# Preparation and Crystal Structure Determination of Some Copper(I) and Silver(I) Substituted Thiourea Complexes

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**Thesis Title** Preparation and Crystal Structure Determination of Some Copper(I) and Silver(I) Substituted Thiourea Complexes

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**Major Program** Physical Chemistry

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| | |
|---|---|
| ชื่อวิทยานิพนธ์ | การเตรียมและหาโครงสร้างผลึกสารประกอบเชิงซ้อนคอปเปอร์(I) และซิลเวอร์(I) ซับสติติวเตดไธโอยูเรียบางตัว |
| ผู้เขียน | นางสาวสุวลักษณ์ แป้นสุข |
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# บทคัดย่อ

ได้ศึกษาโครงสร้างของสารประกอบเชิงซ้อน 5 ชนิด คือ $[Ag(atu)_2]NO_3$ (1), $[Cu_4(ettu)_6 I_4].H_2O$ (2), $[Ag_2(etu)_6](ClO_4)_2$ (3), $[Ag_2(etu)_4Br_2]$ (4), $[Cu(etu)_3]_2SO_4$ (5) และสารประกอบ $(C_6H_5NH)_2CO$ (6) (atu = อะซีทิลไธโอยูเรีย, ettu = เอทิลไธโอยูเรีย, etu = เอทิลีนไธโอยูเรีย, dptu = ไดฟีนิลไธโอยูเรีย) ด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์โดยผลึกเดี่ยว สารประกอบเหล่านี้เตรียมได้จากปฏิกิริยาระหว่างคอปเปอร์(I) หรือซิลเวอร์(I) เฮไลด์ ($Br^-$, $I^-$) หรือ คอปเปอร์(I) หรือคอปเปอร์(II) หรือ ซิลเวอร์(I) แอนไอออน ($NO_3^-$, $ClO_4^-$, $SO_4^{2-}$) กับลิแกนด์ซับสติติวเตดไธโอยูเรียบางตัว ในตัวทำละลายที่เหมาะสม พบว่าโครงสร้างของผลึก (1) อยู่ในระบบมอนอคลินิก กลุ่มปริภูมิ $P2_1/n$, $Z = 4$, $a = 12.0680(6)$, $b = 6.8056(5)$, $c = 17.6552(9)$ Å, $\beta = 108.147(4)°$ โครงสร้างประกอบด้วยแคตไอออนแบบพอลิเมอร์มีซัลเฟอร์เป็นสะพานเชื่อมของ $Ag(atu)_2^+$ และแอนไอออน $NO_3^-$ ซึ่งแยกกันโดยมีแรงวัลเดอร์วาลส์และพันธะไฮโดรเจนเสริมกันในอันตรกิริยาไอออนิก ผลึก (2) อยู่ในระบบออโธรอมบิค กลุ่มปริภูมิ $P2_12_12_1$, $Z = 4$, $a = 11.179(1)$, $b = 18.505(2)$, $c = 22.409(2)$ Å โครงสร้างของ $[Cu_4(ettu)_6I_4]$ เป็นแบบ adamantane cluster ซึ่งมีวงแหวนลักษณะคล้ายรูปเก้าอี้ของ Cu – S – Cu – S – Cu – S 6 วงแหวน อะตอมคอปเปอร์จัดเรียงตัวแบบทรงเหลี่ยมสี่หน้าโดยเกิดพันธะกับอะตอมซัลเฟอร์ของลิแกนด์เอทิลไธโอยูเรียสามโมเลกุลและอะตอมโบรมีนหนึ่งอะตอม ผลึก (3) อยู่ในระบบมอนอคลินิก กลุ่มปริภูมิ $P2_1/c$, $Z = 4$, $a = 6.329(1)$, $b = 24.262(2)$, $c = 12.119(2)$ Å, $\beta = 92.67(1)°$ โครงสร้างประกอบด้วยแคตไอออนซึ่งเป็นไดเมอร์ คือ $Ag_2(etu)_6^{2+}$ และแอนไอออน $ClO_4^-$ ที่แยกจากกัน จุดศูนย์กลางของไดเมอร์เป็นจุดศูนย์กลางของสมมาตรในผลึกนี้โดยอยู่ตรงกลางระนาบ $Ag_2S_2$ ซึ่งเกิดจากอะตอมซิลเวอร์

สองอะตอมและอะตอมซัลเฟอร์สองอะตอม ผลึก (4) อยู่ในระบบมอนอคลินิก กลุ่มปริภูมิ $P2_1/n$, $Z = 4$, $a = 8.975(2)$, $b = 10.457(2)$, $c = 13.158(3)$ Å, $\beta = 103.42(3)°$ โครงสร้างเป็นแบบไดเมอร์โดยมีจุดศูนย์กลางของไดเมอร์เป็นจุดศูนย์กลางของสมมาตร อะตอมซิลเวอร์(I) มีการจัดตัวแบบทรงเหลี่ยมสี่หน้าที่บิดเบี้ยวโดยเกิดพันธะกับลิแกนด์เอทิลไธโอยูเรียสองโมเลกุลและอะตอมโบรมีนสองอะตอม โดยที่อะตอมโบรมีนทำหน้าที่เป็นสะพานเชื่อมในการเกิดไดเมอร์ ผลึก (5) อยู่ในระบบไตรโกนอล กลุ่มปริภูมิ $R3c$, $Z = 6$, $a = 12.750(2)$, $c = 35.083(7)$ Å โครงสร้างประกอบด้วยสองแคตไอออน, $Cu(etu)_3^+$ ซึ่งแต่ละไอออนมีสมมาตรแบบแกนหมุนสาม ส่วนซัลเฟตแอนไอออน ($SO_4^{2-}$) อยู่บนแกนหมุนสาม โดยที่พันธะ S – O พันธะหนึ่งอยู่ในแนวแกนหมุนสามเดียวกับแคตไอออนตัวหนึ่ง ผลึก (6) อยู่ในระบบออโธรอมบิก กลุ่มปริภูมิ $Pna2_1$, $Z = 4$, $a = 9.089(2)$, $b = 11.795(2)$, $c = 10.401(2)$ Å จากการศึกษาพบว่าสารประกอบนี้ไม่เป็นสารประกอบเชิงซ้อนถึงแม้ว่าเตรียมได้จากปฏิกิริยาระหว่างคอปเปอร์(II) ไนเตรตกับลิแกนด์ไดฟีนิลไธโอยูเรีย โครงสร้างที่ได้คือ เอ็น, เอ็น-ไดฟีนิลยูเรีย

