Crystal Structures of Silver(I) Complexes Containing Ethylthiourea and Diethylthiourea Ligands

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Master of Science Thesis in Physical Chemistry

Prince of Songkla University

2003

Thesis title	Crystal Structures of Silver(I) Complexes Containing Ethylthiourea and Diethylthiourea Ligands
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The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of requirement for the Master of Science degree in Physical Chemistry.

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ชื่อวิทยานิพนธ์ โครงสร้างผลึกของสารประกอบเชิงซ้อนซิลเวอร์(I) ที่มีเอทิลไธโอยูเรีย และ ไดเอทิลไธโอยูเรียเป็นลิแกนด์
ผู้เขียน นางสาวเสาวนิต ทรายทอง
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บทคัดย่อ

การศึกษาโครงสร้างผลึกของสารประกอบเชิงซ้อนซิลเวอร์(I) กับลิแกนด์ซับสติติวเตตไธโอยูเรีย คือ $[Ag(ettu)_3Cl]$(1), $[Ag(ettu)_3Br]$(2), $[Ag(detu)_3Br]$(3), $\{[Ag(detu)_3]_2SO_4\}$(4) และ $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ (5) (ettu = เอทิลไธโอยูเรีย, detu = ไดเอทิลไธโอยูเรีย) โดยวิธีการเลี้ยวเบนรังสีเอกซ์ของผลึกเดี่ยว สารประกอบเหล่านี้เตรียมได้จากการทำปฏิกิริยาโดยตรงระหว่างเกลือซิลเวอร์(I) (AgCl, AgBr, Ag_2SO_4 และ AgSCN) กับ ลิแกนด์ซับสติติวเตตไธโอยูเรียข้างต้น ภายใต้สภาวะการทดลองที่เหมาะสม พบว่าสาร(1) เป็นสารประกอบเชิงซ้อนแบบมอนอเมอร์ จัดเป็นสารโคเวเลนต์ มีระบบผลึกเป็นโมโนคลินิก หมู่ปริภูมิ $P2_1/m$ (No.11), $Z = 2$, $a = 7.3489(1)$, $b = 15.3315(1)$, $c = 8.1959(1)$ Å, $\beta = 91.467(1)^\circ$ อะตอมซิลเวอร์จัดตัวเป็นทรงสี่หน้าที่บิดเบี้ยวเล็กน้อยโดยเกิดพันธะโคออร์ดิเนตโคเวเลนต์กับอะตอมซัลเฟอร์สามอะตอมจากเอทิลไธโอยูเรียสามโมเลกุล และคลอรีนหนึ่งอะตอม โมเลกุลมีสมมาตร C_s ผ่านอะตอมซิลเวอร์ คลอรีน และเอทิลไธโอยูเรียหนึ่งโมเลกุล สาร(2) เป็นสารประกอบเชิงซ้อนมอนอเมอร์จัดเป็นสารโคเวเลนต์ เป็น isomorphous และมีโครงสร้างเหมือนกับสาร(1) มีระบบผลึกเป็นโมโนคลินิก หมู่ปริภูมิ $P2_1/m$ (No.11), $Z = 2$, $a = 7.295(2)$, $b = 15.502(3)$, $c = 8.281(2)$Å, $\beta = 91.49(3)^\circ$ โคออร์ดิเนชันรอบอะตอมซิลเวอร์ และโมเลกุลมีสมมาตร C_s เช่นเดียวกับสาร(1) รูปทรงทางเรขาคณิตของสารทั้งสองชนิดนี้เกี่ยวข้องกับพันธะไฮโดรเจนระหว่างโมเลกุล และพันธะไฮโดรเจนภายในโมเลกุลชนิด N-H---X-M (X = เฮไลด์ M = metal) จากผลดังกล่าวเกิดเป็นโครงร่างตาข่าย 2 มิติในผลึกตามแนวแกน *a* และ *b* สาร(3) เป็นสารโคเวเลนต์มอนอเมอร์ มีระบบผลึกเป็นไตรโกนอล หมู่ปริภูมิ $P31c$ (No.159), $Z = 2$, $a = 12.5665(6)$, $c = 9.5805(9)$ Å, $\gamma = 120^\circ$ โคออร์ดิเนชันรอบอะตอมซิลเวอร์เป็นทรงสี่หน้าเกิดพันธะกับอะตอมซัลเฟอร์จากไดเอทิลไธโอยูเรียสามโมเลกุล และโบรมีนหนึ่งอะตอม อะตอมซิลเวอร์และโบรมีนวางตัวอยู่ในตำแหน่งสมมาตรแกนหมุน C_3 สาร(4) เป็นสารประกอบเชิงซ้อนมอนอเมอร์ จัดเป็นสารไอออนิก มีระบบผลึกเป็นเฮกซะโกนอล

หมู่ปริภูมิ $R\bar{3}$ (No.148), $Z = 3$, $a = 12.3745(6)$, $c = 27.603(3)$ Å, $\gamma = 120^\circ$ โครงสร้างประกอบด้วยสองแคตไอออน $[Ag(detu)_3]^+$ ที่เหมือนกันทุกประการ โดยแต่ละแคตไอออนรวมทั้งซัลเฟตแอนไอออน(SO_4^{2-}) มีสมมาตรเป็นแกนหมุนสาม อะตอมออกซิเจนของซัลเฟตทั้งหมดเกิด disorder นอกจากนี้ยังพบว่าเกิดอันตรกิริยาแบบไม่เกิดพันธะระหว่างอะตอมของซิลเวอร์ของแคตไอออนทั้งสอง สาร(5) เป็นสารประกอบเชิงซ้อนที่เป็นสารไอออนิก โมเลกุลเชื่อมต่อกันเป็นสายโซ่อนันต์ มีระบบผลึกเป็นเตตตระโกนอล หมู่ $P4_2/n$ (No.86), $Z = 2$, $a = 18.3911(7)$, $c = 6.2785(5)$Å โครงสร้างประกอบด้วยสายโซ่อนันต์ส่วนที่เป็นแคตไอออน $\{[Ag_2(detu)_4]^{2+}\}_\infty$ และส่วนที่เป็นแอนไอออน $\{[Ag(SCN)_2]_2^{2-}\}_\infty$ แยกจากกัน และสายโซ่เหล่านี้ต่างประกอบด้วยหน่วยย่อยที่เป็นไดเมอร์ที่ซ้ำๆของ $\{[Ag_2(detu)_4]\}^{2+}$ ในส่วนสายโซ่แคตไอออน และ $\{[Ag((SCN)_2)_2]\}^{2-}$ ในส่วนสายโซ่แอนไอออน โคออร์ดิเนชันรอบอะตอมซิลเวอร์ในแต่ละสายโซ่เป็นรูปทรงสี่หน้าที่บิดเบี้ยวเล็กน้อย อะตอมซิลเวอร์ในสายโซ่แคตไอออนเกิดพันธะกับอะตอมซัลเฟอร์จาก detu 4 โมเลกุล และในส่วนสายโซ่แอนไอออนอะตอมซิลเวอร์เกิดพันธะกับอะตอมซัลเฟอร์จากหมู่ไทโอไซยาเนต 4 หมู่ ซึ่งซัลเฟอร์แต่ละอะตอมในแต่ละสายโซ่ต่างทำหน้าที่เป็นสะพานเชื่อมระหว่างซิลเวอร์ที่เป็นอะตอมกลาง 2 อะตอมเกิดเป็นโครงสร้างสายโซ่อนันต์ 1 มิติมีทิศทางขนานตามแกน *c* นอกจากนี้รูปทรงเรขาคณิตของโมเลกุลเกี่ยวข้องกับการเกิดพันธะไฮโดรเจนแบบ N-H---N เกิดเป็นโครงร่างตาข่าย 3 มิติอันเนื่องจากพันธะไฮโดรเจนทั่วทั้งผลึก

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Major Program	Physical Chemistry

Academic year	2003

Abstract

The crystal structures of five silver(I) complexes with substituted thioureas, $[Ag(ettu)_3Cl]$(1), $[Ag(ettu)_3Br]$(2), $[Ag(detu)_3Br]$(3), $\{[Ag(detu)_3]_2SO_4\}$(4) and $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$(5) (ettu = *N*-ethylthiourea, detu = *N,N,*-diethylthiourea) have been studied by single crystal X-ray diffraction method. All complexes were prepared by direct reaction of silver(I) salts such as AgCl, AgBr, Ag_2SO_4 and AgSCN with substituted thiourea under suitable conditions. The monomeric covalent complex (1) crystallizes in a monoclinic system, space group $P2_1/m$ (No.11), $Z = 2$, $a = 7.3489(1)$, $b = 15.3315(1)$, $c = 8.1959(1)$ Å, $\beta = 91.467(1)^\circ$. The silver atom is slightly distorted tetrahedral coordinated by three S atoms from three ettu ligands and one chlorine atom. The molecule has a C_s symmetry via silver, chlorine and one of ettu groups. The covalent complex (2) is isomorphous and isostructural with the complex (1). Crystals of (2) are monoclinic, space group $P2_1/m$ (No.11), $Z = 2$, $a = 7.295(2)$, $b = 15.502(3)$, $c = 8.281(2)$Å, $\beta = 91.49(3)^\circ$. The environment coordination sphere around the silver atom is similar to complex (1) and the molecule has a C_s symmetry as well. The geometries of both complexes involved the inter- and intra-molecular hydrogen bonding type N-H---X-M (X = halides, M = metal) forming 2D network crystal packing along *a* and *b* axes. The monomeric covalent complex (3) is in

a trigonal system, space group $P31c$ (No.159), $Z = 2$, $a = 12.5665(6)$, $c = 9.5805(9)$ Å, $\gamma = 120^{\circ}$. The silver atom is tetrahedrally bonded by three sulfur atoms from three detu molecules and one bromine atom. The silver and bromine atoms are situated at 3 - fold symmetry axis. The monomeric ionic complex (4) crystallizes in a hexagonal-cell, and space group $R\bar{3}$ (No.148), $Z = 3$, $a = 12.3745(6)$, $c = 27.603(3)$ Å, $\gamma = 120^{\circ}$, the structure comprises two dependent cations, $[Ag(detu)_3]^+$, each lies on a crystallographic three fold axis and the sulfate anion (SO_4^{2-}) also lies on a three fold axis and all oxygen atoms are disordered. It is found that there is a non-bonded interaction between the silver atom of these two cations. The polymeric ionic complex (5) crystallizes in a tetragonal system, space group $P4_2/n$ (No.86), $Z = 2$, $a = 18.3911(7)$, $c = 6.2785(5)$ Å. The structure contains polymeric cationic, $\{[Ag_2(detu)_4]^{2+}\}_\infty$, and polymeric anionic, $\{[Ag(SCN)_2]_2^{2-}\}_\infty$, infinite chains. The polymeric chains of these are made of the repeating dimeric units $\{[Ag_2(detu)_4]\}^{2+}$ of cationic chain and $\{[Ag((SCN)_2)_2]\}^{2-}$ of anionic chain. The coordination sphere around the silver atom of each chain is a slightly distorted tetrahedron. The silver atom is bonded to four bridging sulfur atoms from the detu molecules in the cationic part and from four thiocyanate groups in the anionic part. Each of sulfur bridging atoms from each chain is bonded to two silver central atoms to generate the one dimensional infinite chains along the c axis. Furthermore, the geometry of the molecule involves inter-molecular hydrogen bonding type, N-H---N, forming 3D network overall crystal packing.

Acknowledgments

I am extremely grateful to my supervisor, Asst.Prof.Dr. Chaveng Pakawatchai of the Department of Chemistry, Faculty of Science, Prince of Songkla University for many helpful suggestions 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, Asst.Prof.Dr. Pravit Sudkeaw of the Department of Chemistry, Faculty of Science, Prince of Songkla University for his generous hospitality and assistance as well as a critical reading and comments of this manuscript. I also would like to thank another co-supervisor, Dr. Uncharee Tooptakong of the Department of Chemistry, Silpakorn University for her comments and critical review of this manuscript.

Special thanks are extended to the examining committee : Assoc.Prof.Dr. Sumpun Wongnawa and Asst.Prof.Dr. Veerasak Thonglimp for their helpful suggestions and comments during the thesis examination.

I also wish to thank Dr. Narongsak Chaichit of the Department of Physics, Thammasat University for his training on the technique to collect X-ray data for two complexes. In addition, it is my great pleasure to thank Dr. Jonathan Charmant of the School of Chemistry, the University of Bristol, UK. for his kind assistance for his advice on the collection of data, the solution and the interpretation as well as the preparation of data for publication.

Appreciation is also extended to all my teaching staff of the Department of Chemistry and also to many other people who have not been mentioned here for their help and encouragement during my study.

Thank is also extended to the Postgraduate Education and Research Program in Chemistry (PERCH) and the 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 support and encouragement throughout my life.

Saowanit Saithong

The relevancy of the research work to Thailand

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

The main propose of this work is to determine the crystal structures of silver(I) complexes containing S-donor atom ligands. The substituted thiourea ligands, *N*-ethylthiourea(ettu) and *N,N'*-diethylthiourea(detu) ligands, are selected due to the interesting structure that might be formed coordinate bond with silver atom through both sulfur and nitrogen atoms or via one of these atoms. The silver(I) complexes of these ligands have been prepared and studied. The molecular structures, geometries and interactions of these complexes have different types depend on the size and the type of ligand, counterion and recrystallization solvent. The most important method for determination of structures of these complexes is X-ray crystallography. By X-ray crystallographic method it is possible to determine high-resolution three-dimensional structures.

A knowledge of the molecular structure is one of fundamental aim of chemistry and is essential for a better understanding of physical and chemical properties of the materials. This work provide information on structures, hydrogen bonding, and interactions in the solid state. Moreover, the results of this research might be useful as scientific foundation for its application and may possibly be used to design and synthesize crystals with useful properties such as catalysts, semiconductors, superconductors and other materials for using in new technology.

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Lists of abbreviations

° = degree
Å = Angstrom unit (1 Å = 10^{-10} metre)
A.R. = Analytical Reagent
cm^{-1} = wave number
D_c = calculated density
D_m = measured density
EDXRF = Energy Dispersive X-ray Fluorescence
g = gram
$\mathrm{g/cm}^3$ = 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 group IB or group 11 elements are copper(Cu), silver(Ag), and gold(Au). Each of these elements follows a transition metal, Ni, Pd, and Pt, respectively with a completed d shell. These are historically known as coinage metals or nobel metals. The electronic configuration of these elements is $(n-1)d^{10}ns^{1}$. They might be expected to behave as non-transition metals by forming ion M^{+} by the loss of a single electron in the outer most shell or to use the s and p orbitals of that shell to form collinear sp or tetrahedron sp^{3} bonds. In fact, both Cu and Ag form ions M^{+} and bonds of both these types, but Au^{+} is not known and Au(I) shows a marked preference for 2 - as opposed to 4-coordination. Moreover, in these valence states, these elements have some of the characteristic properties with respect to the $(n+1)s^{1}$ configuration of alkalis, for instance, the formation of non-colored diamagnetic ions. But they essentially have nothing in common with the alkalis except their stochiometries in the +1 oxidation state. The first ionization energy is much higher than those of the alkalis due to less effect of the filled d-shell in shielding the outermost s electron from the nuclear charge. Furthermore, the electrons in the outer d-shell are also entailed in metallic bonding because the melting points and heats of sublimation are also much higher than alkalis. At the same time, all these elements exhibit higher valences as a result either of losing more d-electrons, for example, Cu^{2+} and Ag^{2+} or of utilizing d orbitals of penultimate shell in combination with the s orbital of the valence shell. In these higher valence state these elements have some characteristic transition metals properties, namely, the formation of colored paramagnetic ions. This dual behavior greatly complicates the structural chemistry of this group. Little is known of the structural chemistry of these elements in certain oxidation states. In spite of the general similarity in the electronic structures of their atoms, Cu, Ag, and Au differ very considerably in their chemical behavior. There are no simple explanations for many of the differences. Firstly, the valences exhibited in their common compounds are : Cu, 1 and 2, Ag, 1, and Au, 1 and 3. Secondly, the more stable ions of copper is the hydrate Cu^{2+} ions in aqueous chemistry, whereas that of silver is Ag^{+} ion. In contrast to copper and silver, there is no ionic chemistry of gold in aqueous solution.

Apart from obviously similar stoichiometries of compounds in the same oxidation state (which do not always have the same structure), there are some similarities within the group – or at least between two of the three elements :

1. The metals are all crystallize with the same face-centered cubic (fcc) lattice.
2. For Cu_2O and Ag_2O in which the metal atoms are close to two oxygen neighbors and each oxygen is tetragonally surrounded by four metal atoms.
3. Although sequence of the stability constant for halogeno complexes of many metals are F > Cl > Br > I, Cu(I) and Ag(I) belong to the group of ions of the more noble metals, for which it is the reverse.
4. Cu(I) and Ag(I) and to a lesser extent Au(I) form very much the same types of ions and compounds, such as $[MCl_2]^-$, $[Et_2AsMI]_4$, and K_3MCl_3
5. Certain complexes of Cu(II) and Ag(II) are isomorphous, , and Ag(III), Au (III), and Cu(III) also give similar complexes.

(Cotton and Wilkinson, 1976 : 440-441).

Table 1 Some physical and chemical properties of the IB elements.

Properties	Cu	Ag	Au
Electronic configuration	[Ar]$3d^{10}4s^1$	[Kr]$4d^{10}5s^1$	[Xe]$4f^{14}5d^{10}6s^1$
Atomic number	29	47	79
Atomic weight	63.546	107.868	196.967
IE_1 (kJ/mol)	745	731	889
IE_2 (kJ/mol)	1958	2072	1890
Ionic radii (Å)	0.96	1.26	1.37
Metallic radii (Å)	1.28	1.43	1.44
ρ (gcm^{-3})(at 293 K)	8.93	10.5	19.3
mp. (°C)	1084	961	1065
bp. (°C)	2595	2212	2727
aqueous chemistry	Cu(II)	Ag(I)	Au(I)

(Heslop and Jones, 1976)

The types of these complexes formed by M(I) halides or pseudohalides with a groupV or VI Lewis base may depend on the size and type of ligand, counterion, reaction conditions and solvent/crystallization solvent.

Increase in the 'size'of the ligand may give rise to complexes with the same stoichiometry but with a different stereochemistry. For example, $Cu(BF_4)_2$ with *N,N'N''N,'''*-tetramethylthiourea (tmtu) forms a trigonal planar complex (Weininger, *et al.*,1972), while with *N.N'*-dimethylthiourea(dmtu) forms a tetrahedral complex (Tayler, *et.al* 1974), both having a 1:2 stoichiometry.

The change in size of the counterion may also give rise to complexes with different structures. For instance, the 2 :1 adducts of 1,1,4,4,-tetraphenyl-1,3-butadiene (tphb) with $AgClO_4$ form a one-dimension polymeric structure of $[Ag(tphb)(ClO_4)_2]$ while with $AgCF_3SO_3$ form a two-dimensional polymeric structure of $[Ag(tphb)(CF_3SO_3)_2]$ (Ino, *et al.,* 2000). However, the change in the size of the counterion may also give an adduct with similar structures. For example, the 1 : 3 adduct of *N*-diphenylthiourea(dptu) with CuCl, CuBr, and CuI form a monomeric structure and also the same stereochemistry for all of these complexes.(Lamai, 1999)

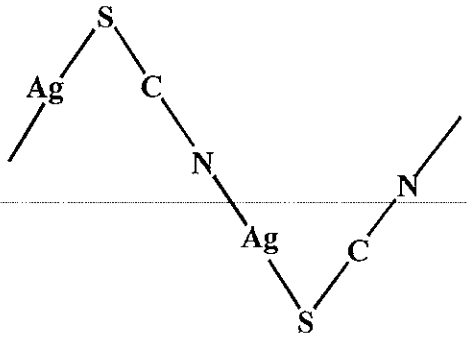
The change in solvent type used for crystallization may give different types of adducts. For instance, crystallization of the 1 : 1 stoichiometries of CuI with triphenylphosphine(PPh_3) from toluene gives a cubane tetramer (Dyason and Healy, 1985), while crystallization from benzene gives a 'step' structure (Churchill, *et al.,* 1975). However, changing the solvent type may also provide a similar structure. For example, crystallization of the 1 : 3 adduct of CuCl with PPh_3 from either a chloroform/ethanol mixture or chloroform gives a monomeric form of $[Cu(PPh_3)Cl]$ complex.(Barron, *et al.,* 1987)

1.1.1 Compounds of Silver(I)

The common oxidation state of silver is +1. The salts $AgNO_3$, $AgClO_3$ and $AgClO_4$ are water soluble but Ag_2SO_4 and $AgOOCCH_3$ are sparingly soluble. The salts of oxo anions are primarily ionic although the water-insoluble halides AgCl and AgBr have the NaCl structure, there appears to be appreciable covalent character in the Ag---X interaction, whereas in compounds such as AgCN (I) and AgSCN (II) with chain structures , the bonds are considered to be predominantly covalent (Cotton and Wilkinson, 1988 : 937-945).

$—Ag—C—N—Ag—C—N—$

(I)



(II)

Table 2 The stereochemistry of silver(I), d^{10}

Coordination number	Geometry	Examples
2^a	Linear	$[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$, AgSCN
3	Trigonal	$(Me_2NC_6H_4PEt_2)_2AgI$
4^a	Tetrahedral	$[Ag(SCN)_4]^{3-}$, $[AgIPR_3]_4$, $[Ag(py)_4]ClO_4$, $[Ag(PPh_3)_4ClO_4$
5	Distorted pentagonal plane	$[Ag(L)]^{2+\,b}$
5	Pentagonal pyramidal	$[Ag(L)]_2^{2+\,b}$
6	Octahedral	AgF, AgCl, AgBr (NaCl structure)

Remark : [a] Most common states .

[b] L is an N_5 Macrocycle. (Cotton and Wilkinson, 1988 : 939-941)

1.1.2 Complexes of Ag(I)

These complexes may be described as being of the type $(AgX)L_n$, X : halides, NO_3^-, $1/2SO_4^{2-}$, ClO_3^-, ClO_4^- and SCN^-, L : sulfur donor ligands. In present work L are substituted thioureas and the value of n varies in the range of 1 to 4.

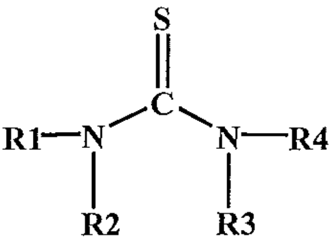
In the past the chemistry of these complexes has been considered to be dominated by linear, two coordinated species. In fact the structural form of some of these $(AgX)L_n$ complexes may be ionic or neutral and may have been observed as monomeric, dimeric or polymeric units with a prevalence of tetrahedral coordination sphere around the metal. The stereochemistry of Ag(I) with soft donor ligands such as thiourea and substituted thioureas is interesting. Complexes may present the different sterochemistry with the same stoichiometries.

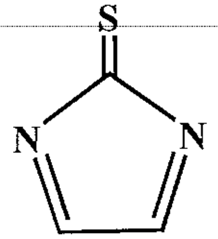
1.2 Thiourea and substituted thioureas

Thiourea and substituted thiourea ligands can form the coordinate covalent bond with silver either via both the sulfur and nitrogen or via one of these atoms. Hard and soft acid and base (HSAB) - hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases - can be applied here (Parr and Pearson, 1983). The silver(I) ion is regarded as an soft acid favoring coordinate to soft bases, such as ligands containing S and unsaturated N. However, S is rather softer than N. Accordingly, silver(I) complexes of these ligands were mostly bound with sulfur but the formation of the nitrogen-silver bond is somewhat difficult. The suspected coordination site of both these possibilities will be illustrated by the vibrational absorption spectra of the complexes. Coordination bond through sulfur will decrease the double bond character of the carbon-to-sulfur bond towards the value of a single bond whereas the bond order of the carbon-to-nitrogen bond is close to the value of a double bond. Therefore, in silver(I) complexes, the C-S stretching frequencies should shift to the lower frequencies while the C-N stretching should change to the higher frequencies. If, however, the coordination bond is through the nitrogen atom, it will attribute to the opposite result. Moreover, The N-H stretching should decrease if the metal is coordinated through the nitrogen and remain substantially unaffected if the bonding is through the sulfur (Suwaluk, 1999, quoted in

Swaminathan, *et al.*, 1964 :1291). Not only the effect from the coordinated site but also the effect from hydrogen bonding as well as the weak-interaction in the molecule leads to the decrease of the N-H stretching. Thus, the accurate molecular structures of Ag(I) complexes have been determined by single crystal X-ray diffraction method.

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'*-diethylthiurea(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

Structures	Names	Remarks
	*N*-ethylenethiourea(etu)	-

1.2 Literature reviews

In the early nineteenth century, most of the metal thiourea and substituted thiourea complexes had been studied only by synthesis and by infrared spectroscopy. The vibrational energies were used to predict the coordinated atoms around the metal and the properties of these complexes are as follows :

Yamaguchi , *et al.* assigned the infrared absorption bands of metal thiourea complexes based on the normal vibration calculation of the thiourea molecule in the region 200 – 3500 cm^{-1} (Yamaguchi, *et al.,* 1958).

Lane, *et al.* studied the infrared absorption spectra of methylthiourea and some metal complexes in the region 200 – 3500 cm^{-1}(Lane, *et al.,* 1959).

By the middle of the nineteenth century, crystallography had become a furnished science used for determination of structures because computer tools have been used systematically to process the data from diffraction experiments. Accordingly, the new experiment diffraction technique resulted in the rapid developments. Since 1960, X–ray crystallography has been mostly utilized as the tool for characterizing the structures of compounds, including silver(I) thiourea and substituted thiourea complexes. Some results are as follows :

Vizzini, *et al.* studied the crystal structure of bis(thiourea) silver(I) chloride, [Ag(tu)$_2$Cl]. The structure is composed of almost trigonal planar AgS$_3$ units bonded together by sulfur bridges to form a spiraling linear polymer in *c*-direction as depicted in figure 1. Each silver atom has four coordination, the fourth coordination position is a long axial Ag-Cl distances of 2.854(5) and 3.035(5)Å, respectively, (Vizzini, *et al.*, 1968).

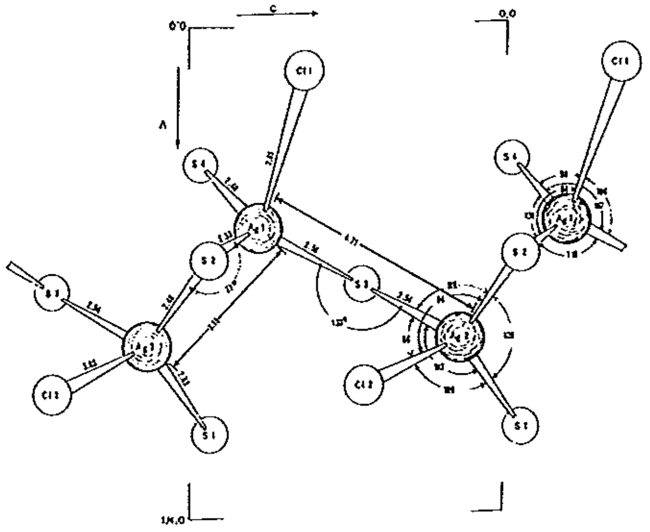
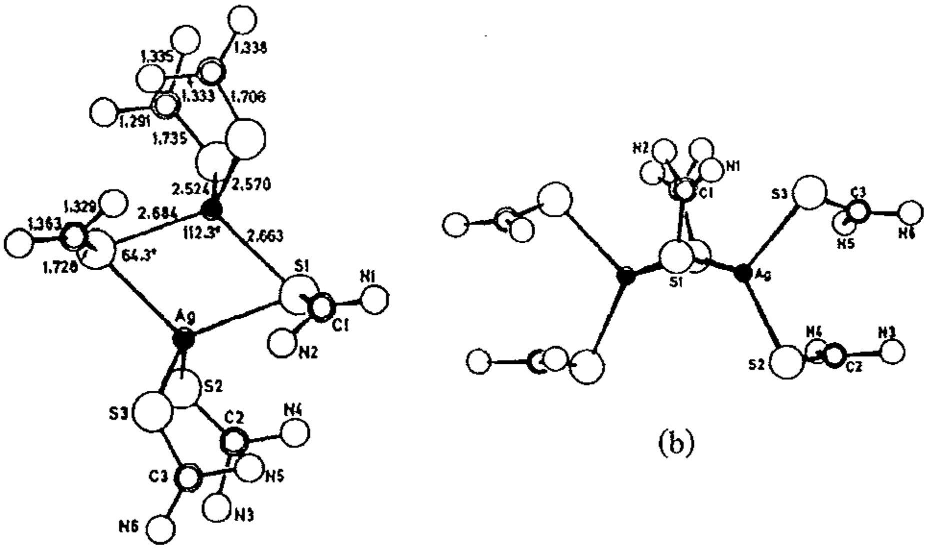


Figure 1 The partial diagram of –Ag-S-Ag- spiraling polymeric chain of bis(thiourea) silver(I) chloride, [Ag(tu)$_2$Cl] plotted down b axis.

Crystal data, monoclinic system, space group $P2_1/a$; $a = 36.70(4)$, $b = 8.24(1)$, $c = 5.87(1)$ Å.; $\beta = 92.50(15)^{\circ}$, $V = 1797.1$, $Z = 8$, $D_m = 2.18$ g/cm^3, $D_c = 2.22$ g/cm^3, $R = 0.062$.

Udupa, *et al.* determined the structure of tris(thiourea) silver(I) perchlorate, [Ag(SC(NH$_2$))$_3$]-ClO$_4$, The determined structure is a binuclear complex of [Ag(SC(NH$_2$))$_3$]$^+$ cations with perchlorate anions. The sulfur atoms of the four thiourea molecules form a distorted coordination tetrahedron around each silver atom (S-Ag-S angles range from 100.5(10) to 115.9(1)^{o}). Two of the six sulfur atoms of the binuclear complex cation act as bridging ligands in a four-membered Ag-S-Ag-S ring, considered as two sets of three-center electron deficient bonds, each Ag contributing a $\sigma(sp^3)$ orbital and each S a nonbonding sp^2 orbital with its electron pair : $\psi_{ED} = \sigma(Ag) + \sigma(Ag') + sp^2(S)$ (ED = electron deficient). This is equivalent to a four-center, four-electron, electron deficient model. The configurations of binuclear complex cation are shown in figure 2 (Udupa, *et al.*, 1972).



(a)

(b)

Figure 2 Configuration of binuclear complex cation $[Ag(SC(NH_2)_2)]_6^{2+}$ (a). Two halves of the complex are related by two-fold axis (b). (H atoms are omitted).

Crystal data, monoclinic system, space group *C2/c*, a = 19.537(8), b = 13.436(6), c = 10.791(5) Å.; β = 103.57(15)^{o} ; Z = 8, D_m = 2.096 g/cm^3, D_c = 2.102 g/cm^3, R = 0.048.

Udupa, *et al.* investigated the crystal structure of thiocyanatobis(thiourea) silver(I). The structure is composed of a complex {[$Ag(SC(NH_2))_3$]SCN} unit , which is associated through weak Ag-S bonds to form centrosymmetric dimers. The silver atom is coordinated by two thiourea sulfur atoms (Ag- S1 (2.482 Å) and Ag-S2 (2.462 Å)) and one S atom from the thiocyanate ligand (Ag-S3 (2.608 Å)) arranged to almost trigonal planar of AgS_3 with Ag atom is displaced by 0.29 Å from S1-S2-S3 plane. Furthermore, the fourth S atom is only weakly bonded, Ag-S1$'$ (3.111 Å) and completed a highly distorted tetrahedral coordination polyhedron around silver atom. The fourth S atom also acts as a bridge to the second half of centrosymmetric dimer [$Ag(tu)_2SCN$]$_2$ form the four-membered ring of Ag_2S_2 (figure 3).

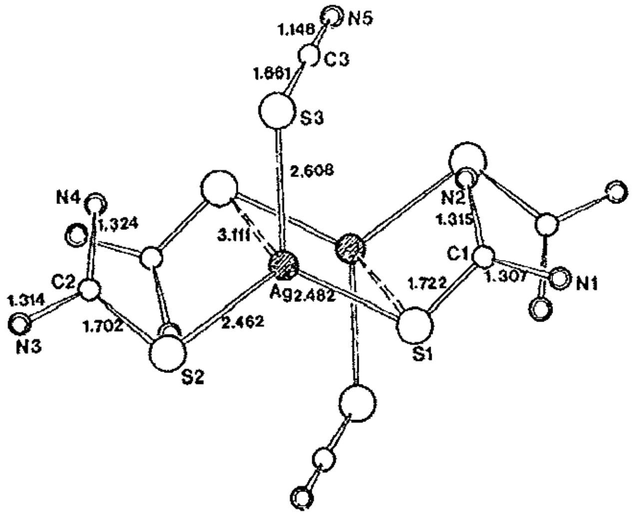


Figure 3 Structure of dimeric complex [$Ag(tu)_2SCN$]$_2$. Two halves of the complex are related by inversion center (H atoms are omitted).

The Ag-S1 bond is approximately in the thiourea molecular plane that can be regarded to non-bonding electron from sp^2 orbital of thiourea sulfur atom. The Ag'-S1 bond, being roughly perpendicular to the thiourea plane must be assumed to be a two center bond, utilizing the electron pair from the sulfur $p\pi$ orbital. The Ag-S2 bond can be interpreted as a normal two center bond, using electrons from non-bonding sulfur sp^2 orbital (Udupa, *et al.,* 1976).

Crystal data, monoclinic system, space group *C2/c*, a = 11.072(3), b = 13.838(4), c = 13.983(4) Å.; β = 111.65(3)$^{\circ}$; Z = 8, D_m = 2.110 g/cm^3, D_c = 2.123 g/cm^3, R = 0.044, R_w = 0.046.

Blake, *et al.* synthesized the cationic complex of [Ag([18]aneS$_6$)]$^+$. The silver atom is coordinated by S atoms from the [18]aneS$_6$ ligand. The complex cation has C_{2h}/*(2/m)* symmetry with Ag^{I} bound to all six thia donors of the [18]aneS$_6$ with two short axial bonds and four significantly longer equaterial bond distances. This 2+4 coordination of these ligand reflects the tendency of d^{10} Ag$^+$ ion to increase its coordination number with soft donor ligands. Two views of the distorted octahedral stoichiometry of the complex cation are shown in figure 4 (Blake, *et al.,* 1989).

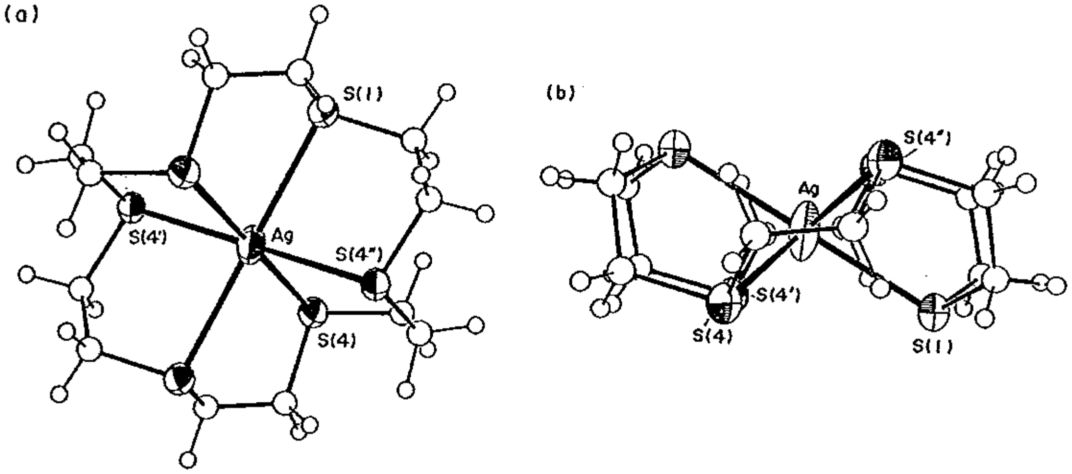


Figure 4 Two views of the structure of [Ag([18]aneS$_6$)]$^+$ with atom numbering scheme adopted.

Crystal data, monoclinic system, space group *I2/m*, a = 5.295(4), b = 13.959(10), c = 13.951(9) Å ; β = 95.15(10)$^{\circ}$; Z = 2, D_c = 1.983 g/cm^3, R = 0.0411, R_w = 0.0564.

Benda, *et al.* synthesized and studied the one-dimension chain of cationic complex of silver pentasulfide, $_{\infty}[\mathrm{Ag}(\mathrm{S}_5)^{-}](\mathrm{MeN}^{+})$. Each silver atom is tetrahedrally coodinated to S atoms from three different $(\mathrm{S}_5)^{2-}$ions and each $(\mathrm{S}_5)^{2-}$ ion makes four bonds to three different silver ions, as shown in figure 5.

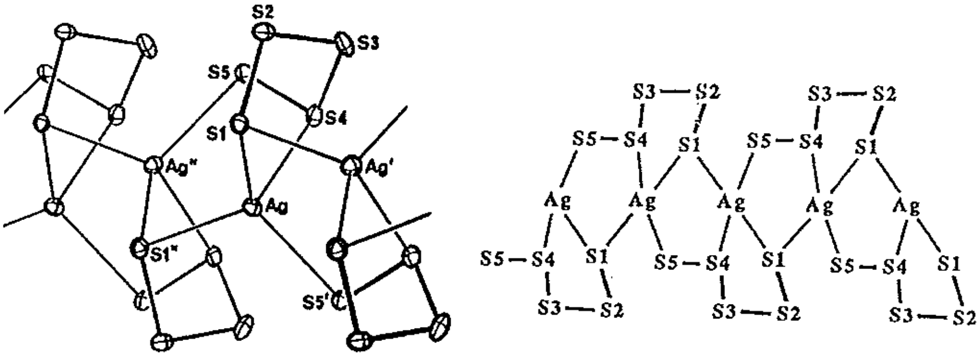


Figure 5 The $_{\infty}[\mathrm{Ag}(\mathrm{S}_5)^{-}]$ chain of $_{\infty}[\mathrm{Ag}(\mathrm{S}_5)^{-}](\mathrm{MeN}^{+})$ and the diagramatic presentation of $_{\infty}[\mathrm{Ag}(\mathrm{S}_5)^{-}]$ showing the connectivities.

