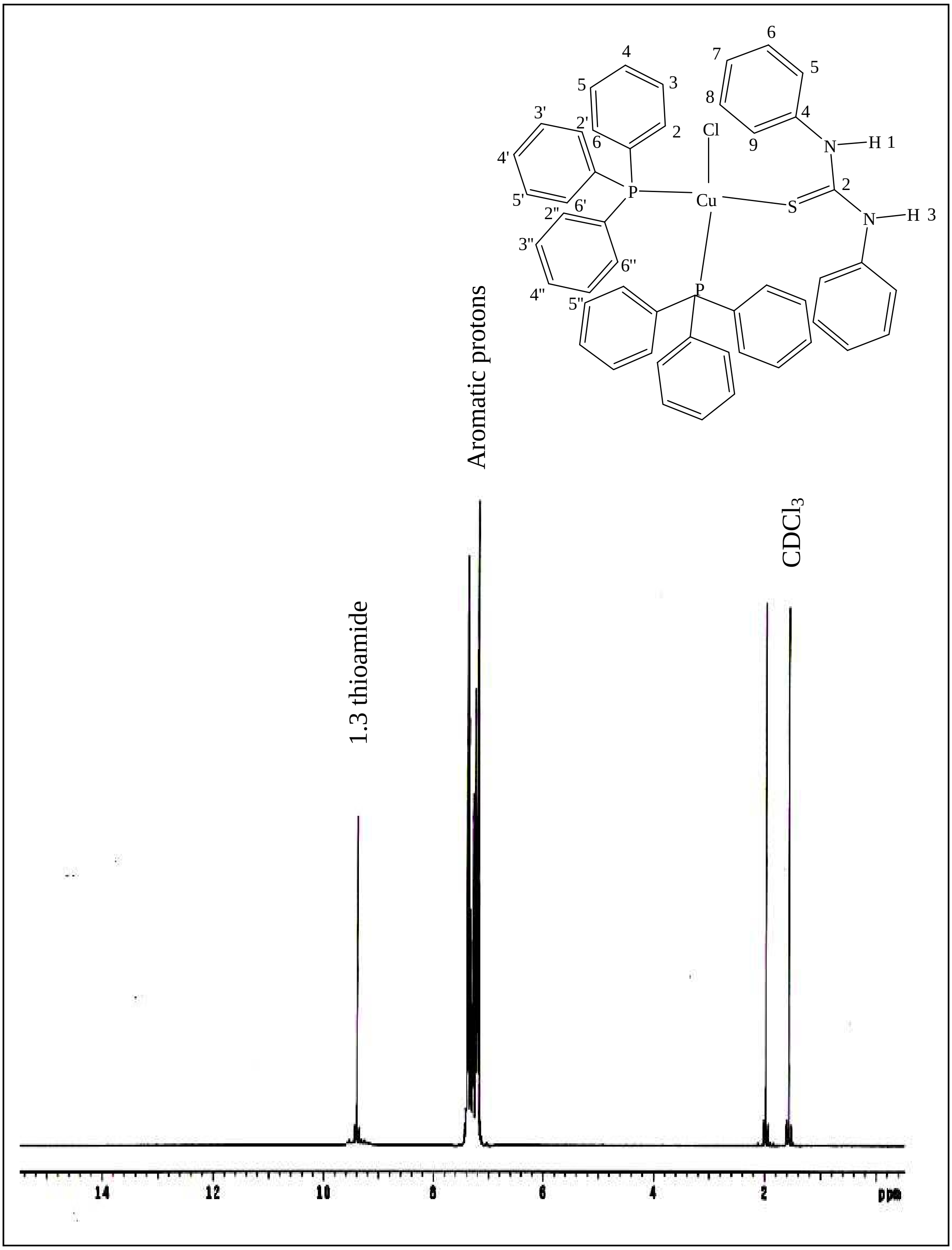


Figure 42 ^{1}H NMR spectrum of [CuCl(PPh$_3$)$_2$(dptu)]·2CH$_3$CN.

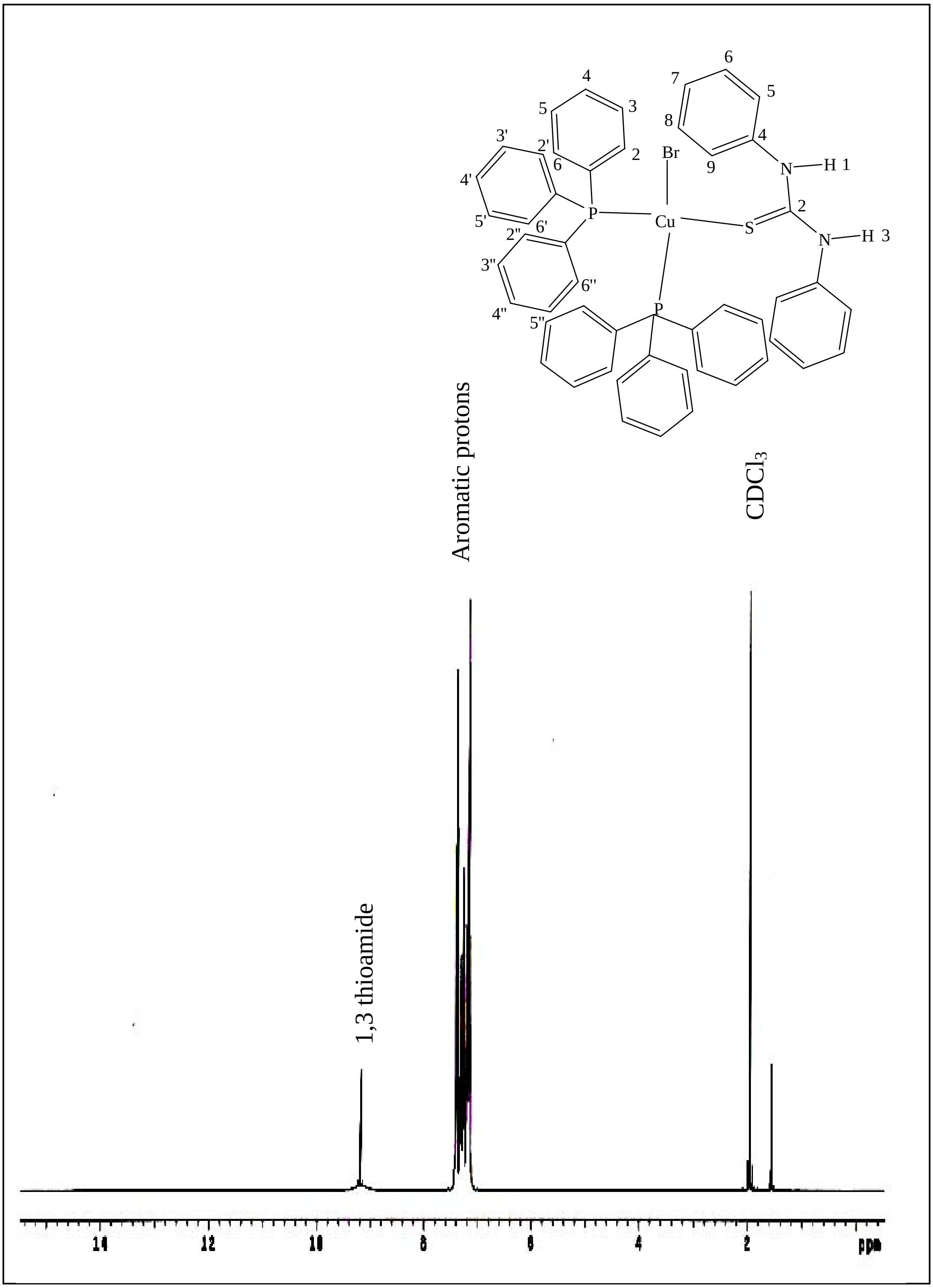


Figure 43 ^{1}H NMR spectrum of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

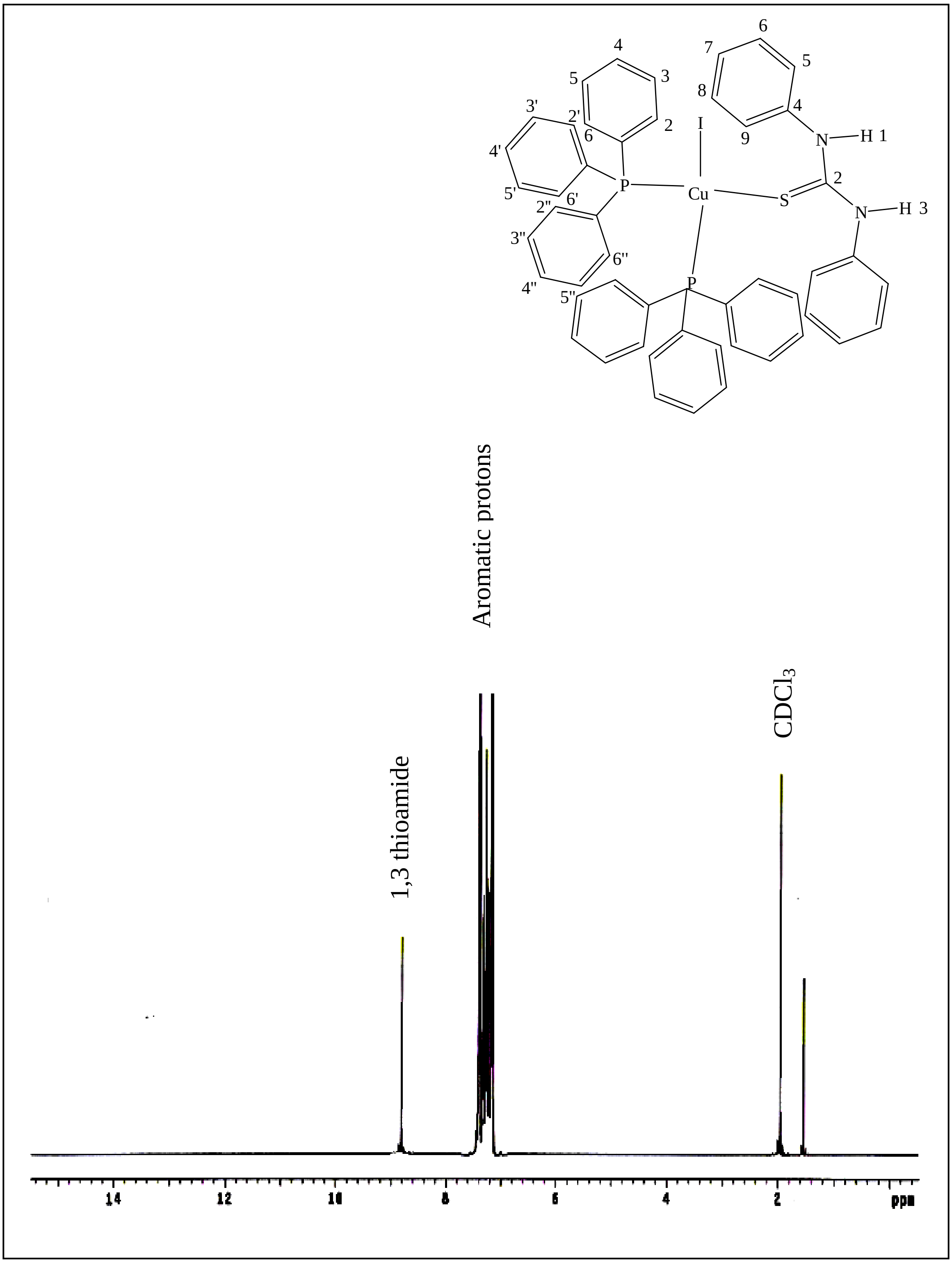


Figure 44 ^{1}H NMR spectrum of [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN.

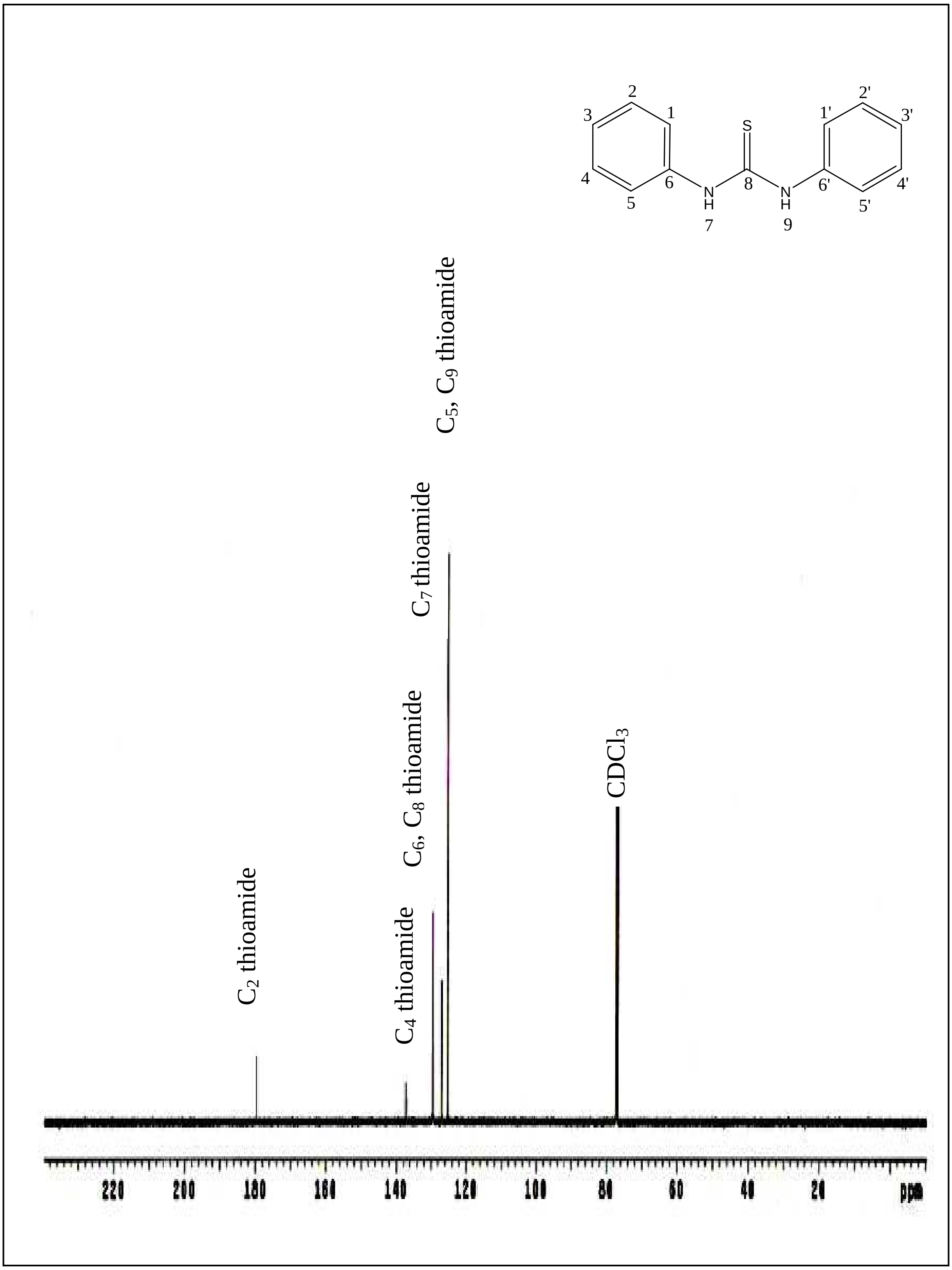


Figure 45 ^{13}C NMR spectrum of *N*,*N'*-diphenylthiourea (dptu).

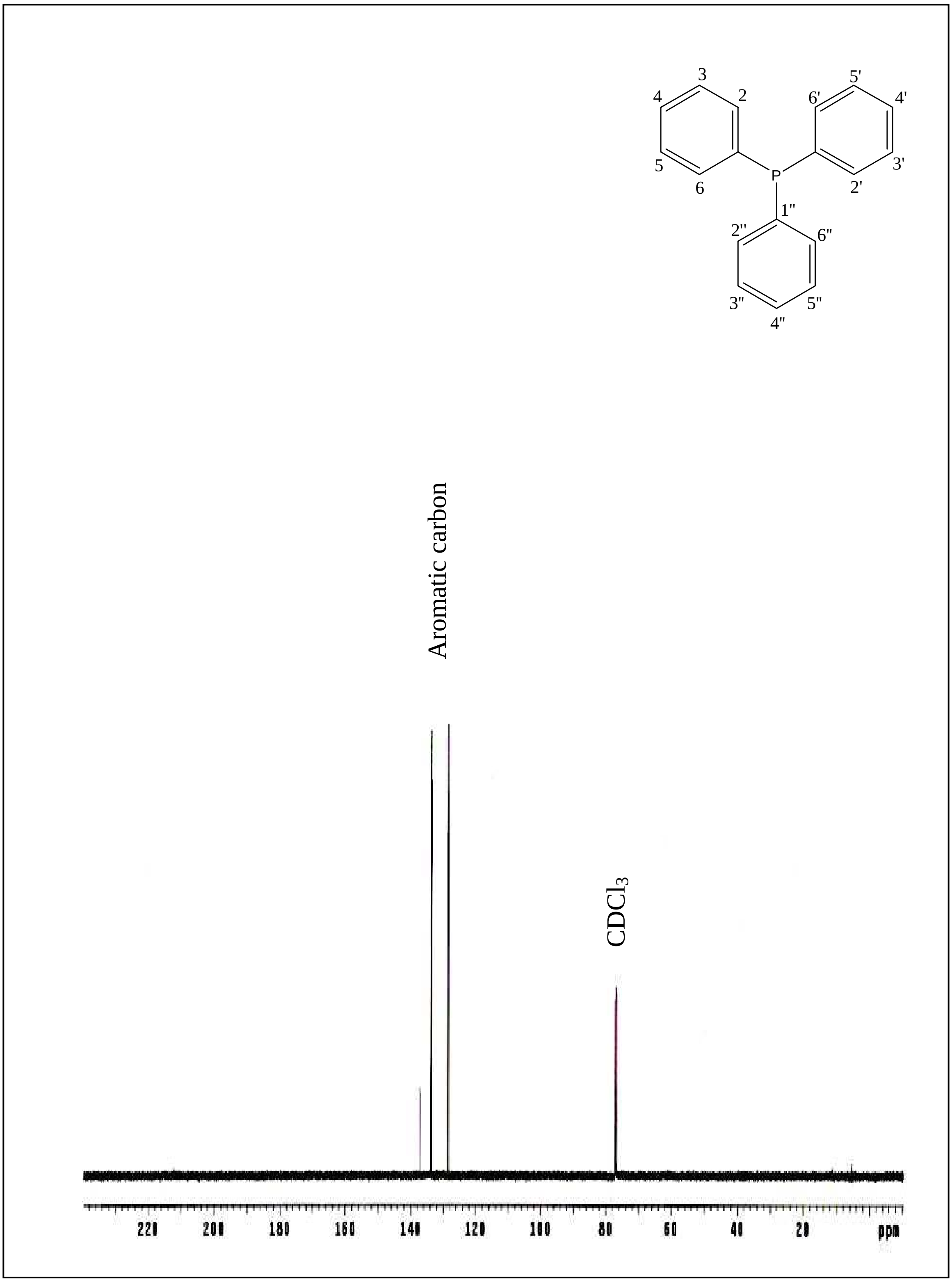


Figure 46 ^{13}C NMR spectrum of Triphenylphosphine (PPh_3).