รวมทั้งได้ศึกษาคุณสมบัติของสารประกอบเหล่านี้โดยใช้วิธีเอกซ์เรย์ฟลูออเรสเซนต์ และอินฟราเรดสเปกโทรสโกปีเพื่อสนับสนุนโครงสร้าง จากการศึกษาพบว่าผลที่ได้จากทั้งสองวิธีสอดคล้องกับโครงสร้างที่ได้

หอสมุด คุณหญิงหลง อรรถกระวีสุนทร
มหาวิทยาลัยสงขลานครินทร์
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**Thesis Title** Preparation and Crystal Structure Determination of Some Copper(I) and Silver(I) Substituted Thiourea Complexes

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**Major Program** Physical Chemistry

**Academic Year** 1999

## Abstract

The crystal structures of 5 complexes, $[Ag(atu)_2]NO_3$ (1), $[Cu_4(ettu)_6I_4].H_2O$ (2), $[Ag_2(etu)_6](ClO_4)_2$ (3), $[Ag_2(etu)_4Br_2]$ (4), $[Cu(etu)_3]_2SO_4$ (5) and a compound, $(C_6H_5NH)_2CO$ (6) (atu = acetylthiourea, ettu = ethylthiourea, etu = ethylenethiourea, dptu = diphenylthiourea) have been studied by single crystal X-ray diffraction methods. These complexes and the compound were prepared by the reaction of copper(I) or silver(I) halides ($Br^-$, $I^-$) or copper(I) or copper(II) or silver(I) anions ($NO_3^-$, $ClO_4^-$, $SO_4^{2-}$) with some substituted thiourea ligands in appropriate solvents. Crystals of (1) are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.0680(6)$, $b = 6.8056(5)$, $c = 17.6552(9)$ Å, $\beta = 108.147(4)°$. The structure consists of sulfur-bridged polymeric cation, $Ag(atu)_2^+$ and anions, $NO_3^-$ with only van der Waals and hydrogen bond forces superposed on ionic interactions. Crystals of (2) are monoclinic, space group $P2_12_12_1$, with $Z = 4$ in a cell of dimensions $a = 11.179(1)$, $b = 18.505(2)$, $c = 22.409(2)$ Å. The structure is a $[Cu_4(ettu)_6I_4]$ adamantane cluster. This cage structure results in the formation of four six-membered Cu – S – Cu – S – Cu – S rings all in the chair conformation. Each Cu atom is coordinated tetrahedrally by three S atoms and an I atom. Crystals of (3) are monoclinic, space group $P2_1/c$, $Z = 4$,

$a = 6.329(1)$, $b = 24.262(2)$, $c = 12.119(2)$ Å, $\beta = 92.67(1)°$. The structure consists of isolated dimeric $Ag_2(etu)_6^{2+}$ cations and $ClO_4^-$ anions. The centre of the dimer is the crystallographic centre of symmetry so that the silver and bridging sulfur atoms form a planar $Ag_2S_2$ unit. Crystals of (4) are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.975(2)$, $b = 10.457(2)$, $c = 13.158(3)$ Å, $\beta = 103.42(3)°$. The structure is built by centrosymmetric dimers. Each silver(I) atom is distorted tetrahedral with the two etu ligands terminal and bromine acting as a bridging. Crystals of (5) are trigonal, space group $R3c$, $Z = 6$, $a = 12.750(2)$, $c = 35.083(7)$ Å. The structure consists of two independent cations, $[Cu(etu)_3]^+$, each lying on a three fold axis. The sulfate ion also lies on a threefold axis with one of the S – O bonds is on this axis common to one of cations. Crystals of (6) are orthorhombic, space group $Pna2_1$, $Z = 4$, $a = 9.089(2)$, $b = 11.795(2)$, $c = 10.401(2)$ Å. The compound is not a complex, although it was prepared by reacting copper(II) nitrate with *N,N'*-diphenylthiourea. It is the structure of *N,N'*-diphenylurea, the sulfur atom in the ligand dptu was substituted by the oxygen atom.

Furthermore, the compounds have been studied by X-ray Fluorescence Spectrometry and Infrared Spectroscopy to support the structures. These results show consistence with the structures.

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Suwaluk Pansook

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# Abbreviations and Symbols

° = degree

Å = Angstrom unit (1 Å = $10^{-10}$ metre)

A.R. = Analytical Reagent

$\mathrm{cm}^{-1}$ = 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

$V$ = volume

# Chapter 1

# INTRODUCTION

## 1.1 Introduction

### 1.1.1 Copper

A chemical element, symbol Cu, atomic number 29, is located in the periodic table between nickel and zinc in the first row of the transition elements and in the same group as others known as coinage metals, silver and gold. The electronic configuration of elemental copper is $[1s^2 2s^2 2p^6 3s^2 3p^6]3d^{10}4s^1$ or $[\mathrm{Ar}]3d^{10}4s^1$. Copper has a single $s$ electron outside the filled $3d$ shell but essentially has nothing in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled $d$ shell is much less effective in shielding the outer $s$ electron from the nuclear charge, so that the first ionization energy of Cu is higher than those of the alkalis. Since the electrons of the $d$ shell are also involved in metallic bonding, the heat of sublimation and the melting point of Cu are also much higher than those of the alkalis. These factors are responsible for the more noble character of copper, and the effect is to make the compounds more covalent and to give them higher lattice energies.