One terminal side of the $(\mathrm{S}_5)^{2-}$ chain, S1, bridges two silver atoms (Ag and Ag$'$) while the other terminal side, S5, is bonded to a third silver atom(Ag$''$) and the third type of Ag-S bond is Ag-S4, involving a β-sulfur atom of $(\mathrm{S}_5)^{2-}$ chain (Benda, *et al.*, 1989).

Crystal data, monoclinic system, space group *Cc*, $a = 10.86(1)$, $b = 18.313(7)$, $c = 9.177(9)$ Å.; $\beta = 139.77(3)^{\circ}$; $Z = 4, D_c = 1.93$ g/cm^3 , $R = 0.044, R_w = 0.052$.

Casals, *et al.* synthesized and characterized the one-dimension structure of $\{[\mathrm{Ag}_{13}(\mu\text{-}\mathrm{SC}_5\mathrm{H}_9\mathrm{NHMe})_{16}]^{13+}\}_n$which contains $\mathrm{Ag}_{10}(\mu\text{-SR})_{16}$ repeating units. The conformation of this repeating unit consists of two tetrahedral and four trigonal planar silver atoms, coordinated by four and three sulfur atoms, respectively. The tetrahedral silver atoms are coordinated by two doubly- and two triply-bridging sulfur atoms whereas the trigonal planar silver atoms are coordinated by one doubly- and two triply-bridging sulfur atoms. The polymeric structure is illustrated in figure 6 (Casals, *et al.*, 1990).

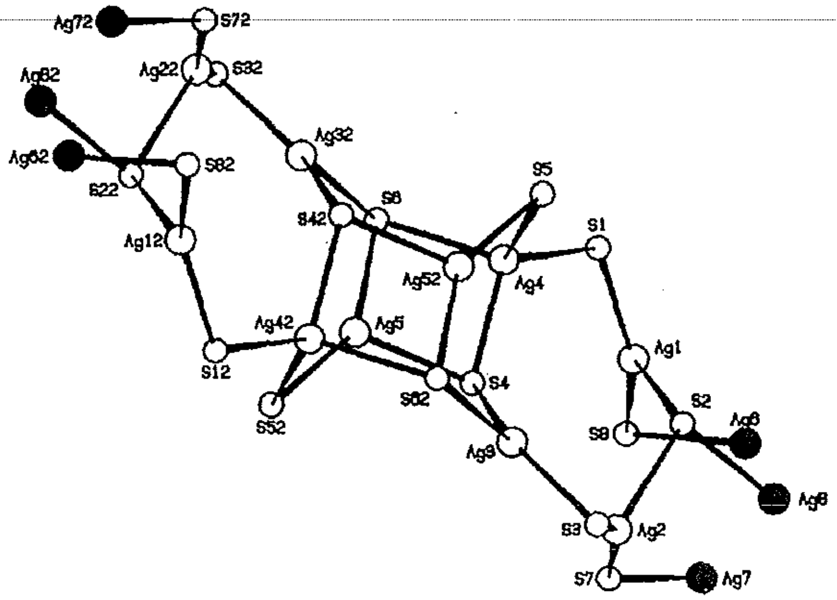


Figure 6 Skeleton of $Ag_{10}(\mu\text{-}SR)_{16}$ unit (Unshaded atoms)

Crystal data, triclinic system, space group $P\bar{1}$, a = 21.129(4), b = 20.383(4), c = 15.172(3) Å.; α = 121.59(3), β = 114.53(4), γ = 96.12(3)° ; Z = 1, R = 0.093, R_w = 0.096.

Casas, *et al.* prepared and investigated the ionic complex, $[Ag(Himnt)_3]NO_3$ (Himnt = 1-methyl-2(2H)-imidazolinethione). The silver ion is trigonally coordinated to three sulfur atoms from three Himnt molecules and the overall Ag-S bonds are chemically equivalent. The trigonal structure is demonstrated in figure 7 (Casas, *et al.*, 1996).

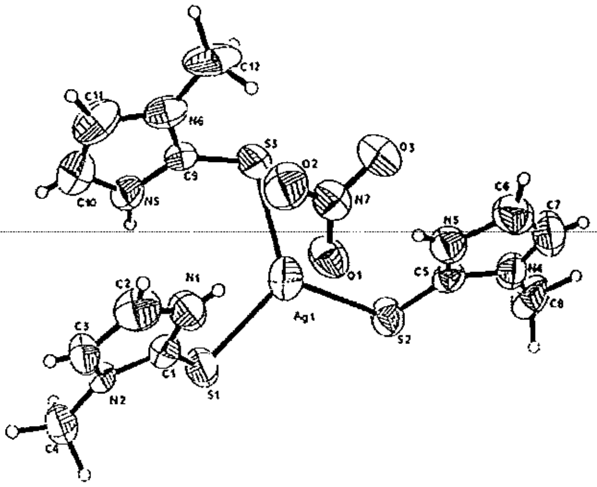


Figure 7 Thermal ellipsoid plot of $[Ag(Himnt)_3]^+$

Crystal data, monoclinic system , space group $P2_1/n$, a = 7.621(2), b = 27.281(5), c = 10.256(4) Å ; β = 107.89(1)° ; Z = 4, D_c = 1.68 g/cm^3 , R = 0.033.

Fun, *et al.* characterized the crystal structure of tris (*N,N'*-diethylthiourea-*S*)-iodosilver(I), $[Ag(detu)_3I]$ (detu = *N,N'*-diethylthiourea). The silver atom is tetragonally coordinated to three sulfur atoms from three detu molecules and to one iodine atom. The structure lies on the three-fold axis which relates the three molecules of ligand. The structure is shown in figure 8 (Fun, *et al.,* 1998).

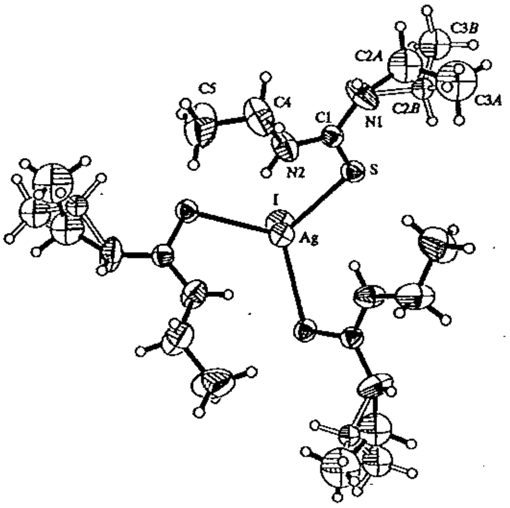
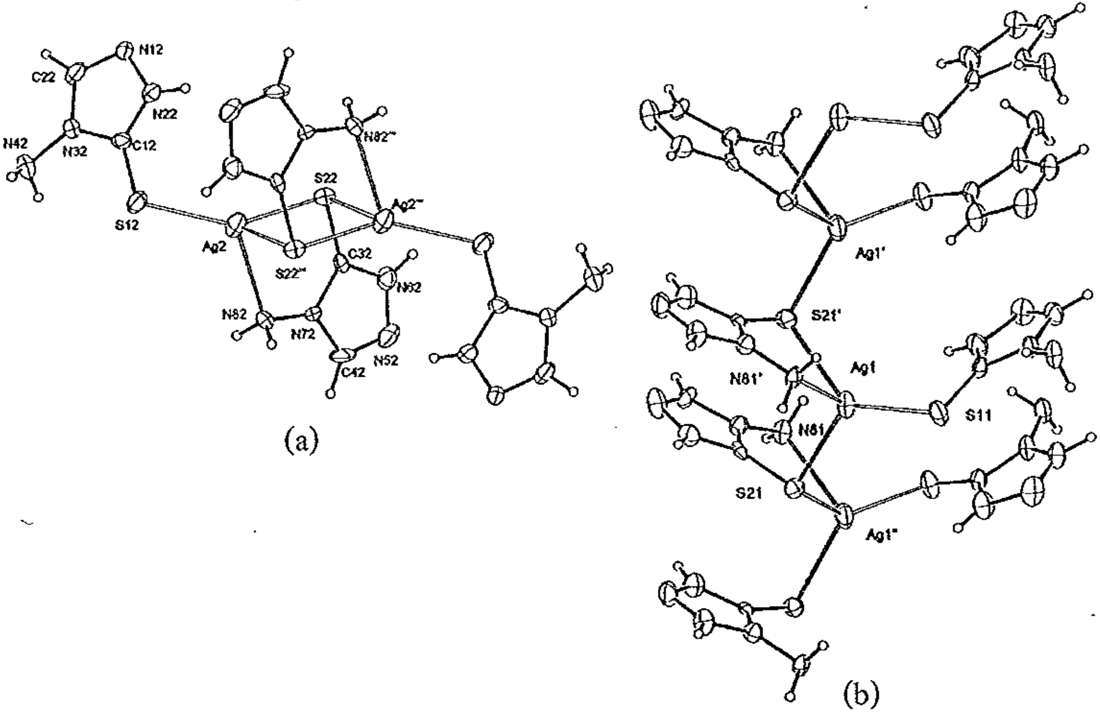


Figure 8 Thermal ellipsoid plot of $[Ag(detu)_3I]$ is drawn at 30% probability.

Crystal data, trigonal system, space group $P31c$, a = 12.792(1), c = 10.256(4)Å, Z = 4, D_c = 1.585 g/cm^3 , R = 0.027, R_w = 0.070.

Biagini, *et al.* prepared and determined the structure of [Ag(HL1)]NO_3 (HL1 = 4-amino-1,2,4,Δ^2-triazoline-5-thione). Unusual dimeric and polymeric species are present in this compound due to the versatile coordination ability of ligand. In centrosymmetric dimeric and polymeric chains a HL1 ligand acts as a monodentate S-coordinated agent and a second HL1 acts as chelating agent through the N, S system and the sulfur atoms bridge to another silver atom. For the dimeric part, the environment around each Ag is described as a distorted tetrahedron with slightly diagonal character in which Ag is coordinated to three S atoms and one N atom. For polymeric chain, molecules of HL1 bridge via the S atom to adjacent Ag atoms so that the chain is generated parallel to the *c* crystallographic axis. Accordingly, the coordination around the Ag atom is tetrahedral with trigonal pyramidal distortion. The structure is shown in figure 9 (Biagini, *et al.,* 2000).



(a)

(b)

Figure 9 Perspective view of the dimeric (a) and polymeric (b) forms of compound [Ag$(HL1)_2$]NO_3. The thermal ellipsoid is drawn at 30% probability level in both (a) and (b).

Crystal data, monoclinic system,space group $P2_1/n$, $a = 12.716(6)$,$b = 25.803(9)$, $c= 7.606(4)$ Å ; $\beta= 90.48(1)^{\circ}$, $Z = 8$, $D_c = 2.141$ g/cm^3 , $R = 0.1809$, $R_w = 0.1023$.

Cox, *et al.* synthesized and characterized mixed-ligand complex of the formula [Ag(PPh)$_3$(pymtH)Br]$_2$ (pymtH = pyridine-2-thione). The structure unit is a dimer, where the two monomers are related by inversion. The double bridging Br atoms generate a strictly planar Ag$_2$Br$_2$ core in which each of doubly bromine-bridge Ag(I) centers is further bonded to one P atom of phosphine and one S atom of thione and displays a distorted tetrahedral environment. The hydrogen atom of the two trans-positioned pymtH participates in two short intra-molecular hydrogen bonds (N---Br = 3.301, H---Br = 2.453 Å and N-H-Br = 168.79(3)°). The structure is shown in figure 10 (Cox,*et. al.* 2000).

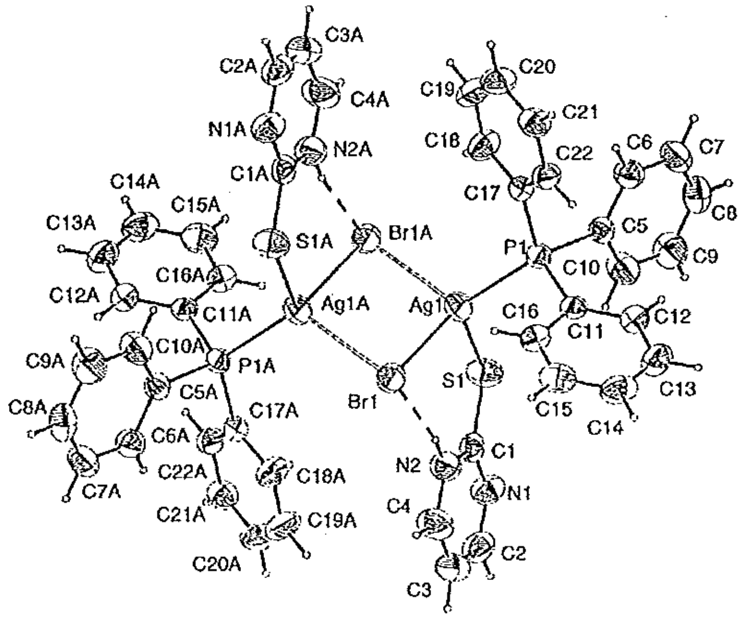
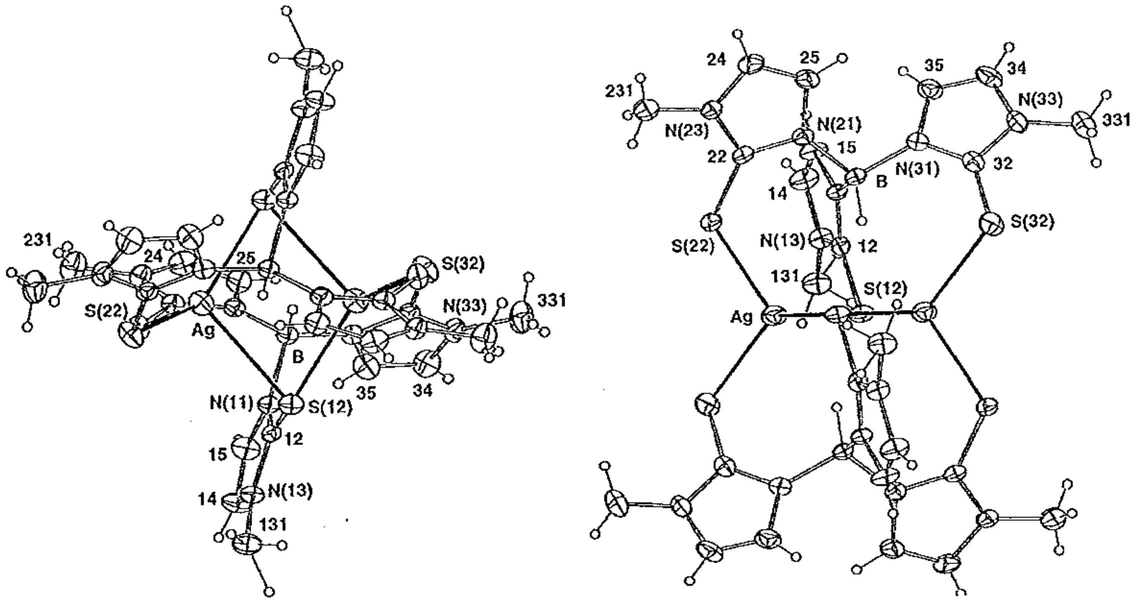


Figure 10 The structure of [Ag(PPh$_3$)(pymtH)Br]$_2$. Displacement ellipsoid is shown at 50% probability level. Dashed lines denote N-H---Br hydrogen bond.

Crystal data, monoclinic system, space group *C2/c*, $a = 27.284(3)$, $b = 9.219(9)$, $c = 18.456(2)$ Å.; $\beta = 108.44(2)^{\circ}$; $Z = 4$, $D_c = 1.695$ g/cm^3, $R = 0.027$, $R_w = 0.063$.

Effendy, *et al.* synthesized and characterized the structure of $[Ag(Tm)]_2$· $2CHCl_3$,(Tm = hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate). The results show the complex to be binuclear accompanied by a pair of chloroform molecules. One half of the dimer,(together with one chloroform molecule) comprises the asymmetric unit of the structure, the dimer being disposed about a crystallographic center of symmetry

The dimeric structure is depicted in two projections as shown in figure 11. The core the dimeric four- membered $[Ag(\mu\text{-}S)_2Ag]$ ring , the sulfur atom of the ring bridging the two silver atoms unsymmetrically (Effendy, *et al.,* 2000).



(a) (b)

Figure 11 Two projections showing the dimer of $[Ag(Tm)]_2 2CHCl_3$ (20% thermal ellipsoid)

Crystal data, triclinic system, space group $P\bar{1}$, a = 11.067(5), b = 10.338(5), c = 9.729(5) Å.; α = 86.53(3), β = 86.53(4), γ = 85.66(4)°; Z = 1 ; D_c = 1.737 g/cm^3, R= 0.051, R_w = 0.054.

Zhong, *et al.* synthesized and studied the coordination compound of silver(I) with 2,5-bis(4′.5′-bis(methylthio)-1′,3′-dithiol-2′-ylidene-1,3,4,6-tetrathiapantalene (TTM-TTP). The product is a polymeric structure of silver(I) coordination, $[\mathrm{Ag(TTM\text{-}TTP)]CF_3SO_4}\}_\infty$. The complex consists of one-dimensional chains in which the silver(I) ion is a distorted square pyramidal coordination. Each silver atom interacts with four sulfur atoms, on the basal plane of the square pyramid, from two TTM-TTP molecules and the fifth coordination site is occupied by one oxygen atom of $\mathrm{CF_3SO_3^-}$ group. One of the TTM-TTP molecules asymmetrically bridges two silver(I) atoms to give a one dimensional waving chain, and the coordinated $\mathrm{CF_3SO_3^-}$ groups sit on the same side of the chain as shown in figure 12 (Zhong, *et al.*, 2001).

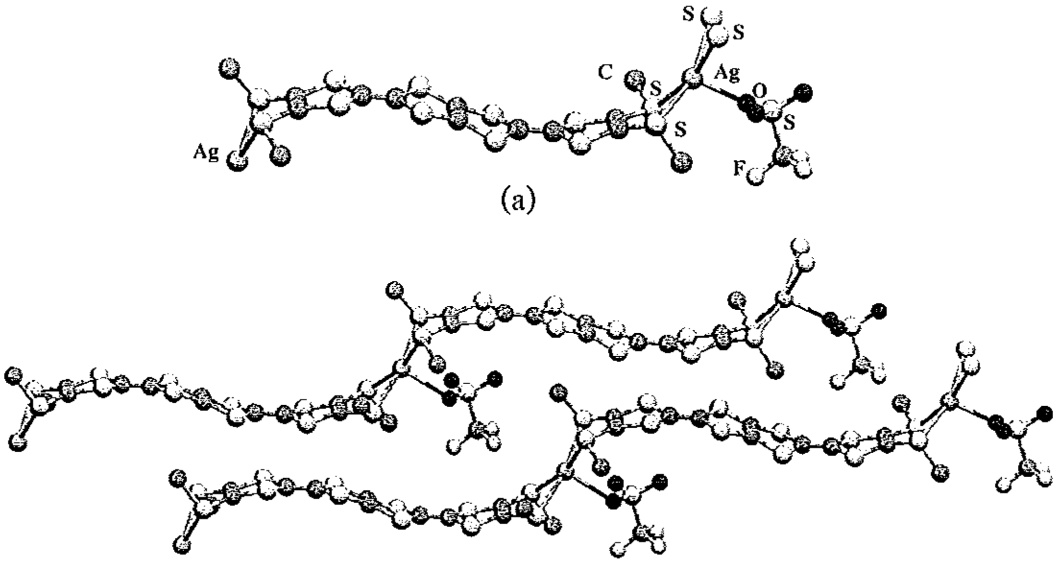


Figure 12 The partial structure of $\{[\mathrm{Ag(TTM\text{-}TTP)]CF_3SO_4}\}_\infty$ (a) and one dimensional waving chain (b)

Crystal data, monoclinic system, space group $P2_1/c$, a = 24.186(1), b = 12.189(1), c = 8.963(1) Å; β = 92.344(2)°; Z = 4, R = 0.021, R_w = 0.049.

1.3 Objectives

1) To prepare single crystals of silver(I) complexes with *N*-ethylthiourea (ettu) and *N,N'*-diethylthiourea(detu) as ligands under appropriate condition, namely, $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$, $[Ag(detu)_3Br]$, $\{[Ag(detu)_3]_2SO_4\}$ and $\{[Ag_2(detu)_4]\text{-}[Ag(SCN)_2]_2\}_\infty$ by varying the mole ratio of reactants, solvent, the reaction temperatures and so on.

2) To characterize the crystal structures of the complexes by using single crystal X-ray diffraction method.

3) To assign the geometry of the complexes in which the sulfur atom act as the donor atom by determining the structures of the complexes, crystal systems, cell parameters, space groups, arrangement of molecules in the unit cell, and also to refine the accurate position of atoms by analyzing the electron density with SHELXTL NT Version 6.12. (Sheldrick, 1998)

4) To study the effect of interactions on the geometry of the molecules and crystal packing.

5) To compare the structures of the complexes synthesized with other silver(I) complexes with the same ligand or the same silver salt.

Chapter 2

METHOD OF STUDY

2.1 Chemicals

Substances (Silver Salts and Ligands)

1) Silver(I) Chloride, AgCl, L.R. grade (Fluka Chemical, Buchs, Switzerland)
2) Silver(I) Bromide, AgBr, L.R. grade (Merch, Darmstadt, Germany)
3) Silver(I) Iodide, AgI, L.R. grade (Fluka Chemical, Buchs, Switzerland)
4) Silver(I) Sulfate, Ag_2SO_4, L.R. grade (BHD Chemical Ltd., England)
5) *N*-Ethylthiourea, $C_3H_7N_2S$, Purm (Fluka Chemical, Buchs, Switzerland)
6) *N,N'*-Diethylthiourea, $C_5H_{12}N_2S$, Purm (Fluka Chemical, Buchs, Switzerland)

Solvents

1) Ethanol, C_2H_5OH, AR Grade (Lab-Scan Analytical Science)
2) Acetronitrile, CH_3CN, AR Grade (Lab-Scan Analytical Science)
3) Distilled Water

2.2 Materials and Instruments

1) UHU Epoxy Adhesive
2) Bee Wax
3) Fiber Glass, 0.1-0.4 mm (diameter)
4) Capillary Tube
5) Computer PC

6) Capillary Melting Point Apparatus, Thomas Hoover, Unimelt 0-360 °C
7) Perkin-Elmer GX FT-IR spectrometer
8) CE Flash 1112 Series EA CHNS-O Analyzer
9) Philips PW 2400 X-ray Fluorescence Spectrometer
10) SMART APEX CCD X-ray Diffractometer

2.3 Preparation of silver(I) complexes

The silver(I) complexes have been synthesized in various approaches from the reaction between silver(I) salts and *N*-ethylthiourea or *N,N'*-diethylthiourea in suitable condition by varying the starting materials, mole ratio of reactants, solvent, reaction temperature, and time of reaction. Nevertheless, there are only 5 single crystals complexes that were appropriated to characterize by X-ray diffraction technique. The preparation of complexes are shown in the following details :

2.3.1 The preparation of [Ag(ettu)$_3$Cl]

N-ethylthiourea or ettu (0.55g, 5.28 mmol) was dissolved in 50 ml acetronitrile at 70 °C and silver(I) chloride (0.25g, 1.74 mmol) was added to this solution. The mixture was heated to the boiling point of acetronitrile about 82-83 °C with continuous stirring for 1 hour. After that, the distilled water (20 ml) was added into the reaction mixture and it was further stirred for 5 hours. After which time, it was filtered and the clear colorless filtrate was kept at ambient temperature, white single crystals of the complex [Ag(ettu)$_3$Cl] were isolated after standing for 3 days. Furthermore, the crystals were separated by suction filtration and thoroughly dried in a silica gel vacuum desiccator.

2.3.2 The preparation of $[Ag(ettu)_3Br]$

N-ethylthiourea (0.25g, 4.13 mmol) was dissolved in 70 ml acetronitrile at 70 °C and silver(I) bromide (0.25g, 1.33 mmol) was added to this solution. The mixture was refluxed on a paraffin oil bath with constant stirring for 7 hours. The solution was filtered and the filtrate was kept to stand at room temperature for 3 days. Upon standing, the clear colorless needle crystals were isolated and dried as 2.3.1.

2.3.3 The preparation of $[Ag(detu)_3Br]$

N,N'-diethylthiourea (0.99g, 7.49 mmol) was dissolved in 70 ml *n*-hexane at ambient temperature. Then, silver(I) bromide (0.32 g, 1.70 mmol) was added to this solution. The mixture was heated to the boiling point of *n*-hexane and refluxed on a paraffin oil bath with constant stirring for 7 hours. After refluxing, it was filtered and the filtrate was allowed to cool slowly to room temperature. Moreover, the suitable colorless needle crystals for X-ray determination were obtained and dried according to 2.3.1.

2.3.4 The preparation of $\{[Ag(detu)_3]_2(SO_4)\}$

Silver(I) sulfate (0.25 g, 0.79 mmol) was added to *N,N'*-diethylthiourea (0.33 g, 2.46 mmol) in 50 ml ethanol at 75 °C with continuous stirring. After that, the gray suspension appeared and slowly changed to black precipitates. The mixture was refluxed for 6 hours and then filtered off. The clear colorless solution was allowed to cool to ambient temperature. Colorless hexagonal crystals were isolated by the slow evaporation of solvent and then they were filtered off and dried as 2.3.1 after standing for a week.

2.3.5 The preparation of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$

Silver(I) thiocyanate (0.23g, 1.39 mmol) was added to *N,N'*-diethylthiourea (0.60g, 4.34 mmol) in a mixture of 30 ml acetronitrile and 30 ml distilled water. A clear colorless solution was obtained by continuous stirring for 5 hours at 50-55 °C. Then, the solution was filtered off and allowed to cool slowly to room temperature before keeping in desiccator containing diethyl ether (Su, *et al.*, 2002). Colorless single crystals suitable for X-ray determination were obtained by slow diffusion of diethyl ether vapor into the clear filtrated solution. The single crystals were kept according to the following 2.3.1.

2.4 Elemental analysis (CHNS)

The composition of C, N, H, and S atoms in complexes were investigated on the CE Flash 1112 Series EA CHNS-O analyzer.

2.5 X-ray fluorescence spectrometry

Ag, S and halides (Cl, Br, and I) qualitative analyses were performed by WDXRF technique using Philips PW 2400 X-ray fluorescence spectrometer.

2.6 Infrared spectroscopy

The vibration spectra were obtained on KBr discs on a Perkin-Elmer GX FT-IR spectroscopy in the range 4000-400 cm^{-1}.

2.7 Single crystal X-ray diffraction

X-ray diffractometry

Fundamental X-ray diffraction experiment consists of the following steps :

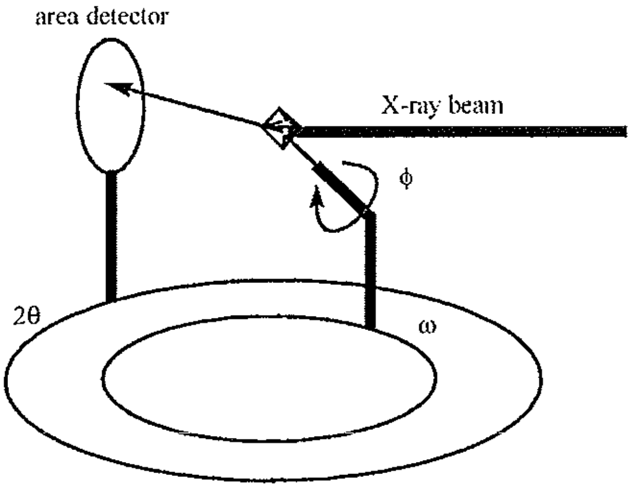
a) Selecting a suitable crystal and mounting it for X-ray study.

b) Collecting some X-ray scattering data to obtain unit cell geometry and preliminary symmetry information before collecting more X-ray scattering data.

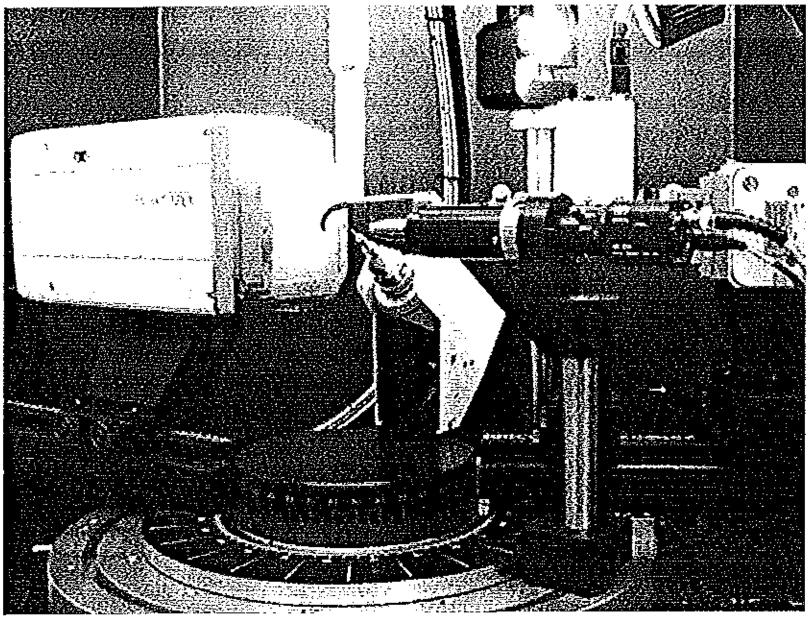
c) Solving and refining the structure.

d) Interpreting the results.

Diffractometer, available in various designs, is the machine used to collect X-ray data. Traditionally, four-circle diffractometers have four axes about which the crystal may be rotated (ϕ -, ω - and χ -circle) plus the circle about with the detector can be rotated (2 θ-circle). With one of these four-circle diffractometers reflections (positions and the intensities) are measured one at a time, the crystal and detector being move under computer control. Recently, X-ray diffractometers have become which record over a considerably larger area and are position-sensitive. Many of diffracted beams can be recorded at the same time. Modern single crystal diffractometers are now exclusively fitted with area detectors. They operate very much like a digital photographic camera but record X-ray information instead of visible light. These detectors are also very sensitive and are thus suited to small crystals in which only weak X-ray scattering can be recorded. An area detector can replace the traditional scintillation of four-circle diffractometer. The size of the area detector is large and the rotation axes are also possible to fix the χ rotation axis because it is no longer necessary to bring all reflection into the horizontal plane in order to record data. In this work the type of detector used is a charge coupled device (CCD) detector with a three-circle diffractometer. This typical three-circle diffractometer has two axes (ϕ, ω) about which the crystal may be rotated plus the circle (2θ) about which the detector is rotated. A typical area detector and a part of SMART APEX CCD X-ray image are shown below:



(a)



(b)

Figure 13 The schematic representation of a three circle diffractomet equipped with an area detector (a) and (b) a part of SMAR APEX CCD X-ray image.

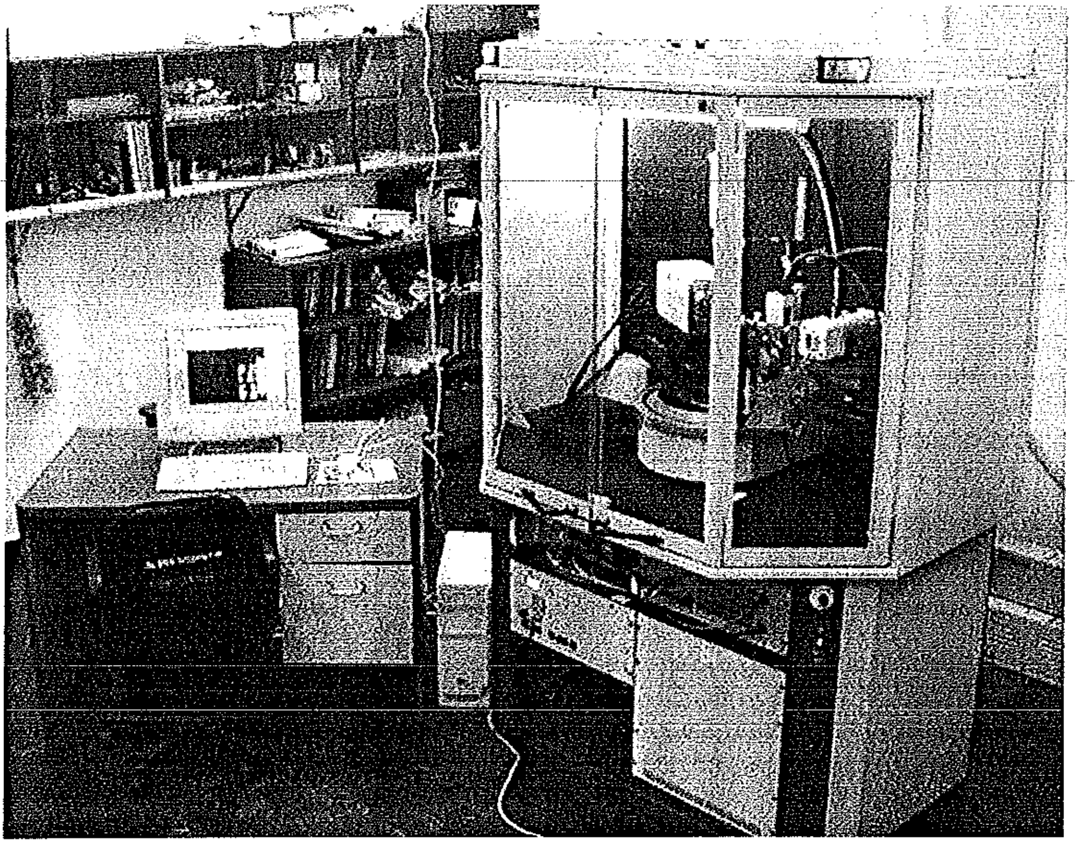


Figure 14 The SMART APEX CCD single crystal X-ray diffractometer.

2.7.1 Selecting a suitable crystal for X-ray studies

Selecting a good single crystal is the important step. The results of an X-ray diffraction experiment are only as good as the quality of the crystal. Without a good crystal everything else is more difficult. The valuable tool, polarizing microscope will probably utilize to inspect, select a good single crystal and check for imperfections of sample. If the crystal is not a single crystal, the diffraction patterns can not be interpreted or structure can not be solved. Considerably, the satisfied crystal to collect the data with X-ray diffraction is:

1) Crystal size

The formal acceptable crystal size for X-ray work on modern diffractometer is approximately 0.1-0.4 mm. and if possible, the crystal should be isotropic in shape. Very large crystal of small molecules can be cut to a smaller size (required size) with razor blade, possibly along a cleavage plane.

2) Crystal shape

Good crystals often have well defined faces and sharp, straight edge as well as it must be homogeneous and pure crystal. It should not have cracks, holes, and concave face or otherwise damaged surfaces or interior. Greatly, it must be a single crystal, in which all molecules or ions obey a regular repeating pattern as well as all unit cells are identical and aligned in the same direction. The crystal quality is shown by the quality of its diffraction.

2.7.2 Crystal mounting

The acceptable crystal has to be mounted in such a way that they can be manipulated in various devices used for intensity measurement and for collecting diffraction data. The glass fiber to be used should have 4 - 5 mm protruding from the end of the brass pin and be accurately centered and parallel to the length of the pin and be preferably attached to a pin with bee wax. Try to mount the samples so that its longest axis is nearly parallel to the fiber or capillary axis. The stationary crystal must be aligned and centered on a camera and must expose to a beam of X-ray. It is essential that the crystal be securely attached to the mounting device so that no slippage can occur during the data collection. Two methods are principally used to mount crystal:

1) Crystals which are not volatile or sensitive to the environment are glued onto a fine glass fiber of borosilicate or quartz with a minimum quantity of an epoxy glue, bee wax or amorphous adhesive.

2) Crystals which are volatile or sensitive, degradable by loss of loosely bound solvent require a special treatment. They will probably be mounted in a thin-walled glass capillary. Alternatively, the crystal can be coated with an inert viscous oil that is a good way to keep out from air and/or moisture and limit the chances of losing solvent and then manipulated under a normal microscope in an open atmosphere.

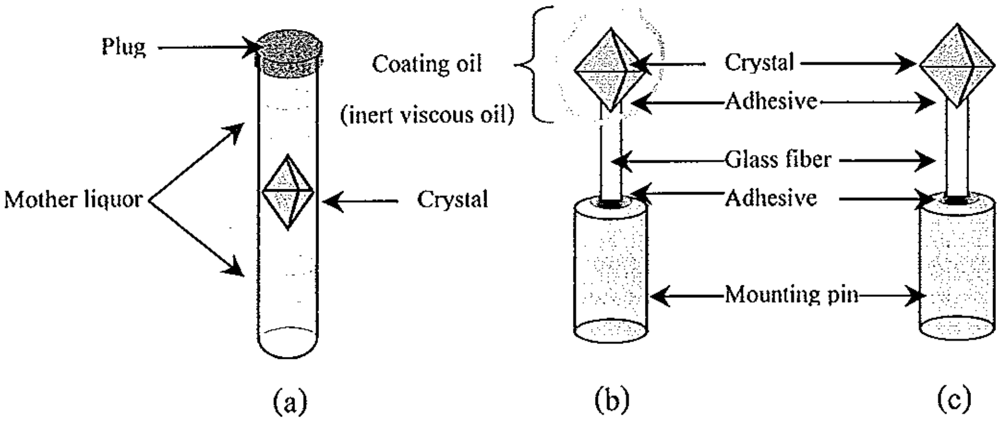


Figure 15 Crystal mounting ; (a) and (b) for sensitive crystal, (c) for stable crystal

2.7.3 Crystal alignment

To obtain accurate unit cell dimensions and to collect good quality data, the crystal must be aligned to the center of the X-ray beam. The mounted crystal is fixed to a goniometer head(figure 16), this gadget has two perpendicular arcs, allowing rotation of the crystal along two perpendicular axes. For further adjustment and centering, the upper part of goniometer head can be moved along two perpendicular sledges. The goniometer head's Z-axis, X-axis and Y-axis adjustment screw (figures 16 and 17) are adjusted until the crystal is on the center of the beam for any rotation as seen by the video camera that the crystal is on the crosshairs intersection on the video screen (figure 18) .