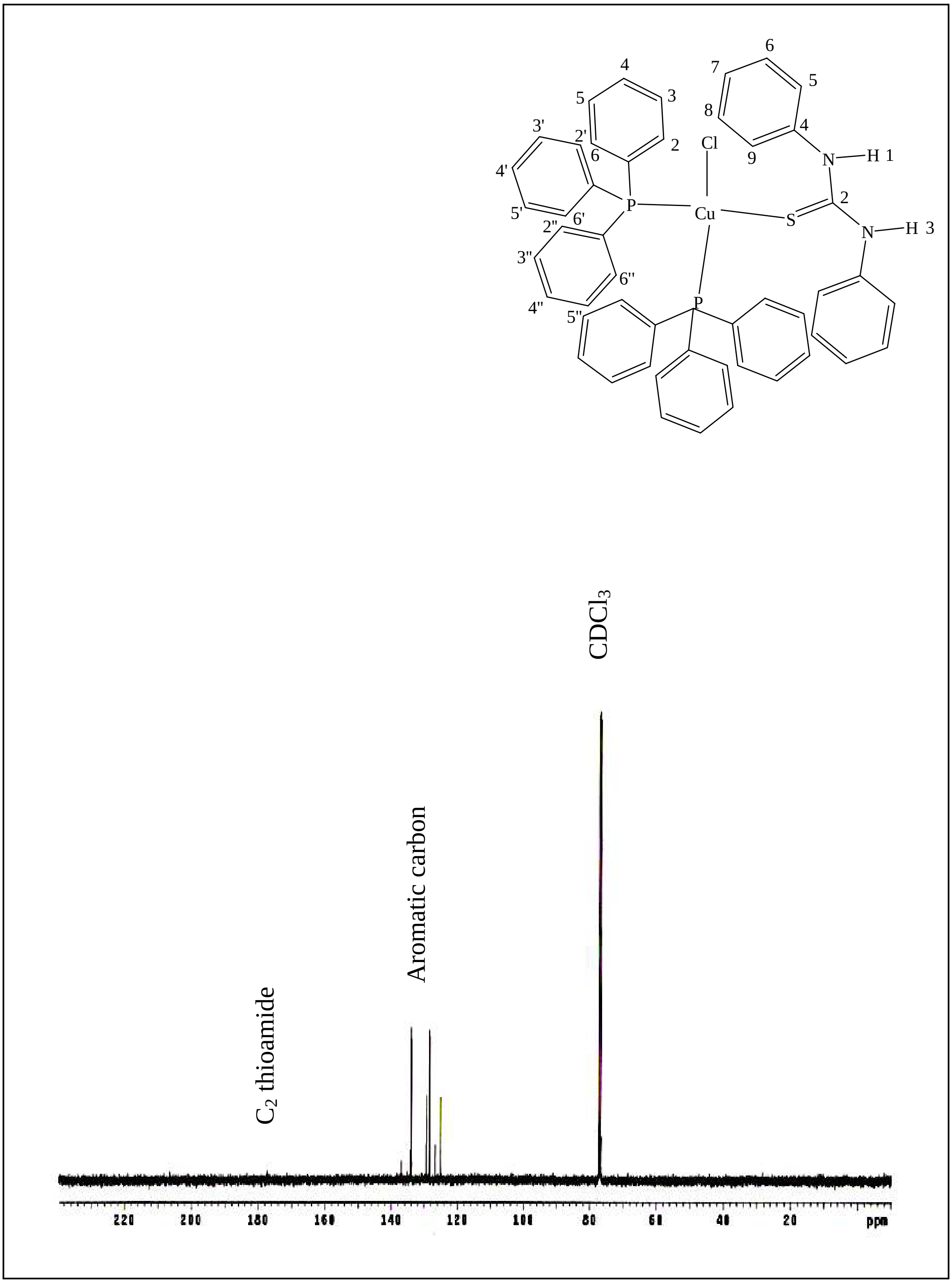


Figure 47 ^{13}C NMR spectrum of $[CuCl(PPh_3)_2(dptu)]\cdot2CH_3CN$.

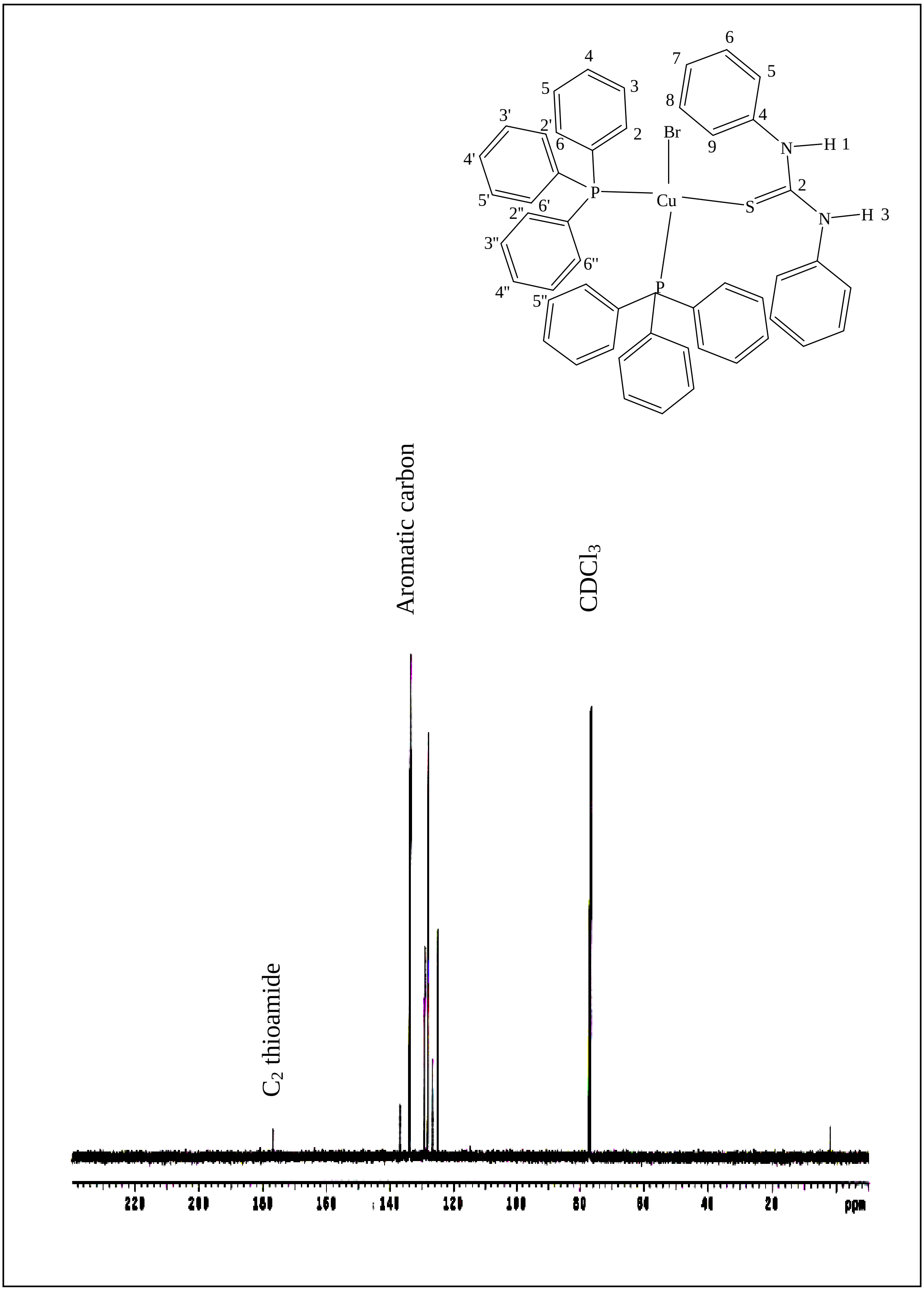


Figure 48 ^{13}C NMR spectrum of [CuBr(PPh$_3$)$_2$(dptu)]·H$_2$O.

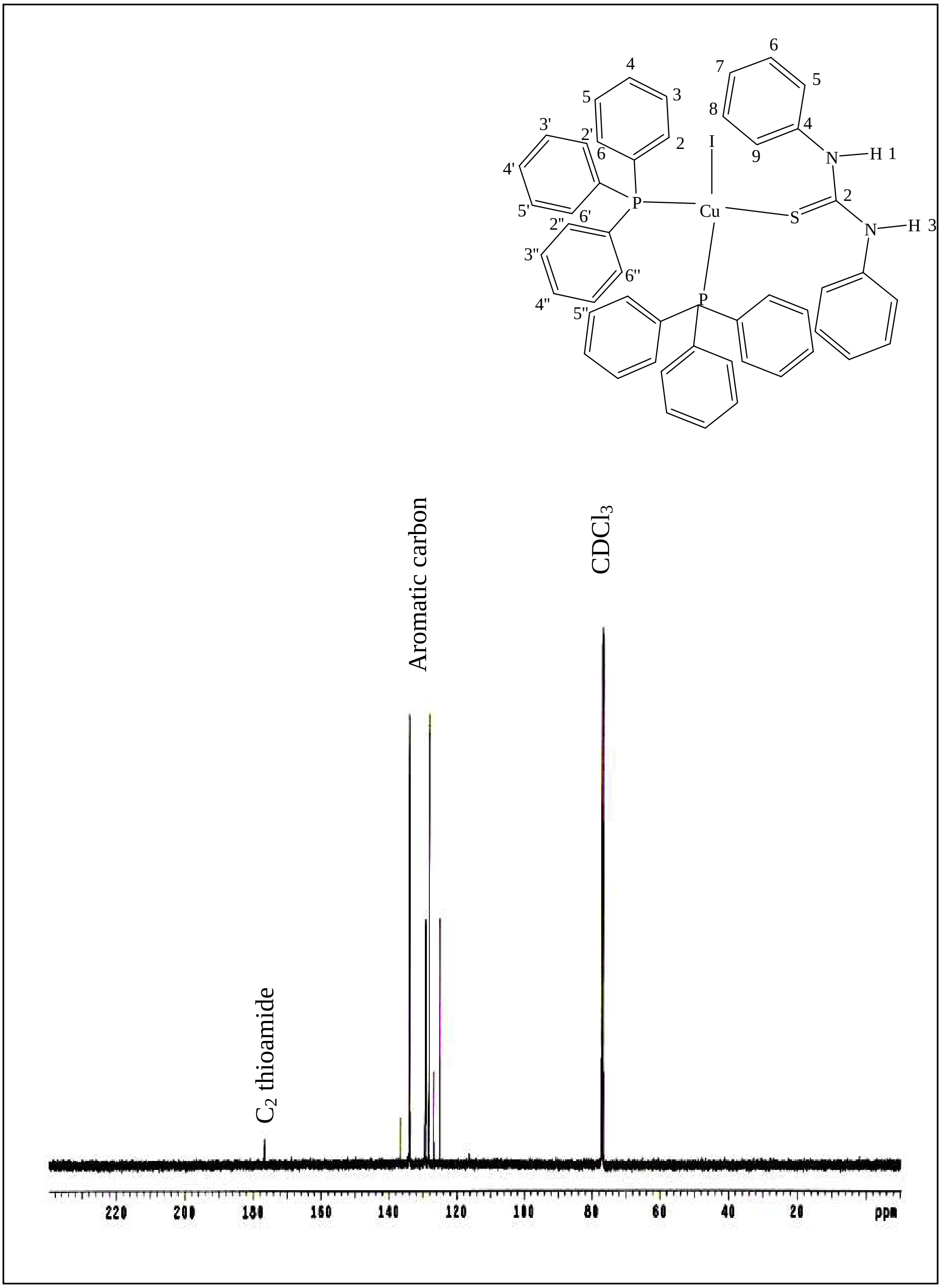


Figure 49 ^{13}C NMR spectrum of [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN.

3.6 Single crystal X-ray diffractometry

3.6.1 Crystal Structures

These results from crystal structure determination using SHELXTL and WinGX program system (Sheldrick, 1998) are shown in Table 4-12, Figure 50-64.

Table 4 The crystallograpraphic data for [CuCl(PPh$_3$)$_2$(dptu)]·2CH$_3$CN.

Empirical formula	$C_{53}H_{48}ClCuN_4P_2S$	
Formula weight	933.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.09460(10) Å	α = 103.0340(1)^o
	b = 12.8345(2) Å	β = 90.6470(1)^o
	c = 18.5790(8) Å	γ = 111.2920(1)^o
Volume	2388.76(11) Å^3	
Z	2	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	972	
Crystal size	0.276 x 0.209 x 0.09 mm^3	
Theta range for data collection	1.76 to 22.50^o	
Index ranges	-11<=h<=11, -13<=k<=13, -20<=l<=20	
Reflections collected	17703	
Independent reflections	6233 [R(int) = 0.0364]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.870 and 0.514	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6233 / 0 / 559	
Goodness-of-fit on F^2	0.984	
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0414, $wR2$ = 0.1174	
R indices (all data)	$R1$ = 0.0525, $wR2$ = 0.1259	
Largest diff. peak and hole	0.355 and -0.345 e. Å^{-3}	

Table 5 Non-hydrogen interatomic distances of [CuCl(PPh$_3$)$_2$(dptu)]·2CH$_3$CN.

Atom	Distance (Å)
Cu(1)-Cl(1)	2.3568(10)
Cu(1)-S(1)	2.3702(10)
Cu(1)-P(1)	2.3090(10)
Cu(1)-P(2)	2.2746(10)
C(1)-S(1)	1.695(4)
C(11A)-P(1)	1.833(4)
C(21A)-P(1)	1.837(4)
C(31A)-P(1)	1.834(4)
C(11B)-P(2)	1.832(3)
C(21B)-P(2)	1.834(3)
C(31B)-P(2)	1.830(3)
N(1)-C(1)	1.330(5)
N(1)-C(11)	1.434(5)
N(2)-C(1)	1.338(4)
N(2)-C(21)	1.425(5)
N(5)-C(7)	1.24(3)
C(5)-N(4)	1.062(10)
C(5)-C(4)	1.442(10)
C(7)-C(6)	1.22(2)
C(6)-C(6)#1	2.30(7)
C(11)-C(12)	1.375(6)
C(11)-C(16)	1.351(6)
C(12)-C(13)	1.362(7)
C(13)-C(14)	1.327(7)
C(14)-C(15)	1.351(7)
C(16)-C(15)	1.419(7)

Table 5 (continued).

Atom	Distance (Å)
C(21)-C(22)	1.344(7)
C(21)-C(26)	1.321(7)
C(22)-C(23)	1.391(9)
C(23)-C(24)	1.346(12)
C(24)-C(25)	1.296(13)
C(26)-C(25)	1.398(10)
C(11A)-C(12A)	1.373(5)
C(11A)-C(16A)	1.376(6)
C(13A)-C(12A)	1.401(6)
C(13A)-C(14A)	1.357(8)
C(14A)-C(15A)	1.357(8)
C(16A)-C(15A)	1.388(7)
C(21A)-C(22A)	1.380(5)
C(21A)-C(26A)	1.381(5)
C(22A)-C(23A)	1.371(6)
C(24A)-C(23A)	1.359(6)
C(24A)-C(25A)	1.371(6)
C(26A)-C(25A)	1.382(6)
C(31A)-C(32A)	1.399(5)
C(31A)-C(36A)	1.357(5)
C(32A)-C(33A)	1.374(6)
C(33A)-C(34A)	1.367(7)
C(34A)-C(35A)	1.364(7)
C(36A)-C(35A)	1.388(6)
C(11B)-C(12B)	1.376(5)
C(11B)-C(16B)	1.377(5)
C(12B)-C(13B)	1.373(5)

Table 5 (continued).

Atom	Distance (Å)
C(13B)-C(14B)	1.365(6)
C(14B)-C(15B)	1.360(6)
C(16B)-C(15B)	1.377(6)
C(21B)-C(22B)	1.379(5)
C(21B)-C(26B)	1.382(5)
C(22B)-C(23B)	1.384(6)
C(23B)-C(24B)	1.365(6)
C(24B)-C(25B)	1.383(7)
C(26B)-C(25B)	1.377(6)
C(31B)-C(32B)	1.378(5)
C(31B)-C(36B)	1.392(5)
C(32B)-C(33B)	1.385(5)
C(33B)-C(34B)	1.368(6)
C(34B)-C(35B)	1.376(6)
C(36B)-C(35B)	1.385(6)

Table 6 Non-hydrogen interbond angles of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$.

Atom	Angle (°)
Cl(1)-Cu(1)-S(1)	109.48(4)
P(1)-Cu(1)-Cl(1)	111.08(4)
P(1)-Cu(1)-S(1)	103.41(4)
P(2)-Cu(1)-P(1)	122.56(4)
P(2)-Cu(1)-Cl(1)	104.03(4)
P(2)-Cu(1)-S(1)	105.83(4)
N(1)-C(1)-S(1)	121.1(3)
N(1)-C(1)-N(2)	117.4(3)
N(2)-C(1)-S(1)	121.5(3)
N(4)-C(5)-C(4)	175.1(10)
N(5)-C(7)-C(6)	172(4)
C(1)-S(1)-Cu(1)	110.41(13)
C(1)-N(1)-C(11)	124.8(3)
C(1)-N(2)-C(21)	124.7(3)
C(7)-C(6)-C(8)	126(4)
C(11)-C(16)-C(15)	119.3(5)
C(12)-C(11)-N(1)	119.8(4)
C(13)-C(12)-C(11)	120.4(5)
C(13)-C(14)-C(15)	121.1(5)
C(14)-C(13)-C(12)	120.7(5)
C(14)-C(15)-C(16)	119.1(5)
C(16)-C(11)-N(1)	120.8(4)
C(16)-C(11)-C(12)	119.4(4)
C(21)-C(22)-C(23)	120.2(7)
C(21)-C(26)-C(25)	119.3(7)
C(22)-C(21)-N(2)	120.7(4)
C(24)-C(23)-C(22)	119.0(8)

Table 6 (continued).