## The Chemistry of Copper(I), $d^{10}$

Copper(I) compounds are diamagnetic and colorless, except where color results from the anion or charge-transfer bands. The relative stabilities of the cuprous and cupric states are indicated by the following potential data :

$$Cu^{+} + e^{-} \rightarrow Cu \qquad E^{0} = 0.52\ V$$

$$Cu^{2+} + e^{-} \rightarrow Cu^{+} \qquad E^{0} = 0.153\ V$$

Whence

$$2Cu^{+} \rightleftharpoons Cu^{2+} + Cu \quad E^{0} = -0.37\ V\ ; \ K = [Cu^{2+}]/[Cu^{+}]^{2} = \sim 10^{6}$$

The relative stabilities of $Cu^{I}$ and $Cu^{II}$ in aqueous solution depend very strongly on the nature of the anions and other ligands present, and vary considerably with solvent or the nature of the neighboring atom in a crystal. In aqueous solutions only low equilibrium concentrations of $Cu^{+}$ ($<10^{-2}$ M) can exist and the only cuprous compounds stable to water are the highly insoluble ones such as CuCl or CuCN. This instability towards water is due partly to the greater lattice and solvation energies and higher formation constants for complexes of the cupric ion, so that ionic $Cu^{I}$ derivatives are unstable.

The equilibrium $2Cu^{I} \rightarrow Cu + Cu^{II}$ can readily be displaced in either direction. Thus with $CN^{-}$, $I^{-}$, and $Me_2S$ (Me = methyl group), $Cu^{II}$ reacts to give the $Cu^{I}$ compound. An excellent illustration of how the stability of the cuprous ion relative to that of the cupric ion may be affected by solvent is the case of acetonitrile. The cuprous ion is very effectively highly solvated by $CH_3CN$, and the cuprous halides have relatively high solubilities (e.g., CuI, 35 g/1 kg $CH_3CN$) vs. negligible solubilities in $H_2O$. $Cu^{I}$ is more stable than $Cu^{II}$ in $CH_3CN$ and the latter is, in fact, a comparatively powerful oxidizing agent.

### Copper(I) Complexes

Copper(I) halide and other complexes are usually obtained by

(a) Direct interaction of ligands with copper(I) halides or the triflate.

(b) Reduction of corresponding copper(II) compounds.

(c) Reduction of $Cu^{2+}$ in the presence of or by the ligand.

The stoichiometries of the compounds give little clue to their structures, which can be very complicated, being mononuclear, binuclear, polynuclear and the copper atom two-, three-, or four-coordinated, or infinite chains. (Cotton and Wilkinson, 1988 : 757-763)

### 1.1.2 Silver

A chemical element, symbol Ag, atomic number 47, is chemically one of the heavy metals and one of the noble metals. Like copper, silver has a single *s* electron outside a completed *d* shell ([Kr] $4d^{10}5s^{1}$), but in spite of the similarity in electronic structures and ionization potentials there are few resemblances between Ag and Cu, and there are no simple explanations for many of the differences. 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 elements :

1. The metals all crystallize with the same face-centered cubic (fcc) lattice.
2. $Cu_2O$ and $Ag_2O$ have the same body-centered cubic structure where the metal atom has two close oxygen neighbors and every oxygen is tetrahedrally surrounded by four metal atoms.

3. Although the stability constant sequence for halo complexes of many metals is 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 $Ag^{I}$ form very much the same types of ions and compounds, such as $[MCl_2]^-$, $[Et_3AsMI]_4$ and $K_2MCl_3$.
5. Certain complexes of $Cu^{II}$ and $Ag^{II}$ are isomorphous.

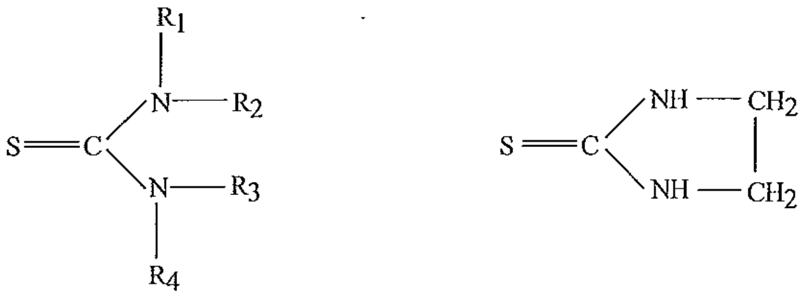
Compounds of Silver(I), $d^{10}$

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

### 1.1.3 Thiourea (tu) and Substituted Thiourea :

Acetylthiourea (atu)
*N*-Ethylthiourea (ettu)
*N*-Ethylenethiourea (etu)
*N*-Methylthiourea (mtu)
*N,N′*-dimethylthiourea (dmtu)
*N*-Phenylthiourea (ptu)
*N,N′*-Diphenylthiourea (dptu)
*N,N′,N″,N‴*-Tetramethylthiourea (tmtu)

These ligands are soft donor ligands, their structures are shown in figure 1.