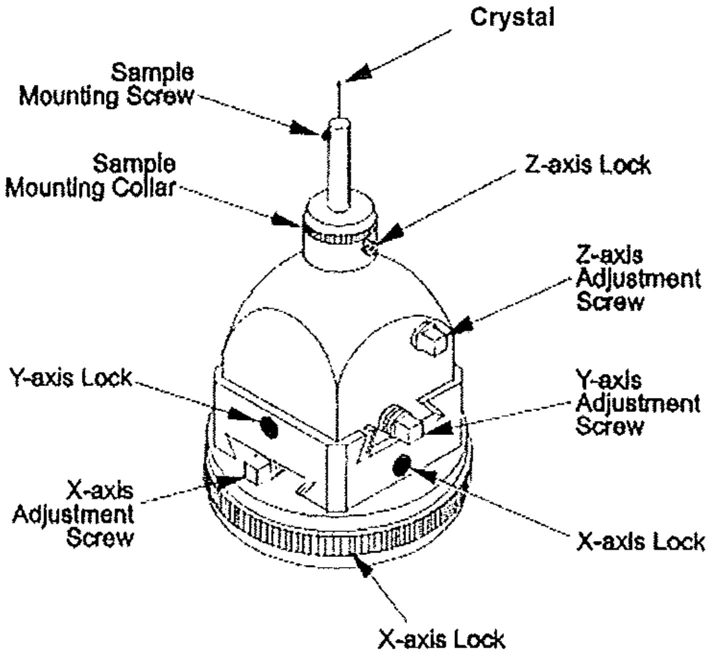


Figure 16 The goniometer head

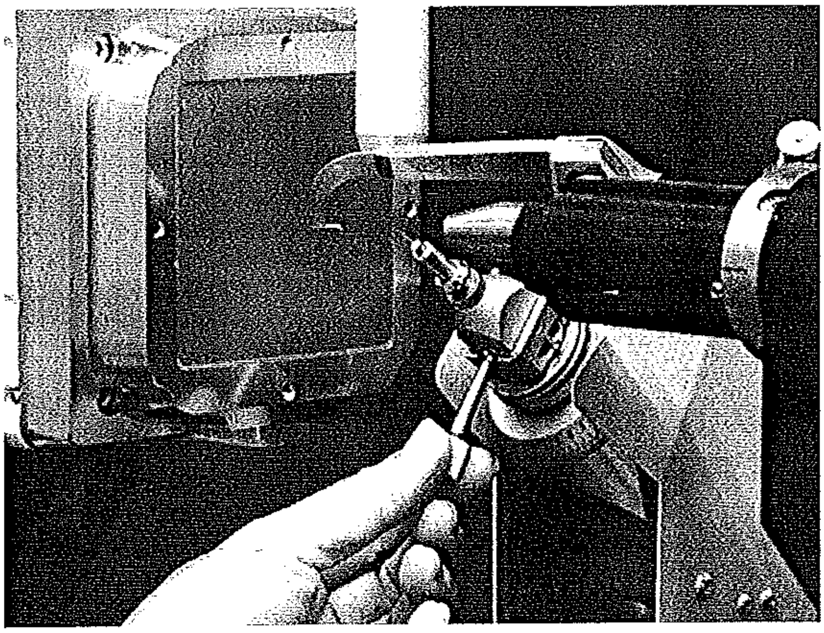


Figure 17 The goniometer head is adjusted in x-axis.

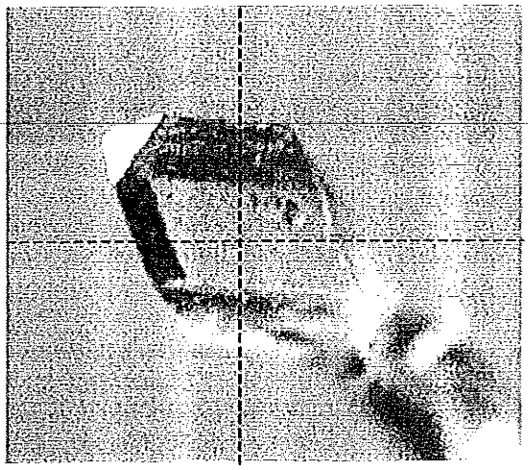


Figure 18 Single crystal centered on crosshairs.

2.7.4 Obtaining unit cell geometry and symmetry

The unit cell can be measured from subset of the complete diffraction pattern. The key step is assigning the correct indices *hkl* to each of observed reflection. From these and the measured Bragg angle for a few reflections, the six unit cell parameters (a, b, c, α, β, γ)and preliminary symmetry information can be calculated via Bragg equation (Clegg, 1998 : 17-18; Guster, *et al.*,1994).

Some reflections from moderate to high intensity are located by simply driving motor while monitoring output for a signal significantly above background (a blind search, all under computer controlled). The crystal orientation, unit cell geometry and reflection indices have to be determined simultaneously. The calculations which are not simple are usually regarded as computer 'black box' method, 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. At this stage, it may be possible to assign the correct space group by comparison of intensities that are equivalent by symmetry, but the decision is made reliably on the basis of the complete data sets.

2.7.5 The measurement of data

An area detector diffractometer can record many diffracted beams at the same time. Normally, the crystal is rotated about one axis and each exposure covers a small angular range, the details depending on the particular characteristic of the detector. In general, reflections are spread over more than one frame and sophisticated computer analysis of large quantities of data is required. Typically, data collections take only a few hours, dependent of the size of structure. Since a large structure just gives more simultaneous reflections. However, longer exposures are advisable for weakly scattering samples. The result of the process is a list of reflections, usually thousands of reflections, each with *hkl* indices and the measured intensity. In addition, from diffractometer measurements, each intensity I has an associated standard uncertainty (s.u.), $\sigma(I)$ that is calculated from the known statistic properties of the X-ray generation and diffraction process, as well as is a measure of the precision or reliability of the measurement. The decision of data collections depends upon about the data collection procedure. These include the maximum Bragg angle to be collected, the time to speed on each measurement, and whether to collect only the fraction of the total pattern depending on the space group symmetry or to include other reflections equivalent by symmetry. For this research, after preliminary crystal quality checking and unit cell parameter determination of all complexes, hemisphere of raw frame data were collected.

2.7.6 Data collection and data reduction

For each Bragg reflection, the raw data typically consist of the Miller indices (h,k,l), the integrated intensity, $I(hkl)$ and its standard deviation, $\sigma(I)$. The intensity of an X-ray beam is proportional to square of the wave amplitude $(I(hkl) \propto |F_o(hkl)|^2)$ (o = observed). The conversion of $I(hkl)$ to $|F_o(hkl)|^2$ and correspondingly $\sigma(I)$ to $\sigma(|F_o|)$ or $\sigma(|F_o|^2)$ involves the application of correction for X-ray background intensity, Lorentz and polarization factor, absorption affects and also radiation damage. This process is known as data reduction. Normally, data reduction is carried out at the end of a data collection. The variety of correction for intensities are utilized to their s.u.'s (associated standard uncertainty). The result of this whole process is a file with the *hkl* indices, the F_o^2 values and their standard uncertainties, $\sigma(F_o^2)$ that usually takes only matter of minute on computer.

For this work, all reflection data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) using SMART program (Bruker, 2000). Raw data frame integration was performed with SAINT(Bruker, 2000), which also applied correction for Lorentz and polarization effects. Absorption corrections were applied using SADABS (Bruker, 2000), provided an empirical absorption correction and put the standard deviations of measure intensities onto an absolute scale. The emperical absorption correction is based on reflection measurements at a diffraction azimuthal angles and/or measurement of equivalent reflections. Besides, the raw file is read twice; the first time to select suitable reflections for refining the absorption parameter, and the second time to apply the corrections.

2.7.7 Solving and refining Structure

2.7.7.1 Solving structure by using SHELXTL NT (Version 6.12)

The integrated reflection data from SAINT and SADAB programs are solved by using SHELXTL NT program (version 6.12) on PC computer at the Department of Chemistry, Faculty of Science, Prince of Songkla University.

SHELXL NT is based on the widely used published domain SHELX-97 program system. This version is a major rewrite in order to incorporate and exposit modern structure solution and refine algorithms. It contains a very large number of improvement and additional facility, such as the automatic space group determination, absorption correction, statistical analysis of reflection data and extensive molecular graphic. The NT version contain six major subprograms for determining and refining the structure of small molecules such as XPREP, XS, XL, XP, XSHELL and XCIF (Appendix A).

The methods used for solving structural model of small molecules are :

a) The heavy atom method

If the position of heavy atom is known then the phases due to this heavy atom can be calculated. Since a heavy atom dominates the phase of all reflections, its phases will approximate to the phases of the overall structure. The position of the heavy atom can be found by the Patterson map.

b) Direct method

The theory of direct methods is based on the phase relationships of a set of reflections which contribute most to the Fourier transform. Direct methods can be used to locate the non-hydrogen atoms in the structure.

2.7.7.2 Refining structure by using SHELXTL NT (Version 6.12)

All atomic positions (x_i, y_i, z_i) have been found by the Patterson method or direct methods may have some errors arise from the approximations of the solution method, error in evaluating the maximum in Fourier synthesis, and error in measuring data. This is lead to the fact that for each reflection *hkl,* the calculated structure factor, (F_c) or the calculated intensity(F_c^2) does not agree exactly with the observed value. The process to obtain the more exact atomic parameters refer to a refinement of the crystal structure that is the essential part of any crystal structure analysis. The method to refine the structure is mostly known as "least squares" that define the best fit of couple sets of $|F_o|$ and $|F_c|$ (o = observed, c = calculated) in order to improve the accurate position of the known atom. The value of these two sets can be compared in various ways. The most fashion is widely used assessment called residual factor or R-factor, defined as :

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

where $F_c(hkl)$ is the calculated structure factor, corresponding to each observed structure factor.

$F_o(hkl)$ is the observed structure factor.

R is calculated as a measure of the precision of the refinement.

Normally the structures are carried out by utilizing F^2 refinement rather than F. Since these allows all of the measured intensities to be used even if the negative intensity. One of the residual factor largely used for $F_o(hkl)$ crystal structure determination is

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

where w is the reflection weight.

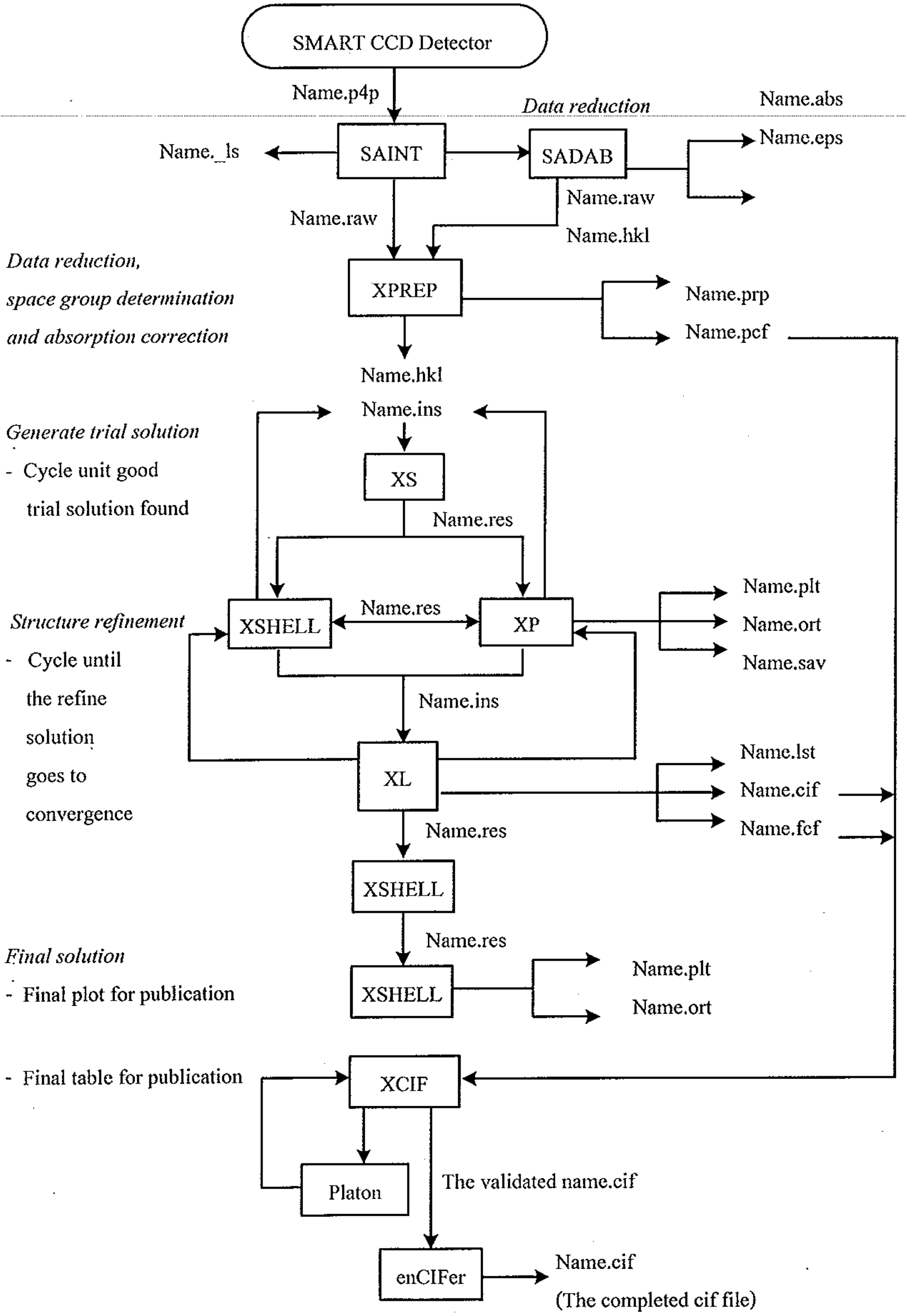
w*R2 is* the conventional name for this residual factor, the *w* indicates that weight are included, and the 2 indicates that F^2 values are used.

For a correct and complete structure determination from well measured data, typically, *R*-factor around 0.02-0.07 and *wR2* based on F^2 is generally higher than those based on *F*. The higher *R*-value indicates to the incorrectness of the derived structure. Much lower *R*-value is needed.

2.7.7.3 Interpreting the result and preparing for publication

The accurate structures were considered insight to the interactions in the structure such as hydrogen bond, weak interaction and so on, affecting to the arrangement of molecules in the unit cell. For accurate data, they were used to plot molecules, unit cells, and other the images of interaction as well as completed crystallographic information file (CIF) for crystallographic data and for publication. Platon (Spek, 2003), Mercury (Bruno, *et al.*, 2002), enCIFer program (Bruno, *et al.*, 2002) and also XL, XP, XCIF subprograms of SHELXTL including with XSHELL are used for performing. Firstly, XL and then XCIF are used for writing CIF files and crystallographic tables. Secondly, all of the CIF files were checked to validate the accurate data by Platon program. After that these accurate CIF files were completed by enCIFer program, which is the convenient interaction package. Not only it utilized for checking syntax error, adding some data such as abstract or some details of structure or preparation methods and author name but also used for viewing the interactions of the structures in three dimension. Finally, all of molecules and unit cells were plotted by XSHELL and some of interacting images involving hydrogen bond and weak interaction between the molecules were drawn by Mercury program. The flowchart of each step are sketched as follows:

A simplified flowchart of structure determination and refinement process



Chapter 3

RESULTS

3.1 Preparation of silver(I) complexes

The appropriated conditions for synthesizing complexes for which single crystal X-ray structures and the physical properties of these complexes have been characterized in this work are illustrated in tables 3, 4 and 5.

Table 3 The summarization of reaction conditions.

Silver(I) salts	Ligand	mole ratio	Solvent (ml)	Temp. (C^o)	Complexes
AgCl	ettu	1:3	$CH_3CN : H_2O$ (50 : 20)	82-83	$[Ag(ettu)_3Cl)]$
AgBr	ettu	1:3	CH_3CN (70)	82-83	$[Ag(ettu)_3Br)]$
AgBr	detu	1:4	n-C_6H_{12} (70)	67-70	$[Ag(detu)_3Br)]$
$AgSO_4$	detu	1:3	EtOH (50)	75	$\{[Ag(detu)_3]_2\ SO_4\}$
AgSCN	detu	1:3	$CH_3CN : H_2O$ (30 : 30)	50-55	$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$

Table 4 The physical properties of silver(I) complexes

Compound	**Appearance**	**Melting point (C°)**
ettu	White powder	108–110
detu	White powder	70-75
[Ag(ettu)$_3$Cl)]	Colorless needle	160-162
[Ag(ettu)$_3$Br)]	Colorless needle	143-145
[Ag(detu)$_3$Br)]	Colorless needle	110-112
{[Ag(detu)$_3$]$_2$ SO$_4$}	Colorless hexagonal	189-191
{[Ag$_2$(detu)$_4$][Ag(SCN)$_2$]$_2$}$_\infty$	Colorless prism	125-127

Table 5 The solubility of complexes at room temperature (28-29 C°)

Complexes Solvent	[Ag(ettu)$_3$Cl)]	[Ag(ettu)$_3$Br)]	[Ag(detu)$_3$Br)]	{[Ag(detu)$_3$]$_2$ SO$_4$}	{[Ag$_2$(detu)$_4$](Ag(SCN)$_2$)}$_\infty$
H_2O	+	-	+	-	-
MeOH	++	++	-	++	-
EtOH	+	+	-	-	-
CH_3CN	+	+	+++	+	-
CH_3COCH_3	++	+++	+	-	-
$CHCl_3$	-	-	-	-	-
$C_4H_{10}O$	+	+	-	-	-
THF	++	++	-	-	+
DMF	+++*	+++	-	++*	++
DMSO	+++	+++	+++	++*	+++
n-C_6H_{12}	+	+	-	-	-
C_7H_8	+	+	+	-	+

Remark:

* : The solution changed color from colorless to yellow brown color

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

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

3.2 Elemental analysis (CHNS)

The composition of C,H , N, and S of silver(I) complexes are shown in table 6.

Table 6 The composition of C, H ,N , and S in complexes.

Complexes		Elemental analysis (%)			
		C	H	N	S
[Ag(ettu)$_3$Cl)]	Calculated	23.03	5.31	18.74	21.10
	Found	22.86	5.48	19.01	21.46
[Ag(ettu)$_3$Br)]	Calculated	21.06	4.85	16.99	19.22
	Found	20.32	5.01	17.02	19.42
[Ag(detu)$_3$Br)]	Calculated	30.28	6.80	14.30	16.46
	Found	30.06	7.06	14.31	16.84
{[Ag(detu)$_3$]$_2$ SO$_4$}	Calculated	33.08	6.66	15.23	20.61
	Found	32.83	6.47	14.99	20.56
{[Ag$_2$(detu)$_4$][Ag(SCN)$_2$]$_2$ }$_\infty$	Calculated	24.02	4.06	14.04	21.55
	Found	23.93	4.08	13.97	22.05

3.3 X-ray Fluorescence Spectroscopy

The X-ray Fluorescence spectra of the compounds are illustrated in figures 19-31.

3.4 Infrared Spectroscopy

The infrared spectra of ligands (ettu and detu) and the complexes are depicted in figures 32-38. Absorption spectra band I, II, III and IV refer to the thioamide band I, II, III and IV, respectively.

3.5 Single crystal X-ray diffraction

The X-ray crystallogaphic data and the structure plots of the overall complexes are depicted in tables 7-27 and figures 39-48, respectively.

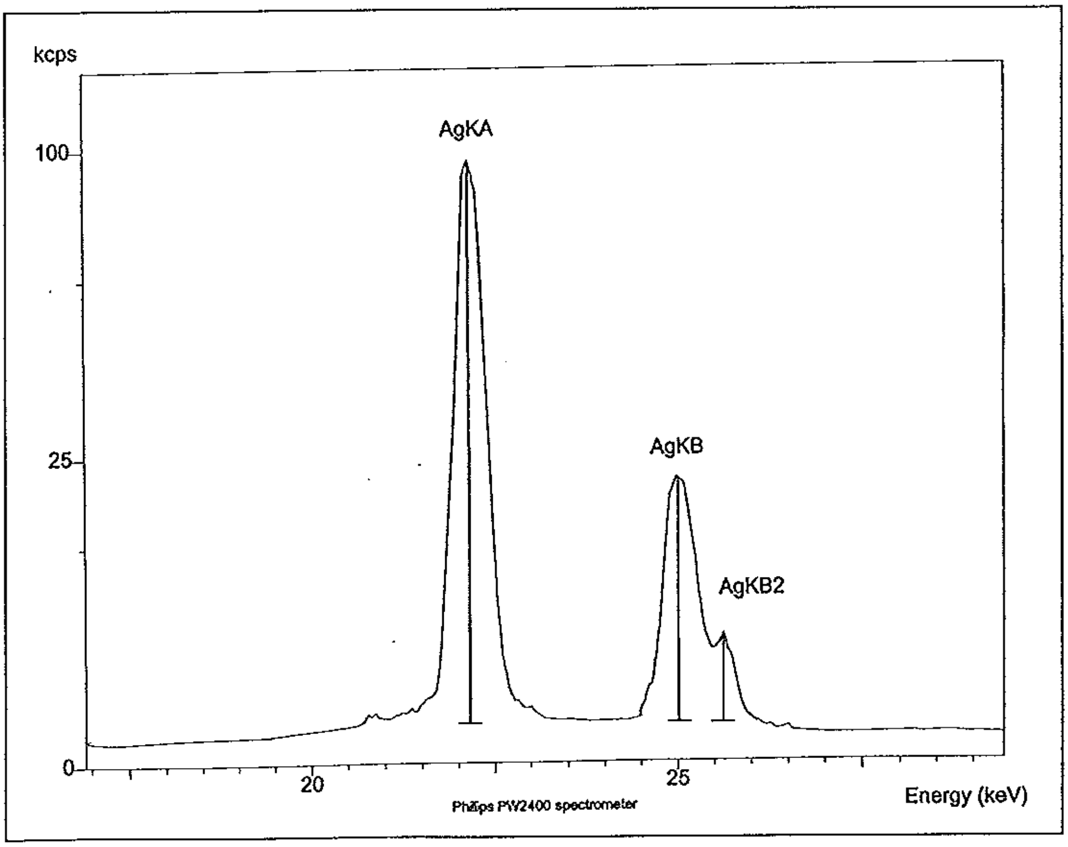


Figure 19 The XRF spectrum of Ag in $[Ag(ettu)_3Cl]$ complex.

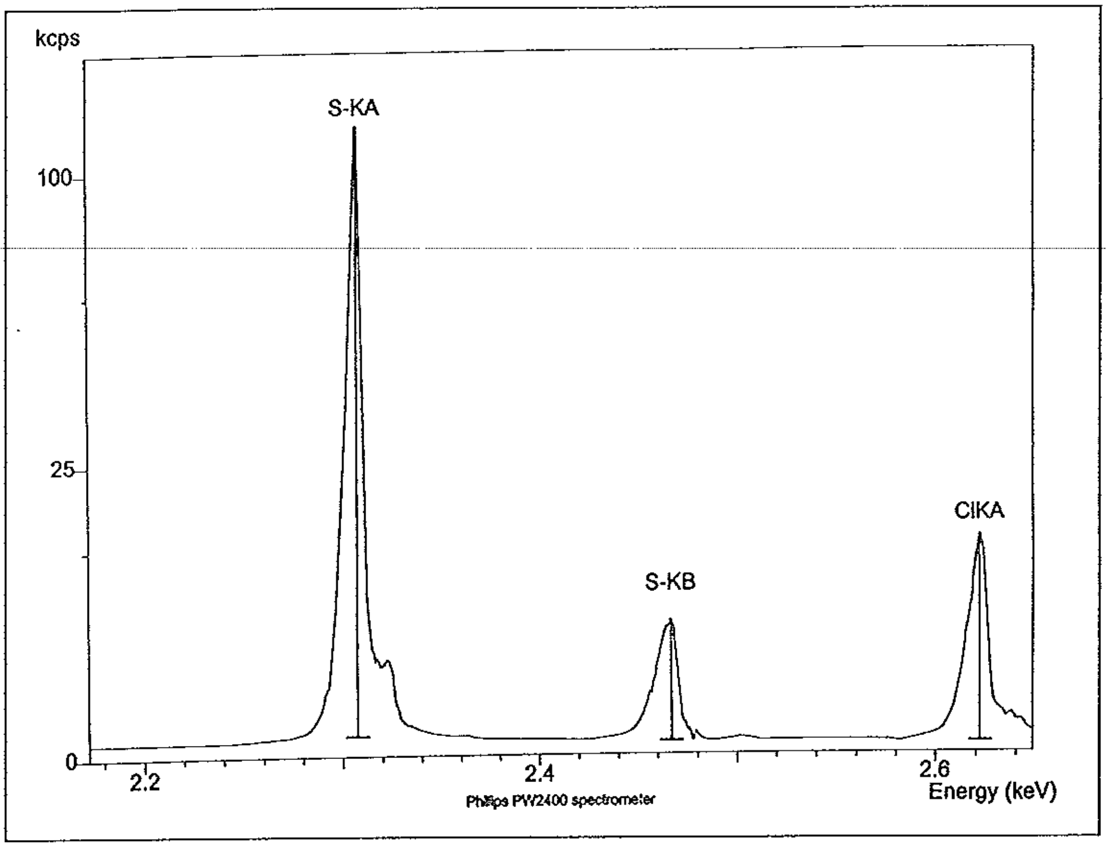


Figure 20 The XRF spectrum of S in [Ag(ettu)$_3$Cl] complex.

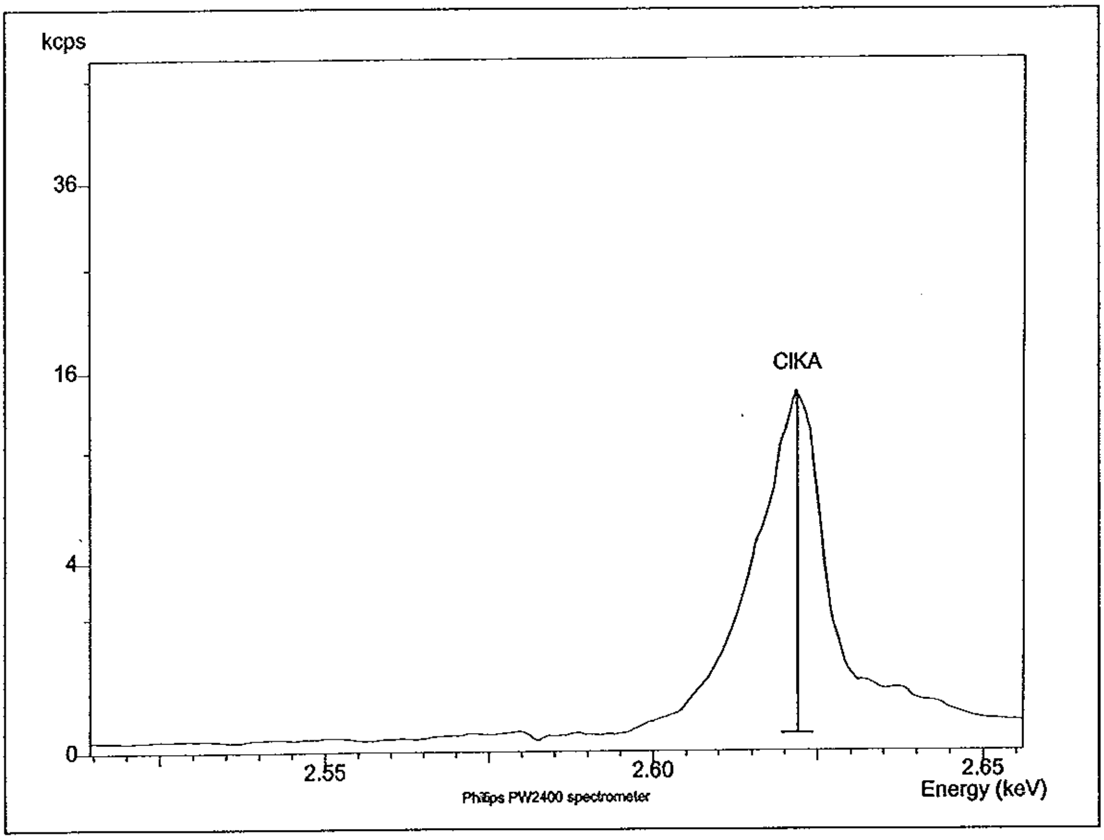


Figure 21 The XRF spectrum of Cl in [Ag(ettu)$_3$Cl] complex.

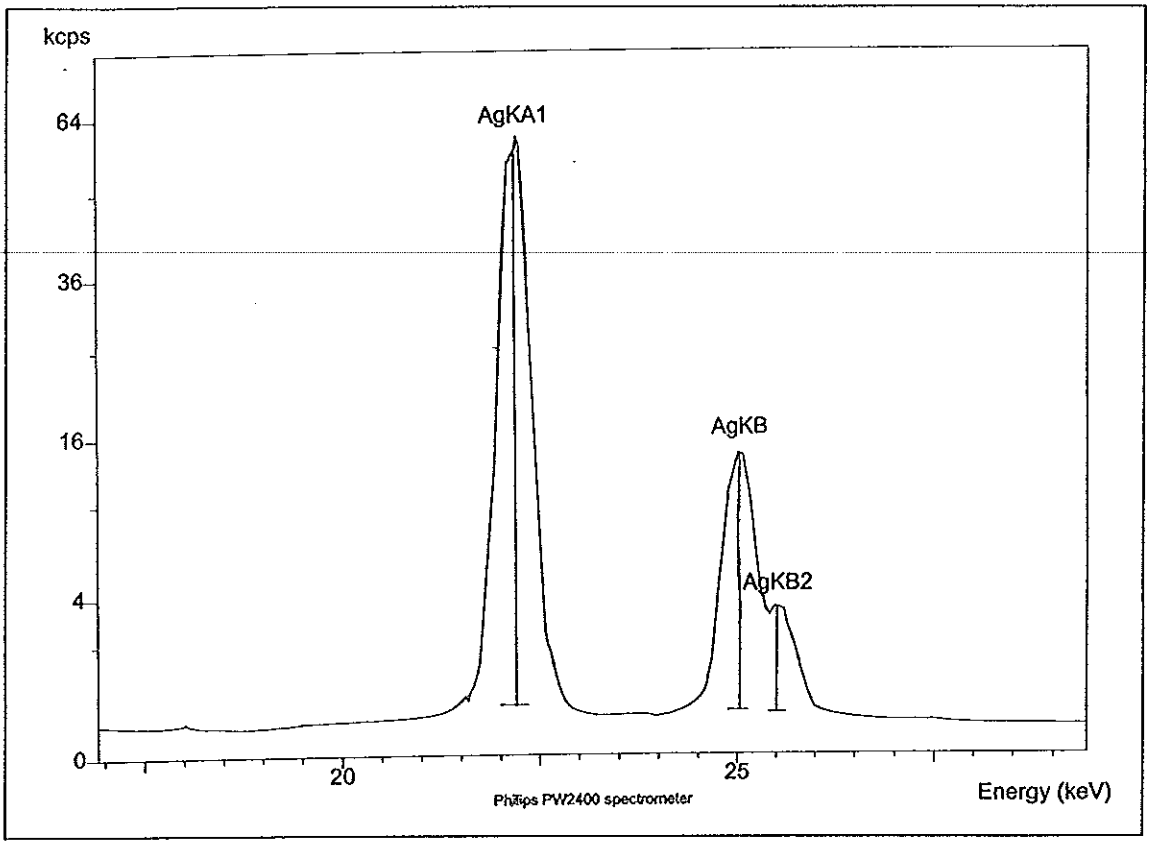


Figure 22 The XRF spectrum of Ag in [Ag(ettu)$_3$Br] complex.

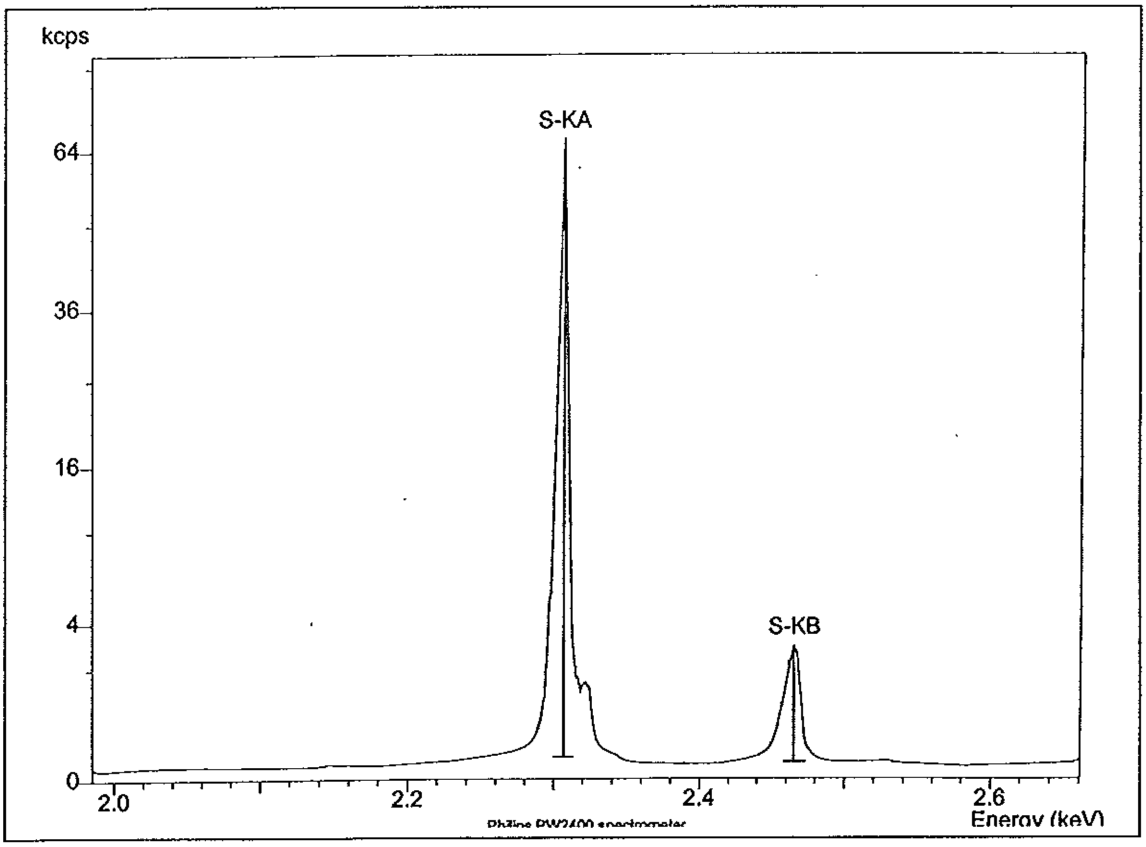


Figure 23 The XRF spectrum of S in [Ag(ettu)$_3$Br] complex.

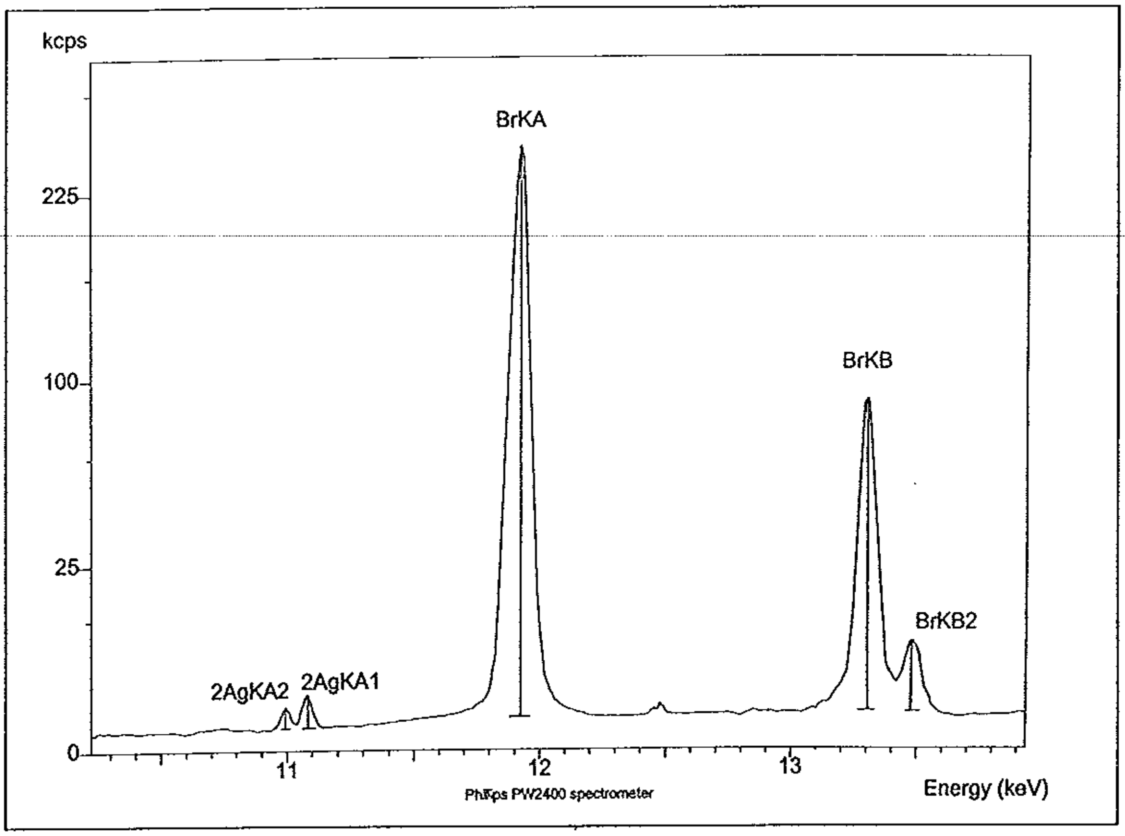


Figure 24 The XRF spectrum of Br in [Ag(ettu)$_3$Br] complex.