Atom	Angle (°)
C(24)-C(25)-C(26)	121.4(9)
C(25)-C(24)-C(23)	120.2(8)
C(26)-C(21)-N(2)	119.5(5)
C(26)-C(21)-C(22)	119.8(5)
C(11A)-P(1)-Cu(1)	112.23(12)
C(11A)-P(1)-C(21A)	103.30(16)
C(11A)-P(1)-C(31A)	102.19(16)
C(21A)-P(1)-Cu(1)	114.73(12)
C(31A)-P(1)-Cu(1)	120.30(12)
C(31A)-P(1)-C(21A)	101.99(16)
C(11B)-P(2)-C(21B)	101.71(15)
C(11B)-P(2)-Cu(1)	116.17(11)
C(21B)-P(2)-Cu(1)	117.61(12)
C(31B)-P(2)-Cu(1)	112.61(12)
C(31B)-P(2)-C(11B)	104.69(15)
C(31B)-P(2)-C(21B)	102.24(15)
C(11A)-C(12A)-C(13A)	120.3(4)
C(11A)-C(16A)-C(15A)	120.4(5)
C(12A)-C(11A)-P(1)	117.1(3)
C(12A)-C(11A)-C(16A)	118.6(4)
C(13A)-C(14A)-C(15A)	119.8(5)
C(14A)-C(13A)-C(12A)	120.2(5)
C(14A)-C(15A)-C(16A)	120.6(5)
C(16A)-C(11A)-P(1)	124.3(3)
C(21A)-C(26A)-C(25A)	120.8(4)
C(22A)-C(21A)-P(1)	123.3(3)
C(23A)-C(22A)-C(21A)	121.1(4)
C(23A)-C(24A)-C(25A)	119.9(4)

Table 6 (continued).

Atom	Angle (°)
C(24A)-C(23A)-C(22A)	120.4(4)
C(24A)-C(25A)-C(26A)	119.8(4)
C(26A)-C(21A)-P(1)	118.6(3)
C(26A)-C(21A)-C(22A)	118.0(4)
C(31A)-C(36A)-C(35A)	120.6(4)
C(32A)-C(31A)-P(1)	121.5(3)
C(33A)-C(32A)-C(31A)	120.4(4)
C(34A)-C(33A)-C(32A)	120.1(4)
C(34A)-C(35A)-C(36A)	120.3(4)
C(35A)-C(34A)-C(33A)	119.9(4)
C(36A)-C(31A)-P(1)	119.8(3)
C(36A)-C(31A)-C(32A)	118.7(4)
C(12B)-C(11B)-P(2)	123.6(3)
C(12B)-C(11B)-C(16B)	117.6(3)
C(13B)-C(12B)-C(11B)	121.2(4)
C(13B)-C(14B)-C(15B)	119.3(4)
C(14B)-C(13B)-C(12B)	120.4(4)
C(14B)-C(15B)-C(16B)	120.4(4)
C(15B)-C(16B)-C(11B)	121.1(4)
C(16B)-C(11B)-P(2)	118.8(3)
C(22B)-C(21B)-P(2)	123.2(3)
C(23B)-C(22B)-C(21B)	121.1(4)
C(23B)-C(24B)-C(25B)	120.0(4)
C(24B)-C(23B)-C(22B)	119.8(4)
C(25B)-C(26B)-C(21B)	120.9(4)
C(26B)-C(21B)-P(2)	118.4(3)
C(26B)-C(21B)-C(22B)	118.4(3)
C(26B)-C(25B)-C(24B)	119.8(4)

Table 6 (continued).

Atom	Angle (°)
C(31B)-C(32B)-C(33B)	120.6(4)
C(32B)-C(31B)-P(2)	124.1(3)
C(32B)-C(31B)-C(36B)	118.8(3)
C(33B)-C(34B)-C(35B)	120.5(4)
C(34B)-C(33B)-C(32B)	120.0(4)
C(34B)-C(35B)-C(36B)	119.6(4)
C(35B)-C(36B)-C(31B)	120.5(4)
C(36B)-C(31B)-P(2)	117.0(3)

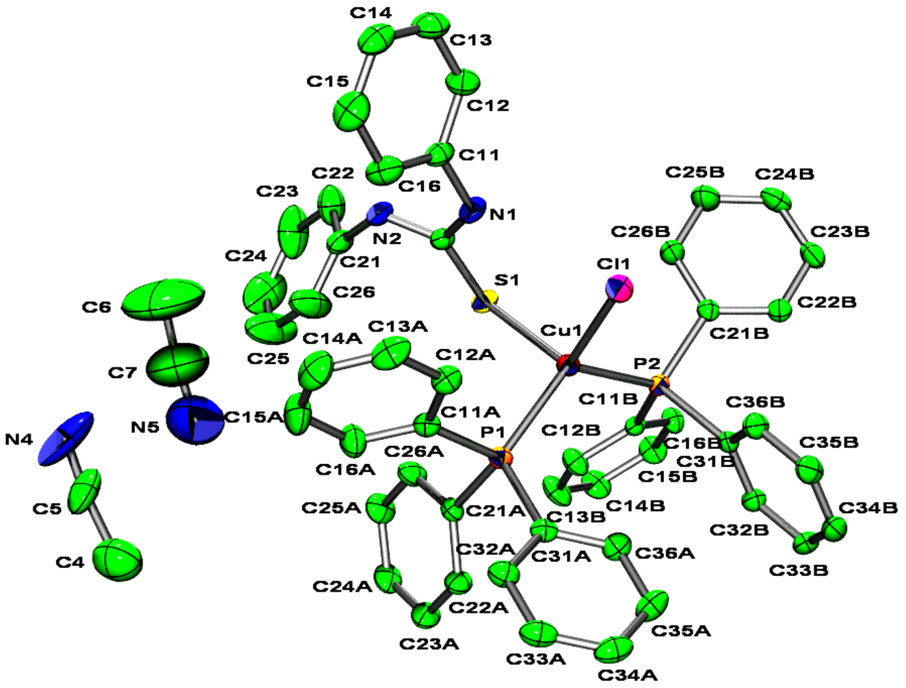


Figure 50 The structure of [CuCl(PPh$_3$)$_2$(dptu)]·2CH$_3$CN.

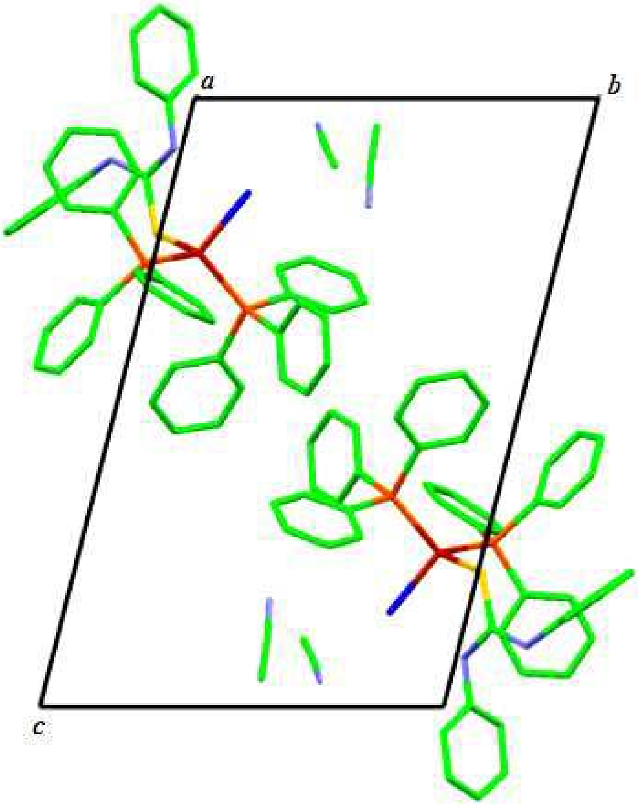


Figure 51 Unit cell contents of [CuCl(PPh_3)$_2$(dptu)]·2CH_3CN. projected down *a*.

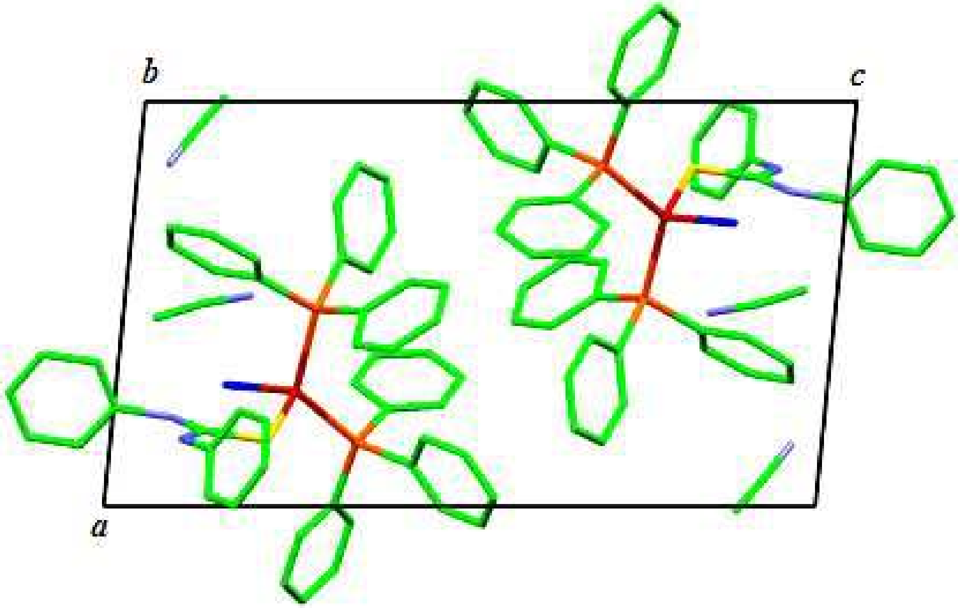


Figure 52 Unit cell contents of [CuCl(PPh_3)$_2$(dptu)]·2CH_3CN. projected down *b*.

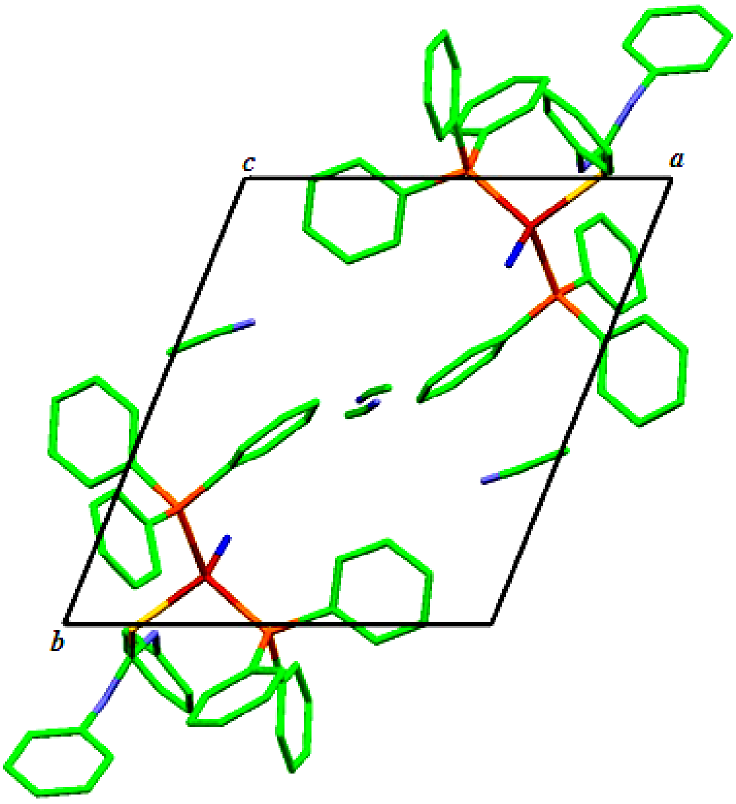


Figure 53 Unit cell contents of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$. projected down *c*.

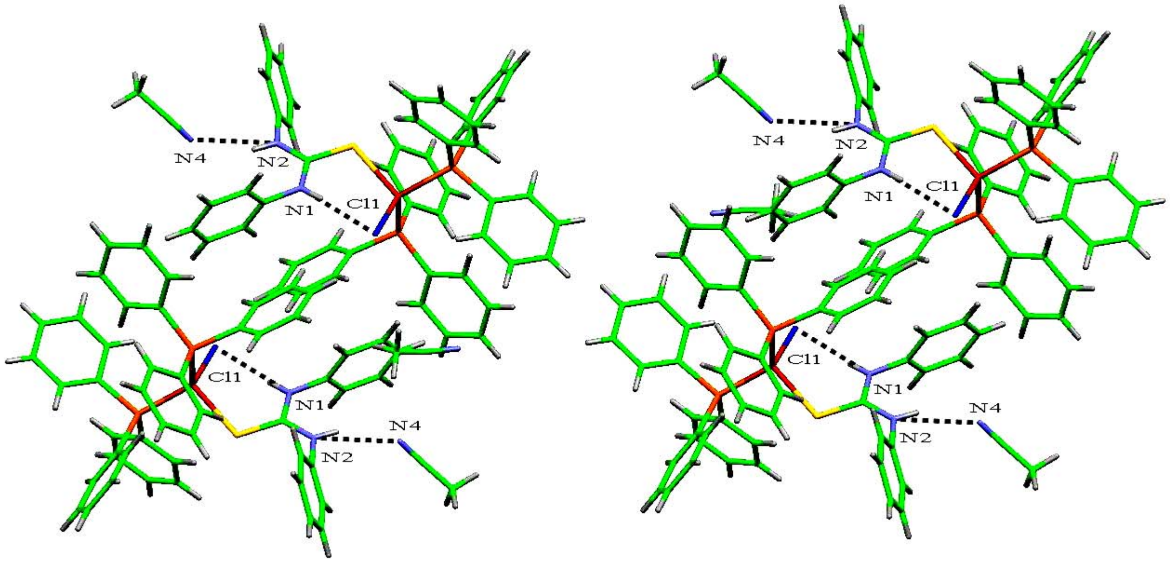


Figure 54 Hydrogen bonding the interaction of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$..

Table 7 The crystallograpraphic data for [CuBr$(PPh_3)_2$(dptu)]·H_2O.

Empirical formula	$C_{49}H_{44}BrCuN_2OP_2S$	
Formula weight	914.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No.2)	
Unit cell dimensions	a = 10.8100(11) Å	α = 73.330(2)^o
	b = 12.2861(13) Å	β = 88.921(2)^o
	c = 18.9086(19) Å	γ = 67.318(2)^o
Volume	2207.7(4) Å^3	
Z	2	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	1.558 mm^{-1}	
F(000)	940	
Crystal size	0.276 x 0.209 x 0.09 mm^3	
Theta range for data collection	1.88 to 25.00^o	
Index ranges	-12<=h<=12, -14<=k<=14, -22<=l<=22	
Reflections collected	20043	
Independent reflections	7765 [R(int) = 0.0626]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.870 and 0.514	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7765 / 3 / 519	
Goodness-of-fit on F^2	0.875	
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0498, $wR2$ = 0.1079	
R indices (all data)	$R1$ = 0.1053, $wR2$ = 0.1231	
Largest diff. peak and hole	0.715 and -0.478 e. Å^{-3}	

Table 8 Non-hydrogen interatomic distances of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

Atom	Distance (Å)
Cu(1)-P(1)	2.2719(13)
Cu(1)-P(2)	2.3110(13)
Cu(1)-S(1)	2.3635(13)
Cu(1)-Br(1)	2.5102(7)
S(1)-C(1)	1.689(5)
P(1)-C(11A)	1.824(4)
P(1)-C(31A)	1.826(5)
P(1)-C(21A)	1.841(5)
P(2)-C(11B)	1.826(4)
P(2)-C(31B)	1.829(5)
P(2)-C(21B)	1.832(5)
N(1)-C(1)	1.336(6)
N(1)-C(11)	1.422(6)
N(2)-C(1)	1.343(5)
N(2)-C(21)	1.425(6)
C(11)-C(16)	1.375(7)
C(11)-C(12)	1.381(7)
C(12)-C(13)	1.396(7)
C(13)-C(14)	1.353(9)
C(14)-C(15)	1.347(1)
C(15)-C(16)	1.382(8)
C(21)-C(26)	1.361(7)
C(21)-C(22)	1.375(7)
C(22)-C(23)	1.370(7)
C(23)-C(24)	1.355(9)
C(24)-C(25)	1.354(9)
C(25)-C(26)	1.383(8)

Table 8 (continued).

Atom	Distance (Å)
C(11A)-C(12A)	1.371(6)
C(11A)-C(16A)	1.376(7)
C(12A)-C(13A)	1.376(7)
C(13A)-C(14A)	1.350(8)
C(14A)-C(15A)	1.353(9)
C(15A)-C(16A)	1.380(7)
C(21A)-C(26A)	1.367(6)
C(21A)-C(22A)	1.373(6)
C(22A)-C(23A)	1.368(7)
C(23A)-C(24A)	1.350(7)
C(24A)-C(25A)	1.367(7)
C(25A)-C(26A)	1.382(7)
C(31A)-C(32A)	1.384(6)
C(31A)-C(36A)	1.391(6)
C(32A)-C(33A)	1.375(6)
C(33A)-C(34A)	1.379(7)
C(34A)-C(35A)	1.376(7)
C(35A)-C(36A)	1.370(6)
C(11B)-C(12B)	1.382(6)
C(11B)-C(16B)	1.399(6)
C(12B)-C(13B)	1.383(6)
C(13B)-C(14B)	1.387(8)
C(14B)-C(15B)	1.375(8)
C(15B)-C(16B)	1.367(7)
C(21B)-C(22B)	1.378(6)
C(21B)-C(26B)	1.394(6)
C(22B)-C(23B)	1.384(7)

Table 8 (continued).