(a) (b)

Figure 1 (a) The structure of thiourea and substituted thiourea

tu, $R_1 = R_2 = R_3 = R_4 = H$

atu, $R_1 = R_2 = R_3 = H$, $R_4 = OCCH_3$

ettu, $R_1 = R_2 = R_3 = H$, $R_4 = C_2H_5$

mtu, $R_1 = R_2 = R_3 = H$, $R_4 = CH_3$

dmtu, $R_1 = R_3 = H$, $R_2 = R_4 = CH_3$

ptu, $R_1 = R_2 = R_3 = H$, $R_4 = C_6H_5$

dptu $R_1 = R_3 = H$, $R_2 = R_4 = C_6H_5$

tmtu, $R_1 = R_2 = R_3 = R_4 = CH_3$

(b) The structure of etu

The ligands are potentially capable of forming coordinate bonds through both sulfur and nitrogen even though the extremely low basicity of the ligand militates against the formation of nitrogen – metal bonds. Both these possibilities will be reflected in the infrared spectra of the complexes. Bonding through sulfur will decrease the bond order of the carbon – sulfur link towards the value for a single bond while the carbon – nitrogen bond approaches the value for a double bond. Hence, in such complexes, the C – S stretching frequency should decrease and that of C – N should increase. If, on the contrary, a nitrogen – metal bond is formed just the opposite effect is to be expected. Furthermore, the N – H frequency should decrease if the metal is coordinated through nitrogen, while remaining substantially unaffected if the bonding is through sulfur. (Swaminathan and Irving, 1964 : 1291)

The stereochemistry of Cu(I) and Ag(I) is interesting not only because of their chemical interest, but also because of their relevance to oxidation-reduction in copper, silver-containing enzymes. With soft ligands, e.g. thiourea and substituted thioureas, complexes with the same stoichiometry may have different stereochemistry.

## 1.2 Review of Literatures

X-ray crystallography has been studied from around 1900s by studying the crystal structure of sodium chloride. However copper(I) halides (CuX, X = Cl, Br, and I ) and oxy anions (CuX, X = $NO_3$, $ClO_4$, $\frac{1}{2}SO_4$) substituted thiourea complexes had been studied only by preparation and infrared spectroscopy in the early 1900s, such as :

Morgan and Brustall studied complexes of copper(I) ethylenethiourea (Morgan and Burstall, 1928).

Yamaguchi, *et al.* assigned the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule (Yamaguchi, *et al.*, 1958).

Lane, *et al.* studied the infrared absorption spectra of methylthiourea and its metal complexes (Lane, *et al.*, 1959).

Benerjee and Sukthankar studied complexes of copper(I) acetylthiourea (Benerjee and Sukthankar, 1962) and copper(I) diphenylthiourea (Benerjee and Sukthankar, 1963).

Malik studied the infrared absorption of complexes of copper(I) diphenylthiourea chloride (Malik, 1968).

After 1960s, the structures of copper(I) and silver(I) thiourea and substituted thiourea complexes have been studied by more widely X-ray crystallography, such as :

Vizzini, Taylor and Amma studied the crystal structure of bis(thiourea) silver(I) chloride, $[Ag(tu)_2Cl]$. The structure is composed of almost trigonal-planar $Ag(S)_3$ units bonded together by a sulfur bridge to form a spiraling linear polymer. The fourth coordination position of each Ag is completed by long axial Ag – Cl distance of 2.854(5) and 3.035(5) Å, respectively, Figure 2 (Vizzini, Taylor and Amma, 1968).

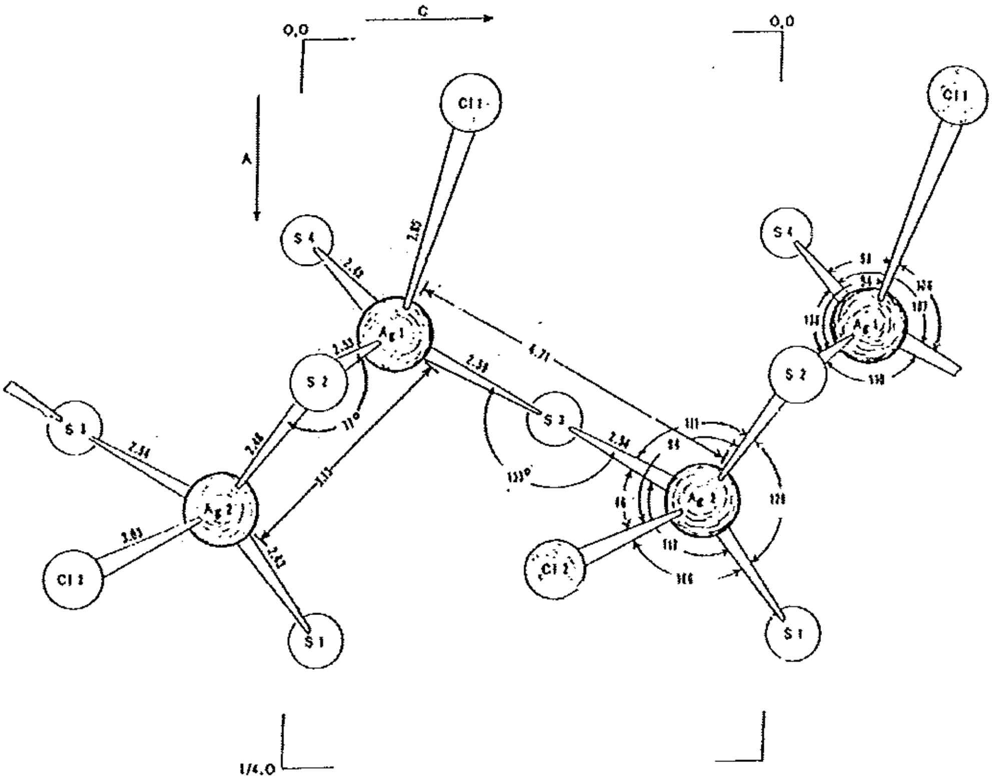


Figure 2 The structure of $Ag(tu)_2Cl$

Crystal data : monoclinic, space group $P2_1/a$ ; $a$ = 36.70(4), $b$ = 8.24 (1), $c$ = 5.87(1) Å ; $\beta$ = 92.50(15) °, $V$ = 1797.1 Å$^3$, $Z$ = 8, $D_c$ = 2.22 g/cm$^3$ , $D_m$ = 2.18 g/cm$^3$ $F(000)$ = 960, $\mu$ = 1.73 mm$^{-1}$ (Mo $K_\alpha$), $N$ = 2699, $R$ = 0.062

The sharp bridge bond can be interpreted as an $Ag_2 - S_2 - Ag_1$ three centers, two electrons, electron deficient bridge bond. However, the broad-angle ($Ag_1 - S_3 - Ag_2$) bridge is readily understandable in terms of two electron-pair donor acceptor linkages.