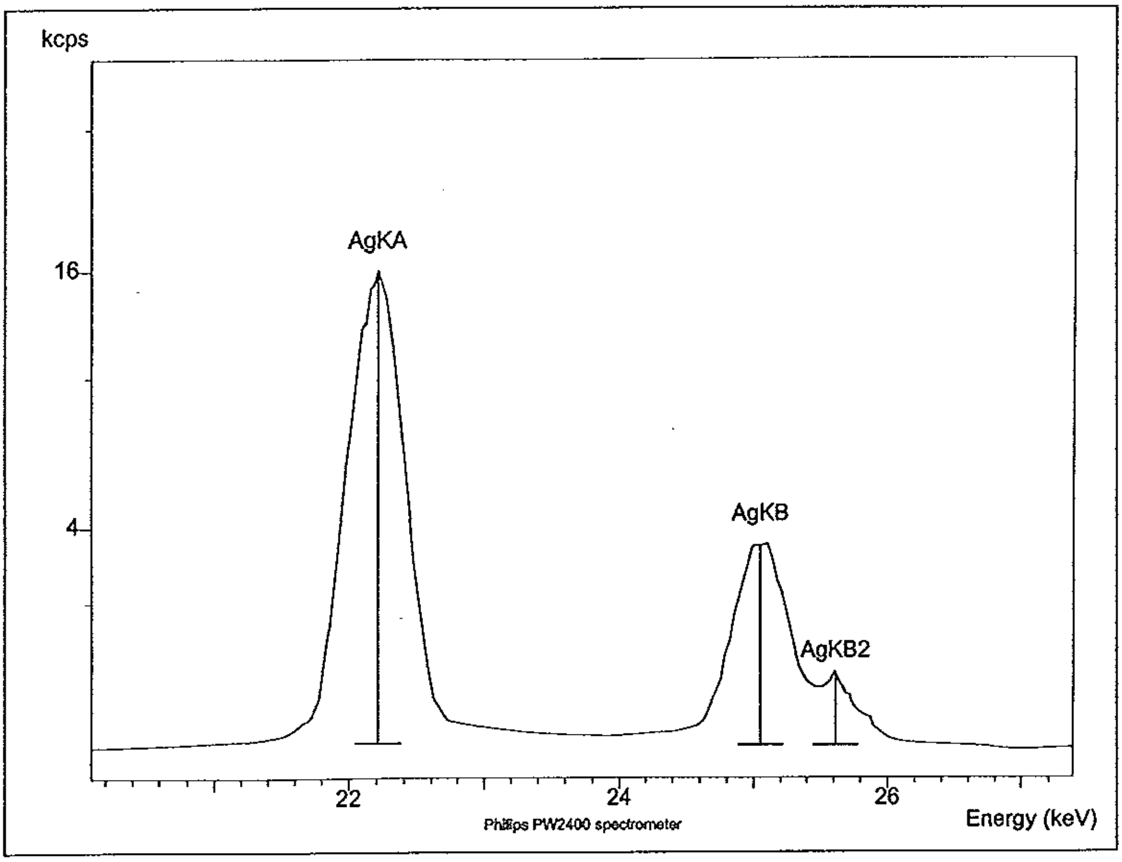


Figure 25 The XRF spectrum of Ag in [Ag(detu)$_3$Br] complex.

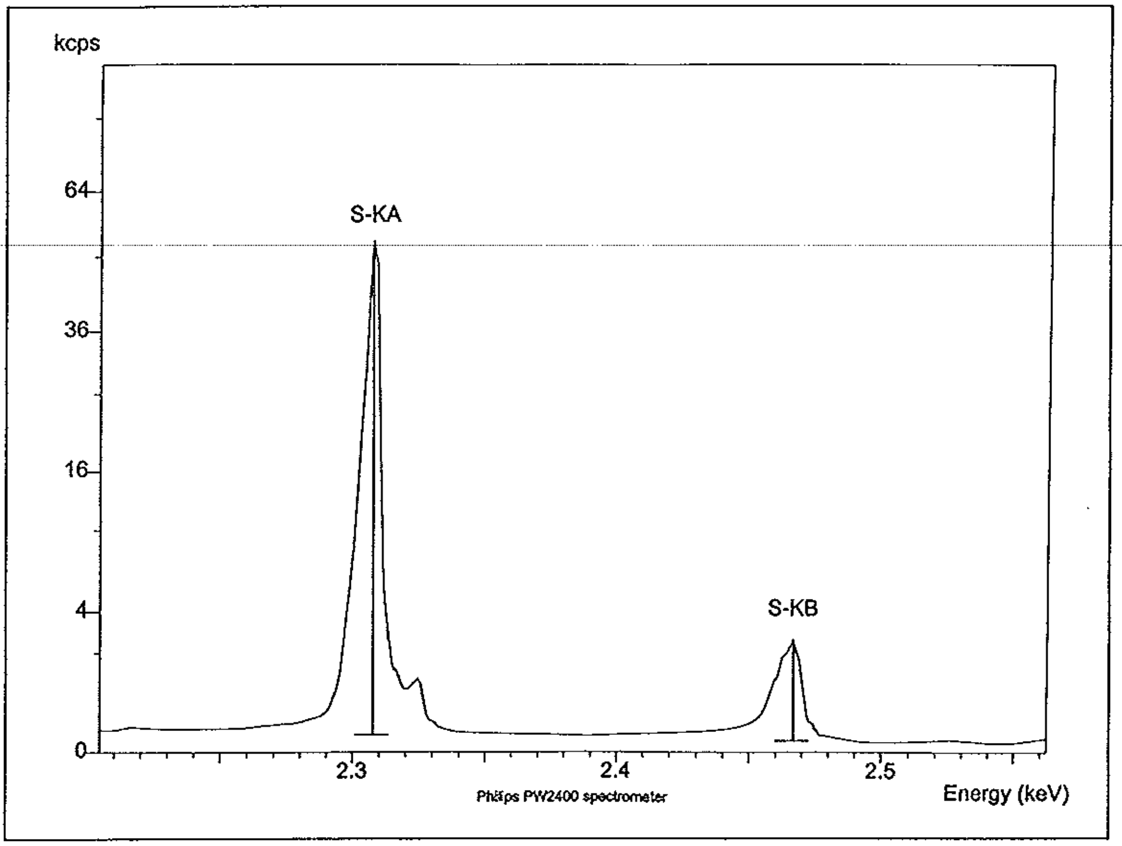


Figure 26 The XRF spectrum of S in [Ag(detu)$_3$Br] complex.

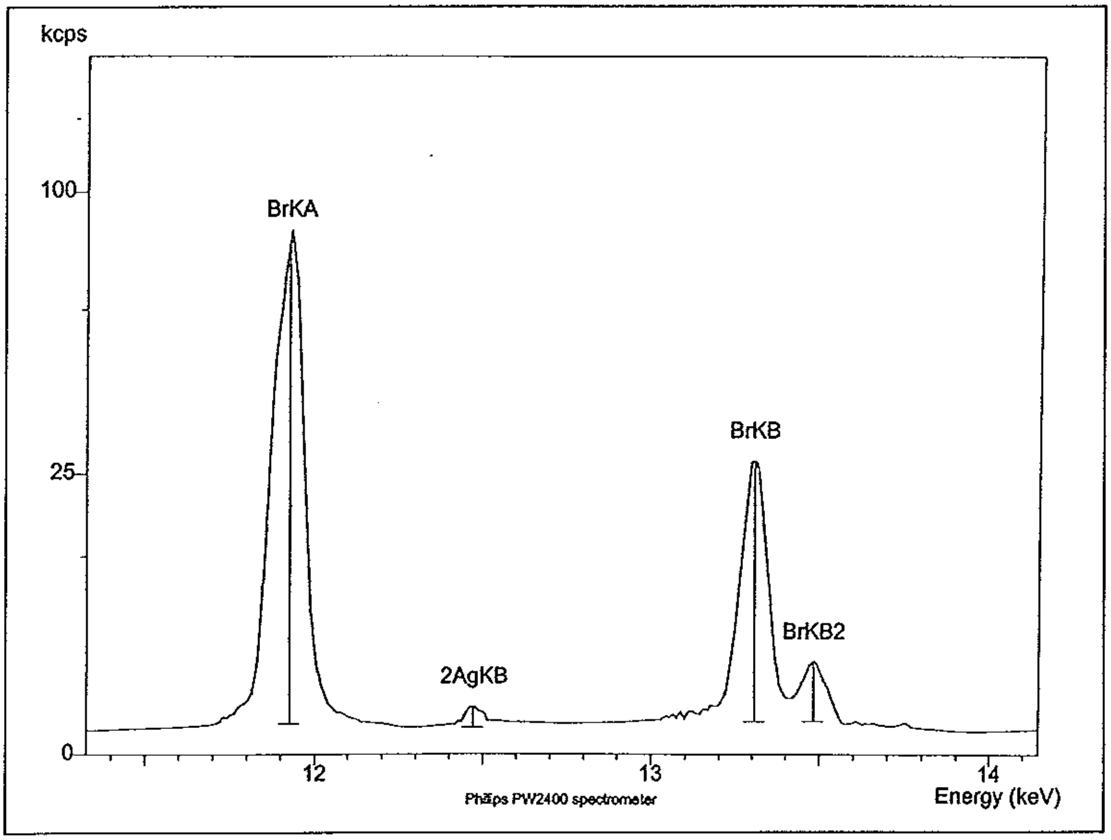


Figure 27 The XRF spectrum of Br in [Ag(detu)$_3$Br] complex.

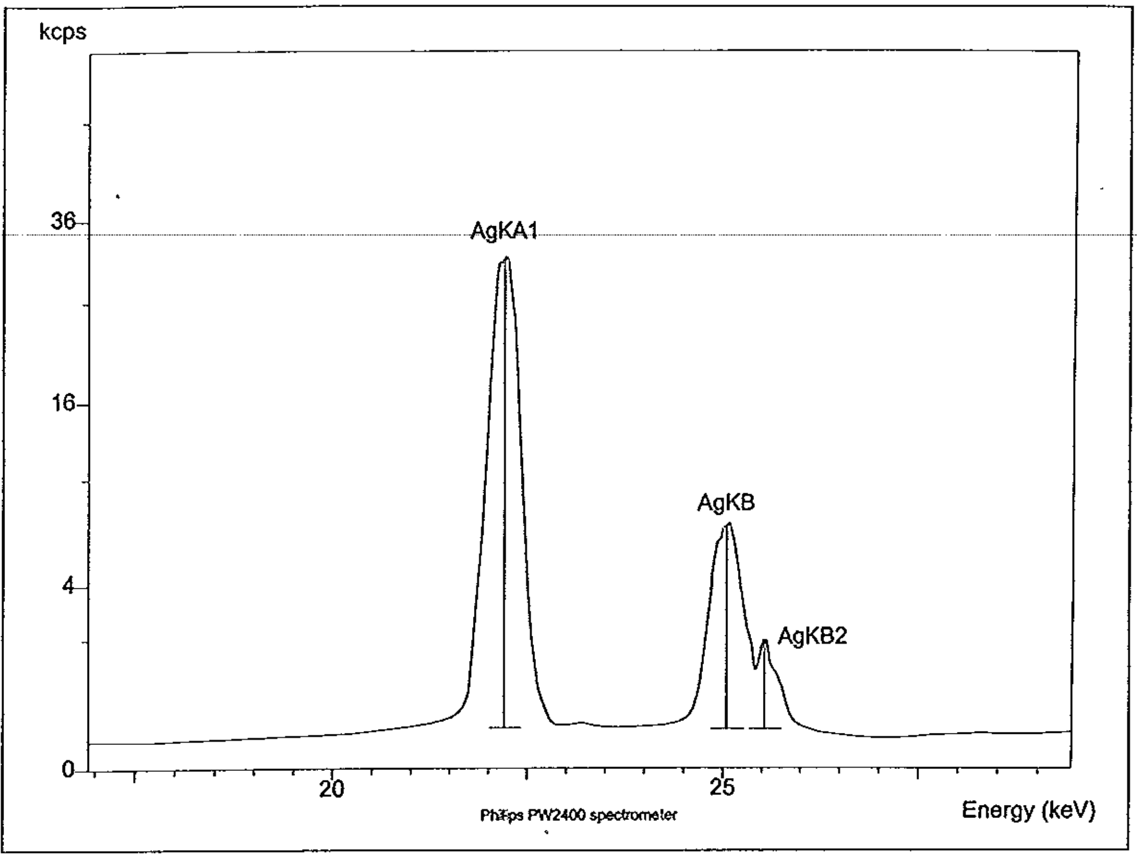


Figure 28 The XRF spectrum of Ag in $\{[Ag(detu)_3]_2SO_4\}$ complex.

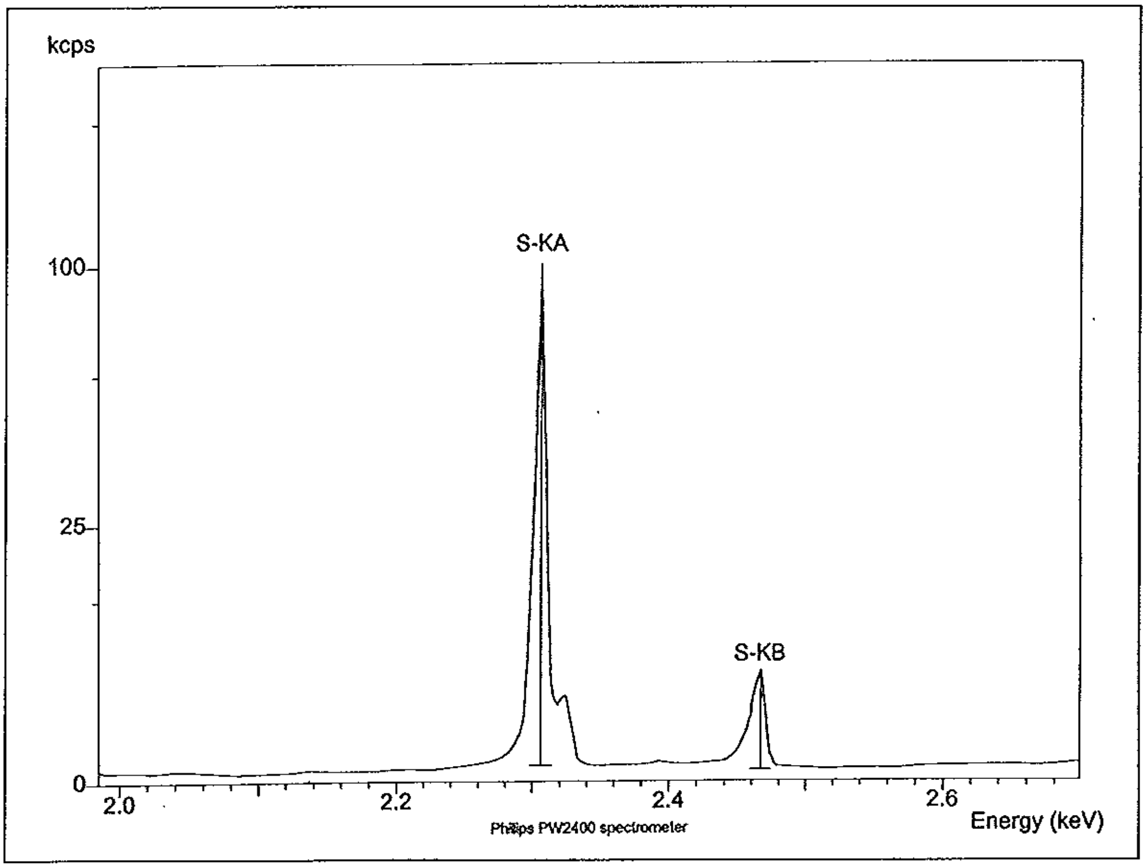


Figure 29 The XRF spectrum of S in $\{[Ag(detu)_3]_2SO_4\}$ complex.

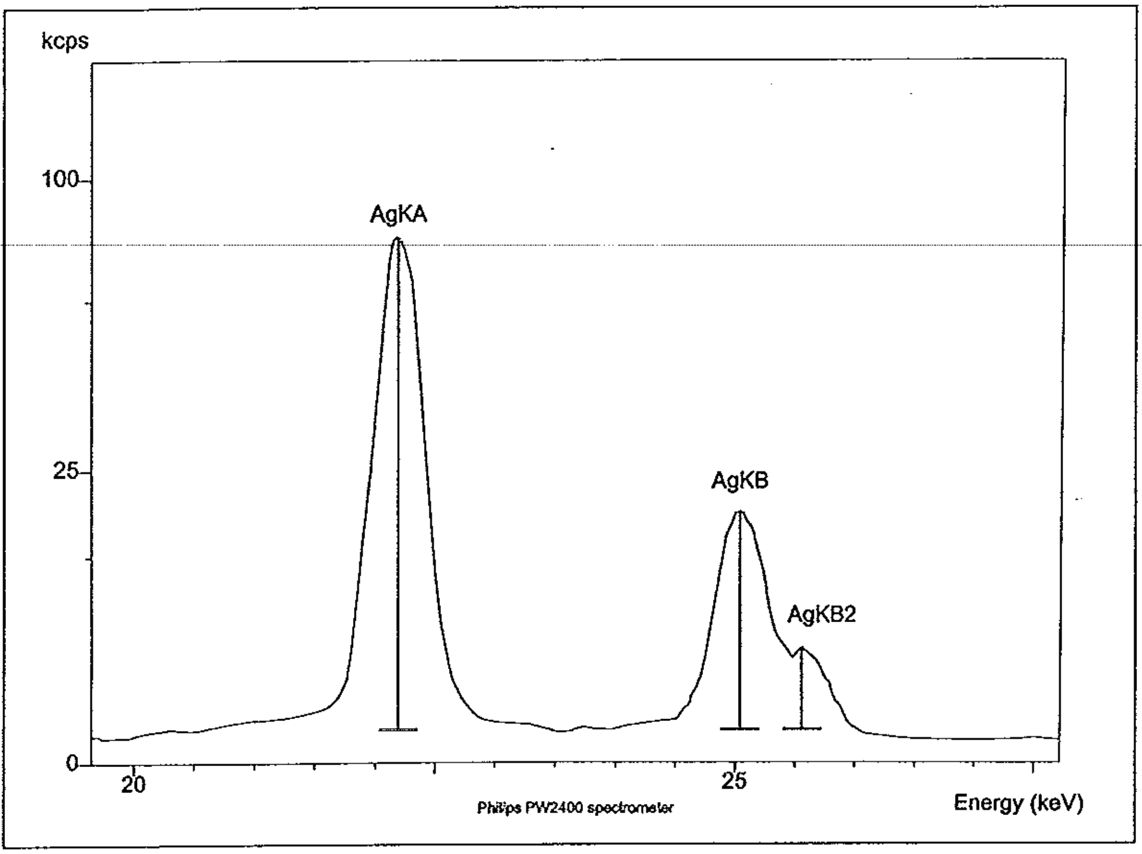


Figure 30 The XRF spectrum of Ag in $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$

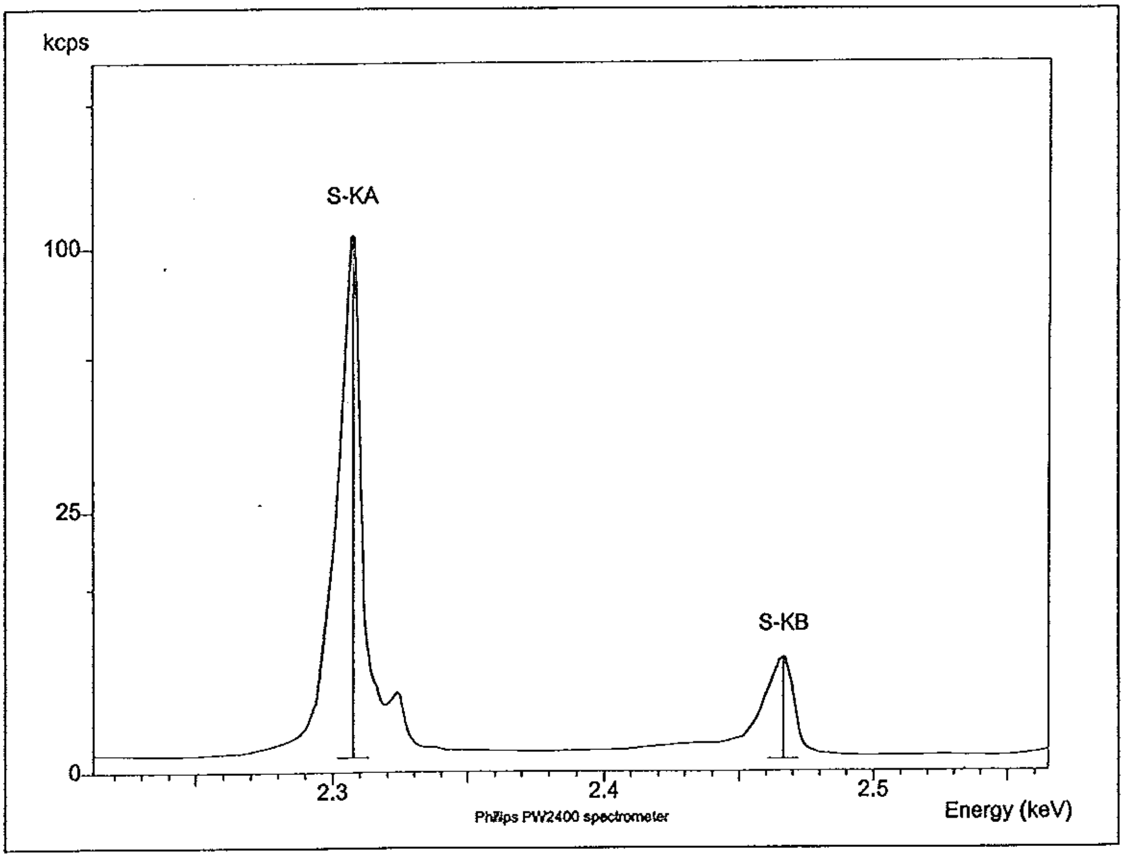


Figure 31 The XRF spectrum of S in $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$

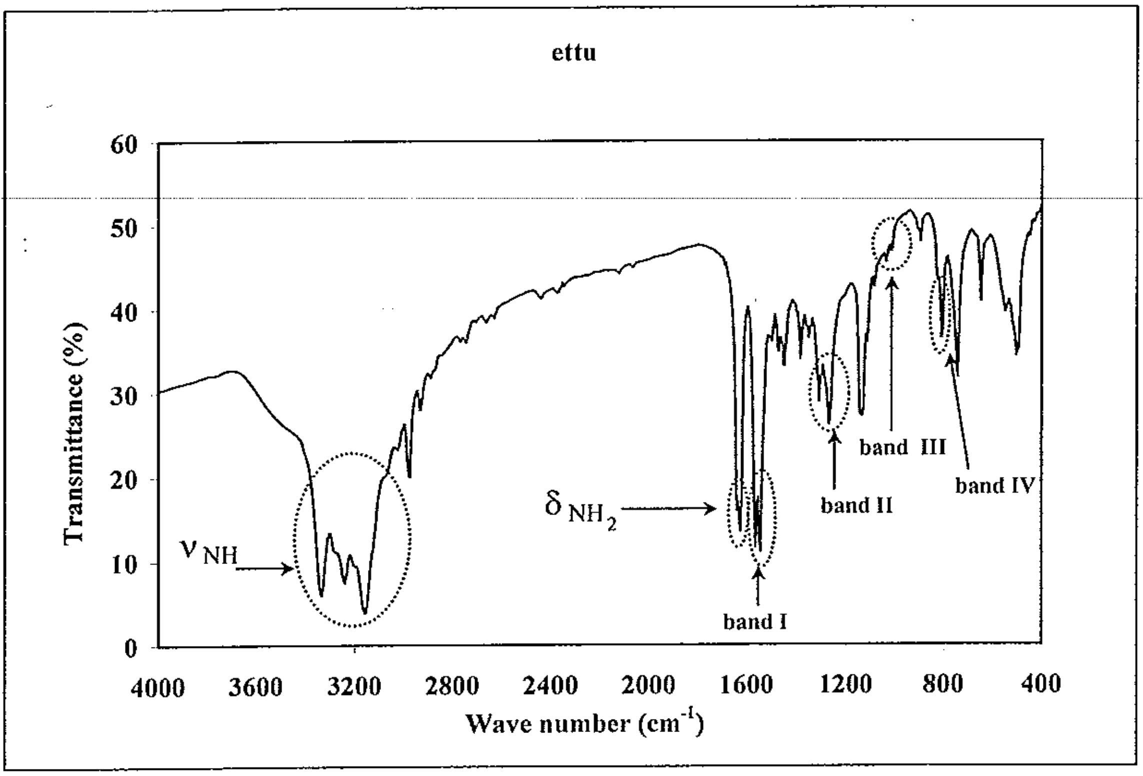


Figure 32 The Infrared spectrum of ettu ligand.

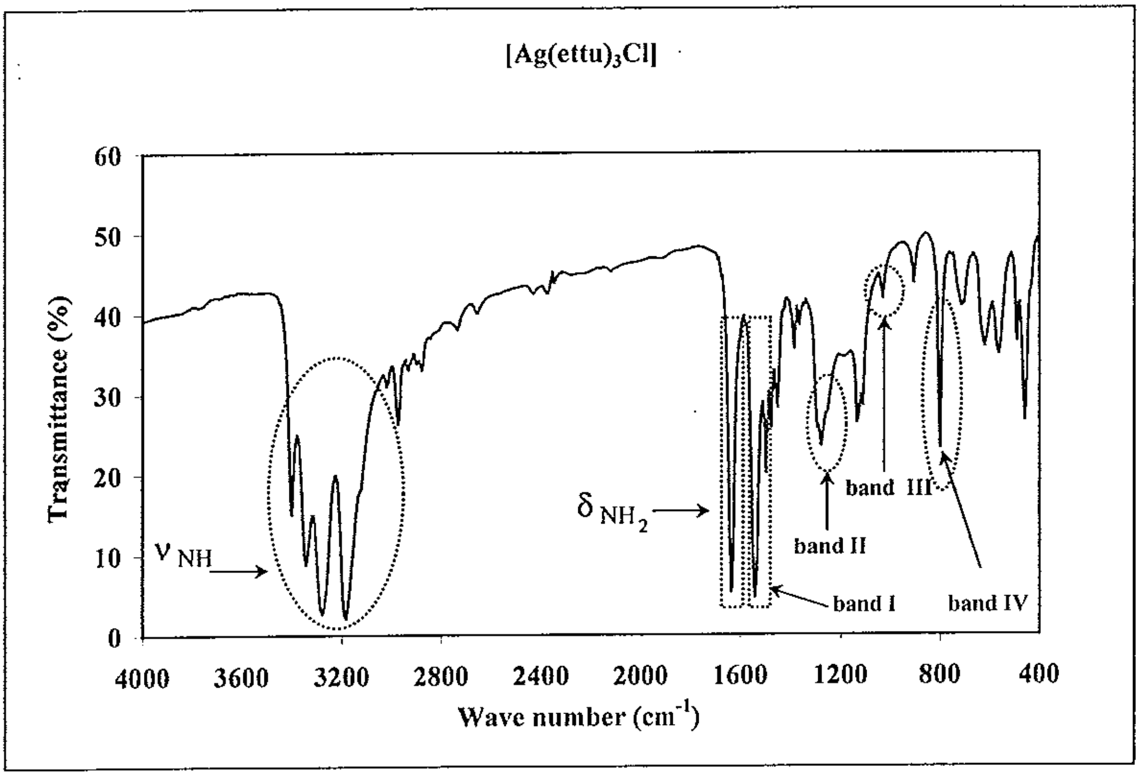


Figure 33 The Infrared spectrum of [Ag(ettu)$_3$Cl] complex.

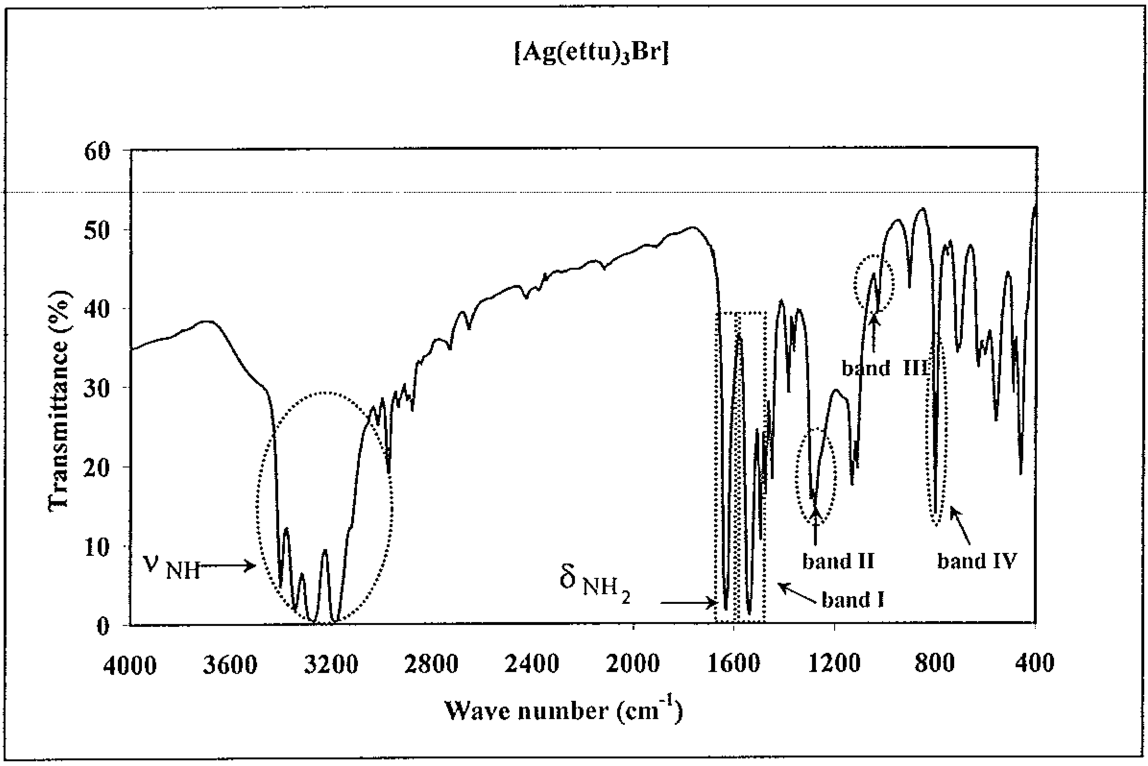


Figure 34 The Infrared spectrum of [Ag(ettu)$_3$Br] complex.

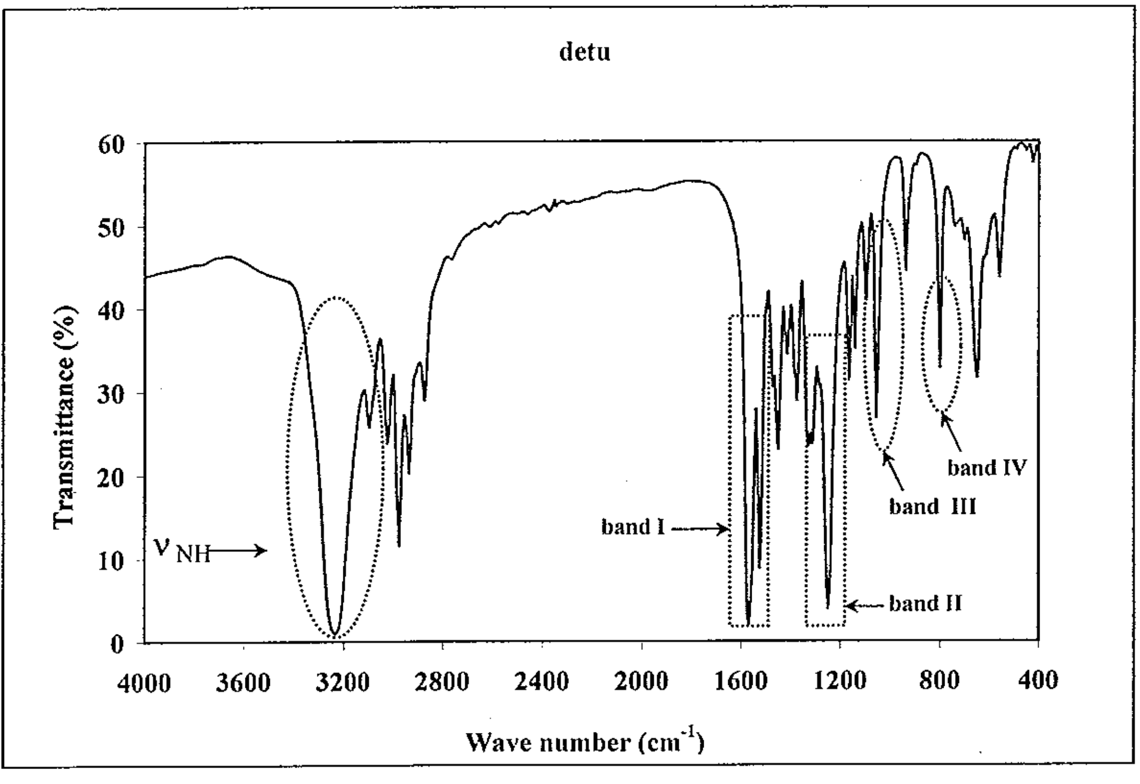


Figure 35 The Infrared spectrum of detu ligand.

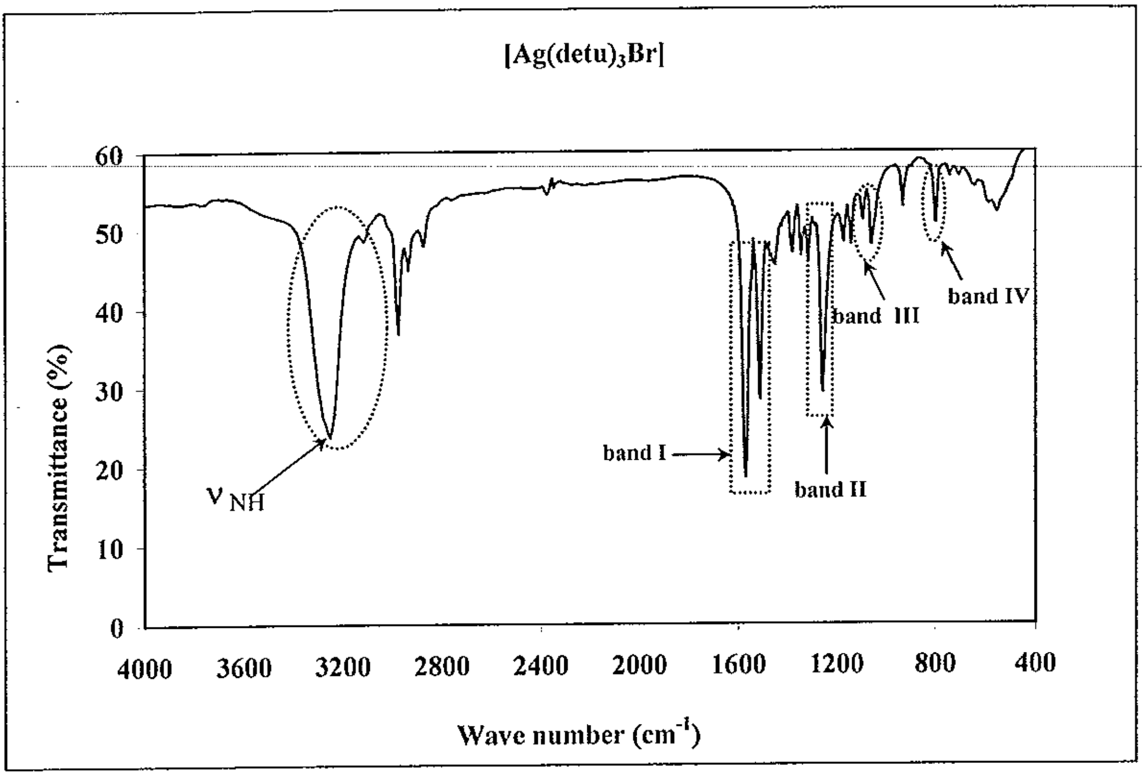


Figure 36 The Infrared spectrum of [Ag(detu)$_3$Br] complex.

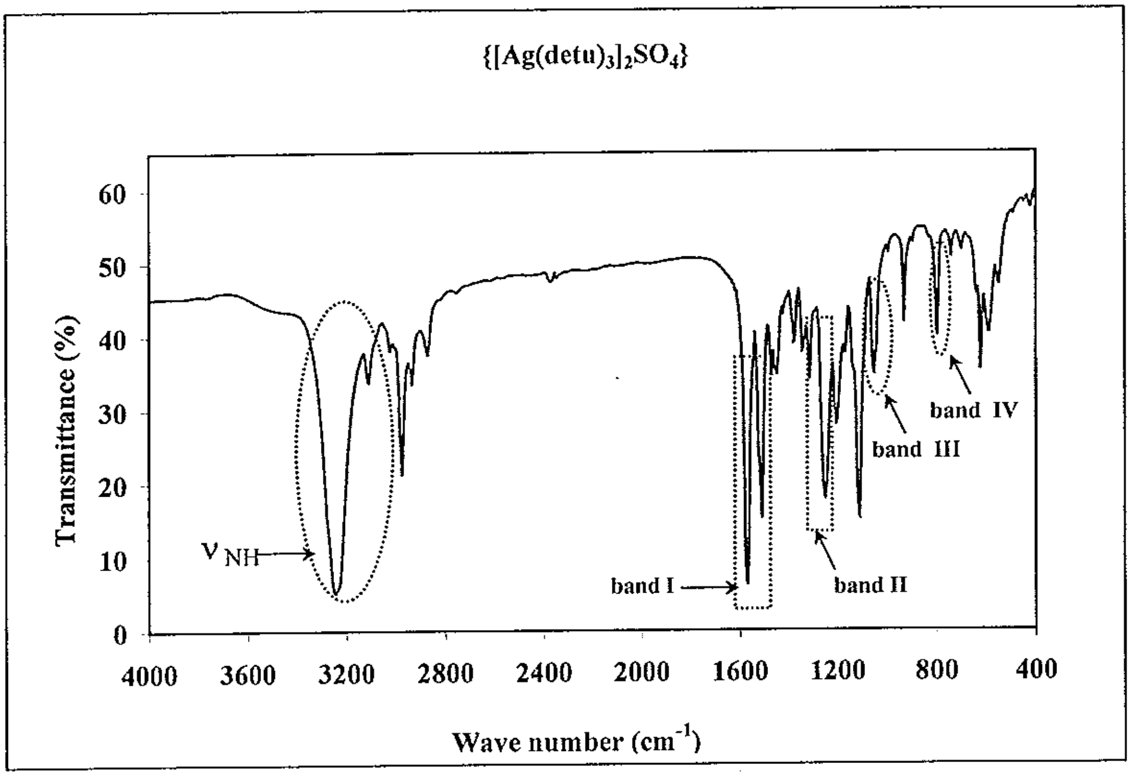


Figure 37 The Infrared spectrum of {[Ag$_2$(detu)$_3$]$_2$SO$_4$} complex.