Atom	Distance (Å)
C(23B)-C(24B)	1.386(8)
C(24B)-C(25B)	1.343(7)
C(25B)-C(26B)	1.372(7)
C(31B)-C(32B)	1.385(6)
C(31B)-C(36B)	1.389(6)
C(32B)-C(33B)	1.383(7)
C(33B)-C(34B)	1.350(9)
C(34B)-C(35B)	1.377(8)
C(35B)-C(36B)	1.368(7)
Cu(1)-P(1)	2.2719(1)
Cu(1)-P(2)	2.3110(1)
Cu(1)-S(1)	2.3635(1)
Cu(1)-Br(1)	2.5102(7)
S(1)-C(1)	1.689(5)
P(1)-C(11A)	1.824(4)
P(1)-C(31A)	1.826(5)
P(1)-C(21A)	1.841(5)
P(2)-C(11B)	1.826(4)
P(2)-C(31B)	1.829(5)
P(2)-C(21B)	1.832(5)
N(1)-C(1)	1.336(6)
N(1)-C(11)	1.422(6)
N(2)-C(1)	1.343(5)

Table 9 Non-hydrogen interbond angles of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

Atom	Angle (°)
P(1)-Cu(1)-P(2)	120.01(5)
P(1)-Cu(1)-S(1)	110.13(5)
P(2)-Cu(1)-S(1)	103.19(5)
P(1)-Cu(1)-Br(1)	100.94(4)
P(2)-Cu(1)-Br(1)	112.94(4)
S(1)-Cu(1)-Br(1)	109.58(4)
C(1)-S(1)-Cu(1)	111.23(16)
C(11A)-P(1)-C(31A)	101.6(2
C(11A)-P(1)-C(21A)	102.0(2)
C(31A)-P(1)-C(21A)	102.9(2)
C(11A)-P(1)-Cu(1)	117.96(15)
C(31A)-P(1)-Cu(1)	111.37(15)
C(21A)-P(1)-Cu(1)	118.71(14)
C(11B)-P(2)-C(31B)	105.8(2)
C(11B)-P(2)-C(21B)	100.8(2)
C(31B)-P(2)-C(21B)	101.2(2)
C(11B)-P(2)-Cu(1)	110.85(15)
C(31B)-P(2)-Cu(1)	111.62(15)
C(21B)-P(2)-Cu(1)	124.75(15)
C(1)-N(1)-C(11)	128.9(4)
C(1)-N(2)-C(21)	126.3(4)
N(1)-C(1)-N(2)	116.8(4)
N(1)-C(1)-S(1)	120.6(3)
N(2)-C(1)-S(1)	122.5(4)
C(16)-C(11)-C(12)	120.6(6)
C(16)-C(11)-N(1)	120.6(5)
C(12)-C(11)-N(1)	118.5(5)

Table 9 (continued).

Atom	Angle (°)
C(11)-C(12)-C(13)	117.4(6)
C(14)-C(13)-C(12)	121.3(6)
C(15)-C(14)-C(13)	121.0(7)
C(14)-C(15)-C(16)	119.5(7)
C(11)-C(16)-C(15)	120.1(6)
C(26)-C(21)-C(22)	120.0(5)
C(26)-C(21)-N(2)	119.7(5)
C(22)-C(21)-N(2)	120.2(5)
C(23)-C(22)-C(21)	119.4(6)
C(24)-C(23)-C(22)	120.9(6)
C(25)-C(24)-C(23)	119.7(6)
C(24)-C(25)-C(26)	120.4(6)
C(21)-C(26)-C(25)	119.6(6)
C(12A)-C(11A)-C(16A)	117.6(4)
C(12A)-C(11A)-P(1)	124.0(4)
C(16A)-C(11A)-P(1)	118.3(4)
C(11A)-C(12A)-C(13A)	122.0(5)
C(14A)-C(13A)-C(12A)	119.4(6)
C(13A)-C(14A)-C(15A)	119.8(6)
C(14A)-C(15A)-C(16A)	121.2(6)
C(11A)-C(16A)-C(15A)	119.8(5)
C(26A)-C(21A)-C(22A)	118.0(4)
C(26A)-C(21A)-P(1)	123.1(3)
C(22A)-C(21A)-P(1)	118.9(4)
C(23A)-C(22A)-C(21A)	121.8(5)
C(24A)-C(23A)-C(22A)	119.5(5)
C(23A)-C(24A)-C(25A)	120.2(5)

Table 9 (continued).

Atom	Angle (°)
C(24A)-C(25A)-C(26A)	119.9(5)
C(21A)-C(26A)-C(25A)	120.5(5)
C(32A)-C(31A)-C(36A)	118.6(4)
C(32A)-C(31A)-P(1)	123.6(4)
C(36A)-C(31A)-P(1)	117.7(4)
C(33A)-C(32A)-C(31A)	120.5(5)
C(32A)-C(33A)-C(34A)	120.2(5)
C(35A)-C(34A)-C(33A)	119.8(5)
C(36A)-C(35A)-C(34A)	120.1(5)
C(35A)-C(36A)-C(31A)	120.8(5)
C(12B)-C(11B)-C(16B)	116.7(4)
C(12B)-C(11B)-P(2)	120.0(4)
C(16B)-C(11B)-P(2)	122.8(4)
C(11B)-C(12B)-C(13B)	122.4(5)
C(12B)-C(13B)-C(14B)	119.0(5)
C(15B)-C(14B)-C(13B)	119.8(5)
C(16B)-C(15B)-C(14B)	120.2(5)
C(15B)-C(16B)-C(11B)	121.8(5)
C(22B)-C(21B)-C(26B)	118.3(5)
C(22B)-C(21B)-P(2)	119.6(4)
C(26B)-C(21B)-P(2)	122.0(4)
C(22B)-C(23B)-C(24B)	119.4(5)
C(25B)-C(24B)-C(23B)	119.9(5)
C(24B)-C(25B)-C(26B)	121.4(5)
C(25B)-C(26B)-C(21B)	120.1(5)
C(32B)-C(31B)-C(36B)	118.0(5)
C(32B)-C(31B)-P(2)	125.8(4)

Table 9 (continued).

Atom	Angle (°)
C(36B)-C(31B)-P(2)	116.2(4)
C(33B)-C(32B)-C(31B)	120.3(5)
C(34B)-C(33B)-C(32B)	120.6(6)
C(33B)-C(34B)-C(35B)	120.1(6)
C(36B)-C(35B)-C(34B)	119.9(6)
C(35B)-C(36B)-C(31B)	121.1(5)

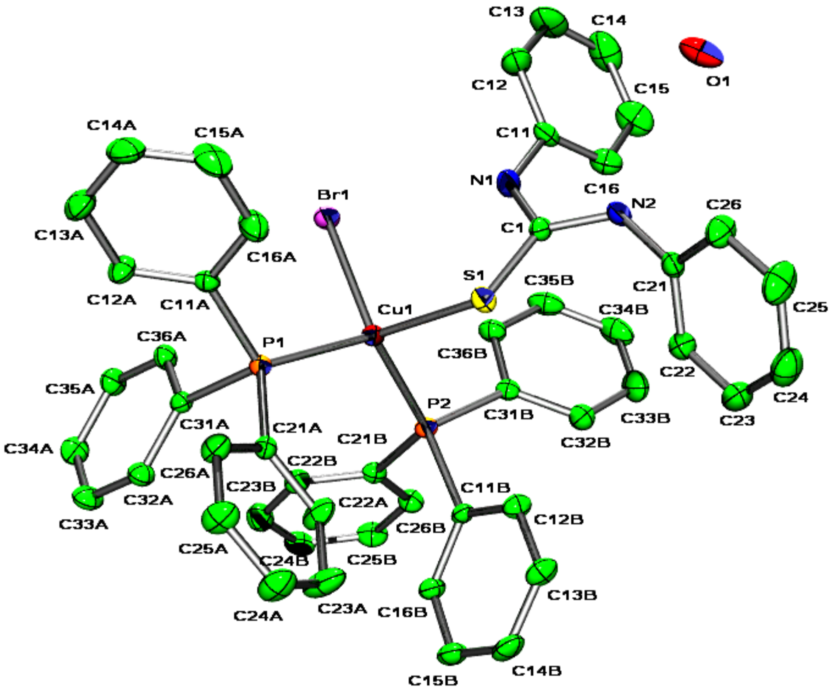


Figure 55 The structure of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$.

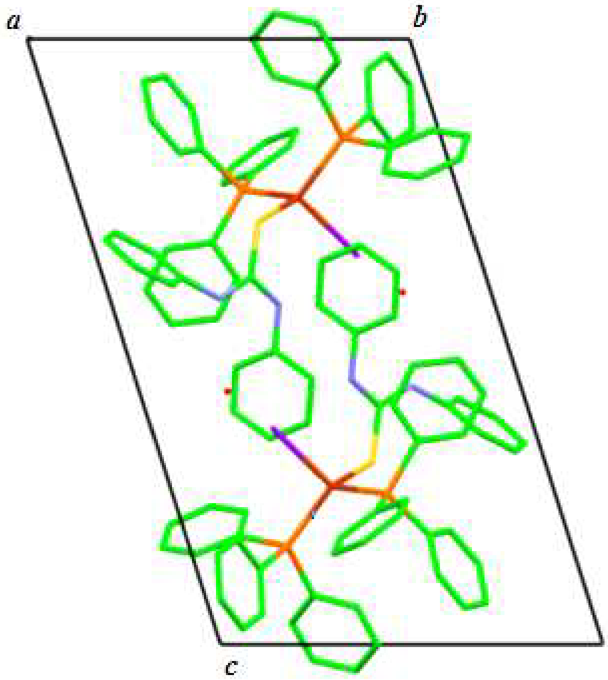


Figure 56 Unit cell contents of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$ projected down *a*.

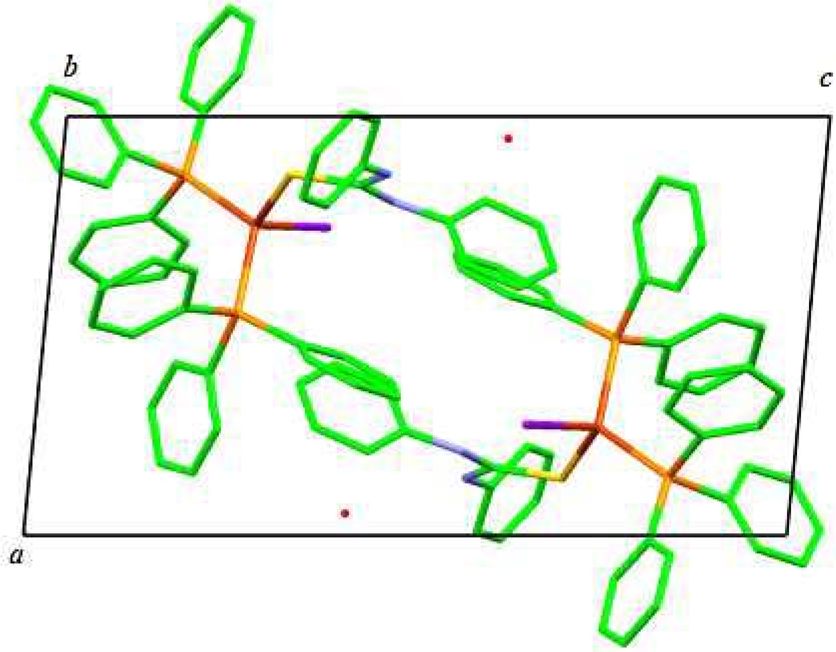


Figure 57 Unit cell contents of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$ projected down *b*.

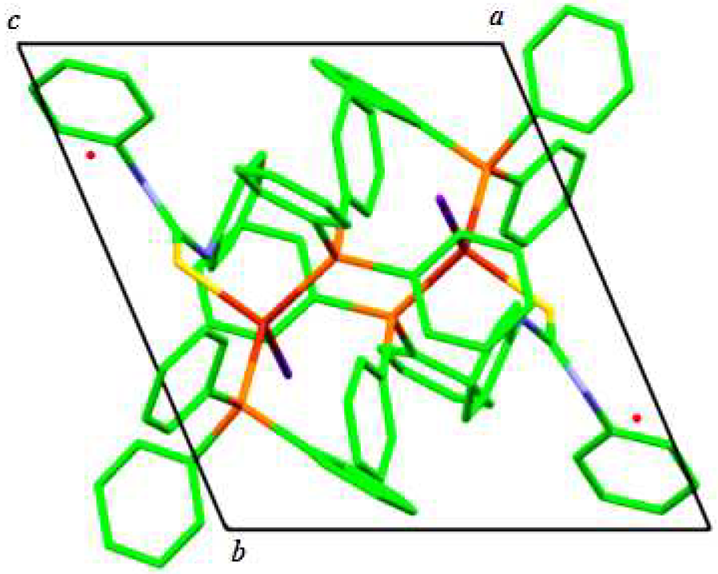


Figure 58 Unit cell contents of [CuBr$(PPh_3)_2$(dptu)]·H_2O projected down *c*.

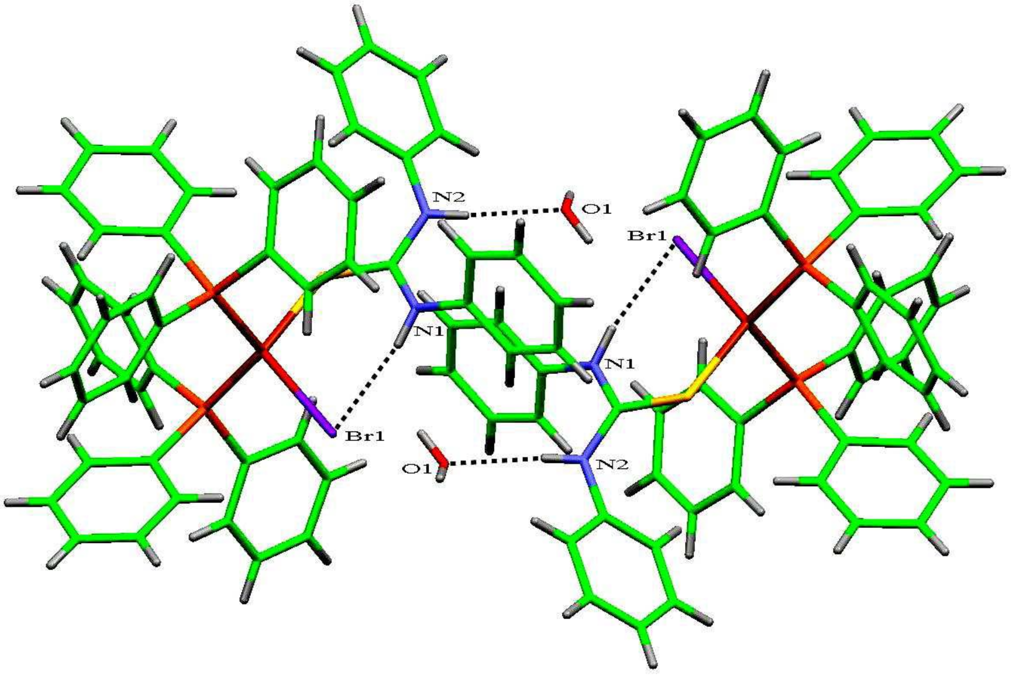


Figure 59. Hydrogen bonding the interaction of [CuBr$(PPh_3)_2$(dptu)]·H_2O

Table 10 The crystallograpraphic data for [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN.

Empirical formula	$C_{51}H_{45}CuIN_3P_2S$	
Formula weight	984.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 13.9088(7) Å	α = 90°
	b = 16.5452(8) Å	β = 90°
	c = 20.2573(10) Å	γ = 90°
Volume	4661.7(4) Å^3	
Z	4	
Density (calculated)	1.403 Mg/m^3	
Absorption coefficient	1.282 mm^{-1}	
F(000)	2000	
Crystal size	0.243 x 0.181 x 0.103 mm^3	
Theta range for data collection	1.59 to 25.00^o	
Index ranges	-16<=h<=16, -19<=k<=19, -24<=l<=24	
Reflections collected	43539	
Independent reflections	8203 [*R*(int) = 0.0300]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.880 and 0.767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8203 / 2 / 539	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2σ(I)]	*R1* = 0.0245, *wR2* = 0.0573	
R indices (all data)	*R1* = 0.0261, *wR2* = 0.0581	
Largest diff. peak and hole	0.443 and -0.161 e.Å^{-3}	

Table 11 Non-hydrogen interatomic distances of [CuI(PPh_3)$_2$(dptu)]·CH_3CN.

Atom	Distance (Å)
Cu(1)-P(1)	2.2996(8)
Cu(1)-P(2)	2.3111(8)
Cu(1)-S(1)	2.3808(8)
Cu(1)-I(1)	2.6718(4)
S(1)-C(1)	1.696(3)
P(1)-C(31A)	1.834(3)
P(1)-C(11A)	1.836(3)
P(1)-C(21A)	1.837(3)
P(2)-C(31B)	1.829(3)
P(2)-C(11B)	1.838(3)
P(2)-C(21B)	1.844(3)
N(1)-C(1)	1.337(4)
N(1)-C(11)	1.418(4)
N(2)-C(1)	1.341(4)
N(2)-C(21)	1.426(4)
C(11)-C(12)	1.378(5)
C(11)-C(16)	1.384(5)
C(12)-C(13)	1.391(5)
C(13)-C(14)	1.355(6)
C(14)-C(15)	1.358(6)
C(15)-C(16)	1.390(5)
C(21)-C(22)	1.339(6)
C(21)-C(26)	1.384(6)
C(22)-C(23)	1.431(8)
C(23)-C(24)	1.364(9)
C(24)-C(25)	1.312(8)
C(25)-C(26)	1.374(7)

Table 11 (continued).

Atom	Distance (Å)
C(11A)-C(16A)	1.382(4)
C(11A)-C(12A)	1.383(4)
C(12A)-C(13A)	1.375(5)
C(13A)-C(14A)	1.358(5)
C(14A)-C(15A)	1.370(5)
C(15A)-C(16A)	1.391(5)
C(21A)-C(22A)	1.387(4)
C(21A)-C(26A)	1.389(4)
C(22A)-C(23A)	1.375(4)
C(23A)-C(24A)	1.365(5)
C(24A)-C(25A)	1.368(5)
C(25A)-C(26A)	1.389(4)
C(31A)-C(36A)	1.375(4)
C(31A)-C(32A)	1.398(4)
C(32A)-C(33A)	1.379(5)
C(33A)-C(34A)	1.368(6)
C(34A)-C(35A)	1.373(6)
C(35A)-C(36A)	1.377(5)
C(11B)-C(16B)	1.382(4)
C(11B)-C(12B)	1.393(4)
C(12B)-C(13B)	1.371(5)
C(14B)-C(15B)	1.373(6)
C(15B)-C(16B)	1.386(5)
C(21B)-C(22B)	1.346(5)
C(21B)-C(26B)	1.362(5)
C(22B)-C(23B)	1.383(5)
C(23B)-C(24B)	1.337(6)

Table 11 (continued).