Weininger, Hunt and Amma studied the crystal structures of tris (ethylenethiourea)copper(I) sulfate, $[Cu(etu)_3]_2SO_4$ and tris(tetramethylthiourea) copper(I) tetrafluoroborate, $[Cu(tmtu)_3BF_4]$. Both structures contains the $Cu^I$ and three sulfur atoms in a planar arrangement. The structure of $[Cu(etu)_3]_2SO_4$ consists of isolated monomeric $Cu(etu)_3^+$ units with planar $CuS_3$ and some N – H --- O hydrogen bonding. The isolated $Cu(etu)_3^+$ ions are propellor-shaped with a left-hand screw, but maintain a trigonal planar $CuS_3$ unit (Figure 3). Another structure consists of monomeric $Cu(tmtu)_3^+$ units with planar $CuS_3$ fragments (Figure 4). $Cu(tmtu)_3^+$ is considerably distorted from trigonal configuration. This distortion arises from steric interactions between adjacent tetramethylthiourea groups (Weininger, Hunt and Amma, 1972).

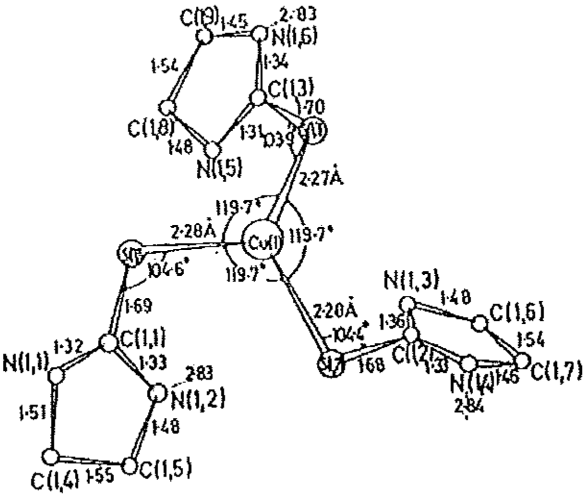


Figure 3 The structure of $[Cu(etu)_3]^+$

Crystal data : monoclinic, space group *Ic* ; $a = 18.916(1)$, $b = 12.772(1)$, $c = 13.974(1)$ Å, $\beta = 96.99(1)°$, $Z = 4$, $D_m = 1.66$ g/cm$^3$, $D_c = 1.66$ g/cm$^3$, $\mu = 17.8$ cm$^{-1}$ (Mo $K\alpha$), $N = 2918$, $R = 0.0478$

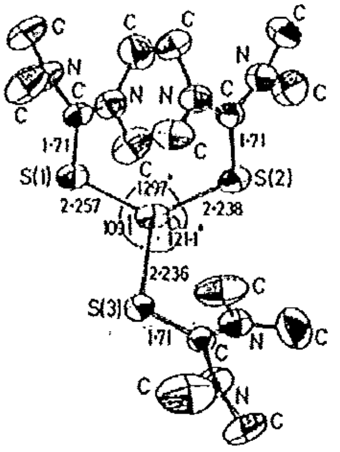


Figure 4 The structure of $[Cu(tmtu)_3]^+$

Crystal data : monoclinic, space group $P2_1/c$ ; $a = 15.987(8)$, $b = 12.596(5)$, $c = 13.495(6)$ Å, $\beta = 102.88(1)°$, $Z = 4$, $D_m = 1.36$ g/cm$^3$, $D_c = 1.34$ g/cm$^3$, $\mu = 11.05$ cm$^{-1}$ (Mo $K\alpha$), $N = 3360$, $R = 0.049$

Raper, Wilson and Clegg studied the crystal structure of [bis{bis(imidazolidine-2-thione)-$\mu_2$-(imidazolidine-2-thione)copper(I)}] diperchlorate, $[Cu_2(imdtH_2)_6](ClO_4)_2$ or $[Cu_2(etu)_6](ClO_4)_2$ (Imidazolidine-2-thione widely known by its trival name, ethylenethiourea.) The structure consists of centrosymmetrically constrained dinuclear complex cations, $[Cu_2(imdtH_2)_6]^{2+}$ (Figure 5), formed by two, edge-sharing, $CuS_4$ tetrahedra, as well as perchlorate anions. The copper(I) atoms have identical $S_4$ coordination with distorted tetrahedral geometry (Raper, Wilson and Clegg, 1992).

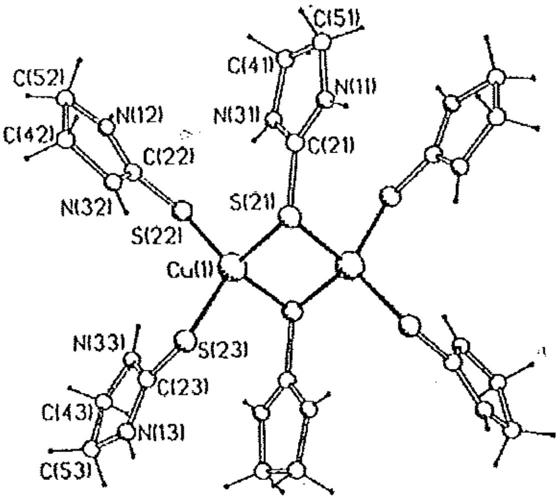


Figure 5 The structure of $[Cu_2(imdtH_2)_6]^{2+}$

Crystal data : monoclinic, space group $P2_1/n$ ; $a = 8.0275(5)$, $b = 26.2252(14)$, $c = 8.5399(6)$ Å, $\beta = 91.707(5)°$, $V = 1797.1$ Å$^3$, $Z = 2$ (dimers), $D_c = 1.735$ g/cm$^3$, $F(000) = 960$, $\mu = 1.73$ mm$^{-1}$ (Mo $K_\alpha$), $N = 2699$, $R = 0.0404$