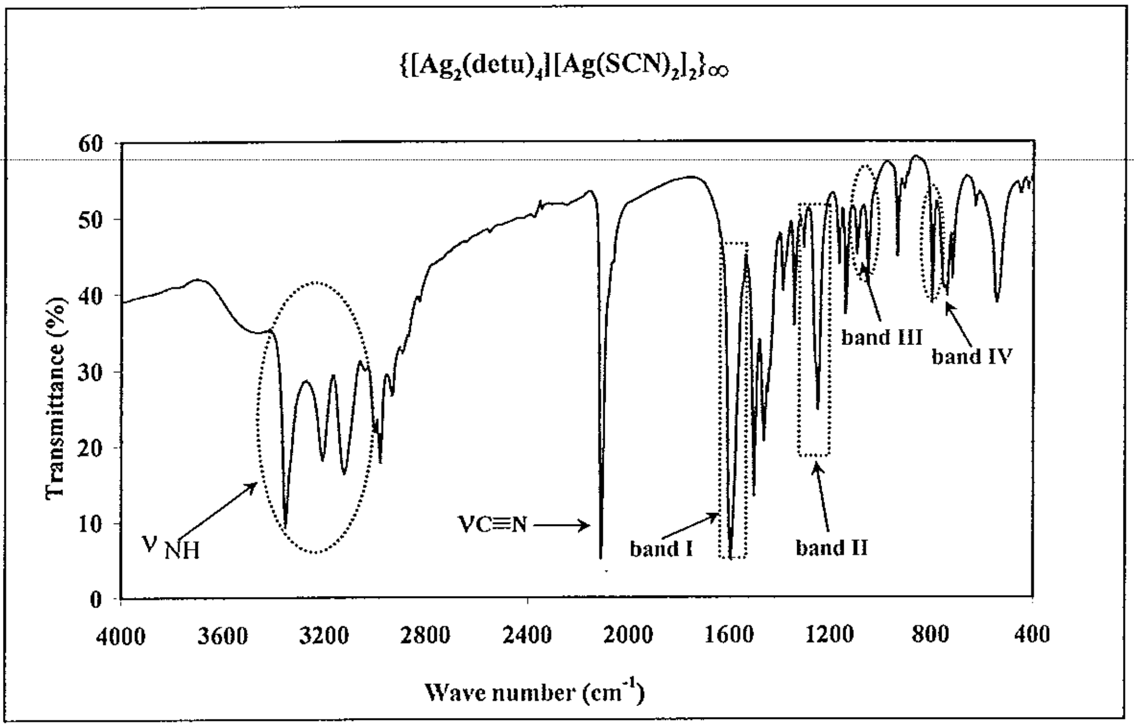


Figure 38 The Infrared spectrum of {[Ag$_2$(detu)$_4$] [Ag(SCN)$_2$]$_2$}$_\infty$

Table 7 Crystal data and structure refinement for [Ag(ettu)$_3$Cl].

Complex	[Ag(ettu)$_3$Cl]	
Empirical formula	$C_9H_{24}AgClN_6S_3$	
Formula weight	455.84	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$ (No. 11)	
Unit cell dimensions	a = 7.3489(1) Å	α = 90°
	b = 15.3315(1) Å	β = 91.467(1)°
	c = 8.1959(1) Å	γ = 90°
Volume	923.13(2) Å^3	
Z	2	
Density (calculated)	1.640 g/cm^3	
Absorption coefficient	1.575 mm^{-1}	
F(000)	464	
Crystal size	0.4 x 0.3 x 0.2 mm^3	
θ range of data collection	3.07 to 30.49°	
Index ranges	-10<=h<=9, -21<=k<=21, -11<=l<=8	
Reflections collected	6843	
Independent reflections	2732 [R(int) = 0.0138]	
Completeness to θ = 30.49°	93.8 %	
Absorption correction	Semi-empirical from equivalents	

Table 7 (continued)

Max. and min. transmission	0.730 and 0.601
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2732 / 0 / 156
Goodness-of-fit on F^2	1.019
Final R indices (for 2511 reflections[$I>2\sigma(I)$])	$R1 = 0.0175$, $wR2 = 0.0435$
R indices (for 2732 reflections)	$R1 = 0.0200$, $wR2 = 0.0441$
Weighting scheme	$w^{-1} = \sigma^2(F_o)^2 + a(P)^2 + b(P)^2$, where $P=[\max(F_o^2)+ 2F_c^2]/3$ a = 0.0233, b = 0.1331
Extinction coefficient	0.0292(15)
Largest diff. peak and hole	0.430 and -0.366 e. Å^{-3}

Table 8 Bond lengths (Å) of non-hydrogen atoms for [Ag(ettu)$_3$Cl].

Atom	Bond length (Å)
Ag-S(1)	2.5321(3)
Ag-S(1)#1	2.5321(3)
Ag-S(2)	2.5910(4)
Ag-Cl	2.6841(4)
S(1)-C(1)	1.724(1)
S(2)-C(2)	1.713(2)
C(1)-N(11)	1.324(2)
C(1)-N(12)	1.325(2)
C(2)-N(21)	1.331(2)
C(2)-N(22)	1.323(2)
N(11)-C(11)	1.466(2)
N(21)-C(21)	1.467(2)
C(11)-C(12)	1.514(2)
C(21)-C(22)	1.490(3)

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

Table 9 Bond angles (°) of non-hydrogen atoms for [Ag(ettu)$_3$Cl].

Atom	Angle (°)
S(1)#1-Ag-S(1)	114.15(2)
S(1)#1-Ag-S(2)	107.13(1)
S(1)-Ag-S(2)	107.13(1)
S(1)#1-Ag-Cl	110.35(1)
S(1)-Ag-Cl	110.35(1)
S(2)-Ag-Cl	107.41(1)
C(1)-S(1)-Ag	108.05(4)
C(2)-S(2)-Ag	112.37(6)
N(11)-C(1)-N(12)	119.4(1)
N(11)-C(1)-S(1)	121.93(9)
N(12)-C(1)-S(1)	118.6(1)
N(22)-C(2)-N(21)	118.9(2)
N(21)-C(2)-S(2)	119.2(1)
N(22)-C(2)-S(2)	121.9(1)
C(1)-N(11)-C(11)	124.9(1)
C(2)-N(21)-C(21)	124.2(2)
N(11)-C(11)-C(12)	110.4(1)
N(21)-C(21)-C(22)	110.9(2)

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

Table 10 Torsion angles (°) for [Ag(ettu)$_3$Cl].

Atom	Angle (°)
S(1)#1-Ag-S(1)-C(1)	169.68(4)
S(2)-Ag-S(1)-C(1)	51.26(5)
Cl-Ag-S(1)-C(1)	-65.37(5)
S(1)#1-Ag-S(2)-C(2)	118.560(9)
S(1)-Ag-S(2)-C(2)	-118.560(9)
Cl-Ag-S(2)-C(2)	0.0
Ag-S(1)-C(1)-N(11)	-15.5(1)
Ag-S(1)-C(1)-N(12)	164.6(1)
Ag-S(2)-C(2)-N(22)	0.0
Ag-S(2)-C(2)-N(21)	180.0
N(12)-C(1)-N(11)-C(11)	-0.3(2)
S(1)-C(1)-N(11)-C(11)	179.8(1)
N(22)-C(2)-N(21)-C(21)	0.0
S(2)-C(2)-N(21)-C(21)	180.0
C(1)-N(11)-C(11)-C(12)	-177.6(2)
C(2)-N(21)-C(21)-C(22)	180.0

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

Table 11 Hydrogen bonds for [$Ag(ettu)_3Cl$] [Å and °].

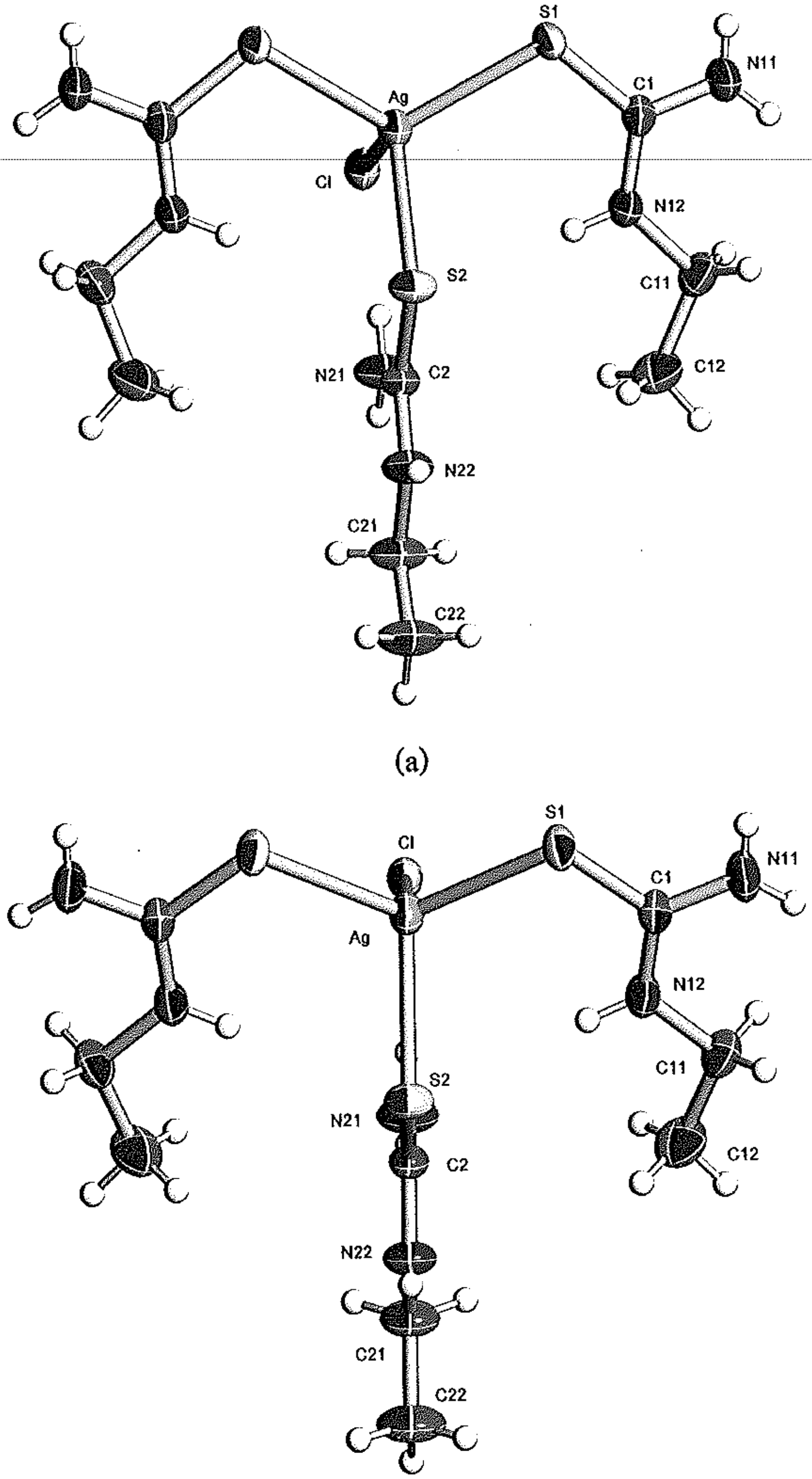
D-H...A	d(H...A)	d(D...A)	<(DHA)
N12-H12---Cl (1-x, 1/2+y, -z)	2.41(2)	3.218(1)	154(2)
N21-H21---Cl (x,y,1+z)	2.67(2)	3.484(2)	180(3)
N22-H22---Cl (x, 1/2-y, 1+z)	2.42(3)	3.275(2)	173(3)

Remark : A = acceptor atom

D = donor atom

d = the distance

< = the angle



(a)

(b)

Figure 39 The molecular plot of [Ag(ettu)$_3$Cl]: (a) All atoms of molecule and (b) The mirror plane in molecule via Ag,Cl, N21, N22, C21, and C22.

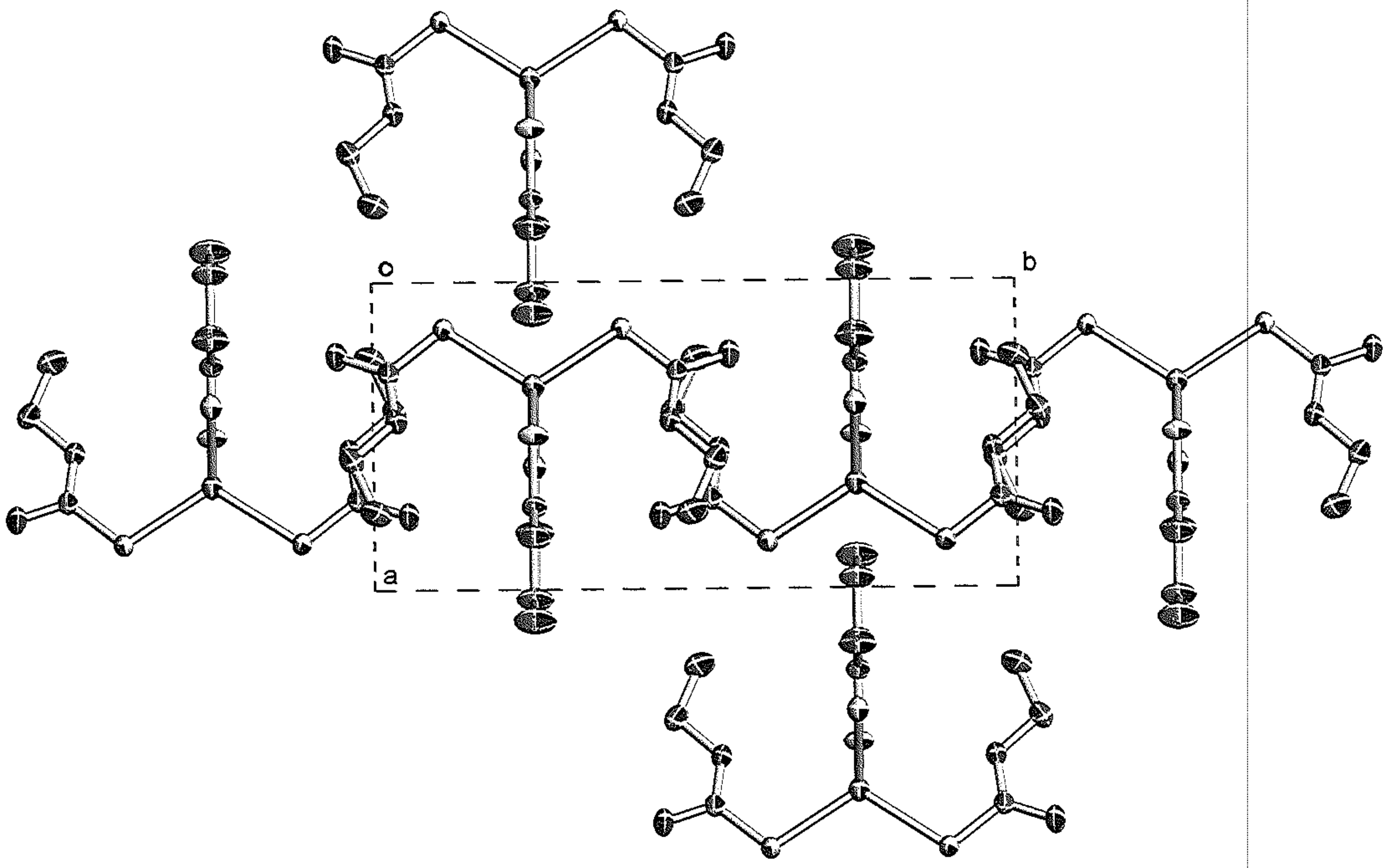


Figure 40 The unit cell contents of $[Ag(ettu)_3Cl]$ plotted down *c* axis .

Table 12 Crystal data and structure refinement for [Ag(ettu)$_3$Br].

Complex	[Ag(ettu)$_3$Br]	
Empirical formula	$C_9H_{24}AgBrN_6S_3$	
Formula weight	500.30	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2$_1$/*m* (No. 11)	
Unit cell dimensions	a = 7.295(2) Å	α = 90°
	b = 15.502(3) Å	β = 91.49(3)°
	c = 8.281(2) Å	γ = 90°
Volume	936.2(3) Å^3	
Z	2	
Density (calculated)	1.775 g/cm^3	
Absorption coefficient	3.545 mm^{-1}	
F(000)	500	
Crystal size	0.4 x 0.3 x 0.2 mm^3	
θ range for data collection	2.46 to 37.63°	
Index ranges	-12<=h<=12, 0<=k<=26, 0<=l<=14	
Reflections collected	5076	
Independent reflections	5076 [*R*(int) = 0.0000]	
Completeness to θ = 37.63°	99.1 %	
Absorption correction	Semi-empirical from equivalents	

Table 12 (continued)

Max. and min. transmission	0.490 and 0.292
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5076 / 0 / 156
Goodness-of-fit on F^2	0.956
Final R indices (for 4069 reflections[$I>2\sigma(I)$])	$R1 = 0.0234$, $wR2 = 0.0501$
R indices (for 5076 reflections)	$R1 = 0.0342$, $wR2 = 0.0524$
Weighting scheme	$w^{-1} = \sigma^2(F_o)^2 + a(P)^2$,
	where P=[max (F_o^2)+ $2F_c^2$]/3
	a = 0.0285
Extinction coefficient	0.0001(3)
Largest diff. peak and hole	0.907 and -0.828 e. Å $^{-3}$

Table 13 Bond lengths (Å) of non-hydrogen atoms for [Ag(ettu)$_3$Br]

Atom	Bond length (Å)
Ag-S(1)#1	2.5260(5)
Ag-S(1)	2.5260(5)
Ag-S(2)	2.5784(8)
Ag-Br	2.7523(8)
S(1)-C(1)	1.720(1)
S(2)-C(2)	1.720(2)
C(1)-N(11)	1.327(2)
C(1)-N(12)	1.330(2)
C(2)-N(21)	1.330(2)
C(2)-N(22)	1.323(2)
N(11)-C(11)	1.469(2)
N(21)-C(21)	1.463(2)
C(11)-C(12)	1.516(2)
C(21)-C(22)	1.503(3)

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

Table 14 Bond angles (°) of non-hydrogen atoms for [Ag(ettu)$_3$Br]

Atom	Angle (°)
S(1)#1-Ag-S(1)	114.18(2)
S(1)#1-Ag-S(2)	108.21(2)
S(1)-Ag-S(2)	108.21(2)
S(1)#1-Ag-Br	108.68(1)
S(1)-Ag-Br	108.68(1)
S(2)-Ag-Br	108.75(2)
C(1)-S(1)-Ag	107.21(5)
C(2)-S(2)-Ag	112.84(6)
N(11)-C(1)-N(12)	119.1(1)
N(11)-C(1)-S(1)	122.44(9)
N(12)-C(1)-S(1)	118.5(1)
N(22)-C(2)-N(21)	118.9(2)
N(21)-C(2)-S(2)	119.3(1)
N(22)-C(2)-S(2)	121.8(1)
C(1)-N(11)-C(11)	124.6(1)
C(2)-N(21)-C(21)	124.4(2)
N(11)-C(11)-C(12)	110.5(1)
N(21)-C(21)-C(22)	110.3(2)

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

Table 15 Torsion angles (°) for [Ag(ettu)$_3$Br].

Atom	Angle (°)
S(1)#1-Ag-S(1)-C(1)	170.65(5)
S(2)-Ag-S(1)-C(1)	50.09(5)
Br-Ag-S(1)-C(1)	-67.85(5)
S(1)#1-Ag-S(2)-C(2)	117.89(1)
S(1)-Ag-S(2)-C(2)	-117.89(1)
Br-Ag-S(2)-C(2)	0.0
Ag-S(1)-C(1)-N(11)	-15.4(1)
Ag-S(1)-C(1)-N(12)	164.2(1)
Ag-S(2)-C(2)-N(22)	0.0
Ag-S(2)-C(2)-N(21)	180.0
S(1)-C(1)-N(11)-C(11)	178.7(1)
S(2)-C(2)-N(21)-C(21)	180.0
N(12)-C(1)-N(11)-C(11)	-0.9(2)
N(22)-C(2)-N(21)-C(21)	0.0
C(1)-N(11)-C(11)-C(12)	-177.3(2)
C(2)-N(21)-C(21)-C(22)	180.0

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

Table 16 Hydrogen bonds for [Ag(ettu)$_3$Br] [Å and °].

D-H...A	d(H...A)	d(D...A)	<(DHA)
N12-H12---Br (1-x, 1/2+y, -z)	2.55(2)	3.318(1)	156(2)
N21-H21---Br (x,y,1+z)	2.66(2)	3.508(2)	177(3)
N22-H22---Br (x, 1/2-y, 1+z)	2.51(2)	3.367(2)	175(2)

Remark : A = acceptor atom

D = donor atom

d = the distance

< = the angle

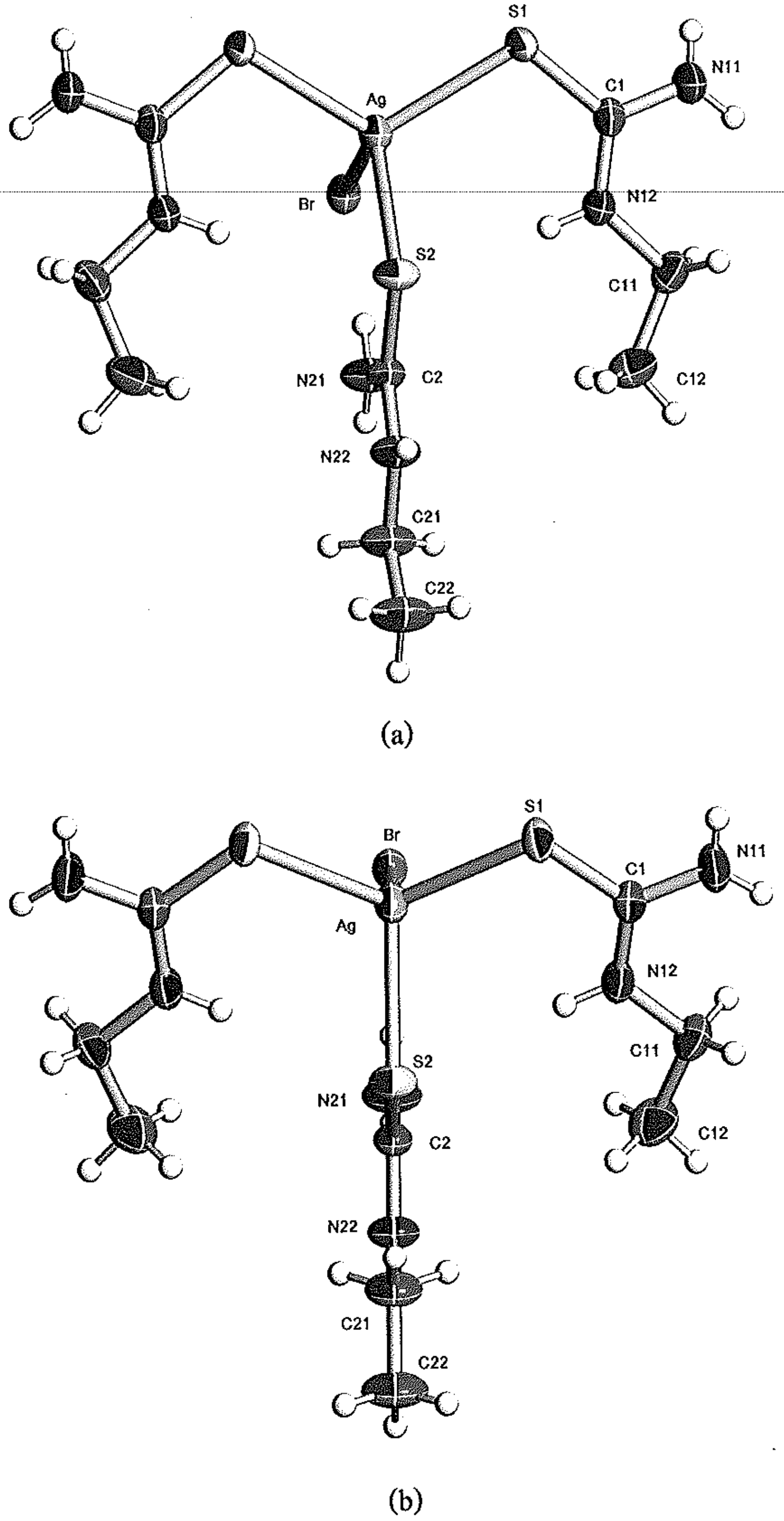


Figure 41 The molecular plot of [Ag(ettu)$_3$Br]: (a) All atoms of molecule and (b) The mirror plane in molecule via Ag, Br, N21, N22, C21, and C22.

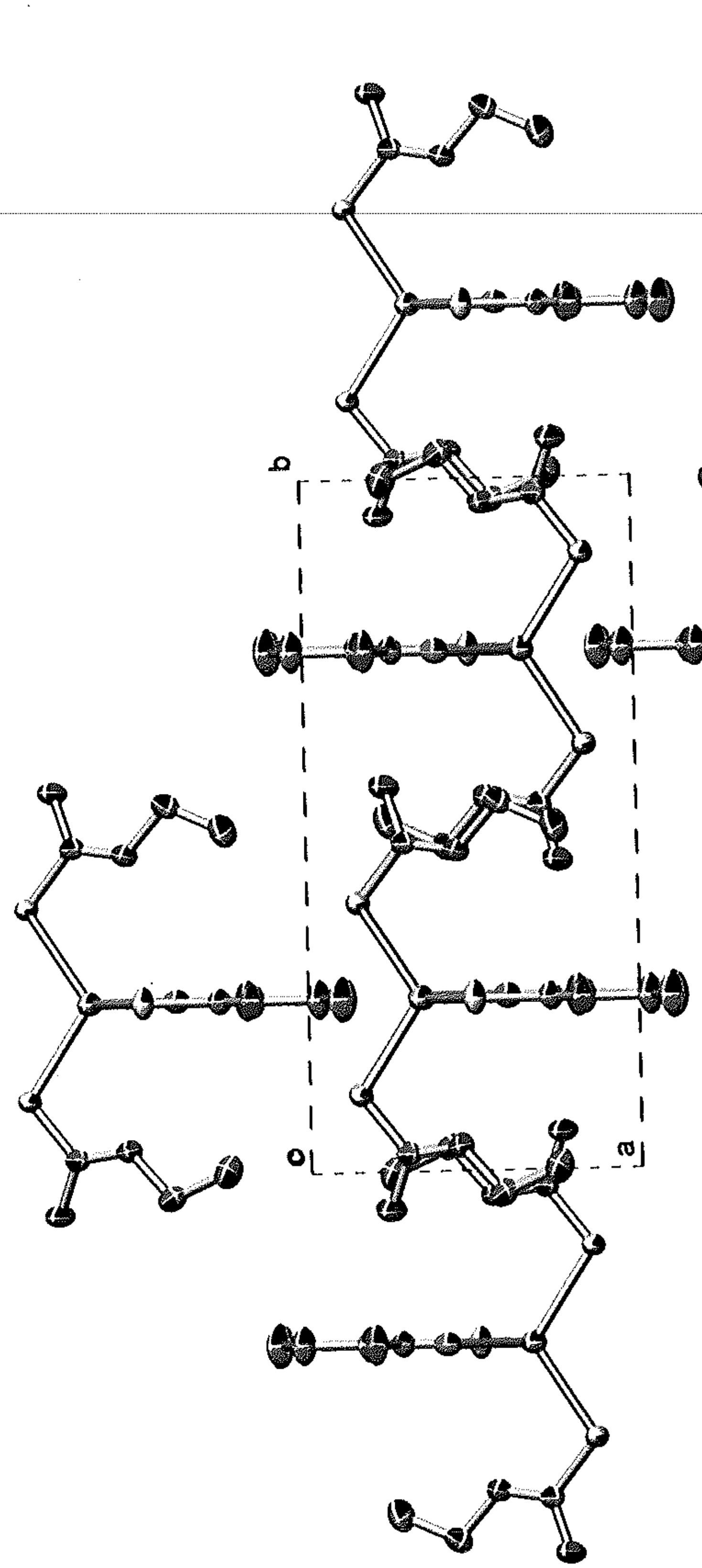


Figure 42 The unit cell contents of [Ag(ettu)$_3$Br] plotted down *c* axis.

Table 17 Crystal data and structure refinement for [Ag(detu)$_3$Br].

complex	[Ag(detu)$_3$Br]	
Empirical formula	$C_{15}H_{36}AgBrN_6S_3$	
Formula weight	584.46	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	*P*31*c* (No. 159)	
Unit cell dimensions	*a* = 12.5665(6) Å	α = 90°
	b = 12.5665(6) Å	β = 90°
	c = 9.5805(9) Å	γ = 120°
Volume	1310.2(2) Å^3	
Z	2	
Density (calculated)	1.481 g/cm^3	
Absorption coefficient	2.544 mm^{-1}	
F(000)	596	
Crystal size	0.4 x 0.3 x 0.2 mm^3	
θ range for data collection	1.87 to 28.29°	
Index ranges	-15<=h<=16, -15<=k<=16, -12<=l<=12	
Reflections collected	7843	
Independent reflections	2028 [R_{int} = 0.0329]	
Completeness to θ = 28.29°	98.9 %	
Absorption correction	Semi-empirical from equivalents	

Table 17 (continued)

Max. and min. transmission	0.600 and 0.494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2028 / 9 / 111
Goodness-of-fit on F^2	1.018
R indices (for 1538 reflections with $[I>2\sigma(I)]$)	$R_1 = 0.0339$, $wR_2 = 0.0764$
R indices (for all 2028 data)	$R_1 = 0.0506$, $wR_2 = 0.0849$
Weighting scheme	$w^{-1} = s^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2) + 2F_c^2]/3$ $a = 0.263$, $b = 0.1669$
Absolute structure (Flack) parameter	0.005(14)
Extinction coefficient	0.0099(12)
Largest diff. peak and hole	0.312 and -0.197 eÅ^{-3}

Table 18 Bond lengths (Å) of non-hydrogen atoms for [Ag(detu)$_3$Br].

Atom	Bond length (Å)
Ag-S(1)	2.583(1)
Ag-S(1)#1	2.583(1)
Ag-S(1)#2	2.583(1)
Ag-Br	2.6337(9)
S(1)-C(1)	1.707(5)
C(1)-N(1)	1.302(6)
C(1)-N(2A)	1.42(2)
C(1)-N(2B)	1.27(1)
N(1)-C(11)	1.45(1)
N(2A)-C(21A)	1.49(1)
N(2B)-C(21B)	1.48(1)
C(11)-C(12)	1.33(2)
C(21A)-C(22A)	1.16(2)
C(21B)-C(22B)	1.14(1)

Symmetry transformations used to generate equivalent atoms:

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

Table 19 Bond angles (°)of non-hydrogen atoms for $[Ag(detu)_3Br]$.

Atom	Angle (°)
S(1)#1-Ag-S(1)	111.86(3)
S(1)#1-Ag-S(1)#2	111.86(3)
S(1)-Ag-S(1)#2	111.86(3)
S(1)-Ag-Br	106.96(3)
S(1)#1-Ag-Br	106.96(3)
S(1)#2-Ag-Br	106.96(3)
C(1)-S(1)-Ag	109.9(2)
N(1)-C(1)-N(2A)	123.7(8)
N(2B)-C(1)-N(1)	112.4(6)
N(1)-C(1)-S(1)	121.5(4)
N(2A)-C(1)-S(1)	112.1(8)
N(2B)-C(1)-S(1)	125.2(5)
C(1)-N(1)-C(11)	124.8(6)
C(1)-N(2A)-C(21A)	122.7(13)
C(1)-N(2B)-C(21B)	132.1(9)
C(12)-C(11)-N(1)	109.2(13)
C(22A)-C(21A)-N(2A)	130(2)

Symmetry transformations used to generate equivalent atoms:

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

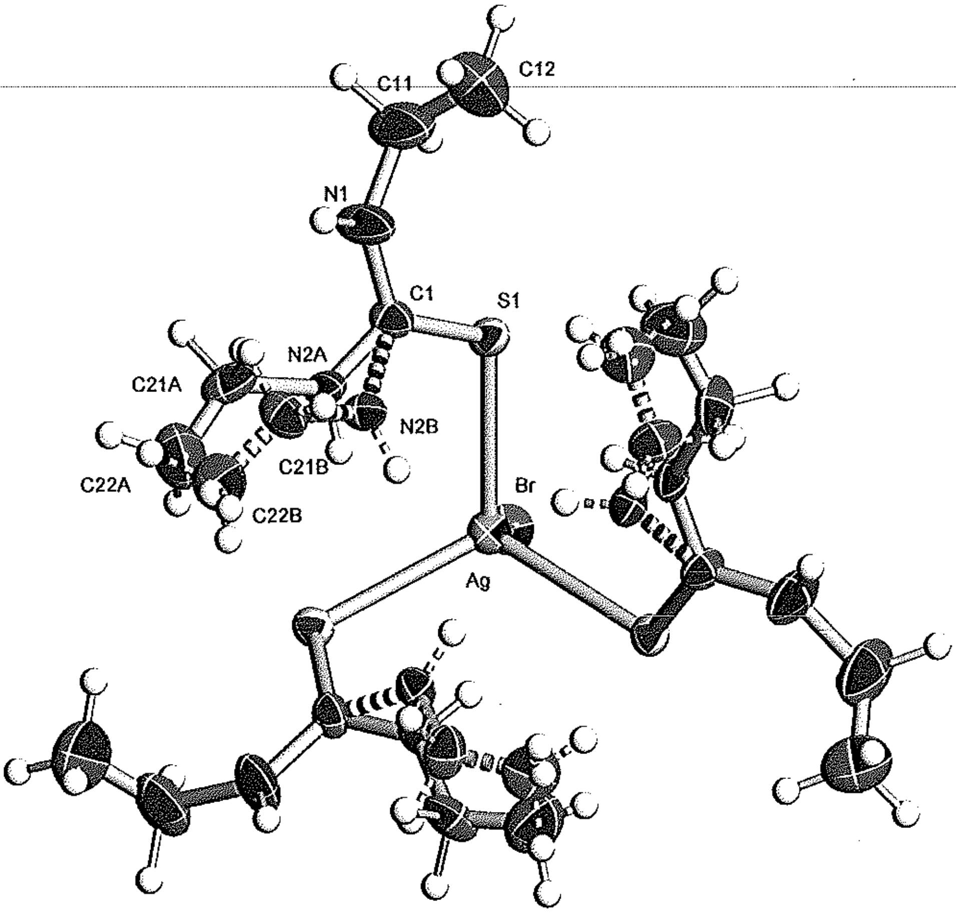


Figure 43 The molecular plot of [Ag(detu)$_3$Br] : the solid lines of N2A, C21A and C22A refer to the major position and the dash lines of N2B, C21B and C22B refer to the minor position.

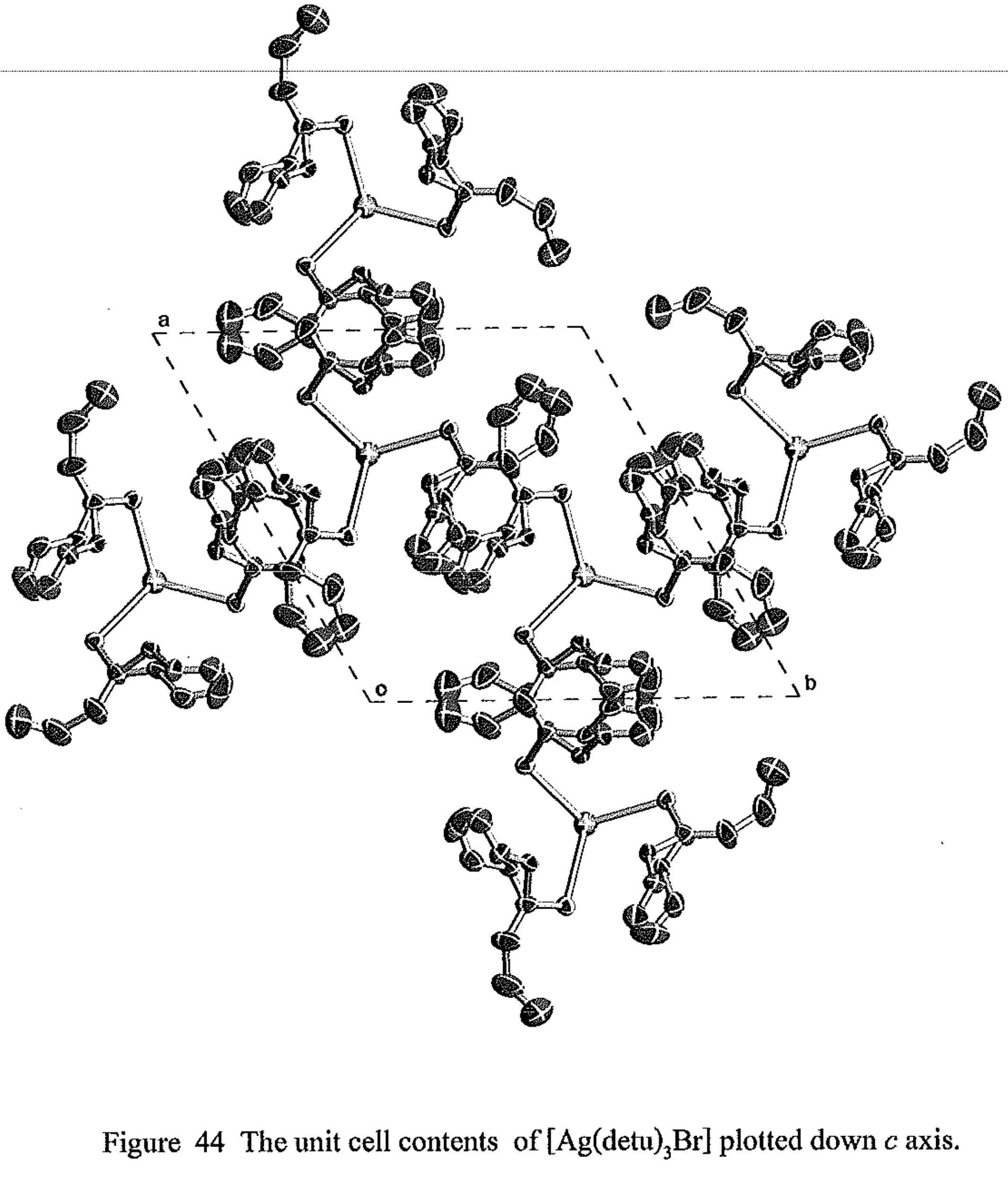


Figure 44 The unit cell contents of [Ag(detu)$_3$Br] plotted down *c* axis.