Atom	Distance (Å)
C(24B)-C(25B)	1.362(6)
C(25B)-C(26B)	1.372(6)
C(31B)-C(36B)	1.363(5)
C(31B)-C(32B)	1.364(5)
C(32B)-C(33B)	1.392(5)
C(33B)-C(34B)	1.360(6)
C(34B)-C(35B)	1.352(7)
C(35B)-C(36B)	1.376(6)
C(2)-C(3)	1.439(9)
C(3)-N(3)	1.133(8)

Table 12 Non-hydrogen interbond angles of [CuI(PPh_3)$_2$(dptu)]·CH_3CN.

Atom	Angle (°)
P(1)-Cu(1)-P(2)	121.35(3)
P(1)-Cu(1)-S(1)	108.74(3)
P(2)-Cu(1)-S(1)	100.90(3)
P(1)-Cu(1)-I(1)	106.82(2)
P(2)-Cu(1)-I(1)	105.72(2)
S(1)-Cu(1)-I(1)	113.47(2)
C(1)-S(1)-Cu(1)	113.00(11)
C(31A)-P(1)-C(11A)	104.70(13)
C(31A)-P(1)-C(21A)	102.11(12)
C(11A)-P(1)-C(21A)	98.51(12)
C(31A)-P(1)-Cu(1)	113.73(9)
C(11A)-P(1)-Cu(1)	118.58(10)
C(21A)-P(1)-Cu(1)	116.82(9)
C(31B)-P(2)-C(11B)	100.05(13)
C(31B)-P(2)-C(21B)	102.74(13)
C(11B)-P(2)-C(21B)	105.82(13)
C(31B)-P(2)-Cu(1)	112.77(9)
C(11B)-P(2)-Cu(1)	120.53(9)
C(21B)-P(2)-Cu(1)	112.83(10)
C(1)-N(1)-C(11)	128.5(3)
C(1)-N(2)-C(21)	127.6(3)
N(1)-C(1)-N(2)	116.8(3)
N(1)-C(1)-S(1)	121.3(2)
N(2)-C(1)-S(1)	121.8(2)
C(12)-C(11)-C(16)	120.0(3)
C(12)-C(11)-N(1)	118.2(3)

Table 12 (continued).

Atom	Angle (°)
C(16)-C(11)-N(1)	121.8(3)
C(11)-C(12)-C(13)	119.9(3)
C(14)-C(13)-C(12)	119.8(4)
C(13)-C(14)-C(15)	120.6(4)
C(14)-C(15)-C(16)	120.9(4)
C(11)-C(16)-C(15)	118.6(4)
C(22)-C(21)-C(26)	121.6(4)
C(22)-C(21)-N(2)	121.1(4)
C(26)-C(21)-N(2)	117.0(4)
C(21)-C(22)-C(23)	117.5(6)
C(24)-C(23)-C(22)	119.2(6)
C(25)-C(24)-C(23)	122.1(6)
C(24)-C(25)-C(26)	120.2(6)
C(25)-C(26)-C(21)	119.4(5)
C(16A)-C(11A)-C(12A)	118.0(3)
C(16A)-C(11A)-P(1)	120.1(2)
C(12A)-C(11A)-P(1)	121.8(2)
C(13A)-C(12A)-C(11A)	120.9(3)
C(14A)-C(13A)-C(12A)	121.2(3)
C(13A)-C(14A)-C(15A)	118.9(3)
C(14A)-C(15A)-C(16A)	120.8(3)
C(11A)-C(16A)-C(15A)	120.2(3)
C(22A)-C(21A)-C(26A)	118.9(3)
C(22A)-C(21A)-P(1)	116.8(2)
C(26A)-C(21A)-P(1)	124.2(2)
C(23A)-C(22A)-C(21A)	120.3(3)

Table 12 (continued).

Atom	Angle (°)
C(24A)-C(23A)-C(22A)	120.8(3)
C(23A)-C(24A)-C(25A)	119.7(3)
C(24A)-C(25A)-C(26A)	120.6(3)
C(25A)-C(26A)-C(21A)	119.6(3)
C(36A)-C(31A)-C(32A)	118.5(3)
C(36A)-C(31A)-P(1)	124.4(2)
C(32A)-C(31A)-P(1)	117.1(2)
C(33A)-C(32A)-C(31A)	120.0(3)
C(34A)-C(33A)-C(32A)	120.8(4)
C(33A)-C(34A)-C(35A)	119.4(3)
C(34A)-C(35A)-C(36A)	120.6(4)
C(31A)-C(36A)-C(35A)	120.7(3)
C(16B)-C(11B)-C(12B)	118.7(3)
C(16B)-C(11B)-P(2)	118.3(2)
C(12B)-C(11B)-P(2)	123.0(2)
C(13B)-C(12B)-C(11B)	120.3(4)
C(14B)-C(13B)-C(12B)	120.7(4)
C(13B)-C(14B)-C(15B)	120.0(4)
C(14B)-C(15B)-C(16B)	120.2(4)
C(11B)-C(16B)-C(15B)	120.0(3)
C(22B)-C(21B)-C(26B)	116.9(3)
C(22B)-C(21B)-P(2)	117.9(3)
C(26B)-C(21B)-P(2)	125.2(3)
C(21B)-C(22B)-C(23B)	121.8(4)
C(24B)-C(23B)-C(22B)	120.5(4)
C(23B)-C(24B)-C(25B)	119.0(4)

Table 12 (continued).

Atom	Angle (°)
C(24B)-C(25B)-C(26B)	119.7(4)
C(21B)-C(26B)-C(25B)	122.1(4)
C(36B)-C(31B)-C(32B)	119.0(3)
C(36B)-C(31B)-P(2)	122.2(3)
C(32B)-C(31B)-P(2)	118.7(2)
C(31B)-C(32B)-C(33B)	120.7(4)
C(34B)-C(33B)-C(32B)	119.2(4)
C(35B)-C(34B)-C(33B)	119.9(4)
C(34B)-C(35B)-C(36B)	121.0(4)
C(31B)-C(36B)-C(35B)	120.0(4)
N(3)-C(3)-C(2)	178.3(8)

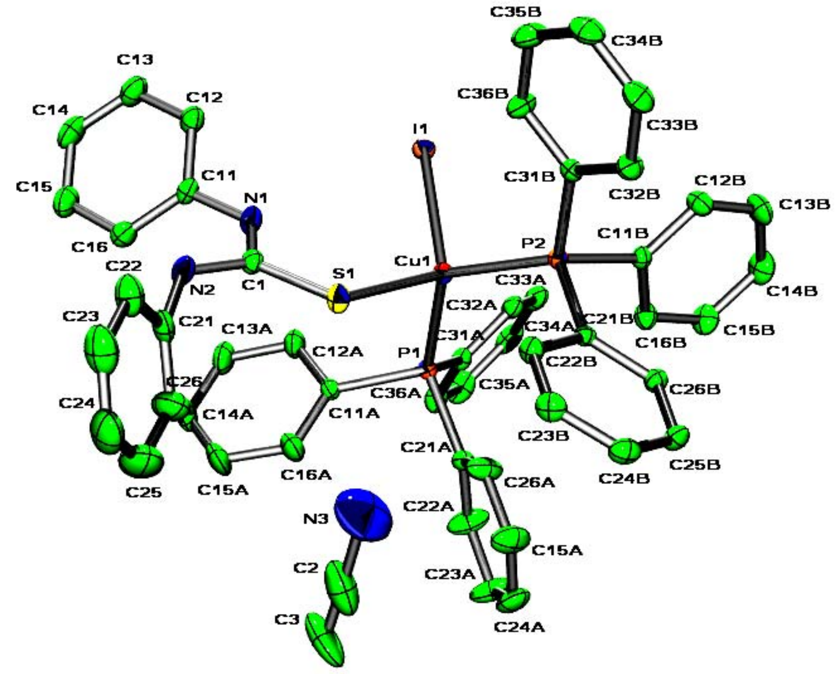


Figure 60 The structure of [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN.

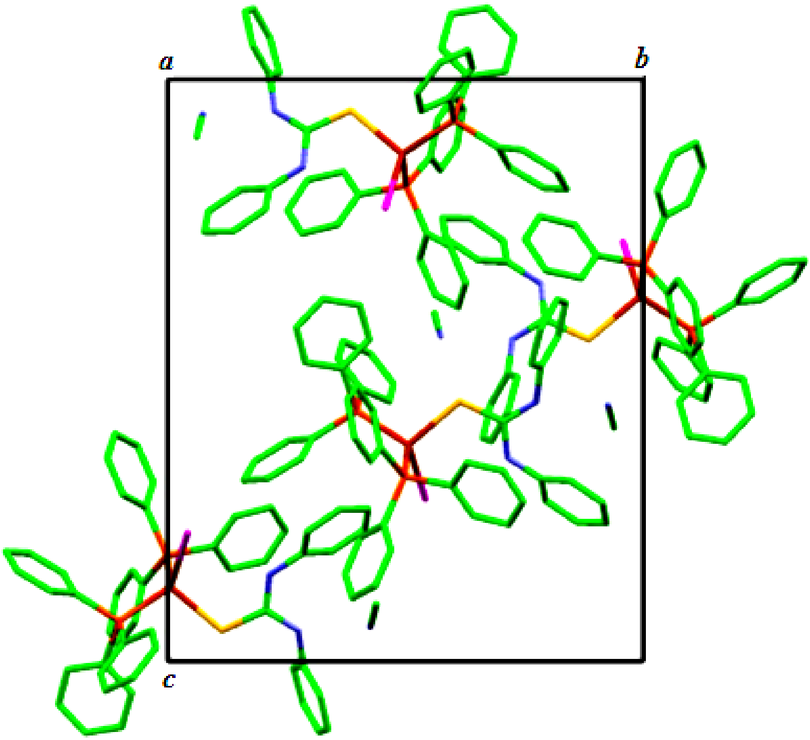


Figure 61 Unit cell contents of [CuI$(PPh_3)_2$(dptu)]·CH_3CN projected down *a*.

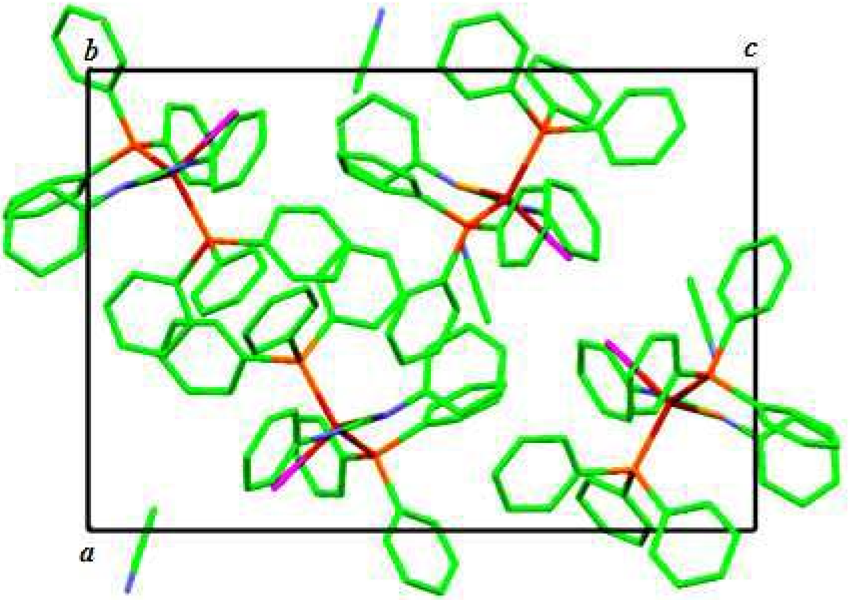


Figure 62 Unit cell contents of [CuI$(PPh_3)_2$(dptu)]·CH_3CN projected down *b*.

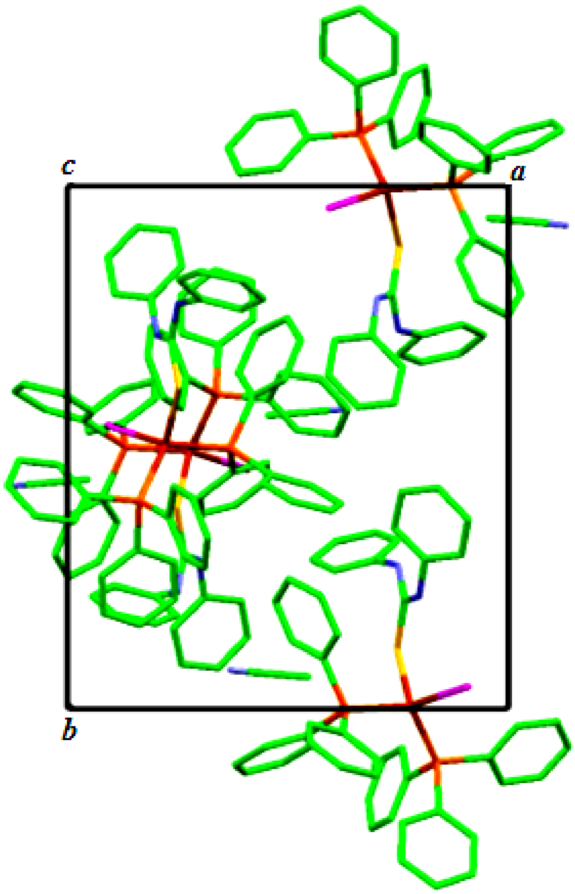


Figure 63 Unit cell contents of [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN projected down *c*.

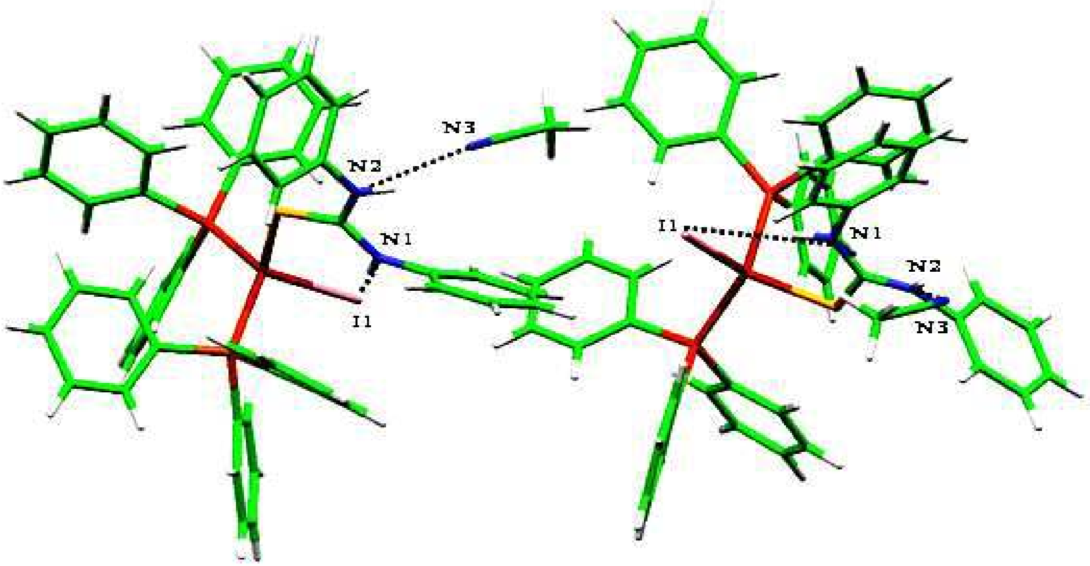


Figure 64 Hydrogen bonding the interaction of [CuI(PPh$_3$)$_2$(dptu)]·CH$_3$CN.

CHAPTER 4

DISCUSSION

4.1 Preparation of complexes

The purpose of this research is to study the structures of copper(I) complexes with mixed ligands of triphenylphosphine (PPh_3) and *N*,*N'*-diphenylthiourea (dptu) by single X-ray diffracton method. The preparation of these complexes has been carried out from direct reactions of copper(I) halides (CuX, X = Cl. Br, I) with *N*,*N'*-diphenylthiourea and triphenylphosphine by varying reactions, mole ratio of reactions, solvent, reaction temperation time. The suitable conditions for preparing all complexes are shown in Table 1. However in this research most preferred mole ratio of the CuX (X = Cl. Br, I) with dptu and PPh_3 of complexes is 1:2:1, In addition, most reaction could form more complexes at temperature in the range of 40-75° because reactants could be more soluble in solvents especially copper salts and crystallization of these complexes was obtained by slowly solvent evaporation. The complexes are colorless solids soluble in acetone, acetonitrile, chloroform, dichloromethane and DMSO, but insoluble in water and ethanol.

4.2 Elemental Analysis

This method was utilized to indicate the quantitative composition of C, H, N and S 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 3.

4.3 X-ray Fluorescence Spectrometry

This method was used to measure the elemental composition of compounds such as Cu, S and halides (Cl, Br, I). From XRF spectra of $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$, $[Cu(PPh_3)_2(dptu)I]\cdot H_2O$ and $[Cu(PPh_3)_2(dptu)I]\cdot CH_3CN$, complexes which the K_α spectrum of Cu, Cl, Br, I appears at 8.04, 2.62, 11.93, 28.67 keV, respectively, represented for copper(I) salts. In addition, S and P atoms are respresented for dptu 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 illustrated in Figures 26-34.

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).

N,N'-diphenylthiourea (dptu) ligand consists of the SCNH group as shown in figure 1., which may be adopted either thione form (S=C-N-H) or the thiol form (H-S-C=N). The free ligands adopt the thione form in the free state and in their complexes (Figure 35-39). This is distinct by the absence of the ν(S-H) band in the region of 2,600-2,550 cm^{-1} and by presence of ν(N-H) in the range 3,100-3400 cm^{-1}.

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 13 The previous studies of infrared absorption spectra for some metal thiourea and substituted thioureas.

Region (cm^{-1})	**Mode of vibration**	**References**
3350	ν(N-H)	Yamaguchi *et al.*, 1958
1600	$\delta(NH_2)$	
1500	ν_s(C-N)	
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)	
3000	ν(N-H)	Creighton *et al.*, 1985
1400	ν(C-N) + δ(C-H)	
1200	ν(C=S) + ν(C-N) + δ(C-H)	
1000	ν(C-N) + ν_s(C=S)	
700	ν_s(C=S) + ν_{as}(C-N)	
2900	ν(N-H)	Karagiannidis *et al.*, 1989
1510	$\nu(NH_2)$	
1320	ν(C=N) + ν(C-N) + ν(C=S)	
1000	ν(C=S) + ν(C-N)	
750	ν(C=S)	

Table 13 (continued).