Bott, *et al.* studied the crystal structure of $[Cu_4(tu)_7](SO_4)_2.H_2O$. It was highlighted by a $[Cu_4(tu)_7]^{4+}$ adamantane cluster. A copper(I) - thiourea cluster of this stoichiometry has not been previously reported. The copper atoms lie in a tetrahedral arrangement in which one of the copper atoms is four-coordinated, while the other three display trigonal planar coordination, figure 6. The copper-thiourea clusters are interlinked by sulfate ions, which strongly interact with the thiourea ligand through hydrogen bonds (Bott, *et al.* 1998).

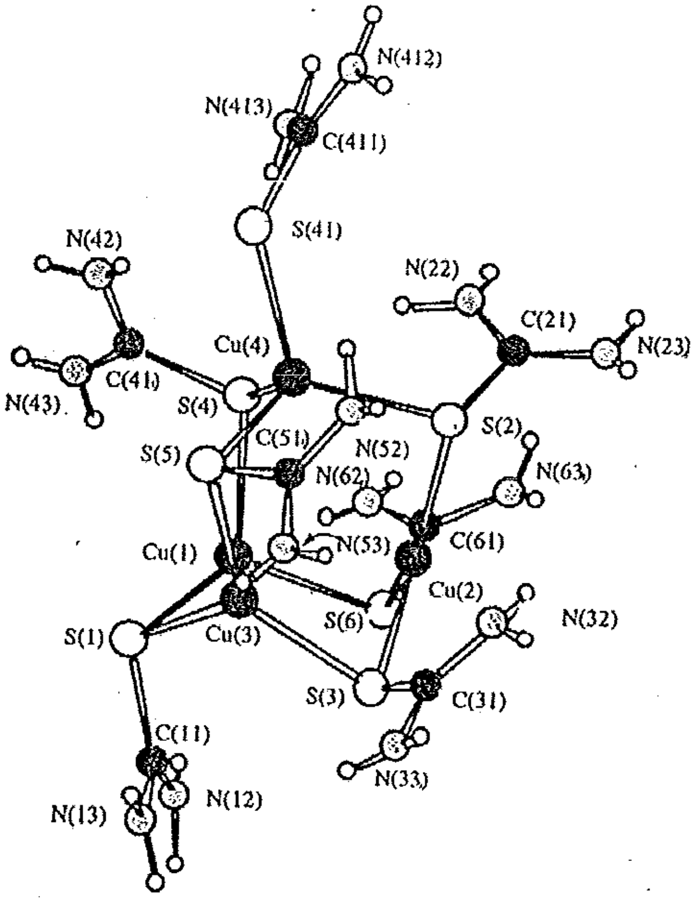


Figure 6 The structure of $[Cu_4(tu)_7]^{4+}$

Crystal data : orthorhombic, space group *Pbca* ; $a = 10.414(3)$, $b = 17.909(3)$, $c = 35.818(3)$ Å , $V = 6680$ Å$^3$, $Z = 8$, $D_c = 1.983$ g/cm$^3$ , $F(000) = 4016$, $\mu = 31.4$ cm$^{-1}$ (Mo $K_\alpha$), $N = 4093$, $R = 0.0447$

The complexes of Cu(I) and Ag(I) thiourea and substituted thioureas, which have already been studied by X-ray crystallography are summarized in Table 1.

Table 1 Copper(I) and silver(I) thiourea and substituted thiourea complexes

| **Formula** | **Metal Steriochemistry** | **Reference** |
|---|---|---|
| $Cu(tu)_3Cl$ | Tetrahedral | Okaya and Knobler, 1964 |
| $[Cu_4(tu)_9](NO_3)_4$ | Tetrahedral | Vranka and Amma, 1966 |
| $Ag(tu)_2Cl$ | Distorted trigonal planar | Vizzini, Taylor and Amma, 1968 |
| $Cu_2(tu)_6(ClO_4)_2$ | Tetrahedral | Havic, 1969 |
| $Cu(tu)_2Cl$ | Trigonal planar | Spofford and Amma, 1970 |
| $Cu(dmtu)_3Cl$ | Tetrahedral | Girling and Amma,1971 |
| $[Cu(etu)_3]_2(SO)_4$<br>$Cu(tmtu)_3(BF_4)$ | Trigonal planar<br>Trigonal planar | Weininger, Hunt and Amma, 1972 |
| $Ag(Mmtu)_3Cl$ | Distorted tetrahedral | Lee and Amma, 1972 |
| $Cu_4(tu)_{10}(SiF_6)_2.H_2O$ | Tetrahedral | Gash, *et al.* 1973 |
| $[Cu(etu)_9(NO_3)_4].6H_2O$ | Tetrahedral | Crumbliss, *et al.* 1974 |
| $Cu(tu)_3(BF_4)$<br>$Cu(dmtu)_3(BF_4)$ | Terahedral<br>Tetrahedral | Talor, Weininger and Amma., 1974 |
| $Cu_4(tu)_6(NO_3)_4.4H_2O$<br>$Cu_4(tu)_9(NO_3)_4.4H_2O$ | Trigonal planar<br>Distorted tetrahedral | Griffith, Hunt and Amma, 1976 |
| $[Cu(etu)_4]NO_3$<br>$Cu_2(etu)_4Cl_2$ | Tetrahedral<br>Cu(1) – Tetrahedral<br>Cu(1) – Trigonal planar | Battaglia, *et al.* 1976 |
| $Ag(tu)_2SCN$ | Distorted tetrahedral | Udupa, Henkel and Krebs, 1976 |
| $[Cu(tu)_4]_2SiF_6$ | Distorted tetrahedral | Hunt, Terry and Amma, 1979 |
| AgCl.2etu<br>AgBr.2etu | Distorted tetrahedral<br>Distorted tetrahedral | Bowmaker, *et al.* 1984 |
| $Cu(dmtu)_2(NO_3)$ | Distorted tetrahedral | Dubler and Bensch,1986 |
| $[Cu(etu)_3]_2SO_4$<br>$[Cu(etu)_4]NO_3$ | Trigonal<br>Quasi-tetrahedral | Bowmaker, *et al.* 1994 |
| $[Cu_4(tu)_7](SO_4)_2.H_2O$ | Cu(1)-tetrahedral<br>Cu(2), Cu(3), Cu(4)-trigonal planar | Bott, *et al.* 1998 |