Table 20 Crystal data and structure refinement for $\{[Ag(detu)_3]_2SO_4\}$.

Complex	$\{[Ag(detu)_3]_2SO_4\}$.
Empirical formula	$C_{30}H_{72}Ag_2N_{12}O_4S_7$
Formula weight	1105.16
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	$R\bar{3}$ (No. 148)
Unit cell dimensions	$a = 12.3745(6)$ Å $\alpha = 90^\circ$
	$b = 12.3745(6)$ Å $\beta = 90^\circ$
	$c = 27.603(3)$ Å $\gamma = 120^\circ$.
Volume	3660.5(4) Å ^{3}
Z	3
Density (calculated)	1.504 g/cm^3
Absorption coefficient	1.147 mm^{-1}
F(000)	1722
Crystal size	0.50 x 0.40 x 0.30 mm^3
θ range for data collection	2.04 to 28.24°
Index ranges	-15<=h<=15, -15<=k<=16, -35<=l<=35
Reflections collected	10752
Independent reflections	1991 [R(int) = 0.0172]
Completeness to $\theta = 28.24^\circ$	98.3 %
Absorption correction	Semi-empirical from equivalents

Table 20 (continued)

Max. and min. transmission	0.710 and 0.661
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1991 / 0 / 99
Goodness-of-fit on F^2	1.062
Final R indices (for 1845 reflections[$I>2\sigma(I)$])	$R1 = 0.0586$, $wR2 = 0.1641$
R indices (for 1991 reflections)	$R1 = 0.0620$, $wR2 = 0.1685$
Weighting scheme	$w^{-1} = \sigma^2(F_o)^2 + a(P)^2 + b(P)^2$, where $P=[\max(F_o^2) + 2F_c^2]/3$ a = 0.098, b = 18.910
Extinction coefficient	0.0001(2)
Largest diff. peak and hole	1.673 and -0.555 e. Å $^{-3}$

Table 21 Bond lengths (Å) of non-hydrogen atoms for $\{[Ag(detu)_3]_2SO_4\}$.

Atom	Bond length (Å)
Ag(1)-S(1)	2.468(1)
Ag(1)-S(1)#1	2.468(2)
Ag(1)-S(1)#2	2.468(2)
Ag(1)-Ag(1)#3	3.286(1)
S(1)-C(1)	1.701(5)
C(1)-N(1)	1.289(7)
C(1)-N(2)	1.352(7)
N(1)-C(11)	1.46(1)
N(2)-C(21)	1.445(9)
C(11)-C(12)	1.48(1)
C(21)-C(22)	1.38(1)
S(2)-O(1A)	1.453(9)
S(2)-O(1A)#4	1.453(8)
S(2)-O(1A)#5	1.453(8)
S(2)-O(1A)#6	1.453(9)
S(2)-O(1A)#7	1.453(8)
S(2)-O(1A)#8	1.453(8)
S(2)-O(1B)	1.47(1)
S(2)-O(1B)#4	1.47(1)
S(2)-O(1B)#5	1.47(1)
S(2)-O(1B)#6	1.47(1)
S(2)-O(1B)#7	1.47(1)

Table 21 (continued)

Atom	Bond length (Å)
S(2)-O(1B)#8	1.47(1)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x+1,z #2 -y+1,x-y,z #3 -x+4/3,-y+2/3,-z+2/3

#4 y,-x+y,-z+1 #5 -y,x-y,z #6 -x,-y,-z+1

#7 -x+y,-x,z #8 x-y,x,-z+1

Table 22 Bond angles (°)of non-hydrogen atoms for {$[Ag(detu)_3]_2SO_4$}.

Atom	Angle (°)
S(1)#1-Ag(1)-S(1)	118.85(1)
S(1)#1-Ag(1)-S(1)#2	118.85(1)
S(1)#2-Ag(1)-S(1)	118.85(1)
S(1)#1-Ag(1)-Ag(1)#3	96.20(3)
S(1)#2-Ag(1)-Ag(1)#3	96.20(3)
S(1)-Ag(1)-Ag(1)#3	96.20(3)
C(1)-S(1)-Ag(1)	105.5(2)
C(1)-N(1)-C(11)	125.1(5)
C(1)-N(2)-C(21)	124.9(6)
N(1)-C(1)-N(2)	119.4(5)
N(1)-C(1)-S(1)	122.2(4)
N(2)-C(1)-S(1)	118.3(4)
N(1)-C(11)-C(12)	113.6(7)
N(2)-C(21)-C(22)	114.9(8)
O(1A)#4-S(2)-O(1A)#5	180.000(2)
O(1A)#4-S(2)-O(1A)	63.1(3)
O(1A)#5-S(2)-O(1A)	116.9(3)
O(1A)#4-S(2)-O(1A)#6	116.9(3)
O(1A)#5-S(2)-O(1A)#6	63.1(3)
O(1A)-S(2)-O(1A)#6	180.000(1)
O(1A)#4-S(2)-O(1A)#7	63.1(3)
O(1A)#5-S(2)-O(1A)#7	116.9(3)

Table 22 (continued)

Atom	Angle (°)
O(1A)-S(2)-O(1A)#7	116.9(3)
O(1A)#6-S(2)-O(1A)#7	63.1(3)
O(1A)#4-S(2)-O(1A)#8	116.9(3)
O(1A)#5-S(2)-O(1A)#8	63.1(3)
O(1A)-S(2)-O(1A)#8	63.1(3)
O(1A)#6-S(2)-O(1A)#8	116.9(3)
O(1A)#7-S(2)-O(1A)#8	180.0(8)
O(1A)#4-S(2)-O(1B)#7	95.8(9)
O(1A)#5-S(2)-O(1B)#7	84.2(9)
O(1A)-S(2)-O(1B)#7	109.7(6)
O(1A)#6-S(2)-O(1B)#7	70.3(6)
O(1A)#7-S(2)-O(1B)#7	48.1(8)
O(1A)#8-S(2)-O(1B)#7	131.9(8)
O(1A)#4-S(2)-O(1B)#4	48.1(8)
O(1A)#5-S(2)-O(1B)#4	131.9(8)
O(1A)-S(2)-O(1B)#4	95.8(10)
O(1A)#6-S(2)-O(1B)#4	84.2(9)
O(1A)#7-S(2)-O(1B)#4	70.3(6)
O(1A)#8-S(2)-O(1B)#4	109.7(6)
O(1B)#7-S(2)-O(1B)#4	118.5(8)
O(1A)#4-S(2)-O(1B)#5	131.9(8)
O(1A)#5-S(2)-O(1B)#5	48.1(8)

Table 22 (continued)

Atom	Angle (°)
O(1A)-S(2)-O(1B)#5	84.2(9)
O(1A)#6-S(2)-O(1B)#5	95.8(10)
O(1A)#7-S(2)-O(1B)#5	109.7(6)
O(1A)#8-S(2)-O(1B)#5	70.3(6)
O(1B)#7-S(2)-O(1B)#5	61.5(8)
O(1B)#4-S(2)-O(1B)#5	180.000(7)
O(1A)#4-S(2)-O(1B)#8	84.2(9)
O(1A)#5-S(2)-O(1B)#8	95.8(9)
O(1A)-S(2)-O(1B)#8	70.3(6)
O(1A)#6-S(2)-O(1B)#8	109.7(6)
O(1A)#7-S(2)-O(1B)#8	131.9(8)
O(1A)#8-S(2)-O(1B)#8	48.1(8)
O(1B)#7-S(2)-O(1B)#8	180.0(5)
O(1B)#4-S(2)-O(1B)#8	61.5(8)
O(1B)#5-S(2)-O(1B)#8	118.5(8)
O(1A)#4-S(2)-O(1B)	70.3(6)
O(1A)#5-S(2)-O(1B)	109.7(6)
O(1A)-S(2)-O(1B)	48.1(8)
O(1A)#6-S(2)-O(1B)	131.9(8)
O(1A)#7-S(2)-O(1B)	84.2(9)
O(1A)#8-S(2)-O(1B)	95.8(9)
O(1B)#7-S(2)-O(1B)	61.5(8)

Table 22 (continued)

Atom	Angle (°)
O(1B)#4-S(2)-O(1B)	118.5(8)
O(1B)#5-S(2)-O(1B)	61.5(8)
O(1B)#8-S(2)-O(1B)	118.5(8)
O(1A)#4-S(2)-O(1B)#6	109.7(6)
O(1A)#5-S(2)-O(1B)#6	70.3(6)
O(1A)-S(2)-O(1B)#6	131.9(8)
O(1A)#6-S(2)-O(1B)#6	48.1(8)
O(1A)#7-S(2)-O(1B)#6	95.8(9)
O(1A)#8-S(2)-O(1B)#6	84.2(9)
O(1B)#7-S(2)-O(1B)#6	118.5(8)
O(1B)#4-S(2)-O(1B)#6	61.5(8)
O(1B)#5-S(2)-O(1B)#6	118.5(8)
O(1B)#8-S(2)-O(1B)#6	61.5(8)
O(1B)-S(2)-O(1B)#6	180.0(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x+1,z #2 -y+1,x-y,z #3 -x+4/3,-y+2/3,-z+2/3

#4 y,-x+y,-z+1 #5 -y,x-y,z #6 -x,-y,-z+1

#7 -x+y,-x,z #8 x-y,x,-z+1

Table 23 Torsion angles (°) for {[Ag(detu)$_3$]$_2$SO$_4$}.

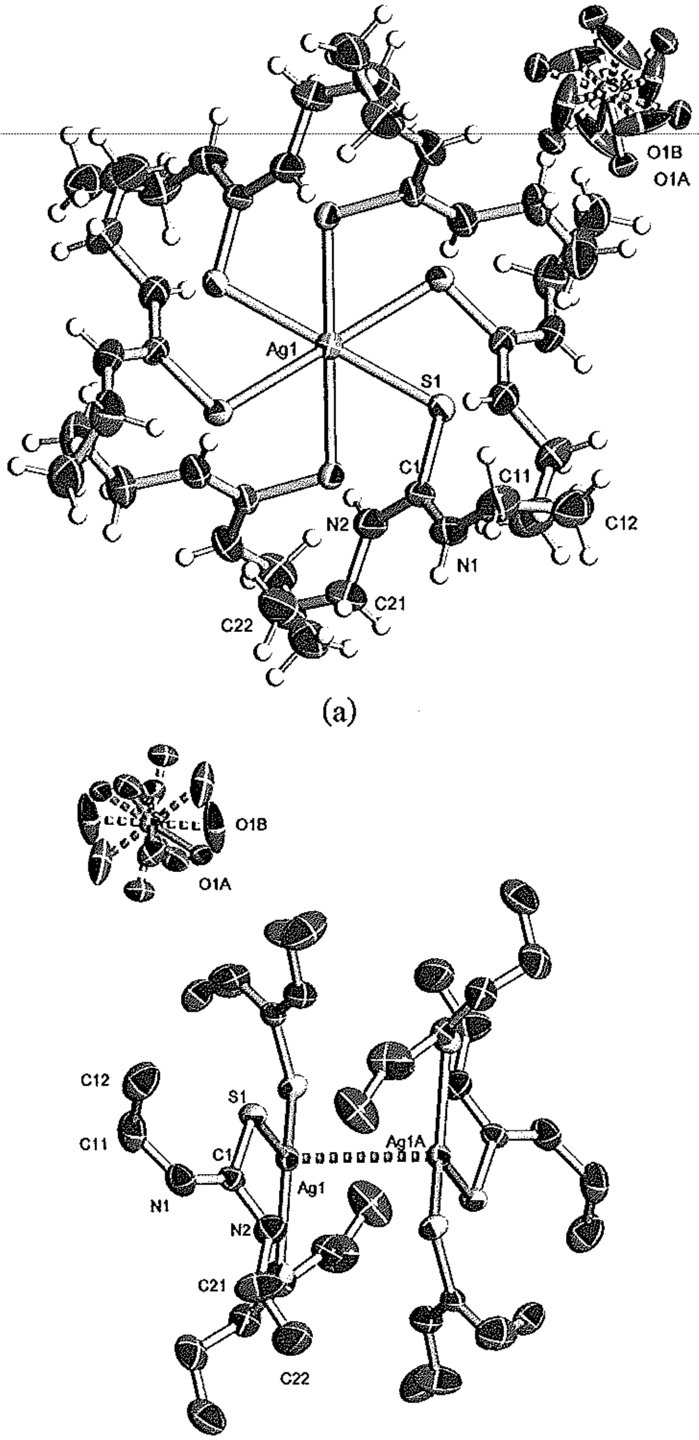
Atom	Angle (°)
Ag(1)-S(1)-C(1)-N(1)	-135.0(4)
Ag(1)-S(1)-C(1)-N(2)	45.5(4)
Ag(1)#3-Ag(1)-S(1)-C(1)	-97.7(2)
S(1)#1-Ag(1)-S(1)-C(1)	2.9(2)
S(1)#2-Ag(1)-S(1)-C(1)	161.7(2)
S(1)-C(1)-N(2)-C(21)	179.9(6)
C(11)-N(1)-C(1)-N(2)	-173.6(6)
C(11)-N(1)-C(1)-S(1)	7.0(9)
N(1)-C(1)-N(2)-C(21)	0.4(9)
C(1)-N(1)-C(11)-C(12)	-91.7(8)
C(1)-N(2)-C(21)-C(22)	160.6(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1,-x+1,z #2 -y+1,x-y,z #3 -x+4/3,-y+2/3,-z+2/3

#4 y,-x+y,-z+1 #5 -y,x-y,z #6 -x,-y,-z+1

#7 -x+y,-x,z #8 x-y,x,-z+1


(a)

(b)

Figure 45 (a) The molecular structure of $\{[Ag(detu)_3]_2SO_4\}$, plotted down *c* axis.

(b) The interaction between silver atoms.

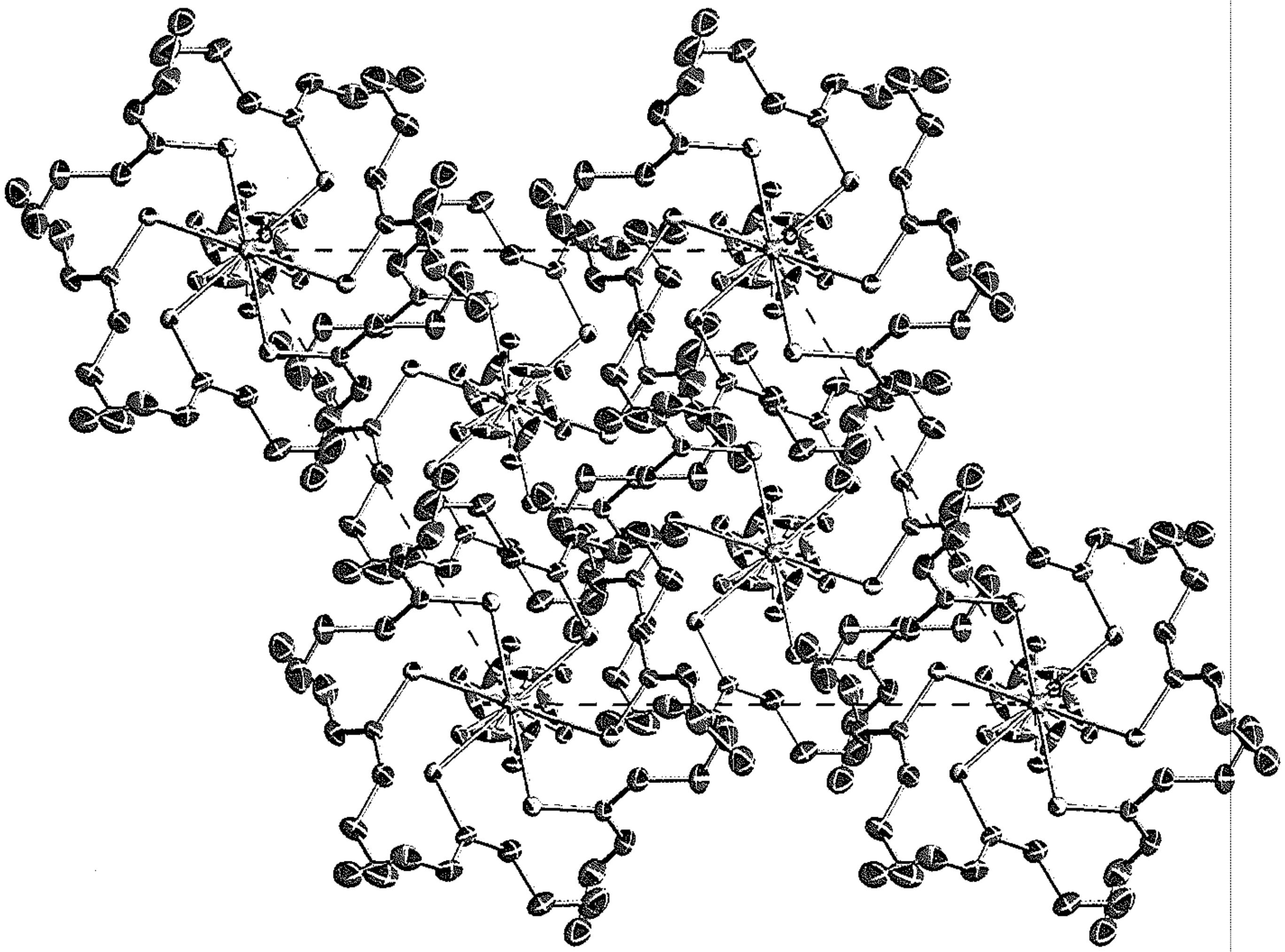


Figure 46 The unit cell contents of $[\{[Ag(detu)_3]_2SO_4\}$ plotted down *c* axis.

Table 24 Crystal data and structure refinement for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Complex	$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$
Empirical formula	$C_{24}H_{48}Ag_4N_{12}S_8$
Formula weight	1192.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$P4_2/n$ (No. 86)
Unit cell dimensions	$a = 18.3911(7)$ Å $\alpha = 90^\circ$.
	$b = 18.3911(7)$ Å $\beta = 90^\circ$
	$c = 6.2785(5)$ Å $\gamma = 90^\circ$
Volume	2123.6(2) Å ^{3}
Z	2
Density (calculated)	1.865 g/cm^3
Absorption coefficient	2.245 mm^{-1}
F(000)	1184
Crystal size	0.41 x 0.32 x 0.25 mm^3
θ range for data collection	1.57 to 28.29°
Index ranges	-24<=h<=20, -24<=k<=20, -8<=l<=8
Reflections collected	13056
Independent reflections	2585 [R(int) = 0.0223]
Completeness to $\theta = 28.29^\circ$	97.5 %
Absorption correction	Semi-empirical from equivalents

Table 24 (continued)

Max. and min. transmission	0.570 and 0.463
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2585 / 0 / 158
Goodness-of-fit on F^2	1.103
Final R indices (for 2170 reflections [$I>2\sigma(I)$])	$R1 = 0.0326$, $wR2 = 0.0792$
R indices (for 2585 reflections)	$R1 = 0.0408$, $wR2 = 0.0833$
Weighting scheme	$w^{-1} = \sigma^2(F_o)^2 + a(P)^2 + b(P)^2$, where $P=[\max(F_o^2)+ 2F_c^2]/3$ a = 0.0363, b = 1.2987
Extinction coefficient	0.00203(19)
Largest diff. peak and hole	0.629 and -0.389 e.Å $^{-3}$

Table 25 Bond lengths (Å) of non-hydrogen atoms for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Atom	Bond length (Å)
Ag(1)-S(1)	2.6190(7)
Ag(1)-S(1)#1	2.6190(7)
Ag(1)-S(1)#2	2.6190(7)
Ag(1)-S(1)#3	2.6190(7)
Ag(2)-S(1)	2.5644(7)
Ag(2)-S(1)#1	2.5644(7)
Ag(2)-S(1)#5	2.5644(7)
Ag(2)-S(1)#6	2.5644(7)
Ag(1)-Ag(2)#4	3.1393(3)
Ag(2)-Ag(1)#7	3.1393(2)
Ag(3)-S(3)	2.6210(8)
Ag(3)-S(3)#8	2.6210(8)
Ag(3)-S(3)#9	2.6240(8)
Ag(3)-S(3)#10	2.6240(8)
Ag(3)-Ag(3)#11	3.1392(3)
Ag(3)-Ag(3)#9	3.1393(2)
S(1)-C(1)	1.740(3)
S(3)-C(3)	1.664(3)
S(3)-Ag(3)#11	2.6240(8)
N(1)-C(1)	1.317(4)
N(1)-C(11)	1.471(4)
N(2)-C(1)	1.317(4)

Table 25 (continued)

Atom	Bond length (Å)
N(2)-C(21)	1.457(4)
N(3)-C(3)	1.142(4)
C(11)-C(12)	1.476(6)
C(21)-C(22)	1.492(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z #2 -y+1/2,x,-z+5/2 #3 y,-x+1/2,-z+5/2

#4 x,y,z+1 #5 y,-x+1/2,-z+3/2 #6 -y+1/2,x,-z+3/2

#7 x,y,z-1 #8 -x+3/2,-y+1/2,z #9 -y+1,x-1/2,z-1/2

#10 y+1/2,-x+1,z-1/2 #11 -y+1,x-1/2,z+1/2

Table 26 Bond angles (°)of non-hydrogen atoms for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Atom	Angle (°)
S(1)#1-Ag(1)-S(1)#2	112.34(2)
S(1)#1-Ag(1)-S(1)#3	112.34(2)
S(1)#2-Ag(1)-S(1)#3	103.87(3)
S(1)#1-Ag(1)-S(1)	103.87(3)
S(1)#2-Ag(1)-S(1)	112.34(2)
S(1)#3-Ag(1)-S(1)	112.34(2)
S(1)#1-Ag(1)-Ag(2)#4	128.06(2)
S(1)#2-Ag(1)-Ag(2)#4	51.94(2)
S(1)#3-Ag(1)-Ag(2)#4	51.94(2)
S(1)-Ag(1)-Ag(2)#4	128.06(2)
S(1)-Ag(2)-S(1)#5	110.70(2)
S(1)-Ag(2)-S(1)#1	107.05(3)
S(1)#5-Ag(2)-S(1)#1	110.70(2)
S(1)-Ag(2)-S(1)#6	110.70(2)
S(1)#5-Ag(2)-S(1)#6	107.05(3)
S(1)#1-Ag(2)-S(1)#6	110.70(2)
S(1)-Ag(2)-Ag(1)#7	126.48(2)
S(1)#5-Ag(2)-Ag(1)#7	53.52(2)
S(1)#1-Ag(2)-Ag(1)#7	126.48(2)
S(1)#6-Ag(2)-Ag(1)#7	53.52(2)
S(3)-Ag(3)-S(3)#8	106.56(4)
S(3)-Ag(3)-S(3)#9	110.99(1)

Table 26 (continued)

Atom	Angle (°)
S(3)#8-Ag(3)-S(3)#9	110.99(1)
S(3)-Ag(3)-S(3)#10	110.99(1)
S(3)#8-Ag(3)-S(3)#10	110.99(1)
S(3)#9-Ag(3)-S(3)#10	106.39(4)
S(3)-Ag(3)-Ag(3)#9	126.72(2)
S(3)#8-Ag(3)-Ag(3)#9	126.72(2)
S(3)#9-Ag(3)-Ag(3)#9	53.19(2)
S(3)#10-Ag(3)-Ag(3)#9	53.19(2)
S(3)-Ag(3)-Ag(3)#11	53.28(2)
S(3)#8-Ag(3)-Ag(3)#11	53.28(2)
S(3)#9-Ag(3)-Ag(3)#11	126.81(2)
S(3)#10-Ag(3)-Ag(3)#11	126.81(2)
Ag(3)#11-Ag(3)-Ag(3)#9	180.0
C(1)-S(1)-Ag(1)	110.30(9)
C(1)-S(1)-Ag(2)	103.31(9)
Ag(2)-S(1)-Ag(1)	74.54(2)
C(3)-S(3)-Ag(3)	96.5(1)
C(3)-S(3)-Ag(3)#11	96.1(1)
Ag(3)-S(3)-Ag(3)#11	73.53(2)
C(1)-N(1)-C(11)	126.8(3)
C(1)-N(2)-C(21)	125.5(3)
N(2)-C(1)-N(1)	119.0(3)

Table 26 (continued)

Atom	Angle (°))
N(1)-C(1)-S(1)	121.0(2)
N(2)-C(1)-S(1)	120.0(2)
N(1)-C(11)-C(12)	111.4(3)
N(2)-C(21)-C(22)	110.6(3)
N(3)-C(3)-S(3)	179.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z #2 -y+1/2,x,-z+5/2 #3 y,-x+1/2,-z+5/2

#4 x,y,z+1 #5 y,-x+1/2,-z+3/2 #6 -y+1/2,x,-z+3/2

#7 x,y,z-1 #8 -x+3/2,-y+1/2,z #9 -y+1,x-1/2,z-1/2

#10 y+1/2,-x+1,z-1/2 #11 -y+1,x-1/2,z+1/2

Table 27 Torsion angles (°) $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Atom	Angle (°)
S(1)#5-Ag(2)-S(1)-C(1)	-13.01(9)
S(1)#1-Ag(2)-S(1)-C(1)	107.73(9)
S(1)#6-Ag(2)-S(1)-C(1)	-131.5(1)
Ag(1)#7-Ag(2)-S(1)-C(1)	-72.27(9)
S(1)#5-Ag(2)-S(1)-Ag(1)	-120.732(9)
S(1)#1-Ag(2)-S(1)-Ag(1)	0.0
S(1)#6-Ag(2)-S(1)-Ag(1)	120.732(9)
Ag(1)#7-Ag(2)-S(1)-Ag(1)	180.0
S(1)#1-Ag(1)-S(1)-C(1)	-98.8(1)
S(1)#2-Ag(1)-S(1)-C(1)	139.6(1)
S(1)#3-Ag(1)-S(1)-C(1)	22.89(9)
Ag(2)#4-Ag(1)-S(1)-C(1)	81.2(1)
S(1)#1-Ag(1)-S(1)-Ag(2)	0.0
S(1)#2-Ag(1)-S(1)-Ag(2)	-121.655(9)
S(1)#3-Ag(1)-S(1)-Ag(2)	121.655(9)
Ag(2)#4-Ag(1)-S(1)-Ag(2)	180.0
S(3)#8-Ag(3)-S(3)-C(3)	94.4(1)
S(3)#9-Ag(3)-S(3)-C(3)	-144.6(1)
S(3)#10-Ag(3)-S(3)-C(3)	-26.6(1)
Ag(3)#11-Ag(3)-S(3)-C(3)	94.4(1)
Ag(3)#9-Ag(3)-S(3)-C(3)	-85.6(1)
S(3)#8-Ag(3)-S(3)-Ag(3)#11	0.0

Table 27 (continued)

Atom	Angle (°)
S(3)#9-Ag(3)-S(3)-Ag(3)#11	120.96(2)
S(3)#10-Ag(3)-S(3)-Ag(3)#11	-120.96(2)
Ag(3)#9-Ag(3)-S(3)-Ag(3)#11	180.0
C(21)-N(2)-C(1)-N(1)	3.8(5)
C(21)-N(2)-C(1)-S(1)	-176.4(3)
C(11)-N(1)-C(1)-N(2)	-178.5(3)
C(11)-N(1)-C(1)-S(1)	1.7(4)
Ag(2)-S(1)-C(1)-N(2)	-96.3(2)
Ag(1)-S(1)-C(1)-N(2)	-18.1(3)
Ag(2)-S(1)-C(1)-N(1)	83.5(2)
Ag(1)-S(1)-C(1)-N(1)	161.7(2)
C(1)-N(1)-C(11)-C(12)	93.1(4)
C(1)-N(2)-C(21)-C(22)	179.6(4)
Ag(3)-S(3)-C(3)-N(3)	154(28)
Ag(3)#11-S(3)-C(3)-N(3)	-132(28)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z #2 -y+1/2,x,-z+5/2 #3 y,-x+1/2,-z+5/2

#4 x,y,z+1 #5 y,-x+1/2,-z+3/2 #6 -y+1/2,x,-z+3/2

#7 x,y,z-1 #8 -x+3/2,-y+1/2,z #9 -y+1,x-1/2,z-1/2

#10 y+1/2,-x+1,z-1/2 #11 -y+1,x-1/2,z+1/2

Table 28 Hydrogen bonds for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ [Å and °].

D-H...A	d(H...A)	d(D...A)	<(DHA)
N1-H1---N3 (1-y, -1/2+x, 1/2+z)	2.14(3)	2.907(1)	156.3(1)

Remark : A = acceptor atom

D = donor atom

d = the distance

< = the angle

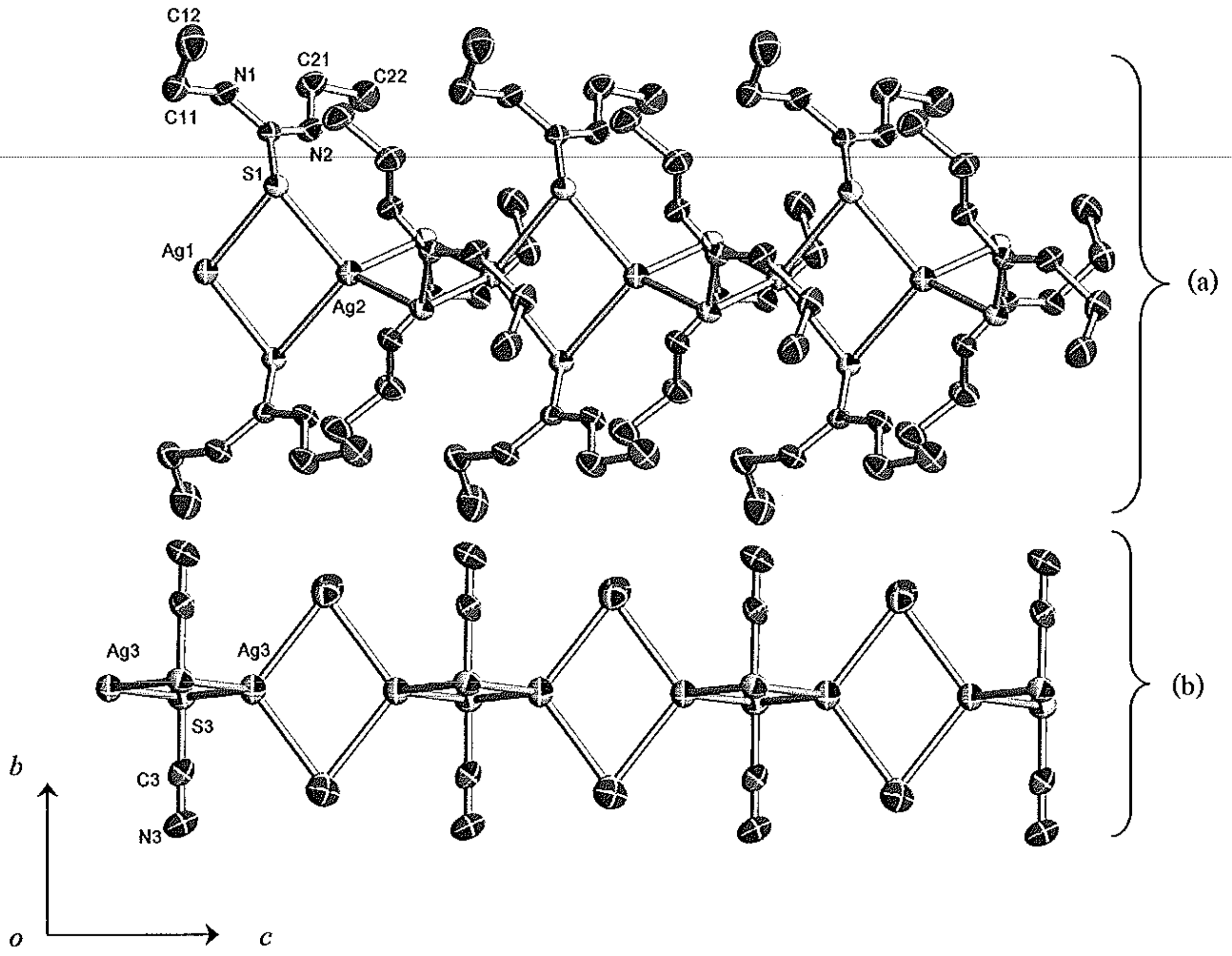


Figure 47 The polymeric structure of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ plotted parallel c axis ; polycation (a) and polyanion (b) (H atoms are omitted).

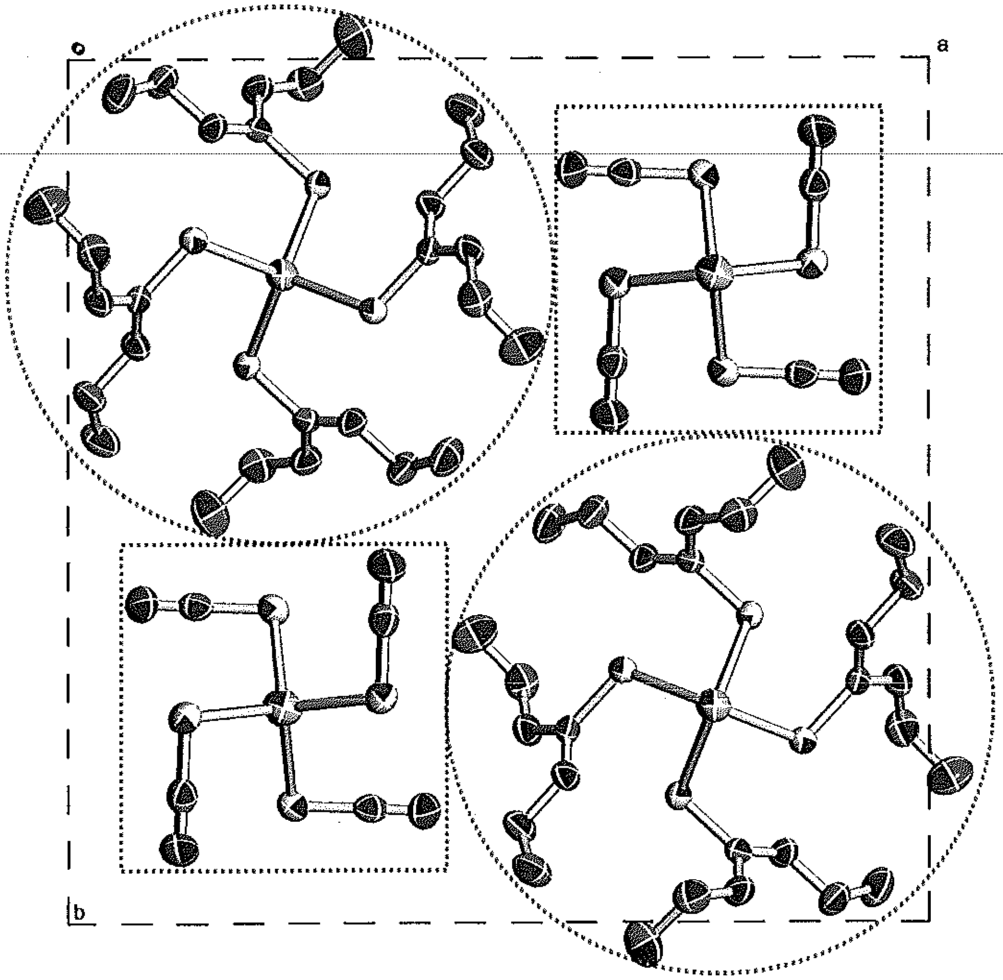


Figure 48 The unit cell contents of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ plotted down *c* axis; the unit cell consists of two chains (red dash circles) refer to cationic segments and two chains (blue dash boxes) refer to anionic segments.

Chapter 4

DISCUSSIONS

4.1 Preparation of silver(I) complexes

The research aims to study the structures of silver(I) complexes containing substituted thioureas such as ettu and detu by X-ray diffraction technique, all complexes must be single crystals. Thus the condition for preparing crystals must be appropriate for this objective. The preparation of these complexes have been carried out from direct reactions between silver(I) salts (AgCl, AgBr, Ag_2SO_4 and AgSCN) and ligands (ettu and detu) by varying reactants, mole ratio of reactants, solvent, reaction temperature and also the condition for crystallization of each complex. The suitable conditions for preparing all complexes are summarized in table 3 (Chapter 3).

In this research, five complexes of $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$, $[Ag(detu)_3Br]$, $\{[Ag(detu)_3]_2SO_4\}$ and $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ have been prepared and structurally determined by X-ray diffraction method for investigating the coordination geometries including the interactions that affect their geometries and crystal packing. The condition and product of each reaction could not be expected. The 1 : 3mole ratio of silver(I) salt and ligands gave the suitable crystals for $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$, $\{[Ag(detu)_3]_2SO_4\}$ and $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ complexes. While, the 1:4 mole ratio produced the suitable crystals of $[Ag(detu)_3Br]$ complex. Specially, the suitable temperature of reactions for synthesizing these silver(I) substituted thiourea complexes are always in the range 50-85 C^o because the silver(I) salts are not readily soluble in organic solvents. The solubility of compounds, called thermodynamic properties, and the nucleation and growth roles, called kinetic properties, affect the formation of their crystals. There are many factors involved in crystallization process, especially, the probability of this process depends upon the concentration of solute, the temperature, the nature of chemical species, the pH, the evaporation rate of solvent and other factors. To obtain crystals suitable for single crystal X-ray diffraction method, hence, these processes are significantly important and must not be negligible. The crystals of $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$, $[Ag(detu)_3Br]$ and $\{[Ag(detu)_3]_2SO_4\}$ have been carried out in organic solvent by slow evaporation of a single solvent. However, the crystals of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ complex has been achieved by using the mixture of solvents to adjust the solubility and to control the rate of solvent evaporation for the crystallization.