Region (cm^{-1})	**Mode of vibration**	**References**
3180-3130 1505-1515 1330-1250 1030-990 900	ν(N-H) ν(NH_2) ν(C=N) + ν(C-N) + ν(C=S) ν(C=S) + ν(C-N) ν(C=S)	Lecomte *et al.*, 1989
3000 1500 1400 700	ν(N-H) ν(C-N) ν(C=S) + ν(C-N) ν(C-N) + ν(N-H) + ν(C=S)	Ferrari *et al.*, 1991
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

The infrared spectra of ligand dptu and three complexes are summarized in Table 14

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 14 The infrared spectra of the ligand dptu and its complexes (cm^{-1}).

Compound	Mode of vibration				
	Band I	Band II	Band III	Band IV	Band V
dptu	3208	1494	1397	1070	757
$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$	3052	1516	1433	1092	743
$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$	3048	1509	1448	1093	742
$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$	3147	1508	1434	1091	742

The infrared spectra of the complexes, the N-H stretching frequency (band I) appears at 3052, 3048 and 3147 cm^{-1} lower than the free ligand (3208 cm^{-1}) is probably due to the hydrogen bonding in the complexes (N-H···X) (X= Cl, Br, I). 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 → Cu 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.

The infrared absorption bands observed near 1500 cm^{-1} are assigned to C-N antisymmetric stretching vibration, [ν(C-N)] which the band of complexes 1, 2, 3 exhibits C-N stretching at 1516, 1509 and 1508 cm^{-1}, respectively These values are blue shifted by about 14-32 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 at the region 1433, 1448 and 1434 cm^{-1} which can be explained as NH vibration plus N-C-N plus C=S stretching vibration, ν(C=S) + ν(C-N) + δ(N-H). The shift of these bands at higher frequency in spectra of complexes, suggest 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 1091 cm^{-1}, respectively have contributed to thioamide band IV, whereas peak of dptu at

1070 cm^{-1}. The spectra show the shift to higher wave number. The shift of these band 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 band in the spectra of the copper substituted thiourea complexes which have been assigned to the particular vibrations indicated the presence of sulfur to metal bonds in the copper complexes.

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

The ^{1}H NMR of ligand diphenylthiourea (dptu) in $CDCl_3$ shows a signals at 7.18-7.55 ppm due to equivalent ring protons (aromatic protons). When this ligand coordinates to the metal via its S electrons, ring protons become magnetically in equivalent and thus expected a signals to aromatic protons for the phosphine and thione ligand. Each of complexes (1), (2) and (3) shows a signals at a low field (7.14-7.43, 7.12-7.44, 7.11-7.45 ppm, respectively) in the solution state. Complexes (1), (2) and (3) show signal due to NH protons (9.33, 9.17, 8.84 ppm, respectively), while free ligand diphenylthiourea shows a single resonance at 8.14 ppm.

The ^{1}H 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 8.84-9.33 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 15 ^{1}H NMR spectra data of the ligand dptu and complexes.

Compound	δ N-H (ppm)
dptu	8.14
$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$	9.33
$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$	9.17
$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$	8.84

The ^{13}C-NMR is to help to solve structures of unknown compounds, plays an important role in determining the structure and diagnodtically of minor impotance, since the carbons of diphenylthiourea, which consists of C=S

The ^{31}C NMR spectra provide more convincing in formation about the monodentate behaviour of thiourea moiety in the complexes. The δ C=S signal appears at δ 177.87 ppm in cmplex (1), δ 176.82 ppm in complex (2) and δ 176.61 ppm in complex (3), which are upfield relative to the free ligand (δ 179.69 ppm). An upfield shift (about 3 ppm) 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 16 ^{13}C NMR spectra data of the ligand dptu and complexes.

Compound	δ C=S (ppm)
dptu	179.69
$[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$	177.87
$[CuBr(PPh_3)_2(dptu)]\cdot H_2O$	176.82
$[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$	176.61

4.6 Crystallography

Crystallographic data for the structures were collected at 293(2) K on a single crystal X-ray diffracometer.

4.6.1 The structure of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$ complex (1)

The monomeric complex (1) of $[CuCl(PPh_3)_2(dptu)]\cdot 2CH_3CN$ consists of one copper(I) central atom, two phosphorus atoms of two triphenyphosphine molecules, one sulfur atom of diphenylthiourea molecule and one chloride atom. The complex (1) crystallizes in triclinic the space group $P\bar{1}$ and $Z = 2$ with cell parameters a = 11.09460(10), b = 12.8345(2), c = 18.5790(8) Å, α = 103.0340(1), β = 90.6470(1), γ = 111.2920(1)^o. The structure of $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$ is shown in Figure 50.

The complex described here, angular deviations from the ideal tetrahedral value of 109.4^o are comparable with several reported four coordinated copper(I) halide complex bearing a heterocyclic thioamide and two monodentate phosphines. In fact, the P(1)-Cu-P(2) angle deviates considerably from the tetrahedral value at 122.56(4)^o compare with the previously observed values in a series of analogous complexes, in $[Cu(PPh_3)_2(py2SH)Cl]$ (P-Cu-P = 122.41(11), P-Cu-Cl = 112.01(10), P-Cu-Cl = 99.17(9), P-Cu-S = 102.38(13)^o) (Aslanidis *et al.*, 1998). A possible explanation for the large value is the steric interaction between the PPh_3 groups.

The Cu-S and Cu-Cl distances are 2.3702(10) Å and 2.3568(10) Å, respectively. The distances of Cu-S and Cu-Cl bond lengths lie in the range normally observed for tetrahedrally coordinated copper(I) complexes with terminal chloride and thione-sulfur donors. The Cu-P(1) and Cu-P(2) distances of 2.3090(10) Å, 2.2746(10) Å, respectively are slightly shorter as compared to the value observed for $[Cu(PPh_3)_3X]$ (Bowmaker *et al.*, 1987). Moreover the presence of intramolecular hydrogen bonds between the chloride and the N(1)H hydrogen [N(1)H···Cl = 3.182(3) Å] could be responsible for the moderate narrowing of the S-Cu-Cl angle (109.48(4)°). The hydrogen atom, involving the interaction, N(2)-H(2A)...N(4), is orientated at a distance of 2.980(7) Å from N(4), which the corresponding angle of 145.0°.

Table 17 Hydrogen bonding of [CuCl(PPh_3)$_2$(dptu)]·2CH_3CN complex.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...Cl(1)	0.86	2.34	3.182(3)	167.1
N(2)-H(2A)...N(4)#1	0.86	2.23	2.980(7)	145.0

4.6.2 The structure of [CuBr(PPh_3)$_2$(dptu)]·H_2O complex (2)

The monomeric complex (2) of [CuBr(PPh_3)$_2$(dptu)]·H_2O crystallizes in triclinic space group $P\bar{1}$ and Z = 2 with cell parameters a = 10.8100(11), b = 12.2861(13), c = 18.9086(19) Å, α = 73.330(2), β = 88.921(2) and γ = 67.318(2)^o. The crystal structure of [CuBr(PPh_3)$_2$(dptu)]·H_2O is composed of discrete molecules with no crystallographically impose symmetry. The coordination around the metal is pseudo-tetrahedral with two phosphorus atoms of two triphenylphosphine molecules, one sulfur atom of diphenylthiourea molecule and one bromide atom This arrangement is considerably distorted since the P angle at the metal site, P1-Cu1-P2 with value of 120.01(5)°, is much larger than the tetrahedral value, 109.4°. This higher angle is counterbalanced by the bond P1-Cu1-Br, P2-Cu1-Br and P1-Cu1-S1, P2-Cu1-S1 whose values are 100.94(4)°, 112.94(4)° and 110.13(5)°, 103.19(5)° respectively. The distorted is due to steric imposition of the bulky phosphine ligand and was observed previously in a series of analogous complex, [Cu(PPh_3)$_2$(memimtH)Br] (P-Cu-P = 130.9(0)°) (Karagiannidis *et al.*, 1998).

The Cu-S distance of (2.3635(13) Å) is close to the value observed in tetrahedrally coordinated copper(I) halide complexe, [CuBr(1κS-imzSH)(PPh_3)$_2$]·H_2O with thione-S donor, (Cu-S = 2.366(2) Å) (Lobana *et al.*, 2008) and 2.373(2) Å for [CuBr(1κS-bzimSH)(PPh_3)$_2$]·CH_3COCH_3 (Lobana *et al.*, 2008). The crystal structure of [CuBr(PPh_3)$_2$ (dptu)]·H_2O is shown in Figure 55.

The Cu-P(1) and Cu-P(2) distances of 2.2719(13) and 2.3110(13) Å respectively, are significantly longer than those observed in the structure of [CuBr(1κS-bzimSH)(PPh_3)$_2$]·CH_3COCH_3 (2.309(2) and 2.291(2) Å). The short non-bonding distance in the molecule H(N)···Br1 can be accepted as an intramolecular hydrogen bond with the geometry N(1)-H(1)...Br(1) = 3.282(4) Å and the water molecule in the crystal lattice and is engaged in intermolecular H-bonding with amide group of thiourea ligand, N(2)-H(2)...O(1) = 2.986(6) Å).

Table 18 Hydrogen bonding of $[CuBr(PPh_3)_2(dptu)]\cdot H_2O$ complex.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Br(1)	0.86	2.45	3.282(4)	161.7
N(2)-H(2)...O(1)#1	0.86	2.16	2.986(6)	160.0

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

4.6.3 The structure of $[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$ complex (3).

The monomeric complex, $[CuI(dptu)(PPh_3)_2]\cdot CH_3CN$, crystallizes in orthorhombic system space group $P2_12_12_1$, Z = 4 with cell parameters a = 13.9088(7), b = 16.5452(8) and c = 20.2573(10) Å. This complex (3), the Cu atom is bonded to two phosphorus atoms of triphenylphospine ligands, one sulfur atom of the 1,3-imidazoline-2-thione ligand and one bromine atom to complete its tetra-coordination similar to complexes (1) and (2) with above stoichiometry in asymmetric unit. The Cu(I) atom displays a distorted tetrahedral environment (Figure 60) which the angles around Cu lie in the ranges 100.90(3)–113.47(2)°. The Cu-S bond distance of 2.3808(8) Å is longer than in the analogous complexes with chloride (2.364(2) Å) (Cox *et al.*, 1999).and bromide (2.375(1) Å) (Karagiannidis *et al.*, 1990). This Cu-S bond distance increases in the order Cl〈Br〈I with the decreasing in electronegativity of the halogen atom. The Cu-I bond distance, 2.6718(4) Å, is comparable with 2.6658(8) Å in similar type of complex of copper(I) iodide with phenylthiourea $[CuI(PPh_3)_2(ptu)]$ (Nimthong *et al.*, 2008). The Cu-P bond distances, (2.2996(8), 2.3111(8) Å) are close to other monomeric complexes with two triphenylphosphine and substituted thiourea ligands in the literature, which Cu-P bond distances, (2.2908(15), 2.3024(16) Å) (Nimthong *et al.*, 2008) and 2.2847(9), 2.2850(9) (La-O *et al.*, 2008). In complex (3), the weak intramolecular hydrogen bonding between the amide group and iodide atom is observed N(1)-H(1)...I(1) = 3.544(3) Å, and acetonitrile molecule in the crystal lattice and is engaged in intermolecular H-bonding with imino nitrogen of diphenylthiourea (N(2)-H(2)...N(3)).

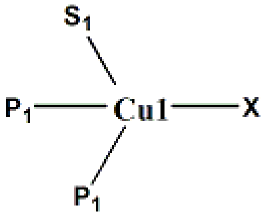
Table 19 Hydrogen bonding of $[CuI(PPh_3)_2(dptu)]\cdot CH_3CN$ complex.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...N(3)#1	0.856(18)	2.18(2)	2.997(6)	159(4)
N(1)-H(1)...I(1)	0.885(18)	2.67(2)	3.544(3)	170(3)

Symmetry transformations used to generate equivalent atoms:

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

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



Complexes	[CuCl(PPh$_3$)$_2$(dptu)]· 2CH$_3$CN	[CuBr(PPh$_3$)$_2$(dptu)]· H$_2$O	[CuI(dptu)(PPh$_3$)$_2$]· CH$_3$CN
Cu1-X	2.3568(10)	2.5102(7)	2.6718(4)
Cu1-S1	2.3702(10)	2.3635(13)	2.3808(8)
Cu1-P1	2.3090(10)	2.2719(13)	2.2996(8)
Cu1-P2	2.2746(10)	2.3110(13)	2.3111(8)
P1-Cu1-P2	122.56(4)	120.01(5)	121.35(3)
P1-Cu1-S1	103.41(4)	110.13(5)	108.74(3)
P2-Cu1-S1	105.83(4)	103.19(5)	100.90(3)
P1-Cu1-X	111.08(4)	100.94(4)	106.82(2)
P2-Cu1-X	104.03(4)	112.94(4)	105.72(2)
S1-Cu1-X	109.48(4)	109.58(4)	113.47(2)

CHAPTER 5

CONCLUSION

The purpose of this research is to synthesize and characterize a series of copper(I) halide complexes with triphenylphosphine(PPh_3) and *N*,*N'*-diphenylthiourea(dptu) to give mononuclear complexes of the general formula $[Cu(PPh_3)_2(dptu)X]$ (X = Cl, Br, I). These complexes have been characterized by elemental analysis, XRF, IR and NMR spectroscopy. The crystal structures of these complexes have been determined by single crystal X-ray diffraction methods.

The complex of $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$ crystallizes in triclinic system space group $P\bar{1}$ with cell parameters a = 11.09460(10), b = 12.8345(2), c = 18.5790(8) Å, α = 103.0340(1), β = 90.6470(1), γ = 111.2920(1)^{o}, Z = 2, R = 0.0414.

The complex of $[Cu(PPh_3)_2(dptu)Br]\cdot H_2O$ crystallizes in triclinic system space group $P\bar{1}$ with cell parameters a = 10.8100(11), b = 12.2861(13), c = 18.9086(19)Å, α = 73.330(2), β = 88.921(2) and γ = 67.318(2)^{o}, Z = 2, R = 0.0498

The complex of $[Cu(PPh_3)_2(dptu)I]\cdot CH_3CN$ crystallizes in orthorhombic system space group $P2_12_12_1$ with cell parameters a = 13.9088(7), b = 16.5452(8) and c = 20.2573(10) Å, Z = 4, R = 0.0245

The experimental results show a series of complexes of copper(I) halides with PPh_3 and dptu ligands for 1:2:1 CuX : PPh_3 : dptu stoichiometry. Geometry of copper in all complexes is distorted tetrahedral bonded to two phosphorus atoms of two triphenylphosphine molecules, one sulfur atom of diphenylthiourea molecule and one halide atom.

The substituted thiourea and triphenylphosphine complexes have attracted considerable attention because of their various application properties. An increasing investigation of the complexes of these groups has focused on acquiring well-defined solid-state structures in order to understand about the nature versatile coordination chemistry.

BIBLIOGRAPHY

Alexander, Y.V., Felix, D. S., Nail, G. Z., Maria, G.B., Dmitry, B. K., Vasiliy, V.B., Igor, A.L.2006. Copper(I) complexes of *N*-thioacylamido(thio) phosphates and Triphenylphosphine. *Inorganica Chimica Acta*. 359, 475-483

.

Aslanidis, P., Hadjikakou, S. K., Karagiannidis, P., Gdaniec, M. and Kosturkiewicz, Z. 1993. Four-Coordinate Copper(I) iodide Complexes with Triphenylphosphine Heterocyclic Thiones Ligands.The Crystal Structure of [Cu(PPh_3)$_2$(pymtH)I]. *Polyhedron*. 12, 2221-2226.

Aslanidis, P., Hadjikakou, S.K., Karagiannidis, P. and Cox, P.J. 1998. Synthesis and characterization of copper(I) complexes with triphenylphosphine and heterocyclic thione ligands: the crystal structure of (thiazolidine-2-thione)(bis-triphenylphosphine)copper(1) chloride. *Inorganica Chimica Acta*. 271, 243-247.

Belicchi-Ferrari, M., Bisceglie, F., Buluggiu, E., Pelosi, G. And Tarasconi, P. 2009. Synthesis, characterization and crystal structure of triphenylphosphine copper(I) methylpyruvate thiosemicabazones. *Polyhedron*. 28, 110-1168.

Bowmaker, G.A., Dyason, J.C., Healy, P.C., Engelhardt, L.M., Pakawatchai, C., Patrick, V.A. and White, A.H. 1987. Lewis-base Adducts of Group 11 Metal(I) Compounds. Part 27. Solid-state Phosphorus-31 Cross-polarization Magic-angle Spinnig Nuclear Magnetic Resonance, Far-infrared and Structural Studies on the Mononuclear 2:1 Adducts of triphenylphosphine with Copper(I) Halides. *J. Chem. Soc. Dalton Trans*. 1099-1106.

Clegg, W. 1998. *Crystal Structure Determination*. New York : Oxford University Press.

Cox, P.J., Aslanidis, P., Karagiannidis, P. and Hadjikakou, S.K. 1999. Synthesis, spectroscopic and computational studies plus crystal structure of [(bis-benzo-1,3-thiazolidine-2-thione)(bistriphenylphoshine)copper(I)] [chloro(benzothiazolidine-2-thione)(bistriphenylphoshine)copper(I)]. *Polyhedron*. 18, 1501–1506.

Creighton, J.R., Gardiner, D.J., Gorvin, A.C., Gutteridge, C., Jackson, A.R.W., Raper, E.S., Sherwood, P.M.A.1985. Copper(I) halide complexes of imidazole thiones: Crystal structure of dimeric monochloro bis(1-methylimidazoline-2-thione) copper(I). *Inorganica Chimica Acta*. 103, 195-205

Dyason, J.C.,Engelhardt, L.M., Pakawatchai, C., Healy, P.C. and White, A.H. 1985. Lewis-Base Adducts of Group 1B Metal(I) Compounds. XXI+ The Crystal and Molecular Structures of the Unsolvated Forms of Dibomotris (triphenylphosphine)dicopper(I) and ‘step’ Tetrabtromotetrakis (triphenylphosphine) tetracopper(I). *Aust. J. Chem*. 38, 1243-1250.

Ferrari, M.B., Fava, G.G., Lanfranchi, M., Pelizzi, C. and Tarasconi, P. 1991. Synthesis, spectroscopic and structural characterization of chlorobis(methyl) pyruvate thiosemicabazone copper(I) and chlorobis(triphenylphosphine) (methyl pyruvate thiosemicarbazone) copper(I) toluene solvate. *Inorg. Chim. Acta*. 181, 253-262.