Cu(I) and Ag(I) thiourea and substituted thiourea complexes give rise to a wide range of stoichiometries and geometric configurations including polynuclear species. Compounds may even present a different stereochemistry with the same stiochiometry and, for instance, they may exhibit two kinds of coordination of the central metallic atom in the same adduct. With this in mind, several spectroscopic studies have been carried out, the determination of the crystal structures by X-ray diffraction often brings about the ultimate structure decision.

In this thesis, Cu(I) and Ag(I) substituted thiourea complexes have been synthesized and characterized by X-ray crystallography.

## 1.3 Objective

1. To synthesize single crystals of some copper(I) and silver(I) substituted thiourea complexes in suitable solvents by varying mole ratio of reactants.
2. To determine crystal structures of complexes (synthesized in 1.) by X–ray diffraction techniques.
3. To apply Xtal program to solve structures of complexes.
4. To compare the crystal structures of the complexes studied with those of similar complexes, which have already been studied.
5. To present the research in academic conferences or publish in chemistry journals.

# Chapter 2

# METHOD OF STUDY

## 2.1 Materials and Instruments

1. Capillary Melting Point Apparatus, Thomas Hoover, Unimelt 0 - 360°C
2. Thermometer, Gallenkamp, England 0 - 360°C
3. Perkin-Elmer 783 Infrared Spectrophotometer
4. Spectrace 5000 X-ray Fluorescence
5. PW 1720 X-ray Generator (Philips), Weissenberg Camera (Enraf Nonius FR550)
6. Xtal Version 3.5, 3.6
7. Microscope Olympus Bin Steriom VTII
8. UHU Epoxy Adhesive
9. Film AGFA-GEVAERT CURIXRP1 100 AFW
10. Fiber glass, 0.1 - 0.4 mm (in diameter)
11. Capillary tube
12. Diskette 1.44 MB, 3.5 inch
13. Hot plate stirrer with Magnetic bar
14. Computer
    - Unix workstation (Dec Alpha 4/166)
    - PC (Hewlett Packard, Vectra VL)
15. Printer Hewlett Packard, Laser Jet 5 MP

## 2.2 Chemicals

Products of Fluka Chemical, Buchs, Switzerland

1. Acetylthiourea, $C_3H_6N_2OS$, purum
2. *N,N′*-Dimethylthiourea, $C_3H_8N_2S$, purum
3. *N,N′*-Diphenylthiourea, $C_{13}H_{12}N_2S$, purum
4. *N,N′*-Ethylenethiourea, $C_3H_6N_2S$, purum
5. *N*-Ethylthiourea, $C_3H_8N_2S$, purum
6. *N*-Methylthiourea, $C_2H_6N_2S$, purum
7. *N*-Phenylthiourea, $C_7H_8N_2S$, purum
8. Silver(I) acetate, $AgC_2H_3O_2$, purum
9. Silver(I) carbonate, $Ag_2CO_3$, purum
10. Silver(I) chloride, AgCl, purum
11. Silver(I) iodide, AgI, purum
12. Silver(I) thiocyanate, AgSCN, purum

Products of BDH Chemical Ltd., England

1. Copper(I) bromide, CuBr, L.R. grade
2. Copper(I) chloride, CuCl, L.R. grade
3. Silver(I) sulfate, $Ag_2SO_4$, L.R. grade

Products of E. Merck, Darmstadt, Germany

1. Silver(I) bromide, AgBr, L.R. grade
2. Copper(II) nitrate 2.5 hydrate, $Cu(NO_3)_2 . 2\frac{1}{2}H_2O$, L.R. grade
3. Copper(II) sulfate pentahydrate, $CuSO_4 . 5H_2O$, L.R. grade

Products of Lab-Scan Analytical Science

1. Ethanol, $C_2H_5OH$, A.R. grade
2. Acetonitrile, $CH_3CN$, A.R. grade

Product of Aldrich Chemical Co., Inc., USA

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

Product of Farmitalia Carlo Erba, Miland

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

Product of Sigma Chemical Co., USA

Silver(I) perchlorate, $AgClO_4$, L.R. grade

## 2.3 Preparation of Complexes

Preparation of Cu(I) and Ag(I) substituted thiourea complexes have been performed in many ways ; varying reactants, mole ratios of reactants, solvents and reaction temperature. However, there were 6 compounds the crystals of which were suitable to be studied by X-ray diffraction methods. The following detail is about the methods of crystal preparation of these compounds :

### 2.3.1 $[Ag(atu)_2]NO_3$

$AgNO_3$ (0.25 g, 1.5 mmol) was added to acetylthiourea (0.87 g, 7.4 mmol) in ethanol (50 mL) at room temperature with continuous stirring for 3 h. After which time it was filtered and the fitrate then left at room temperature. After 1 day, the solution yielded a black precipitate. It was filtered off the filtrate left to stand again. Upon standing, the product formed light brown prismatic crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

### 2.3.2 $[Cu_4(ettu)_6 I_4].H_2O$

CuI (0.25 g, 1.3 mmol) was added to *N*-ethylthiourea (0.35 g, 3.3 mmol) in ethanol (50 mL) at 60 °C with continuous stirring for 3 h. Then it was filtered and allowed to cool to room temperature. Slow evaporation of the solvent yielded colorless needles. They were isolated, washed and dried as in 2.3.1.