4.2 Elemental analysis

This method was utilized to indicate the quantitative composition of C, H, N and S in complexes. 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. These affect the higher or lower quantitative values of the results. Thus these factors must not be negligible. The experimental and calculated data are compared in table 6 (chapter 3).

4.3 X-ray fluorescence spectrometry

This method was used for checking the elemental composition of compounds such as Ag, S and halides (Cl and Br). It was only fundamentally qualitative analyses. The Ag, Cl and Br are represented for silver(I) salts, the K_α spectrum of Ag, Cl, and Br appear at 22.25, 2.63 and 11.92 keV, respectively. In addition, S atom is represented for substituted thioureas, ettu and detu ligands, and for some silver(I) salts such as Ag_2SO_4 and AgSCN. The K_α spectrum of sulfur is at 2.32 keV. The XRF spectra for all complexes are illustrated in figures 19-31.

4.4 Infrared spectroscopy

Characterization of complexes was mainly based on X-ray diffraction studies. Nevertheless, infrared spectroscopy is a good indicator of incorporation of metal ion and ligands into the complex systems. IR spectra were recorded on KBr discs in the region 4000-400 cm^{-1} on Perkin-Elmer Spectrum GX FT-IR spectrometer providing the information of the coordination mode of ligands. The infrared spectrum of isolated molecule is determined by arrangement of atoms in space and by the forces between atoms. When a ligand coordinated, all of these forces change. The changes are to be expected both in the vibrational spectral features associated with the free ligand and those systems to which it attached. Both ettu and detu ligands contain the thioamide group (NHCS) which may utilize either the thione form H-N-C=S or thiol form N=C-S-H. The salient feature of the solid state IR spectra of the compounds exhibit the dominance of thione form of these ligands, deduced by the presence of N-H stretching [ν(N-H)] at around 3400-3000 cm^{-1} region and by the absence of any evidence for S-H stretching [ν(S-H)] at approximately 2500-2600 cm^{-1} (Hadjikakou, *et al.*, 1991; Singh and Dikshit, 1995); thus, ligands in free state and their complexes adopt the thione form. They should give rise to four characteristic thioamide bands at wave number around 1510 (band I), 1320 (band II), 1000 (band III) and 750 (band IV) cm^{-1} (Bellany , *et al.*, 1996, quoted in Cox, 2000) with respect to ν(C-H)+ δ(N-H), ν(C=S)+ν(C=N)+ν(C-H), ν(C-N)+ν(C-S), and ν(C-S) mode of vibration, respectively.

In general thioamide bands are pronounced in the infrared spectra of these ligands and their complexes. Most of thioamide band II and III have contributions from ν(C-S) and ν(C-N) but the ν(C-S) stretching contributes more than the ν(C-N). These bands are difficult to decide the coordination site on the basis of the shift of these thioamide bands in some complexes. The main feature of the infrared spectra of the complexes is the major perturbation of thioamide band IV, in the region about 800 cm^{-1}. This is obviously indicative of thione sulfur coordination to metal.

The previous studies of infrared absorption spectra for some metal thiourea and substituted thioureas have been assigned as follows :

Yamaguchi, *et al.* investigated and assigned absorption bands of some metal thiourea complexes in 2-35 μ region based on the normal vibration calculation of thiourea molecule (Yamaguchi, *et al.,* 1958). Lane, *et al.* studied the infrared spectra of some metal methylthiourea complexes in the region 15 μ (200-1500 cm^{-1}) and assigned the mode of vibration of complexes as well as compared with free ligand (Lane, *et al.,* 1959). Singh and Dikshit characterized the molecular structures and studied the vibrational spectra of mixed ligand Cu(I) complexes containing triphenylphosphine, halide and *N,N'*-dimethyl-*N'*-phenylthiourea (dmptu), *N,N'*-dibutyl-*N'*-phenylthiourea (dbptH) and 1,3-thiazoliline-2-thione(tzdtH) (Singh and Dikshit,1995). All these ligands contain thioamide group (NHCS) with respect to four characterictic thioamide region namely I, II, III, and IV bands for 1500, 1300, 1000, and 800 cm^{-1}, respectively. The mode of vibration of these previous reports are selected and summarized in table 29.

Table 29 The previous studies of infrared absorption spectra for some metal thiourea and substituted thioureas.

Region (cm^{-1})	Mode of vibration	References
3000-3500	ν(N-H)	Yamaguchi, *et al.*, 1958
1600	$\delta(NH_2)$	
1500	ν_s(C-N)	
1400	δ(N-H)+ν(C=N)+ν(C=S)	
1100	ν(C-S)	
700	ν_s (C-N))+ν(C=S)	
3000	ν(N-H)	Lane, *et al.*, 1959
1600	$\delta(NH_2)$	
1550-1560	δ(N-H)+ν_{as}(C-N)	
1470-1490	δ(N-H)+ν_s(C-N)+ν(C=S)	
1300	ν_{as}(C-N)+δ(N-H)	
1100	ν(C-S)+ν(C-N)	
1000	ν(C-N)+ $\delta(NH_2)$+ν(C=S)	
800	ν(C=S)+ν_s (C-N))	
1500	ν(N-H)+δ(N-H)	Singh, *et al.*, 1995
1300	ν(C=S)+ν(C=N)+ ν(C-H)	
1000	ν(C-N)+ν(C-S)	
800	ν(C-S)	
1510	ν(N-H)+δ(N-H)	Bellany, *et al.*, 1996, quoted in Cox, 2000
1320	ν(C=S)+ν(C=N)+ ν(C-H)	
1000	ν(C-N)+ν(C-S)	
750	ν(C-S)	

Infrared spectroscopy of ettu, detu and its complexes

The infrared spectra of ettu and detu complexes are essentially restricted to the "thioamide band". The frequencies of absorption bands observed at the region 3000-3500 cm^{-1} can be assigned to N-H stretching vibrations. These bands of all silver(I) complexes appear at higher wave number than the free ligand is probably owing to the hydrogen bonding in complexes ; this suggests that N-H stretching [ν(N-H)] is somewhat difficult to vibrate in these complexes. The ν(N-H) of free ligands and their complexes are shown as follows :

Compound	ν(N-H) (cm^{-1})
ettu	3334, 3239, 3155
$[Ag(ettu)_3Cl]$	3400, 3342, 3277, 3184
$[Ag(ettu)_3Br]$	3401, 3275, 3186
detu	3234, 3094
$[Ag(detu)_3Br]$	3248, 3112
$\{[Ag(detu)_3]_2SO_4\}$	3243, 3110
$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$	3353, 3207, 3121

The bands observed near 1600 cm^{-1} region can be indicated to NH_2 bending vibration correspond to only ettu ligand and its complexes. Whilst, these absorptions disappear in detu molecule and its complexes due to the lack of NH_2 group in the molecules. These bands of ettu and its complexes are shown as follows :

Compound	$\delta(NH_2)$ (cm^{-1})
ettu	1636, 1625
$[Ag(ettu)_3Cl]$	1630
$[Ag(ettu)_3Br]$	1630

The strong bands observed at the region 1493–1595 cm^{-1} can be explained as thioamide band I, N-H bending [δ(N-H)] plus C-N antisymmetric stretching [ν_{as}(C-N)]. This band in free ettu molecule splits into two peaks at 1561 and 1543 cm^{-1} and in its complexes are observed at 1537 and 1493 cm^{-1} for both [$Ag(ettu)_3Cl$] and [$Ag(ettu)_3Br$] with 24 and 50 cm^{-1} significantly decreased, respectively. Consequently, the decrease in the C-N stretching frequencies due to the intra- and inter-molecular hydrogen bonding effects between H atom on N atom and halides (Cl and Br). These factors will be probably reduce the increasing double bond character of C-N in complexes.

For complexes of detu ligand, the absorption spectra of δ(N-H) bending in [$Ag(detu)_3Br$] appear at 1568 cm^{-1} . This observation can be attributed to the nature of N-H rocking. While this band of {[$Ag(detu)_3]_2SO_4$} shift to higher frequency by 3 cm^{-1} ; resulted in a short contact between Ag atoms in cation [$Ag(detu)_3]^+$. Besides, the bands of ν(C-N) observed at 1509 and 1508 cm^{-1} for [$Ag(detu)_3Br$] and {[$Ag(detu)_3]_2SO_4$} are lower than these of the detu free state. The decreasing frequencies of these complexes may be indicated to the inductive effect of the Br atoms and the disorder effect in [$Ag(detu)_3Br$] molecule and may be attributed to the short contact interaction between cations in {[$Ag(detu)_3]_2SO_4$} as well. The higher band of δ(N-H) in the $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ complex found at 1595 cm^{-1}. The increasing frequency is about 27 cm^{-1}, involving the bridging of sulfur atom bonded to adjacent silver atoms. Thus, nitrogen atom of detu ligands of the cationic complex, $\{[Ag_2(detu)_4]^{2+}\}_\infty$ close to another nitrogen atom led to the rigidity of vibration, which results the vibration mode of N-H rocking shifted to the higher frequencies. The decrement frequency of ν(C-N) band found at 1503 cm^{-1} is due to the hydrogen bonding interaction between H atoms bonded to N atoms from cationic chain and N atoms from thiocynate groups in anionic chain which reflect the single bond character of carbon to nitrogen in cationic part has been increased. In addition, the sharp absorption band at 2107 cm^{-1} can be attributed to C≡N bond stretching [ν(C≡N)] from anionic segment, $\{[Ag(SCN)_2]_2^{2-}\}_\infty$. The thioamide band I of ligands and their complexes are displayed as follows :

Compound	Thioamide band I (cm^{-1})	
	δ(N-H)	ν(C-N)
ettu	1561	1543
$[Ag(ettu)_3Cl]$	1537	1493
$[Ag(ettu)_3Br]$	1537	1493
detu	1568	1522
$[Ag(detu)_3Br]$	1568	1509
$\{[Ag(detu)_3]_2SO_4\}$	1569	1508
$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$	1595	1503

Moreover, the bands at region 1459-1474 cm^{-1} can be implied to C-N stretching. The absorption band of $[Ag(ettu)_3X]$, X = Cl and Br, rise to higher frequency by about 4 cm^{-1}. In $[Ag(detu)_3Br]$ complex, this band drops to lower position by about 12 cm^{-1}. This band of $\{[Ag(detu)_3]_2SO_4\}$ observed at the same position of free detu. In contrast to $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$, this band appears at the lower position by 11 cm^{-1}. For all free ligands and their complexes the absorption bands assigned at 1448-1450 cm^{-1} refer to CH_3 bending found at the same region.

The absorption spectra found at the region around 1246-1328 cm^{-1} have contributed to thioamide band II. Accordingly, modest sharp peak of ettu at 1307 and 1266 cm^{-1} that can be supported to ν(C=S) and ν(C=N), respectively. In its complexes, the first peak appears at 1292 cm^{-1} that move to the lower position by about 15 cm^{-1} for both $[Ag(ettu)_3Cl]$ and $[Ag(ettu)_3Br]$. Nevertheless, the another one change to higher region by 9-10 cm^{-1} in both complexes. This is owing to the decrease of double bond character in carbon-to-sulfur bond and the increase of double bond character in carbon-to-nitrogen bond. In detu ligand, the absorption band of V(C=S) splits into two peaks at 1328 and 1310 cm^{-1} appear at higher than its complexes. The sharp band observed at 1246 cm^{-1} in detu corresponds to the band of C-N antisymmetric stretching and NH-bending. In [Ag(detu)$_3$Br] and {[Ag(detu)$_3$]$_2$SO$_4$} complexes, these bands are increased by 3-9 cm^{-1}. This behavior illustrated the greater double bond character of carbon-to-nitrogen bond. This is due to the intermolecular hydrogen bonding from H atoms bonded to N atoms in $\{[Ag_2(detu)_4]\}_{\infty}^{+}$ cationic chain to N atom in the anionic chain. This factor is identified by X-ray data.

Compound	Thioamide band II (cm^{-1})	
	V (C=S)	V(C=N)
ettu	1307	1266
[Ag(ettu)$_3$Cl]	1292	1276
[Ag(ettu)$_3$Br]	1292	1275
detu	1328, 1310	1246
[Ag(detu)$_3$Br]	1313	1255
{[Ag(detu)$_3$]$_2$SO$_4$}	1312	1249
{[Ag$_2$(detu)$_4$][Ag(SCN)$_2$]$_2$}$_\infty$	1304	1245

Besides, a conspicuous band exhibited at 1142 and 1111 cm^{-1} for ettu ligand and at 1161 and 1137 cm^{-1} for detu ligand are also supported to C=S stretching. The stronger peak at 1142 cm^{-1} for all ettu complexes changed to lower position by 10 - 11 cm^{-1}. In contrast, another peak at 1111 cm^{-1} remains almost constant in this energy. However, in comparing with detu ligand and its complexes, all complexes of detu ligand show a weaker peak at the higher energy by about 2 - 8 cm^{-1} for both [Ag(detu)$_3$Br] and [Ag(detu)$_3$]$_2$SO$_4$}complexes, however, these peaks are absent for {[Ag$_2$(detu)$_2$](Ag(SCN)$_2$)$_2$}$_\infty$ complex.

The bands manifested at region 1010-1093 cm^{-1} can be indicated to the C-N stretching plus C-S stretching refer to thioamide band III but ν(C-S) dominates more than ν(C-N). This observation can be explained by considerably change in the nature of the nitrogen-to-carbon bond and the C=S bond on coordination of complexes. All complexes of ettu revealed at 1027 cm^{-1} that can be considered to the bands at 1032 and 1010 cm^{-1} of free ettu, which have been assigned to a vibration consisting of C-N stretching plus C-S stretching. The corresponding bands of these complexes have been found at the decrease frequency because of the dominant of the C-S stretching carbon-to-sulfur bond in these complexes. In contrast, these bands observed at 1093 and 1053 cm^{-1} of detu for which it is difficult to decide the coordination site of detu complexes from the shift of thioamide band III. The thioamide band III of compounds are given as follows :

Compound	Thioamide band III (cm^{-1}) ν(C-S) + ν (C-N)
ettu	1032, 1010
$[Ag(ettu)_3Cl]$	1027
$[Ag(ettu)_3Br]$	1027
detu	1093, 1053
$[Ag(detu)_3Br]$	1090, 1059
$\{[Ag(detu)_3]_2SO_4\}$	1049
$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$	1092, 1049

Finally, the vibration spectra assigned at about 800 cm^{-1}, attributed to C-S stretching refer to thioamide IV band. It is particularly affected with the bands in free ligands at 805 and 798 cm^{-1} for ettu and detu respectively replaced with a peak in the lower frequency for complexes. This is due to the C=S stretching motion become very small. The result of lower shift of all complexes can be compared with thioamide band IV of free ligands as shown in table below. Moreover the vibration band of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ at 717 cm^{-1} deduced the C-S stretching of thiocyanate group. The thioamide band IV of compounds are given as follows :

Compound	Thioamide band IV (cm^{-1}) ν(C-S)
ettu	805
$[Ag(ettu)_3Cl]$	799
$[Ag(ettu)_3Br]$	798
detu	798
$[Ag(detu)_3Br]$	795
$\{[Ag(detu)_3]_2SO_4\}$	796
$\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$	796

All infrared spectroscopic data are summarized in the table 30 for ettu ligand and its complexes and table 31 for detu ligand and its complexes.

Specially, the ionic complexes $\{[Ag(detu)_3]_2SO_4\}$ contains sulfate group, the IR spectrum show the band refer to ν(S-O) from SO_4^{2-} at 1109 and 621 cm^{-1}. The first band of this complex shifts to lower frequency and another one shifts to higher position compared with Ag_2SO_4 (1117 and 618 cm^{-1})(Appendix C). This may be owing to the disorder of SO_4^{2-} group in the complex. The spectrum of the ionic complex $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ consists of thiocyanate has been compared with simple thiocyanate, AgSCN. In simple thiocyanate, there are the $\nu(C\equiv N)$ stretching vibration at about 2102 and 2086 cm^{-1}, a ν(CS) stretching at about 719 cm^{-1} and a δ(SCN) band at about 456 cm^{-1}. In anionic part $\{[Ag(SCN)_2]_2^{2-}\}_\infty$,where SCN^- anion is S-bridging bonded, the V(C≡N) mode rise to 2107 cm^{-1}, the V(C-S) drop to 717 cm^{-1} and the bending mode of SCN is extremely weak and splits in to two peaks at 452 and 446 cm^{-1} (Appendix C) because N of thiocyanate group interact with hydrogen atom of the amide group in $\{[Ag_2(detu)_4]\}_\infty^+$ cationic part as a intermolecular hydrogen bonding.

Table 30 The infrared spectra of ettu ligand and its complexes

compounds	Bands							
	ν(NH)	$\delta(NH_2)$	ν(CN)+ $\nu(CH_3)$	ν(CS)	Thioamide bands			
					I	II	III	IV
ettu	3334	1636	1470	1142	1561	1307	1032	805
	3239	1625	1448	1111	1543	1266	1010	
	3155							
$[Ag(ettu)_3Cl]$	3400	1630	1474	1131	1537	1292	1027	799
	3342		1448	1109	1493	1276		
	3277							
	3184							
$[Ag(ettu)_3Br]$	3401	1630	1474	1130	1537	1292	1027	798
	3344		1448	1109	1493	1275		
	3275							
	3186							

Table 31 The infrared spectra of detu ligand and its complexes

compounds	Bands							
	ν(NH)	$\delta(NH_2)$	ν(CN)+ $\nu(CH_3)$	ν(CS)	Thioamide bands			
					I	II	III	IV
detu	3234	-	1471	1161	1568	1328	1093	798
	3094		1449	1137	1522	1310	1053	
						1246		
$[Ag(detu)_3Br]$	3248	-	1459	1169	1568	1313	1090	795
	3112		1450	1138	1509	1255	1059	
$\{[Ag(detu)_3]_2\ SO_3\}$	3243		1470	1165	1569	1312	1049	796
	3110		1450	1109	1508	1249		
$\{[Ag_2(detu)_2](Ag(SCN)_2)_2\}$	3353	-	1460	-	1595	1304	1092	796
	3207		1448	-	1503	1245	1049	
	3121							

4.2 Single crystal X-ray diffraction

Since the vast majority of X-ray crystallography is conducted to elucidate the molecular structures and it still be a major tool for studying hydrogen bonding interactions despite the well-known limitation of this technique in previously locating hydrogen atoms. Indeed, the relative strength of individual hydrogen bond can be inferred to the molecular arrangement in crystal structure.

Although hydrogen bonds are rather stronger than the other inter-molecular interactions, they are clearly weak bonds (typically < 10 kcal/mol)(Brammer, *et al.*, 1998). The hydrogen bond, D-H---A, is generally considered to comprise two components. A hydrogen atom is covalent bonded to an electronegative element, i.e., N, O, S or even C, known as the donor atom (D), lead to the polar D-H bond in which the hydrogen carries a partial positive charge. The hydrogen atom can then interact with an acceptor (A) ; A = halides (F, Cl, Br, I), O, N. The interaction is predominantly electrostatic forces. Thus, their effects can be anticipated to be quite sensitive to surroundings and the existence of the other hydrogen bonds lead to mutual distortion of molecular structure (Aullon, *et al.*, 1998; Brammer, *et al.*, 1999; Brammer, *et al.*, 2001; Rivas, *et al.*, 1998). In the previous work, Orpen and Martin (Orpen and Martin 1998) have shown recently even intra-molecular geometries in solid state such as covalent bond lengths, angles and so on, can be affected substantially by their molecular and crystal environment. Thus, the inter- and intramolecular interactions and other weak interactions are significantly important for the molecular arrangement.

In this work, the crystal structures of the complexes, intramolecular interactions and/or intermolecular interactions of $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$, $[Ag(detu)_3Br]$, $\{[Ag(detu)_3]_2SO_4\}$ and $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ have been determined, in order to gain an insight of the structures and also the interactions in the crystal. The crystal structures of the complexes are discussed as follows :

4.2.1 Description of the crystal structure of [Ag(ettu)$_3$Cl]

The monomeric complex of tris (*N*-ethylthiourea)chlorosilver(I), [Ag(ettu)$_3$Cl], consists of a silver central atom, which is tetragonally coordinated by three ettu molecules via sulfur atoms and by one chlorine atom. The silver-chlorine and one of ettu groups lie in the crystallographic mirror plane and the remaining two ligands are related by this plane. The distances of Ag-S(1) , Ag-S(2) and Ag-Cl are 2.5321(3), 2.5910(4) and 2.6841(4) Å, respectively; and the angles of S(1)-Ag-S(1)#1 [where #1 refer to crystallographic equivalent position, x, -y+1/2, z], S(1)-Ag-S(2), S(1)-Ag-Cl and S(2)-Ag-Cl are 114.15(1), 107.129(10), 110.35(1) and 107.41(1)°, respectively. The factor of intra- and intermolecular interactions of hydrogen bond in this complex (figure 49) affect the distorted tetrahedral coordination around silver atom. The hydrogen atoms involving these interactions (N-H---Cl) are orientated at the distances of 2.41(2) and 2.67(2)Å for inter-interaction for donor atoms (N12 and N21) and are located at a distance of 2.42(3)Å for intra-interaction for N22 donor atom. The corresponding angles of both inter- and intra-interactions N12-H12---Cl, N21-H21---Cl and N22-H22---Cl are 154(2), 180(3) and 173(3)°. The structure of this complex is shown in figures 39-40 and the crystallographic data are given in tables 7-11.

4.2.2 Description of the crystal structure of [Ag(ettu)$_3$Br]

The monomeric complex of tris(*N*-ethylthiourea)bromosilver(I), [Ag(ettu)$_3$Br], is isomorphous with [Ag(ettu)$_3$Cl] complex. The structure contains one silver atom, three ettu molecules and one bromine atom. The silver, bromine and one of ettu groups lie in the crystallographic mirror plane as well. The distances of Ag-S (1), Ag-S(2) and Ag-Br are 2.5260(5), 2.5784(8) and 2.7523(8) Å, respectively; and the angles of S(1)-Ag-S(1)#1, S(1)-Ag-S(2), S(1)-Ag-Br and S(2)-Ag-Br are 114.18(2), 108.21(2), 108.68(1) and 108.75(2)°, respectively. Like [Ag(ettu)$_3$Cl], the tetrahedral coordination around silver atom is distorted due to the factor of intra- and inter-molecular interactions of hydrogen bonds in complex. The hydrogen atoms, involving these interactions are situated at a distance of 2.53(2) and 2.66(2)Å for inter-interactions for donor atoms (N12 and N21) and oriented at a distance of 2.50 (2)Å for intra-interaction for N22 donor atom. The corresponding angles of both inter- and intra-interactions N12-H12---Br, N21-H21---Br and N22-H22---Br are 155(2), 177 (3) and 175(2)°, respectively. The structure of this complex is shown in figures 41-42 and the crystallographic data are given in tables 12-16.

Since both of these complexes are isomorphous structures, the bond lengths and bond angles of silver environment and also hydrogen bonding are compared in tables 32-34.

The significant difference of Ag-S(1), Ag-X (X = Cl, Br) distances including the angle difference of S(1)-Ag-S(1)#1 and S(1)-Ag-S(2) of [Ag(ettu)$_3$Br] compared with [Ag(ettu)$_3$Cl] may be due to the size of bromine is larger than chlorine atom (Van der Waals radii of Cl and Br are 1.80 and 1.95 Å (Ladd, 1994)). There are inter- and intra-molecular hydrogen bonds in [Ag(ettu)$_3$X], (X = Cl and Br) complexes as shown in figures 49–50. Each molecule interacts with other molecules by inter-hydrogen bonds, forming chains that run approximately along (001) plane.

Table 32 Bond lengths (Å) in isomorphous complexes [Ag(ettu)$_3$X], (X =Cl and Br).

Atomic Bond	Bond length (Å) (X= Cl)	Bond length (Å) (X = Br)
Ag-S(1)	2.5321(3)	2.5260(5)
Ag-S(1)#1	2.5321(3)	2.5260(5)
Ag-S(2)	2.5910(4)	2.5784(8)
Ag-X	2.6841(4)	2.7523(8)

Table 33 Bond angles (°) in isomorphous complexes [Ag(ettu)$_3$X], (X =Cl and Br).

Bond angle	Angle (°) (X= Cl)	Angle (°) (X = Br)
S(1)#1-Ag-S(1)	114.15(2)	114.18(2)
S(1)-Ag-S(2)	107.13(1)	108.21(2)
S(1)-Ag-X	110.35(1)	108.68(1)
S(2)-Ag-X	107.41(1)	108.75(2)

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

Table 34 Hydrogen bonds of inter- and intra-molecular interaction for isomorphous complexes $[Ag(ettu)_3X]$, (X =Cl and Br).

Hydrogen bonds	D-H---A	Distance (Å)		Angle (°)
		H---A	D---A	<(DHA)
Inter-molecular interaction	N12-H12---Cl N12-H12---Br (1-x, 1/2+y, -z)	2.41(2) 2.55(2)	3.218(1) 3.318(1)	154(2) 156(2)
	N21-H21---Cl N21-H21---Br (x,y,1+z)	2.67(2) 2.66(2)	3.484(2) 3.508(2)	180(3) 177(3)
Intra-molecular interaction	N22-H22---Cl N22-H22---Br (x, 1/2-y, 1+z)	2.42(3) 2.51(2)	3.275(2) 3.367(2)	173(3) 175(2)

Remark : A = acceptor atom (A = Cl and Br)

D = donor atom (D = N12, N21 and N22)

< = the angle

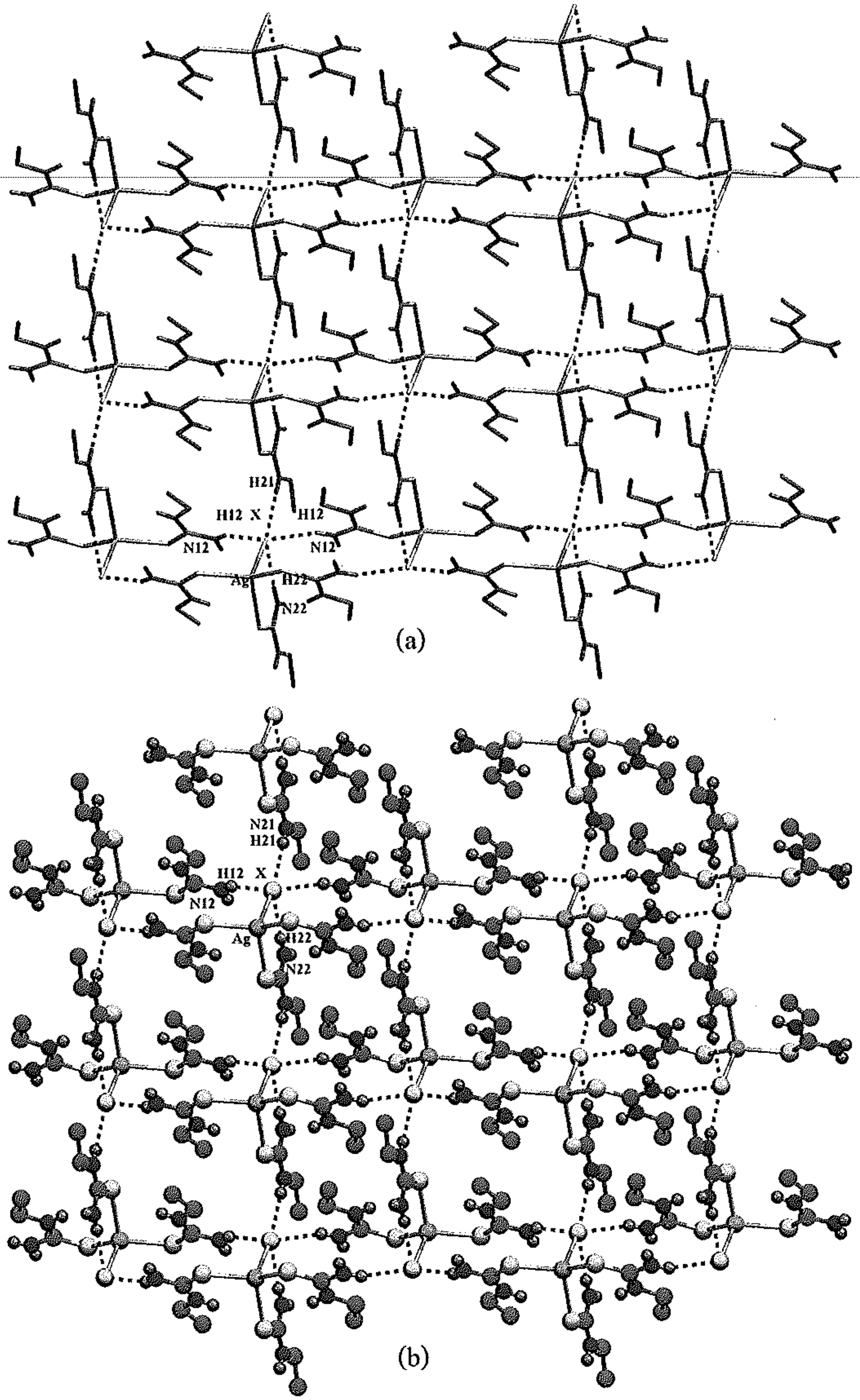


Figure 49 The inter- and intra-molecular interactions of hydrogen bonding in crystal packing structure of [Ag(ettu)$_3$X], (X =Cl and Br) : (a) capped stick plot and (b) ball and stick plot.

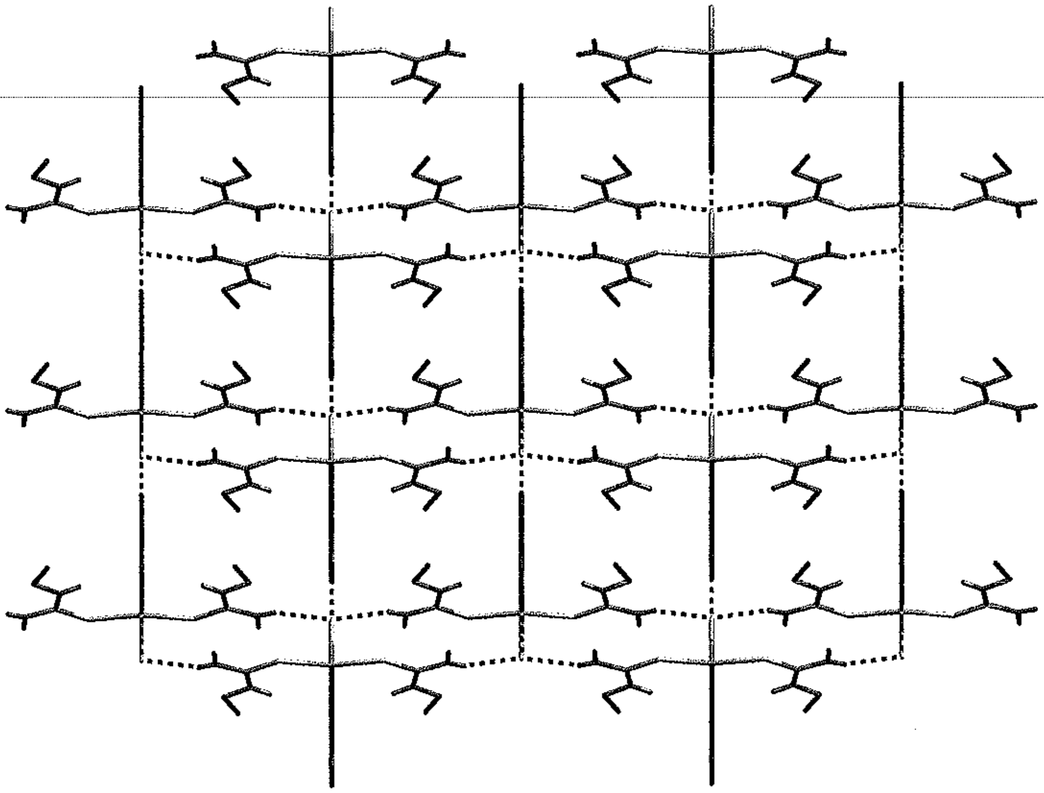


Figure 50 The other view of inter- and intra-molecular interactions of hydrogen bonding in crystal packing structure of [Ag(ettu)$_3$X], (X =Cl and Br) plotted down *c* axis forming the 2D chains along (001) plane.

4.2.3 Description of the crystal structure of [Ag(detu)$_3$Br]

The monomeric structure of tris(diethylthiourea)bromosilver(I), [Ag(detu)$_3$Br], is isomorphous with tris(diethylthiourea)iodosilver(I), [Ag(detu)$_3$I], that has been reported (Fun, *et al.* 1998). The molecule comprises three detu molecules and one bromine atom. The silver atom is tetrahedrally coordinated by three sulfur atoms from different detu molecules and one bromine atom. The metal is situated at a special position and lies on a crystallographic three fold axis which relates the three detu ligands, hence, all three Ag-S bonds are equal. The S1-Ag-S1#1 angle (#1, -x+y, -x+1, z), 111.86(3)°, is larger than the corresponding angle, 111.50(3)°, of the previous studied complex,[Ag(detu)$_3$I]. While the Ag-S1 distances 2.583(1) Å and the Ag-Br distance 2.6337(9) Å are shorter than the previous report iodide complex, (2.593(1) and 2.774(1) Å for Ag-S1 and Ag-I distances, respectively). This may be owing to the smaller size of bromine atom than the iodine atom which results in the enlargement of S1-Ag-S1#1 angle. Additionally, the N2-C21-C22 part is disordered, which can be spitted into two parts, N2A-C21A-C22A and N2B-C21B-C22B (A and B refer to the major position, 56.51%, and the minor position, 43.49%, respectively). The positions of all detu molecules are significantly far from Br atom. It is note that there is no significant hydrogen bonding involving the bromine and amide groups. The molecular and the unit cell plots are illustrated in figures 43-44. The figure 51 is given showing view plot similar to the tree.

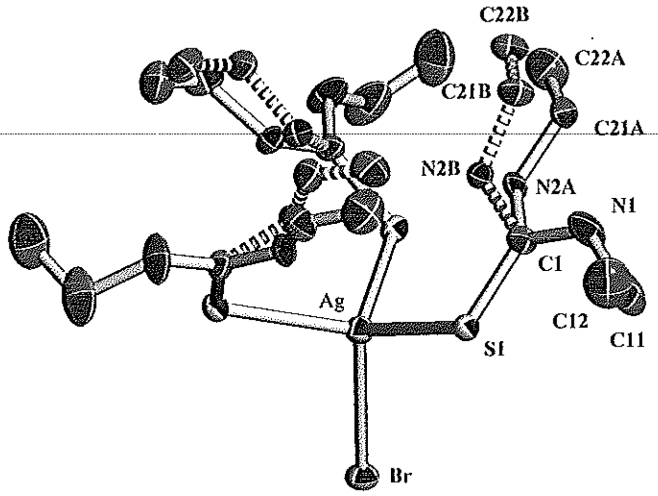


Figure 51 View of the tree, [Ag(detu)$_3$Br] showing disordered structure and H atoms are excluded for clarity (the dash line refer to the bond of the minor position)

4.2.4 Description of the crystal structure of {[Ag(detu)$_3$]$_2$SO$_4$]}

The ionic structure of bis(tris-diethylthiourea)silver(I) sulfate, {[Ag(detu)$_3$]$_2$-SO$_4$}, consists of two dependent [Ag(detu)$_3$]$^+$ cations with an inversion center between the two Ag atoms and a SO$_4^{2-}$ anion. The silver atom is trigonally coordinated by three sulfur atoms from different detu molecules, the symmetry is defined by space group $R\bar{3}$. Each cation is situated with silver atom on a crystallographic 3-fold axis. The distances of Ag(1)-S(1) is 2.468(1)Å, while S(1)-Ag(1)-S(1)#1 (#1, -x+y,-x+1,z) is equal to 118.85(1)°. It has been found experimentally that there is an inter-molecular non-bonded distance between pairs of silver atoms (Ag(1)---Ag(1)#1), 3.286(1)Å and the angle S(1)-Ag(1)-Ag(1)#1 is 96.40(10)°. This interaction and also steric effect of ligand molecules between two dependent cations affect slightly distorted trigonal-planar around silver atom of two cations. Consequently, the total angles around Ag1 is 356.6(1)°, result from the planarity distorted from ideal trigonal planar about 3.45°.

In addition, the factor from the disorder of sulfate anions close to one of three detu molecules also affect the distorted trigonal geometry of Ag ions. Furthermore, Ag(1) is located at lower and higher position from the trigonal planar of three sulfur atom of the ligands about 0.268 Å as shown in figure 52. The whole molecule plotted down *c* axis, the view of Ag(1)---Ag(1)#1 interaction and the unit cell plotted down *c* axis are illustrated in figures 45a, 45b and 46 respectively.

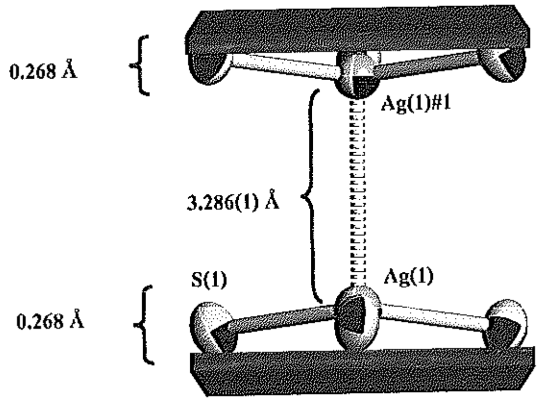


Figure 52 View of the orientation and the interaction distance of Ag(1) and Ag(1)#1 atom.