Jianping, L. and Kazuyuki, T. 1996. Synthesis and Crystal Structure of A Binuclear Copper(I) Bromide Complex of Benz-1,3-thiazolidine-2-thione and Triphenylphosphine, $[Cu(bztzdtH)(PPh_3)Br]_2$. *Polyhedron*. 15, 2127-2130.

Karagiannidis, P., Aslanidis, P., Papastefanou, S., Mentzafos, D., Hountas, A. and Terzis, A. 1989. Cu(I) with Heterocyclic Thiones and Triphenylphosphine as Ligands. The Crystal Structure of $[Cu(tzdtH)_2(PPh_3)_2].NO_3$. *Inorgica Chimica Acta*. 156, 265-270.

Karagiannidis, P., Aslanidis, P. and Kessissoglou, D.P. 1989. Mononuclear and Binuclear Cu(I) Complexes with Metal-Sulfur Ligation. *Inorgica Chimica Acta.* 156, 47-56.

Karagiannidis, P., Aslanidis, P., Papastefanou, S., Mentzafos, D., Hountas, A. and Terzis, A. 1990. Synthesis and Characterization of Copper(I) halide Complexes with Heterocyclic Thiones and Triphenylphosphine as Ligands.The X-ray Crystal Structure of Copper(I)1-methyl-1,3-imidazoline-2-thione bis(triphenylphosphine)bromide, [Cu(PPh_3)$_2$meimtH)Br]. *Polyhedron. 9,* 981-986.

Lane, T.J., Yamaguchi, A.Y., Quagliano, J.V., Ryan, J.A. and Mizushima, S. 1959. Infrared Absorption Spectra of Inorganic Coordination Complexes. Infrared Studies of Methylthiourea and its Metal Complexes. *J. C. S. Dalton. Trans,* 3824-3236.

La-o, L., Pakawatchai, C., Saithong, S. and Skelton**,** B.W. 2009. Chlorido(1,3-dimethylthiourea-*κS*)bis(triphenylphosphine-*κP*)copper(I) acetonitrile hemisolvate. *Acta Cryst*. E65, m926

Lecomte, C., Skoulika, St., Aslanidis, P., Karagiannidis, P. and Papastefanou, St. 1989. Copper(I) Bromide Complexes with Heterocyclic Thiones and Triphenylphosphine as Ligands.The X-ray Crystal Structure of Coppet(I) Pyrimidine-2-thione Bis(triphenylphosphine)Bromide [Cu(PPh_3)$_2$(PymtH)Br]. *Polyhedron*. 8, 1103-1109.

Lobana, T. S. and Castineiras, A. 2002. Metal_ heterocyclic thione interactions.13. Pyridine-2-thione derivatives of copper(I): crystal structure of dinuclear [bromo(pyridine-2-thione)(tri-p-tolylphosphine)copper(I)]2 complex. *Polyhedron*. 21, 1603-1611.

Lobana, T. S., Khanna, S., Butcher, R. J., Hunter, A.D. and Zeller, M. 2006. Synthesis, Crystal structures and multinuclear NMR spectroscopy of copper(I) complexes with benzophenone thiosemicarbazone. *Polyhedron*. 25, 2755–2763.

Lobana, T. S., Sharma, R., Pannu, A.P.S., Hundal, G., Butcher, R. and Castineiras, A. 2007. Synthesis and structures of monomeric [chloro(isatin-3-thiosemicarbazone)bis(triphenylphosphine)]copper(I) and dimeric [dichlorobis(thiophene-2-carbaldehyde thiosemicarbazone)bis(triphenylphosphine)] dicopper(I)] complexes. *Polyhedron*. 26, 2621–2628.

Lobana, T. S., Kumari P. and Butcher, R. J. 2008. Cyclopentanone thiosemicarbazone (Hcptsc) induces a new bonding pattern in $(Ph_3P)Cu(\mu\text{-}Br)(\mu_3\text{-}S,N\text{-}Hcptsc)CuBr(PPh_3)$ dimmer. *Inorganic Chemistry Communications*. 11, 11-14.

Lobana,T. S., Sultana, R. and Hundal, G. 2008. Heterocyclic thioamides of copper(I): Synthesis and crystal structures of copper complexes with 1,3-imidazoline-2-thiones in the presence of triphenyl phosphine. *Polyhedron*. 27, 1008–1016

Lobana, T. S., Sharma, Sharma, R., Castineiras, A., Hundal, G. and Butcher, R. J. 2009. Theinfluence of substituents (R) at N^1 atom of thiophene-2-carbaldehyde thiosemicarbazones $\{(C_4H_3S)HC^2{=}N^3\text{-}N(H)\text{-}\ C^1({=}S)N^1HR\}$on bonding nuclearity and H-bonded networks of copper(I) complexes. *Inorganica chimica Acta*.

Nimthong, R., Pakawatchai, C., Saithong, S. and Charmant, P.H. 2008. Iodido(*N*-phenylthiourea)bis(triphenylphosphine)copper(I). *Acta Crystallographica Section E*.64, 977.

Sherman Hsu, C.P. In: F. Settle, Editor. 1997. *Handbook of Instrumental Techniques for Analytical Chemistry*. Prentice Hall: Upper Saddle River, p249

Sheldrick, G.M. 2008. SHLLXTL NT Version 6.12, Bruker Analytical X-ray System, Inc: Madison, WI, USA.

Singh R. and Dikshit S. K. 1995. Synthesis and characterization of mixed ligand copper(I) complexes containing halids, triphenylarsine and N,N'-dimethyl-N'-phenylthiourea (dmptH), N,N'-dibutyl-N'-phenylthiourea (dbptH) or 1,3-thiazolidine-2-thione (tzdtH). The X-ray crystal structure of $[Cu(PPh_3)_2(dmptH)Cl]$, *Polyhedron*. 14. 1799-1807.

Skoulika, S., Aubry, A., Karagiannidis, P., Aslanidis, P. and Papastefanou, S. 1991. New Copper(I) Chloride Complexes with Heterocyclic Thiones and Triphenylphosphine as Ligands. Crystal Structure of $[Cu(PPh_3)_2(bzimtH_2)Cl]CH_3COCH_3$ and $[Cu(PPh_3)_2(nbzimtH_2)Cl]$. *Inorganic Chimica Acta*. 183, 207-211.

Swaminathan, K. and Irving, H. M. N. H. 1964. Infrared Absorption Spectra of Complexes of thiourea", J. *Inorg. Nucl. Chem*. 26, 1291-1294.

Yamaguchi, A., Penland, R.B., Mizushima, S., Lane, T.J., Curran, C. and Qungliano, J.V. 1958. Infrared Absorption Spectra of Inorganic Coordination Complexes. XIV. Infrared Studies of Some Metal Thiourea Complexes. *J. Amer. Chem. Soc*. 80, 527-529.

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

Fw = Formula weight

APPENDIX B

Table 21 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters ($Å^2$ x 10^3) of $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$.

Atom	x	y	z	U(eq)
C(21B)	9935(3)	13598(3)	3233(2)	47(1)
N(2)	8327(3)	8326(3)	999(2)	64(1)
C(21A)	5172(3)	8976(3)	3377(2)	50(1)
C(11B)	8978(3)	12245(3)	4272(2)	44(1)
N(1)	7785(3)	9803(3)	814(2)	66(1)
C(11A)	4348(3)	8703(3)	1848(2)	54(1)
C(31B)	7585(3)	13574(3)	3849(2)	46(1)
C(31A)	3849(3)	10344(3)	2998(2)	50(1)
C(1)	8124(3)	9294(3)	1287(2)	51(1)
C(11)	7558(4)	9360(4)	23(2)	60(1)
C(21)	8584(5)	7619(4)	1423(2)	71(1)
C(22B)	10366(4)	14780(3)	3492(2)	58(1)
C(32B)	7495(3)	13936(3)	4597(2)	55(1)
C(12B)	10054(4)	12977(3)	4754(2)	59(1)
C(16A)	3911(5)	7535(4)	1793(3)	85(1)
C(26A)	6012(4)	8395(4)	3307(3)	71(1)
C(36A)	4165(4)	11446(4)	3401(2)	63(1)
C(33B)	6814(4)	14643(3)	4842(3)	68(1)
C(36B)	6954(4)	13908(3)	3345(2)	64(1)
C(22A)	4453(4)	8950(3)	3979(2)	64(1)
C(24A)	5396(5)	7794(4)	4416(3)	79(1)
C(32A)	2534(4)	9624(4)	2837(2)	65(1)
C(33A)	1587(4)	10028(5)	3089(3)	74(1)

Table 21 (continued).

Atom	x	y	z	U(eq)
C(13A)	3540(5)	8274(6)	565(3)	90(2)
C(12)	8478(5)	9843(4)	-419(3)	81(1)
C(34B)	6203(4)	14969(4)	4341(3)	75(1)
C(12A)	4184(4)	9074(4)	1229(2)	65(1)
C(16B)	8310(4)	11179(3)	4402(2)	67(1)
C(23A)	4568(5)	8365(4)	4492(2)	81(1)
C(13)	8278(6)	9428(5)	-1170(3)	95(2)
C(26B)	10711(4)	13137(4)	2799(3)	72(1)
C(13B)	10441(4)	12661(4)	5348(2)	74(1)
C(35B)	6266(4)	14607(4)	3591(3)	73(1)
C(23B)	11557(4)	15491(4)	3337(2)	71(1)
C(24B)	12324(4)	15020(4)	2921(3)	81(1)
C(25A)	6118(5)	7798(4)	3822(3)	82(1)
C(14B)	9764(5)	11602(4)	5471(3)	80(1)
C(34A)	1925(5)	11136(5)	3502(3)	78(1)
C(25B)	11901(5)	13838(4)	2646(3)	91(2)
C(14)	7180(6)	8573(5)	-1490(3)	88(2)
C(15B)	8704(5)	10862(4)	4996(3)	87(2)
C(35A)	3204(5)	11846(4)	3658(3)	81(1)
C(16)	6440(5)	8481(5)	-295(3)	91(2)
C(14A)	3107(5)	7126(6)	523(3)	104(2)
C(15A)	3297(6)	6753(5)	1127(4)	109(2)
C(22)	9750(6)	7522(4)	1448(4)	105(2)
C(15)	6243(6)	8073(5)	-1080(3)	100(2)
C(26)	7654(8)	7030(6)	1779(4)	148(3)
C(23)	9978(9)	6804(6)	1847(6)	156(4)
C(24)	9016(15)	6209(10)	2203(5)	186(5)

Table 21 (continued).

Atom	x	y	z	U(eq)
C(25)	7894(13)	6303(9)	2170(6)	220(6)
Cu(1)	7152(1)	11085(1)	2537(1)	46(1)
P(2)	8413(1)	12604(1)	3464(1)	43(1)
P(1)	5139(1)	9816(1)	2702(1)	46(1)
S(1)	8363(1)	9891(1)	2214(1)	55(1)
Cl(1)	6999(1)	11925(1)	1552(1)	63(1)
C(5)	812(9)	3466(6)	714(4)	125(2)
C(4)	-93(7)	3896(8)	1105(5)	169(3)
N(4)	1531(10)	3224(8)	430(4)	213(4)
N(5)	4787(12)	4981(13)	1759(10)	303(7)
C(7)	4990(30)	4790(30)	1097(17)	720(20)
C(6)	5340(40)	4690(30)	473(12)	1100(40)

Table 22 Non – hydrogen atom thermal parameters (Å^{2}x 10^3) of $[Cu(PPh_3)_2(dptu)Cl]\cdot 2CH_3CN$.

Atom	U11	U22	U33	U23	U13	U12
C(21B)	51(2)	49(2)	44(2)	15(2)	4(2)	20(2)
N(2)	93(2)	69(2)	48(2)	16(2)	17(2)	50(2)
C(21A)	51(2)	48(2)	51(2)	17(2)	4(2)	14(2)
C(11B)	49(2)	47(2)	41(2)	12(2)	9(2)	24(2)
N(1)	100(3)	71(2)	44(2)	14(2)	12(2)	52(2)
C(11A)	50(2)	63(2)	51(2)	16(2)	7(2)	21(2)
C(31B)	47(2)	40(2)	53(2)	14(2)	11(2)	17(2)
C(31A)	49(2)	65(2)	43(2)	22(2)	6(2)	25(2)
C(1)	55(2)	59(2)	48(2)	17(2)	14(2)	29(2)
C(11)	77(3)	77(3)	43(2)	17(2)	10(2)	48(2)
C(21)	104(4)	71(3)	61(3)	24(2)	29(3)	54(3)
C(22B)	66(3)	57(2)	51(2)	15(2)	10(2)	23(2)
C(32B)	53(2)	55(2)	57(3)	12(2)	10(2)	21(2)
C(12B)	66(3)	53(2)	55(2)	18(2)	-6(2)	18(2)
C(16A)	105(4)	60(3)	74(3)	12(2)	-1(3)	14(3)
C(26A)	73(3)	78(3)	84(3)	46(2)	27(2)	38(2)
C(36A)	59(2)	71(3)	63(3)	12(2)	1(2)	30(2)
C(33B)	73(3)	66(3)	73(3)	15(2)	31(2)	34(2)
C(36B)	74(3)	64(2)	66(3)	27(2)	16(2)	36(2)
C(22A)	79(3)	70(3)	56(3)	28(2)	18(2)	34(2)
C(24A)	108(4)	71(3)	67(3)	36(2)	8(3)	33(3)
C(32A)	54(2)	77(3)	71(3)	28(2)	9(2)	27(2)
C(33A)	54(3)	112(4)	73(3)	42(3)	14(2)	39(3)
C(13A)	89(3)	128(5)	55(3)	5(3)	-9(3)	54(3)
C(12)	93(3)	98(3)	59(3)	32(3)	15(3)	36(3)

Table 22 (continued).

Atom	U11	U22	U33	U23	U13	U12
C(34B)	74(3)	63(3)	106(4)	31(3)	40(3)	40(2)
C(12A)	67(3)	73(3)	58(3)	15(2)	2(2)	30(2)
C(16B)	63(3)	65(3)	70(3)	30(2)	-4(2)	13(2)
C(23A)	119(4)	80(3)	61(3)	36(2)	29(3)	46(3)
C(13)	118(5)	121(4)	59(3)	39(3)	28(3)	51(4)
C(26B)	70(3)	59(2)	91(3)	22(2)	29(2)	28(2)
C(13B)	76(3)	80(3)	61(3)	19(2)	-13(2)	23(2)
C(35B)	76(3)	75(3)	97(4)	45(3)	28(3)	47(2)
C(23B)	77(3)	57(2)	70(3)	25(2)	9(2)	10(2)
C(24B)	63(3)	89(3)	94(4)	47(3)	24(3)	17(3)
C(25A)	93(3)	81(3)	99(4)	48(3)	17(3)	49(3)
C(14B)	88(3)	92(3)	66(3)	40(3)	-4(3)	31(3)
C(34A)	77(3)	125(4)	64(3)	35(3)	20(2)	67(3)
C(25B)	78(3)	83(3)	122(4)	39(3)	48(3)	34(3)
C(14)	123(5)	113(4)	55(3)	22(3)	7(3)	76(4)
C(15B)	92(3)	80(3)	91(4)	55(3)	0(3)	15(3)
C(35A)	90(4)	94(3)	71(3)	5(2)	6(3)	59(3)
C(16)	75(3)	123(4)	71(3)	14(3)	12(3)	39(3)
C(14A)	87(4)	105(5)	91(4)	-21(4)	-19(3)	30(3)
C(15A)	124(5)	66(3)	107(5)	-4(3)	-15(4)	17(3)
C(22)	109(4)	73(3)	136(5)	25(3)	-18(4)	41(3)
C(15)	89(4)	118(4)	86(4)	2(3)	-19(3)	44(3)
C(26)	191(7)	157(6)	190(8)	117(6)	118(6)	125(6)
C(23)	173(8)	100(5)	203(10)	21(5)	-67(7)	73(5)
C(24)	327(17)	197(10)	133(7)	84(7)	48(9)	187(11)
C(25)	337(16)	242(11)	244(12)	196(11)	195(12)	211(12)
Cu(1)	51(1)	50(1)	41(1)	13(1)	5(1)	21(1)

Table 22 (continued).

Atom	U11	U22	U33	U23	U13	U12
P(2)	50(1)	44(1)	39(1)	11(1)	6(1)	21(1)
P(1)	46(1)	51(1)	45(1)	17(1)	6(1)	19(1)
S(1)	64(1)	68(1)	44(1)	14(1)	7(1)	38(1)
Cl(1)	84(1)	66(1)	52(1)	25(1)	5(1)	36(1)
C(5)	191(8)	99(4)	77(4)	-17(3)	-9(5)	70(5)
C(4)	120(6)	201(8)	175(8)	52(7)	25(6)	43(6)
N(4)	335(12)	272(9)	91(5)	-25(5)	17(6)	224(9)
N(5)	178(10)	231(14)	500(20)	86(15)	60(12)	73(9)
C(7)	880(50)	420(30)	780(40)	50(30)	570(40)	210(30)
C(6)	1680(90)	1220(60)	620(40)	360(40)	970(50)	710(60)

Table 23 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters ($Å^2$ x 10^3) of [Cu(PPh$_3$)$_2$(dptu)Br]·H$_2$O.

Atom	x	y	z	U(eq)
Cu(1)	2591(1)	5770(1)	2616(1)	37(1)
Br(1)	2653(1)	6818(1)	3568(1)	52(1)
S(1)	1367(1)	4509(1)	3015(1)	44(1)
P(1)	1408(1)	7428(1)	1630(1)	33(1)
P(2)	4692(1)	4380(1)	2496(1)	35(1)
N(1)	2028(4)	4366(4)	4382(2)	52(1)
N(2)	1371(4)	2854(3)	4284(2)	45(1)
C(1)	1629(5)	3854(4)	3945(3)	39(1)
C(11)	2506(5)	3865(5)	5149(3)	48(1)
C(12)	2016(7)	4610(6)	5602(3)	75(2)
C(13)	2602(5)	4144(5)	6335(2)	101(3)
O(1)	-530(5)	7708(5)	4185(2)	108(2)
C(14)	3629(9)	3018(8)	6588(4)	102(3)
C(15)	4078(7)	2283(7)	6150(4)	91(2)
C(16)	3522(6)	2707(6)	5421(3)	66(2)
C(21)	1175(5)	2034(4)	3940(3)	44(1)
C(22)	2121(6)	1489(5)	3515(3)	58(2)
C(23)	1929(8)	681(5)	3202(3)	81(2)
C(24)	840(8)	389(6)	3322(4)	82(2)
C(25)	-84(7)	913(6)	3749(4)	86(2)
C(26)	82(6)	1740(5)	4065(3)	63(2)
C(11A)	-130(4)	8606(4)	1790(2)	37(1)
C(12A)	-466(5)	9854(4)	1505(3)	51(1)
C(13A)	-1677(6)	10711(5)	1601(3)	69(2)
C(14A)	-2574(7)	10319(6)	1981(4)	86(2)
C(15A)	-2255(6)	9092(7)	2284(4)	101(3)

Table 23 (continued).

Atom	x	y	z	U(eq)
C(16A)	-1040(6)	8225(5)	2195(3)	74(2)
C(21A)	845(4)	7155(4)	809(2)	36(1)
C(22A)	1640(6)	6121(5)	620(3)	66(2)
C(23A)	1307(7)	5894(6)	-2(4)	85(2)
C(24A)	138(6)	6673(5)	-427(3)	71(2)
C(25A)	-678(6)	7711(5)	-256(3)	66(2)
C(26A)	-320(5)	7951(4)	363(3)	52(1)
C(31A)	2394(4)	8337(4)	1247(3)	38(1)
C(32A)	2619(5)	8646(4)	506(3)	48(1)
C(33A)	3426(5)	9284(5)	263(3)	59(2)
C(34A)	4014(5)	9627(5)	754(3)	60(2)
C(35A)	3799(5)	9324(4)	1491(3)	55(1)
C(36A)	2996(5)	8689(4)	1736(3)	44(1)
C(11B)	4574(5)	3619(4)	1815(2)	37(1)
C(12B)	3688(5)	3040(4)	1880(3)	47(1)
C(13B)	3437(5)	2581(5)	1336(3)	57(2)
C(14B)	4088(6)	2713(5)	697(3)	66(2)
C(15B)	4960(6)	3301(5)	612(3)	59(2)
C(16B)	5212(5)	3730(4)	1163(3)	48(1)
C(21B)	6127(5)	4785(4)	2209(3)	39(1)
C(22B)	5900(5)	5964(4)	1765(3)	49(1)
C(23B)	6961(6)	6275(5)	1504(3)	64(2)
C(24B)	8269(6)	5390(6)	1696(3)	61(2)
C(25B)	8496(5)	4244(6)	2137(3)	59(2)
C(26B)	7454(5)	3916(5)	2391(3)	48(1)
C(31B)	5437(4)	3136(4)	3365(3)	39(1)
C(32B)	5767(6)	1889(5)	3474(3)	59(2)

Table 23 (continued).

Atom	x	y	z	U(eq)
C(33B)	6390(6)	1029(5)	4151(4)	75(2)
C(34B)	6698(6)	1390(7)	4710(3)	80(2)
C(35B)	6359(6)	2627(7)	4619(3)	72(2)
C(36B)	5723(5)	3488(5)	3957(3)	52(1)

Table 24 Non – hydrogen atom thermal parameters (Å^2 x 10^3) of [Cu(PPh$_3$)$_2$(dptu)Br]·H$_2$O.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	41(1)	38(1)	32(1)	-13(1)	4(1)	-15(1)
Br(1)	80(1)	54(1)	39(1)	-24(1)	12(1)	-38(1)
S(1)	52(1)	51(1)	36(1)	-11(1)	2(1)	-29(1)
P(1)	35(1)	33(1)	31(1)	-10(1)	3(1)	-14(1)
P(2)	36(1)	38(1)	33(1)	-14(1)	1(1)	-13(1)
N(1)	73(3)	49(2)	42(3)	-12(2)	3(2)	-33(2)
N(2)	61(3)	54(2)	34(2)	-14(2)	12(2)	-37(2)
C(1)	39(3)	40(3)	45(3)	-16(2)	8(2)	-20(2)
C(11)	60(4)	64(3)	33(3)	-13(3)	11(3)	-40(3)
C(12)	117(6)	76(4)	52(4)	-35(3)	17(4)	-48(4)
C(13)	170(9)	127(7)	49(5)	-49(5)	23(5)	-89(6)
O(1)	105(5)	157(5)	72(4)	-38(4)	40(3)	-63(4)
C(14)	148(8)	131(7)	45(4)	-9(5)	-24(5)	-85(6)
C(15)	79(5)	115(6)	68(5)	-12(5)	-14(4)	-38(4)
C(16)	58(4)	86(4)	56(4)	-24(3)	12(3)	-30(3)
C(21)	56(3)	43(3)	38(3)	-9(2)	4(3)	-25(3)
C(22)	65(4)	56(3)	58(4)	-19(3)	15(3)	-29(3)
C(23)	121(6)	60(4)	65(4)	-31(3)	24(4)	-32(4)
C(24)	111(6)	66(4)	79(5)	-26(4)	-11(4)	-44(4)
C(25)	73(5)	80(5)	127(7)	-44(5)	6(5)	-45(4)
C(26)	53(4)	65(4)	86(5)	-33(3)	16(3)	-32(3)
C(11A)	37(3)	45(3)	28(3)	-13(2)	4(2)	-15(2)
C(12A)	37(3)	44(3)	66(4)	-18(3)	9(3)	-9(2)
C(13A)	66(4)	53(3)	71(4)	-23(3)	3(4)	-3(3)
C(14A)	70(5)	87(5)	72(5)	-30(4)	26(4)	3(4)
C(15A)	62(5)	97(5)	106(6)	-2(5)	53(4)	-13(4)

Table 24 (continued)

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(16A)	58(4)	60(4)	79(5)	-3(3)	28(3)	-11(3)
C(21A)	37(3)	34(2)	36(3)	-9(2)	2(2)	-13(2)
C(22A)	62(4)	45(3)	68(4)	-24(3)	-23(3)	10(3)
C(23A)	82(5)	84(4)	73(5)	-54(4)	-16(4)	8(4)
C(24A)	78(4)	73(4)	62(4)	-36(3)	-21(3)	-16(4)
C(25A)	65(4)	73(4)	55(4)	-31(3)	-22(3)	-15(3)
C(26A)	48(3)	49(3)	54(3)	-21(3)	-8(3)	-10(3)
C(31A)	36(3)	37(3)	38(3)	-13(2)	7(2)	-11(2)
C(32A)	51(3)	55(3)	47(3)	-19(3)	17(3)	-29(3)
C(33A)	62(4)	75(4)	53(4)	-25(3)	25(3)	-38(3)
C(34A)	49(3)	62(3)	81(5)	-25(3)	28(3)	-34(3)
C(35A)	65(4)	55(3)	57(4)	-19(3)	8(3)	-35(3)
C(36A)	50(3)	43(3)	46(3)	-13(2)	5(3)	-24(2)
C(11B)	47(3)	32(2)	31(3)	-15(2)	0(2)	-12(2)
C(12B)	43(3)	55(3)	49(3)	-25(3)	7(3)	-21(3)
C(13B)	60(4)	62(3)	62(4)	-36(3)	-4(3)	-25(3)
C(14B)	87(5)	58(4)	58(4)	-38(3)	-3(3)	-19(3)
C(15B)	73(4)	61(3)	45(3)	-28(3)	8(3)	-18(3)
C(16B)	52(3)	53(3)	48(3)	-27(3)	13(3)	-20(3)
C(21B)	41(3)	49(3)	36(3)	-18(2)	1(2)	-22(2)
C(22B)	44(3)	51(3)	52(3)	-19(3)	2(3)	-16(3)
C(23B)	72(4)	67(4)	63(4)	-18(3)	12(3)	-39(4)
C(24B)	56(4)	90(4)	58(4)	-31(4)	18(3)	-45(4)
C(25B)	40(3)	78(4)	61(4)	-28(3)	5(3)	-21(3)
C(26B)	41(3)	55(3)	46(3)	-15(3)	5(3)	-18(3)
C(31B)	34(3)	45(3)	38(3)	-14(2)	4(2)	-14(2)
C(32B)	69(4)	53(3)	50(4)	-14(3)	4(3)	-20(3)

Table 24 (continued)

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(33B)	81(5)	51(3)	64(5)	3(3)	-2(4)	-9(3)
C(34B)	74(5)	97(5)	40(4)	0(4)	-4(3)	-18(4)
C(35B)	62(4)	109(5)	43(4)	-30(4)	5(3)	-27(4)
C(36B)	57(3)	61(3)	38(3)	-16(3)	1(3)	-21(3)

Table 25 Non – hydrogen atom coordinates (x 10^4) and isotropic thermal parameters ($Å^2$ x 10^3) of $[Cu(PPh_3)_2(dptu)I]\cdot CH_3CN$.

Atom	x	y	z	U(eq)
Cu(1)	2775(1)	5062(1)	6279(1)	37(1)
I(1)	4073(1)	5421(1)	7206(1)	41(1)
S(1)	2474(1)	6144(1)	5532(1)	48(1)
P(1)	3374(1)	3981(1)	5695(1)	33(1)
P(2)	1316(1)	4986(1)	6821(1)	35(1)
N(1)	2974(2)	7145(2)	6493(1)	53(1)
N(2)	2499(2)	7751(2)	5536(2)	60(1)
C(1)	2643(2)	7067(2)	5877(2)	44(1)
C(11)	3105(2)	7863(2)	6866(2)	50(1)
C(12)	3936(3)	7941(2)	7230(2)	58(1)
C(13)	4082(3)	8628(2)	7613(2)	73(1)
C(14)	3411(4)	9222(3)	7620(2)	81(1)
C(15)	2585(3)	9145(2)	7269(2)	78(1)
C(16)	2408(3)	8459(2)	6891(2)	64(1)
C(21)	1984(3)	7847(2)	4932(2)	61(1)
C(22)	1053(3)	7649(3)	4886(3)	104(2)
C(23)	566(5)	7846(4)	4285(4)	138(3)
C(24)	1070(6)	8195(3)	3783(3)	118(2)
C(25)	1987(6)	8369(3)	3836(3)	105(2)
C(26)	2469(4)	8209(2)	4413(2)	78(1)
C(11A)	4570(2)	4072(2)	5319(1)	38(1)
C(12A)	4851(2)	3589(2)	4796(2)	54(1)
C(13A)	5732(3)	3692(3)	4500(2)	65(1)
C(14A)	6354(3)	4269(3)	4712(2)	68(1)
C(15A)	6092(3)	4752(2)	5231(2)	72(1)
C(16A)	5197(2)	4665(2)	5530(2)	55(1)

Table 25 (continued).

Atom	x	y	z	U(eq)
C(21A)	2700(2)	3669(2)	4958(1)	35(1)
C(22A)	2584(2)	4244(2)	4465(1)	45(1)
C(23A)	2164(2)	4036(2)	3875(2)	54(1)
C(24A)	1824(2)	3273(2)	3772(2)	54(1)
C(25A)	1896(2)	2708(2)	4263(2)	54(1)
C(26A)	2336(2)	2897(2)	4858(2)	42(1)
C(31A)	3424(2)	3040(2)	6172(1)	37(1)
C(32A)	2590(2)	2813(2)	6511(2)	52(1)
C(33A)	2569(3)	2097(2)	6860(2)	64(1)
C(34A)	3360(3)	1606(2)	6885(2)	72(1)
C(35A)	4184(3)	1833(2)	6561(2)	69(1)
C(36A)	4215(2)	2544(2)	6207(2)	53(1)
C(11B)	1240(2)	4544(2)	7652(1)	41(1)
C(12B)	481(3)	4699(2)	8083(2)	56(1)
C(13B)	474(3)	4367(3)	8703(2)	74(1)
C(14B)	1210(4)	3892(2)	8911(2)	75(1)
C(15B)	1968(3)	3733(2)	8497(2)	64(1)
C(16B)	1988(2)	4060(2)	7867(2)	49(1)
C(21B)	380(2)	4477(2)	6329(2)	41(1)
C(22B)	571(3)	4319(3)	5691(2)	77(1)
C(23B)	-104(3)	3969(3)	5279(2)	91(2)
C(24B)	-980(3)	3784(3)	5505(2)	78(1)
C(25B)	-1190(3)	3926(3)	6151(2)	102(2)
C(26B)	-510(3)	4269(3)	6554(2)	87(2)
C(31B)	787(2)	5979(2)	6979(1)	40(1)
C(32B)	1126(3)	6425(2)	7495(2)	66(1)
C(33B)	723(3)	7172(2)	7648(2)	78(1)

Table 25 (continued).

Atom	x	y	z	U(eq)
C(34B)	21(3)	7477(2)	7253(3)	85(1)
C(35B)	-283(4)	7051(3)	6723(3)	103(2)
C(36B)	89(3)	6299(2)	6585(2)	74(1)
C(2)	443(5)	5613(5)	4015(4)	157(3)
C(3)	-534(6)	5680(4)	4243(3)	127(2)
N(3)	-1308(5)	5742(4)	4410(4)	174(3)

Table 26 Non – hydrogen atom thermal parameters (Å^{2}x 10^3) of [Cu(PPh$_3$)$_2$(dptu)I]·CH$_3$CN.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	37(1)	34(1)	38(1)	-4(1)	-1(1)	2(1)
I(1)	43(1)	46(1)	36(1)	-2(1)	-6(1)	1(1)
S(1)	68(1)	40(1)	37(1)	2(1)	-5(1)	2(1)
P(1)	34(1)	31(1)	33(1)	-3(1)	0(1)	1(1)
P(2)	34(1)	33(1)	38(1)	0(1)	0(1)	2(1)
N(1)	74(2)	36(2)	49(2)	4(1)	-14(1)	-3(1)
N(2)	80(2)	41(2)	60(2)	14(1)	-21(2)	-8(1)
C(1)	49(2)	40(2)	44(2)	7(1)	-3(1)	-4(1)
C(11)	61(2)	38(2)	50(2)	1(2)	2(2)	-9(1)
C(12)	70(2)	49(2)	55(2)	5(2)	-12(2)	-5(2)
C(13)	89(3)	59(2)	71(3)	-4(2)	-22(2)	-17(2)
C(14)	101(3)	59(2)	81(3)	-20(2)	8(3)	-25(2)
C(15)	77(3)	50(2)	107(3)	-17(2)	16(3)	-1(2)
C(16)	54(2)	56(2)	81(2)	-8(2)	-1(2)	-5(2)
C(21)	85(3)	41(2)	56(2)	3(2)	-17(2)	18(2)
C(22)	76(3)	113(4)	123(4)	27(3)	-35(3)	-6(3)
C(23)	114(5)	133(6)	167(7)	16(5)	-72(5)	-14(4)
C(24)	166(6)	80(4)	107(4)	22(3)	-55(5)	18(4)
C(25)	164(6)	86(4)	65(3)	11(3)	-15(3)	23(4)
C(26)	115(4)	63(2)	57(2)	9(2)	-2(2)	16(2)
C(11A)	37(1)	39(2)	37(2)	2(1)	0(1)	6(1)
C(12A)	47(2)	55(2)	59(2)	-13(2)	7(2)	2(2)
C(13A)	56(2)	79(3)	60(2)	-10(2)	16(2)	17(2)
C(14A)	45(2)	87(3)	72(2)	9(2)	16(2)	3(2)
C(15A)	50(2)	82(3)	85(3)	-6(2)	7(2)	-24(2)
C(16A)	50(2)	59(2)	56(2)	-14(2)	7(2)	-14(2)

Table 26 (continued).

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(21A)	32(1)	40(2)	33(1)	-3(1)	0(1)	2(1)
C(22A)	52(2)	41(2)	43(2)	2(1)	-1(1)	0(1)
C(23A)	62(2)	62(2)	37(2)	8(2)	-4(2)	0(2)
C(24A)	51(2)	72(2)	40(2)	-10(2)	-9(1)	-1(2)
C(25A)	50(2)	53(2)	58(2)	-14(2)	-7(2)	-8(2)
C(26A)	45(2)	40(2)	39(2)	-3(1)	-5(1)	0(1)
C(31A)	43(2)	36(2)	32(1)	-2(1)	-6(1)	1(1)
C(32A)	57(2)	44(2)	54(2)	5(2)	9(2)	1(2)
C(33A)	75(3)	56(2)	59(2)	13(2)	13(2)	-7(2)
C(34A)	106(3)	50(2)	60(2)	19(2)	-10(2)	1(2)
C(35A)	76(3)	56(2)	74(2)	18(2)	-6(2)	18(2)
C(36A)	47(2)	56(2)	57(2)	7(2)	-1(2)	7(2)
C(11B)	48(2)	35(1)	38(2)	-1(1)	-1(1)	-2(1)
C(12B)	69(2)	49(2)	52(2)	1(2)	11(2)	-1(2)
C(13B)	101(3)	73(3)	48(2)	-7(2)	18(2)	-21(2)
C(14B)	118(4)	61(2)	44(2)	9(2)	-15(2)	-38(2)
C(15B)	77(3)	47(2)	68(2)	16(2)	-29(2)	-16(2)
C(16B)	56(2)	38(2)	54(2)	5(2)	-11(2)	-9(1)
C(21B)	39(1)	38(2)	45(2)	1(1)	-8(1)	-2(1)
C(22B)	46(2)	115(4)	69(2)	-37(2)	-7(2)	5(2)
C(23B)	70(3)	127(4)	76(3)	-49(3)	-13(2)	-4(3)
C(24B)	73(3)	80(3)	81(3)	-9(2)	-31(2)	-25(2)
C(25B)	72(3)	146(5)	88(3)	6(3)	-8(2)	-59(3)
C(26B)	70(2)	133(4)	58(2)	-2(3)	4(2)	-50(3)
C(31B)	35(2)	36(2)	48(2)	4(1)	3(1)	3(1)
C(32B)	77(3)	44(2)	77(2)	-10(2)	-17(2)	9(2)
C(33B)	101(3)	43(2)	90(3)	-18(2)	-3(3)	4(2)

Table 26 (continued).

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(34B)	80(3)	44(2)	131(4)	-3(3)	14(3)	26(2)
C(35B)	98(3)	65(3)	147(5)	-13(3)	-42(3)	42(3)
C(36B)	79(3)	58(2)	84(3)	1(2)	-25(2)	23(2)
C(2)	136(5)	192(8)	143(6)	-30(6)	26(5)	62(5)
C(3)	161(6)	112(5)	107(4)	8(4)	7(4)	71(4)
N(3)	162(5)	167(6)	193(6)	67(5)	59(5)	103(5)

VITAE

Name Miss Ladawan Duangmuengmai

Student ID 5010220190

Education Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science (Chemistry)	Yala Rajabhat University	2007

Scholarship Awards during Enrolment

Center of Excellence for Innovation in Chemistry Commission on Higher Education, (PERCH-CIC)