4.2.5 Description of the crystal structure of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$

The polymeric structure of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ consists of discrete cationic and anionic infinite chains. The $\{[Ag_2(detu)_4]^{2+}\}_\infty$ polycation is generated by infinite connecting of $\{[Ag_2(detu)_4]\}^{2+}$ dimeric units which half of dimers related by $\bar{4}$ axis, whereas the $\{[Ag(SCN)_2]_2^{2-}\}_\infty$ polyanion generated by infinite repeating dimeric units the $\{[Ag(SCN)_2]_2\}^{2-}$ which half of dimers related by twofold axis running along the Ag---Ag distance. Both cationic and anionic polymers run parallel to *c* axis as shown in figure 47. In cationic polymeric part the environment of each silver atom is described as slightly distorted tetrahedron bonded to four bridging sulfur atoms from detu molecules and each bridging atom shared with two adjacent silver atoms from detu molecules and each bridging atom shared with two adjacent silver atoms to form the one dimension infinite chain. Like in cationic part, local environment of each silver atom in anionic chain is described as a slightly distorted tetrahedron whereas it is coordinated and bridged by sulfur atoms from thiocyanate group. Previous structural work on silver(I) thiocyanate substituted systems is sparse. The complexes $Ag(tu)_2SCN$, tu = thiourea, was studied (Udupa, *et al.*,1976). The structure comprises a pair of –(NCS-Ag)(tu)(NCS-Ag)(tu) strings, linked together by inversion center to be a one-dimensional polymer. Each Ag atom is trigonal planar by two bridging thiourea sulfur atoms and one terminal S atom of thiocyanate ligand. One of the two thiourea S atoms is weakly coordinated to a second Ag center forming a dimeric complex, $[Ag(tu)_2SCN]_2$ unit. Unlike the reported silver(I) thiocyanato system as mentioned, each S atom of thiocyanate group act as bridging atom coordinated to two silver atoms with the Ag-S distances 2.6210(8) Å longer than Ag-S of terminal SCN group (2.608(2) Å). For the cationic polymeric part in this complex, each detu ligand bonded to silver ions via a bridging sulfur atom, The Ag-S distances 2.6190(7) Å for Ag(1)-S(1) and 2.5644(7) Å for Ag(2)-S(1) are longer than that found in S-terminal substituted thiourea ligands in this work such as $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$ and $\{[Ag(detu)_3]SO_4\}$ which are 2.5321(3), 2.5260(5) and 2.458(1) Å, respectively. There is the intermolecular hydrogen bonding of N-H---N type between H atom on one of N atoms from detu molecule of cationic segment and N atom from thiocyanate group of anion. This factor affects the distorted tetrahedral coordination around silver atoms in both cationic and anionic chains. The hydrogen atom, involving this interaction, N(1)-H(1)---N(3), is orientated at a distance of 2.14(3) Å from N(3). The corresponding angle is 156.(4)°. The molecular structure and the unit cell plots are depicted in figures 47-48 and the packing of hydrogen bonding plots are shown in figures 53 (a) and 53 (b).

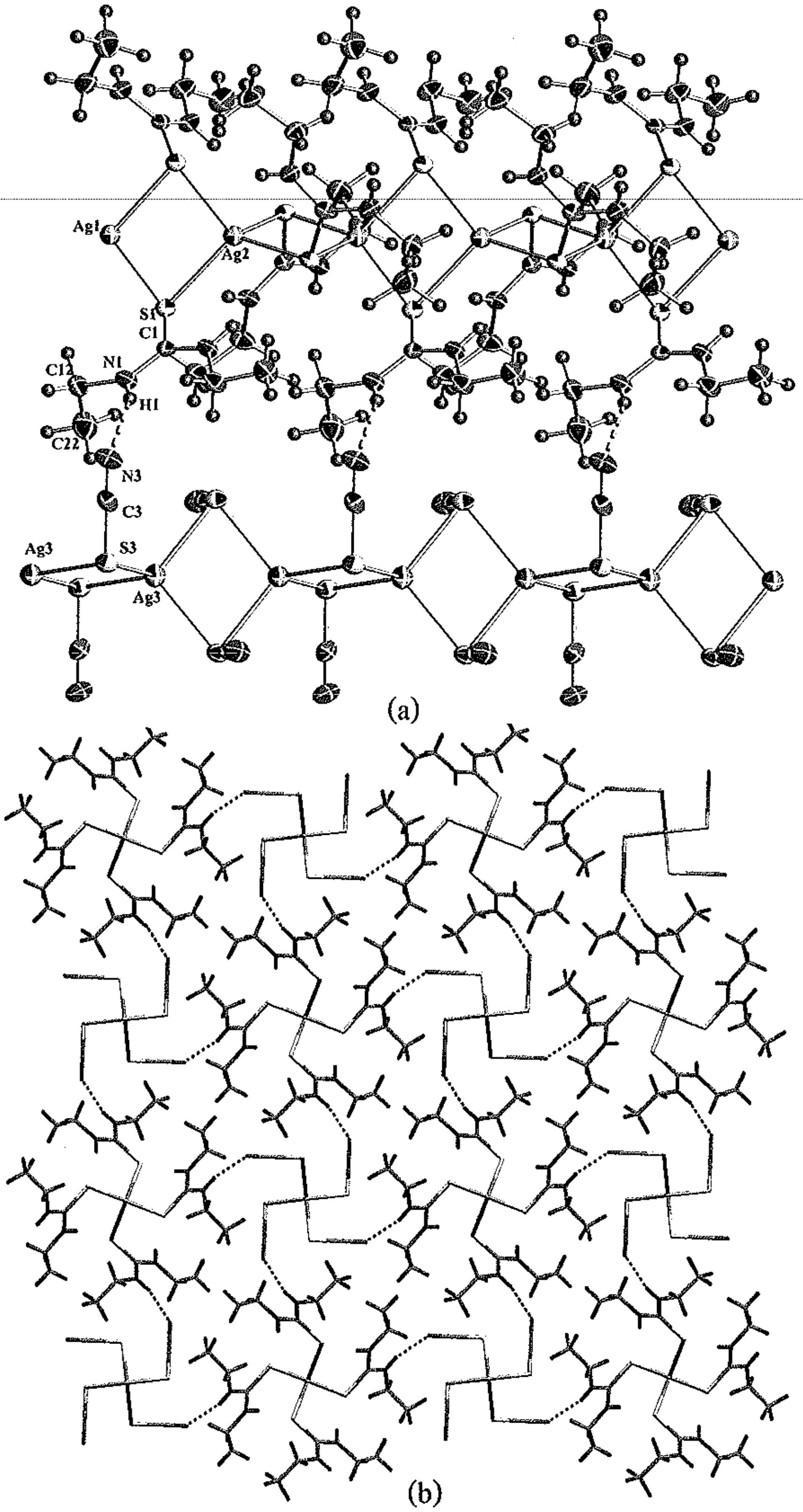


Figure 53 (a) The inter-molecular hydrogen bonding between cationic and anionic polymeric chains.

(b) The other view of hydrogen bonding depicted in (001) plane.

Chapter 5

CONCLUSION

Silver(I) salts form complexes in various stoichiometries and structural patterns with ettu and detu ligands. In this work, their complexes have been prepared and structurally characterized. They are neutral complexes, $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$ and $[Ag(detu)_3Br]$ and two ionic complexes $\{[Ag(detu)_3]_2SO_4\}$ and $\{[Ag_2(detu)_4]$-$[Ag(SCN)_2]_2\}_\infty$. In these complexes, the basic substituted thioureas are retained with S donor in the coordination sphere of silver. Characterization of the complexes was mainly based on X-ray diffraction studies. Nevertheless, infrared spectroscopy is a good indicator of incorporation of metal ion and ligands and other techniques were used in this work.

The crystal structures of $[Ag(ettu)_3Cl]$ and $[Ag(ettu)_3Br]$ are isomorphous. Both complexes crystallized in the monoclinic system with the space group $P2_1/m$. The R-factor for $[Ag(ettu)_3Cl]$ and $[Ag(ettu)_3Br]$ are 0.0175 for 2511 observed reflections and 0.0234 for 4069 observed reflections, respectively. Both structures are neutral monomers for which the coordination around silver is distorted tetrahedral and coordinated to three S terminal ettu ligands and halide atoms. The unit cell contains two discrete tetrahedral molecular structures and each molecule has a C_s symmetry via silver, halide and one of ettu groups. The crystal packing of these complexes have been involved the hydrogen bond system of metal-bound halides (this work refers to Cl and Br).

The monomeric complex of $[Ag(detu)_3Br]$ crystallized in a trigonal system, space group $P31c$, R = 0.0339 and $Rw2$ = 0.0764 for 1538 observed reflections. The structure is also a neutral monomer for which silver displays a tetrahedral environment bonded to three S terminal detu ligands and one Br atom with a crystallographic C_3 symmetry axis passes through silver and Br atoms. Additionally the $-NHCH_2CH_3$ group is disordered. The unit cell contains three discrete tetrahedral molecules.

The complex of $\{[Ag(detu)_3]_2SO_4\}$ crystallized in the hexagonal system, space group $R\bar{3}$. *R* and *Rw*2 are 0.0586 and 0.1641 for 1845 observed reflections. The structure consists of two dependent monomeric cation and one SO_4^{2-} counterion. This counterion presented in disordered fashion. The silver atom lies on a crystallogphic three fold axis with a trigonal planar geometry. The effect of non-bonding interaction between silver atoms of two cations lead to the trigonal planar around silver slightly distorted.

The ionic polymeric complex of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ crystallized in tetragonal system, space group $P4_2/n$, $R = 0.0326$ and $Rw2 = 0.792$ for 2170 observed reflections. Silver ions are tetrahedrally coordinated by bridging S atoms from detu molecules for cationic part and by bridging S atoms from thiocyanate groups for anionic part. Each part forms infinite covalent bond and lie in the parallel direction along c axis. Each cationic polymeric chain is closed to anionic chain forming hydrogen bonding network (N1-H1---N3) in three-dimension of crystal packing.

Moreover, the complexes have been studied by X-ray Fluorescence spectrometry to preliminarily support the composition of elements such as silver, sulfur and halides. Infrared spectroscopy was used to confirm the mode of vibrations of the ligands both in the free state compared with that in the complexes. The change of vibrational energy of C=S and C-N in the complexes have been determined owing to the coordination site of ligands. The inter- and/or intra-molecular hydrogen bond interactions perturb the vibration of $V(C-N)$ and $VN-H$ in the spectra of $[Ag(ettu)_3Cl]$, $[Ag(ettu)_3Br]$ and $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$ and also the weak interaction between silver atoms affect $\{[Ag(detu)_3]_2SO_4\}$ structure.

In the solid-state, the knowledge of molecular structure and the effect of hydrogen bonding is greatly important. It is one of fundamental aim of chemistry and is essential for proper understanding of physical and chemical properties of the materials.

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Appendix

Appendix A

SHELTL NT program (version 6.12)

SHELTL NT version 6.12 is an integrated system for the determination of crystal structures from diffraction data. The programs have been highly used to optimize calculations times, memory and disk space requirements. All calculations are valid for all space group in conventional setting, otherwise, there is almost on limit on the number of unique atom is limited to 5,000 for structure refinement and 10,000 or more for all other calculation.

SHELTL is a major rewrite in order to incorporate and exploit modern structure solution and refining algorithms. These programs consist of five major sub programs and XSHELL program, developing to make the interaction with the mouse and menu feature of Windows NT, are as follows :

XPREP : This program is automatically applied for space group determination, absorption correction, scaling and merging of different data sets, index transformations, reflection statistics, reciprocal space plots and contoured Patterson section. There are mainly two stages for operating by XPERP. The first stage, XPREP reads the new data file name.raw or name.hkl (This name is generated by SADABS program, program for absorption correction with the SMART system) and parameter file name.p4p written by diffratometer controlled program. The second stage, XPREP write the crystal data file name.ins and new reflection data file name.hkl used by the XS and XL subprogram. Besides, this program writes log of all operations to the file name.prp and writes a CIF format name.pcf

XS : This program is utilized for solving structure by “phase annealing” direct method or automated Patterson interpretation based on superposition minimum functions. It reads the resulting file of XPREP program (name.ins and name.hkl) and writes the solution in the form of crystal data to file nam.res and a listing file name.lst. The module calculated normalized structure factor E_s, performs the Patterson interpretation and use direct method of structure calculation. The structure factors of all elements (but not ions) are stored internally. The program checks the symmetry data entered by a user. Because of the presence of symmetry elements, the reciprocal domain being studied will have equivalent spots ; the experimental data are survived to enable a set of independent reflection to be selected.

XL : This program is used for Least-squares refinements. It reads name.res, obtained by editing the name.res (file from XS program or a previous XL job, e.g. via XP), and write the new result file name.res and new listing file name.lst. Furthermore, this program can produce the CIF format files name.cif crystal data, atoms and requirement result and name.fcf, observed and calculated structure factors.

XP : This program is the old fashion, applied for providing interactive molecular graphic and publication quality diagrams. It reads the file name.res from structure solution and requirement and it can write name.ins for next requirement run. Moreover, XP also calculates plot file (name.plt) save file (name.sav) and orthogonal file (name.ort)

XCIF : This program is used for preparation of crystallographic data tables for publication via CIF format. It reads name.cif, name.pcf and name.fcf and write table.

XSHELL : This program is utilized for Least-squares refinements similar to XP, but it is powerful for graphic data or final solution plot for publications. It reads name.res and name.hkl, obtained by editing the name.res (file from XS program or a previous XL job, e.g. via XP), and writes the new result file name.res, new listing file name.lst and also name.cif. This program can be used together with previous five program of SHELTL NT 6.12.

Appendix B

Table 35 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Ag(ettu)$_3$Cl]

Atom	x	y	z	U(eq)
Ag	3400(1)	2500	1262(1)	36(1)
Cl	6013(1)	2500	-968(1)	32(1)
S(1)	1536(1)	3886(1)	1047(1)	38(1)
S(2)	4997(1)	2500	4117(1)	36(1)
C(1)	2935(2)	4750(1)	1568(2)	32(1)
C(2)	7322(2)	2500	4004(2)	30(1)
N(11)	4525(2)	4636(1)	2334(2)	37(1)
N(12)	2390(2)	5551(1)	1190(2)	51(1)
N(21)	8329(2)	2500	5377(2)	39(1)
N(22)	8149(2)	2500	2588(2)	46(1)
C(11)	5785(2)	5338(1)	2810(2)	42(1)
C(12)	7501(2)	4964(1)	3595(3)	56(1)
C(21)	10326(3)	2500	5435(3)	47(1)
C(22)	11036(4)	2500	7153(3)	61(1)

Table 36 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for non-hydrogen of $[Ag(ettu)_3Cl]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag	35(1)	26(1)	45(1)	0	-4(1)	0
Cl	38(1)	27(1)	32(1)	0	2(1)	0
S(1)	29(1)	23(1)	62(1)	2(1)	-8(1)	1(1)
S(2)	25(1)	52(1)	31(1)	0	-1(1)	0
C(1)	32(1)	25(1)	38(1)	-1(1)	4(1)	0(1)
C(2)	27(1)	33(1)	29(1)	0	-3(1)	0
N(11)	34(1)	25(1)	52(1)	-1(1)	-4(1)	-2(1)
N(12)	48(1)	24(1)	79(1)	5(1)	-16(1)	-1(1)
N(21)	28(1)	61(1)	27(1)	0	-3(1)	0
N(22)	28(1)	81(1)	29(1)	0	0(1)	0
C(11)	41(1)	34(1)	52(1)	-5(1)	1(1)	-8(1)
C(12)	40(1)	57(1)	70(1)	-7(1)	-8(1)	-8(1)
C(21)	29(1)	75(2)	37(1)	0	-6(1)	0
C(22)	40(1)	100(2)	43(1)	0	-13(1)	0

The anisotropic displacement factor exponent takes the form :

$$-2\pi^2[U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + 2 U_{12}h k a^* b^* + 2 U_{13}hl a^*c^* + 2 U_{23}kl b^* c^*]$$

Table 37 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Ag(ettu)_3Cl]$

Atom	x	y	z	U(eq)
H(11)	4800(30)	4129(14)	2660(20)	49(5)
H(12)	3110(30)	5998(14)	1330(20)	56(6)
H(13)	1500(30)	5582(15)	670(30)	61(6)
H(14)	5990(30)	5666(15)	1870(30)	63(6)
H(15)	5140(30)	5721(14)	3520(20)	56(5)
H(16)	8130(30)	4608(16)	2840(30)	71(6)
H(17)	7280(30)	4605(16)	4530(30)	73(7)
H(18)	8330(40)	5370(20)	3970(40)	103(9)
H(21)	7790(40)	2500	6230(30)	46(7)
H(22)	7490(40)	2500	1700(40)	55(7)
H(23)	9230(50)	2500	2550(40)	76(10)
H(24)	10750(30)	3008(15)	4840(30)	74(7)
H(25)	10570(30)	2985(17)	7730(30)	90(8)
H(26)	12300(50)	2500	7190(40)	85(11)

Table 38 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for [Ag(ettu)$_3$Br].

Atom	x	y	z	U(eq)
Ag	3348(1)	2500	1310(1)	18(1)
Br	5957(1)	2500	-1031(1)	16(1)
S(1)	1483(1)	3868(1)	1048(1)	22(1)
S(2)	4981(1)	2500	4109(1)	20(1)
C(1)	2909(2)	4712(1)	1574(2)	20(1)
C(2)	7332(2)	2500	3994(2)	17(1)
N(11)	4502(2)	4596(1)	2353(2)	22(1)
N(12)	2392(2)	5508(1)	1173(2)	31(1)
N(21)	8351(2)	2500	5349(2)	22(1)
N(22)	8160(2)	2500	2592(2)	26(1)
C(11)	5785(2)	5292(1)	2800(2)	25(1)
C(12)	7504(2)	4925(1)	3605(2)	31(1)
C(21)	10357(2)	2500	5408(2)	26(1)
C(22)	11058(3)	2500	7130(3)	42(1)

Table 39 Anisotropic displacement parameters (Å^{2}x 10^3) for non-hydrogen atoms of [Ag(ettu)$_3$Br.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag	18(1)	15(1)	21(1) 0	0(1)	0	0
Br	19(1)	16(1)	15(1)	0	1(1)	0
S(1)	17(1)	14(1)	34(1)	2(1)	-4(1)	0(1)
S(2)	14(1)	30(1)	16(1)	0	0(1)	0
C(1)	20(1)	16(1)	23(1)	0(1)	3(1)	0(1)
C(2)	15(1)	20(1)	15(1)	0	-1(1)	0
N(11)	20(1)	16(1)	30(1)	0(1)	-2(1)	-2(1)
N(12)	28(1)	15(1)	48(1)	3(1)	-10(1)	-1(1)
N(21)	15(1)	38(1)	13(1)	0	0(1)	0
N(22)	14(1)	48(1)	16(1)	0	0(1)	0
C(11)	23(1)	21(1)	31(1)	-3(1)	0(1)	-5(1)
C(12)	23(1)	32(1)	38(1)	-4(1)	-4(1)	-4(1)
C(21)	15(1)	43(1)	20(1)	0	-2(1)	0
C(22)	21(1)	81(2)	22(1)	0	-7(1)	0

Table 40 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [Ag(ettu)$_3$Br]

Atom	x	y	z	U(eq)
H(11)	4800(20)	4071(11)	2640(20)	24(4)
H(12)	3070(30)	5927(13)	1310(20)	40(6)
H(13)	1440(30)	5552(14)	640(30)	48(6)
H(14)	6090(20)	5602(12)	1860(20)	28(5)
H(15)	5090(20)	5688(11)	3550(20)	26(4)
H(16)	8290(30)	5356(14)	3920(30)	51(6)
H(17)	7230(30)	4615(13)	4510(30)	42(6)
H(18)	8140(30)	4575(13)	2910(30)	46(6)
H(21)	7810(40)	2500	6250(40)	45(8)
H(22)	7530(30)	2500	1700(30)	11(5)
H(23)	9240(40)	2500	2540(30)	29(7)
H(24)	10770(30)	2976(12)	4810(20)	38(5)
H(25)	10670(30)	2991(13)	7670(30)	53(6)
H(26)	12300(40)	2500	7160(40)	52(9)

Table 41 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Ag(detu)$_3$Br] .

Atom	x	y	z	U(eq)
Ag	3333	6667	6689(1)	74(1)
Br	3333	6667	9438(1)	88(1)
S(1)	1743(1)	4469(1)	5902(1)	67(1)
C(1)	858(4)	4529(4)	4586(5)	73(1)
N(1)	-117(6)	3546(4)	4143(7)	128(2)
N(2A)	1490(19)	5635(15)	3798(14)	61(4)
N(2B)	948(13)	5508(9)	4086(12)	72(3)
C(11)	-675(9)	2356(8)	4827(14)	175(5)
C(12)	-374(12)	1628(11)	4141(17)	204(6)
C(21A)	930(20)	5894(17)	2566(16)	78(6)
C(22A)	930(20)	6790(20)	2260(30)	109(8)
C(21B)	185(14)	5723(10)	3069(17)	100(5)
C(22B)	380(30)	6679(19)	2760(30)	186(12)

Table 42 Anisotropic displacement parameters ($Å^2$x 10^3) for non-hydrogen atoms of $[Ag(detu)_3Br]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag	79(1)	79(1)	65(1)	0	0	39(1)
Br	104(1)	104(1)	57(1)	0	0	52(1)
S(1)	62(1)	66(1)	67(1)	7(1)	-2(1)	28(1)
C(1)	81(3)	59(2)	72(3)	-7(2)	-14(2)	30(2)
N(1)	124(4)	68(3)	156(6)	-1(3)	-76(4)	21(3)
N(2A)	55(8)	58(6)	61(6)	6(5)	0(6)	22(7)
N(2B)	60(6)	56(4)	85(6)	0(4)	-23(4)	18(4)
C(11)	133(6)	103(6)	237(13)	-6(7)	-92(7)	20(5)
C(12)	209(12)	150(8)	274(17)	24(9)	-11(11)	106(9)
C(21A)	88(15)	77(10)	80(10)	3(7)	-3(8)	50(10)
C(22A)	117(11)	109(11)	103(11)	16(8)	-9(8)	58(8)
C(21B)	78(8)	91(6)	106(9)	0(6)	-32(7)	24(5)
C(22B)	250(30)	210(20)	190(20)	-62(17)	-101(19)	190(20)

Table 43 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for [Ag(detu)$_3$Br].

Atom	x	y	z	U(eq)
H(1)	-456	3605	3389	154
H(11A)	-389	2453	5784	210
H(11B)	-1562	1993	4840	210
H(12A)	-618	1572	3182	306
H(12B)	-785	824	4553	306
H(12C)	499	1960	4191	306
H(2A)	2224	6175	4043	73
H(21A)	1283	5706	1764	93
H(21B)	74	5263	2589	93
H(22A)	1346	7396	2976	164
H(22B)	102	6616	2177	164
H(22C)	1353	7088	1391	164
H(2B)	1568	6171	4396	86
H(21C)	191	5315	2211	120
H(21D)	-651	5285	3419	120
H(22D)	705	7220	3550	278
H(22E)	-373	6637	2467	278
H(22F)	962	6986	2011	278

Table 44 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\AA^2$x 10^3) for $\{[Ag(detu)_3]_2SO_4\}$.

Atom	x	y	z	U(eq)
Ag(1)	6667	3333	3929(1)	50(1)
S(1)	5933(1)	4845(1)	4025(1)	56(1)
C(1)	7242(4)	6246(4)	4122(2)	54(1)
N(1)	7302(5)	7003(4)	4455(2)	78(1)
N(2)	8243(5)	6571(5)	3835(2)	76(1)
C(11)	6343(9)	6722(7)	4819(3)	98(2)
C(12)	5416(9)	7083(8)	4672(4)	111(3)
C(21)	9418(7)	7726(8)	3871(4)	119(3)
C(22)	10413(9)	7711(10)	3657(4)	136(4)
S(2)	0	0	5000	40(1)
O(1A)	679(9)	1334(8)	4906(4)	55(2)
O(1B)	673(9)	724(17)	4571(4)	103(6)

Table 45 Anisotropic displacement parameters (Å^{2}x 10^3) for non-hydrogen atoms of $\{[Ag(detu)_3]_2SO_4\}$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	52(1)	52(1)	46(1)	0	0	26(1)
S(1)	45(1)	53(1)	69(1)	-11(1)	-2(1)	23(1)
C(1)	49(2)	47(2)	56(2)	5(2)	-6(2)	18(2)
N(1)	81(3)	55(2)	79(3)	-13(2)	-12(2)	21(2)
N(2)	71(3)	62(3)	87(3)	4(2)	9(2)	27(2)
C(11)	133(7)	83(4)	79(4)	-29(3)	-1(4)	54(5)
C(12)	118(6)	88(5)	125(7)	-9(5)	31(5)	50(5)
C(21)	72(4)	72(4)	184(10)	22(5)	23(5)	14(4)
C(22)	89(6)	126(8)	153(9)	-50(7)	10(6)	24(5)
S(2)	33(1)	33(1)	53(1)	0	0	17(1)
O(1A)	54(5)	37(4)	72(6)	4(4)	14(4)	21(4)
O(1B)	32(5)	177(16)	39(5)	2(7)	8(4)	6(6)

Table 46 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\{[Ag(detu)_3]_2SO_4\}$.

Atom	x	y	z	U(eq)
H(1)	7958	7731	4464	93
H(2)	8176	6051	3614	91
H(111)	6742	7155	5117	118
H(112)	5911	5834	4886	118
H(121)	5779	7971	4700	166
H(122)	4697	6675	4878	166
H(123)	5172	6836	4342	166
H(211)	9322	8386	3724	143
H(212)	9608	7930	4211	143
H(221)	11177	8381	3784	204
H(222)	10370	6929	3723	204
H(223)	10386	7814	3313	204

Table 47 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\AA^2$x 10^3) for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Atom	x	y	z	U(eq)
Ag(1)	2500	2500	12500	49(1)
Ag(2)	2500	2500	7500	50(1)
Ag(3)	7500	2500	-638(1)	59(1)
S(1)	3543(1)	2913(1)	9928(1)	41(1)
S(3)	6363(1)	2612(1)	1858(1)	51(1)
N(1)	4644(1)	2221(2)	8041(4)	51(1)
N(2)	4211(1)	1692(1)	11051(5)	46(1)
N(3)	6296(2)	4136(2)	1894(5)	68(1)
C(1)	4183(1)	2223(1)	9647(4)	38(1)
C(11)	4706(2)	2774(2)	6356(6)	60(1)
C(12)	5253(3)	3331(3)	6901(8)	82(1)
C(21)	4744(2)	1106(2)	11068(7)	57(1)
C(22)	4611(3)	605(2)	12898(7)	70(1)
C(3)	6328(2)	3516(2)	1877(5)	49(1)

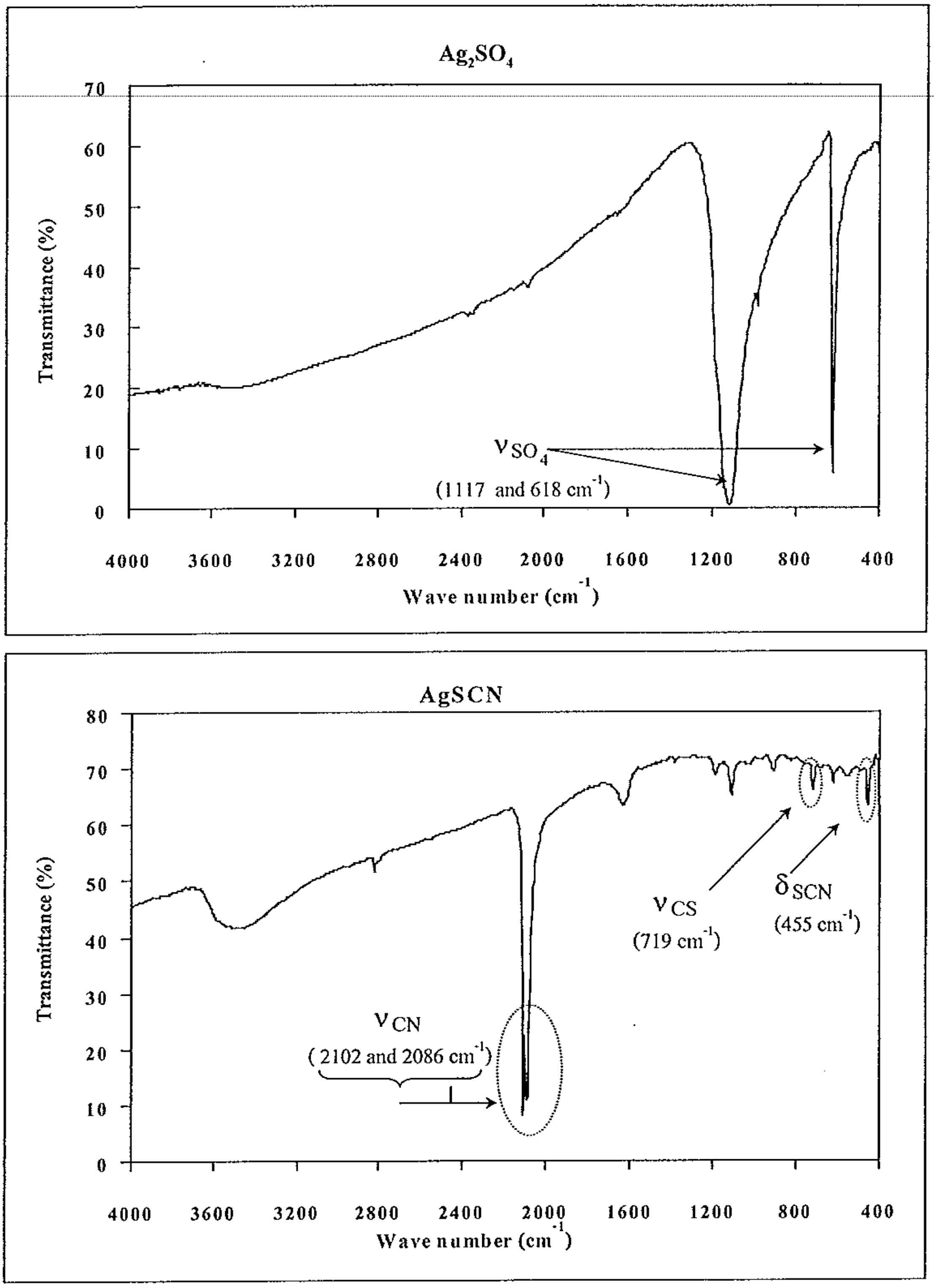
Table 48 Anisotropic displacement parameters ($Å^2$x 10^3) for non-hydrogen atoms of $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	49(1)	49(1)	50(1)	0	0	0
Ag(2)	51(1)	51(1)	47(1)	0	0	0
Ag(3)	68(1)	58(1)	52(1)	0	0	3(1)
S(1)	40(1)	36(1)	47(1)	-4(1)	0(1)	1(1)
S(3)	47(1)	49(1)	57(1)	-4(1)	-3(1)	-6(1)
N(1)	44(1)	51(2)	58(2)	10(1)	12(1)	7(1)
N(2)	42(1)	44(1)	52(2)	7(1)	12(1)	6(1)
N(3)	65(2)	53(2)	84(2)	-20(2)	-7(2)	2(1)
C(1)	31(1)	39(1)	44(1)	-2(1)	0(1)	-3(1)
C(11)	57(2)	71(2)	52(2)	10(2)	7(2)	2(2)
C(12)	102(4)	72(3)	72(3)	14(2)	4(3)	-22(3)
C(21)	54(2)	49(2)	69(2)	10(2)	15(2)	14(2)
C(22)	76(3)	57(2)	75(3)	18(2)	11(2)	20(2)
C(3)	39(2)	59(2)	50(2)	-12(1)	-3(1)	-2(1)

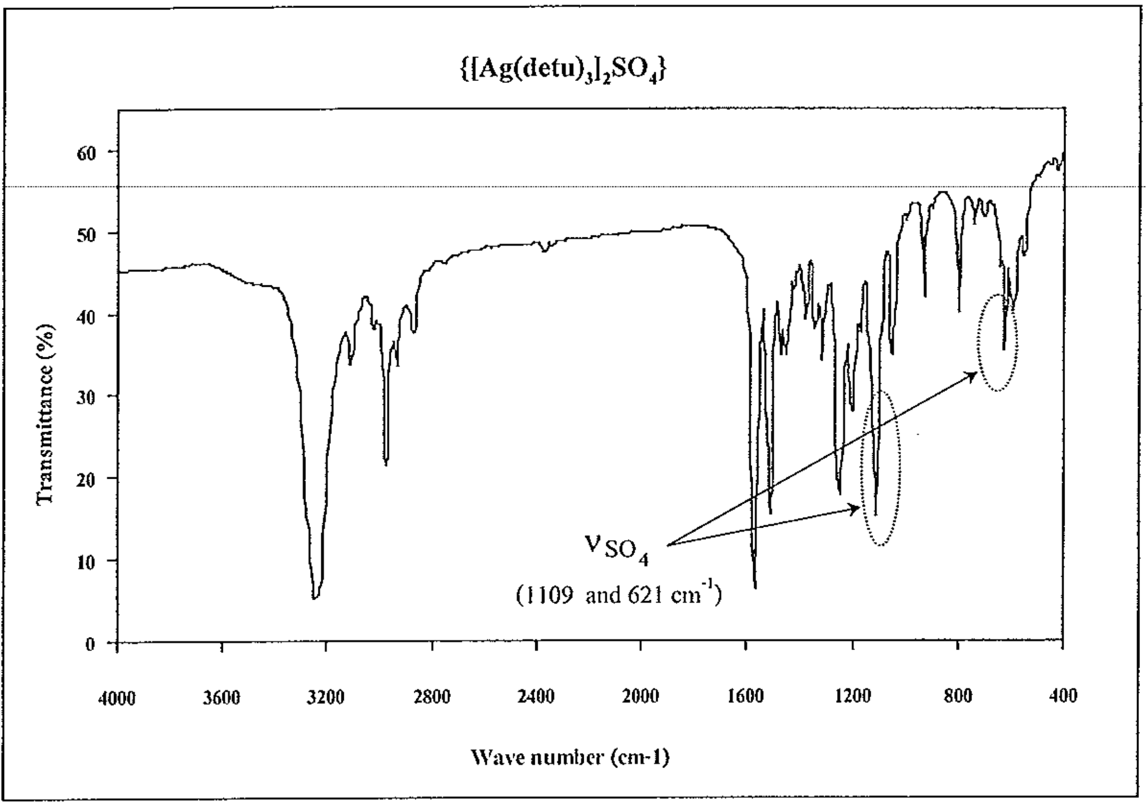
Table 49 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\{[Ag_2(detu)_4][Ag(SCN)_2]_2\}_\infty$.

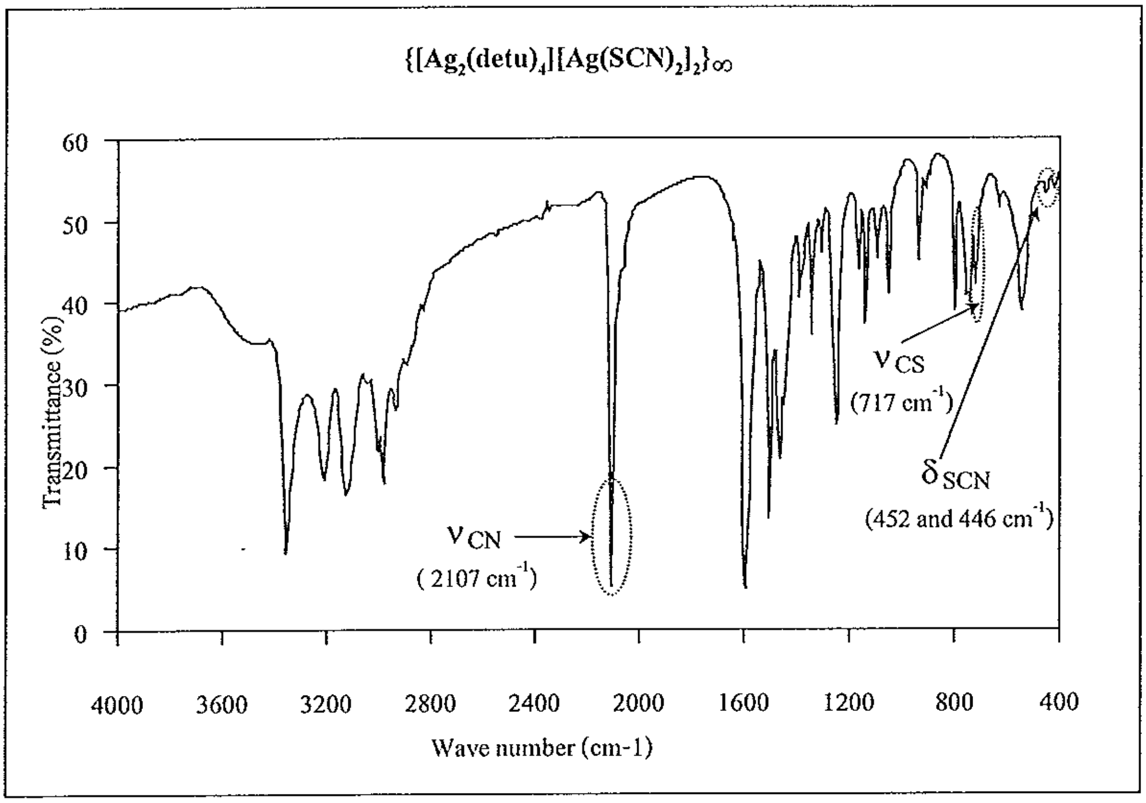
Atom	x	y	z	U(eq)
H(1)	4943(16)	1890(17)	8020(50)	41(8)
H(2)	3952(18)	1689(18)	11820(60)	44(10)
H(111)	4790(20)	2550(20)	5070(70)	82(13)
H(112)	4220(20)	2964(19)	6010(60)	70(11)
H(121)	5350(30)	3670(30)	5550(90)	130(19)
H(122)	5760(30)	3070(30)	7050(90)	140(20)
H(123)	5060(40)	3640(30)	8290(110)	170(20)
H(211)	5210(20)	1330(20)	11120(70)	88(14)
H(212)	4740(20)	880(20)	9820(70)	73(13)
H(221)	4720(30)	950(30)	14150(90)	113(18)
H(222)	4980(20)	230(30)	12920(60)	85(12)
H(223)	4170(20)	380(20)	12900(70)	87(14)

Appendix C



The IR spectra of Ag_2SO_4 and AgSCN





The IR spectra of {[Ag$_2$(detu)$_3$]$_2$SO$_4$} and {[Ag$_2$(detu)$_4$][Ag(SCN)$_2$]$_2$}$_\infty$

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