### 2.3.4 $[Ag_2(etu)_6](ClO_4)_2$

$AgClO_4$ (0.25 g, 1.2 mmol) was added to *N*-ethylenethiourea (0.61 g, 6.0 mmol) in ethanol (50 mL) at room temperature with continuous stirring for 3 h. Then it was filtered and the fitrate left to stand at room temperature. Upon standing, the solution yielded colorless prisms which were isolated, washed and dried as in 2.3.1.

### 2.3.4 $[Ag_2(etu)_4Br_2]$

AgBr (0.50 g, 2.7 mmol) was added to *N*-ethylenethiourea (0.81g, 7.9 mmol) in distilled water (70 mL) at 70 °C with continuous stirring for 3 h. Then it was filtered and allowed to cool slowly to room temperature. Upon standing, the solution yielded colorless needles. They were isolated, washed and dried as in 2.3.1.

### 2.3.5 $[Cu(etu)_3]_2SO_4$

$CuSO_4.5H_2O$ (0.5 g, 2.0 mmol) was slowly added to *N*-ethylenethiourea (0.61 g, 6.0 mmol) which dissolved in distilled water (70 mL) at 70 °C with continuous stirring for 3 h. Then it was filtered and allowed to cool slowly to room temperature. Upon standing, the solution yielded colorless prisms which were isolated, washed and dried as in 2.3.1.

2.3.6 $(C_6H_5NH)_2CO$

$Cu(NO_3)_2.2\frac{1}{2}H_2O$ (1.16 g, 5.0 mmol) was added to *N,N′*-diphenylthiourea (3.43 g, 15.0 mmol) in acetonitrile (100 mL) at 60 °C with continuous stirring for 3 h. Then it was filtered and allowed to cool slowly to room temperature. After 1 day, the solution yielded a blue precipitate. It was filtered off and the filtrate left to stand. Upon standing, the solution yielded light brown prisms. They were isolated, washed and dried as in 2.3.1

## 2.4 X-ray Fluorescence Spectrometry

Cu or Ag, S and/or halides (Cl, Br or I) qualitative analyses were performed by EDXRF techniques on Spectrace 5000 X-ray Fluorescence.

## 2.5 Infrared Spectrophotometry

Infrared spectra were obtained on KBr discs on a Perkin-Elmer 783 Infrared Spectrophotometer in the range 4000 - 200 $cm^{-1}$.

## 2.6 Crystal Structure Determination

### 2.6.1 The preparation and selection of samples

2.6.1.1 Select a suitable crystal

If a crystal is satisfactory for collecting X-ray diffraction data, two main requirements must be met :

(1) It must possess uniform internal structure, a crystal must be pure at the molecular, ionic or atomic level. It must be a single crystal. It should not be grossly fractured, bent or otherwise physically distorted.

(2) It must be of proper size and shape, 0.2 - 0.5 mm.

### 2.6.1.2 Crystal mounting

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

(1) Crystals, not volatile or sensitive to the environment, are glued onto a thin glass fiber with an expoxy glue (Figure 7a). All crystals were mounted by this method.

(2) Crystals, air-sensitive or degradable by loss of loosely bound solvents, require special treatment. They may be sealed in thin-walled glass capillary tubes (Figure 7b). Alternatively, the crystals can be coated with an inert viscous oil and then manipulated without difficulty under a normal microscope in the open atmosphere.

### 2.6.1.3 Optical alignment

The mounted crystal was attached to a goniometer head (Figure 8), this device holds the crystal in place on a camera and allows it to be oriented in the x-ray beam by means of translational and angular motions. The head is designed to be screwed onto a rotating spindle in the camera and the crystal can be adjusted (aligned) so that either a direct or a reciprocal crystal axis is on the axis of rotation.

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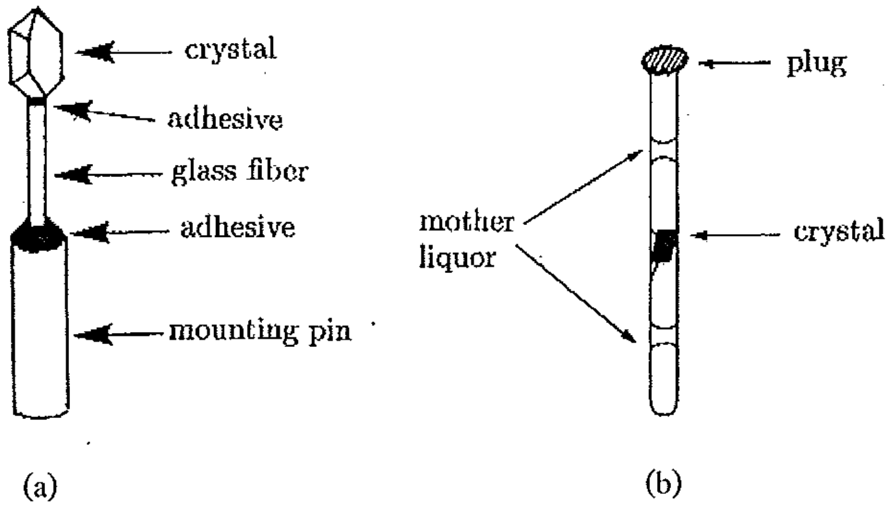

Figure 7 Crystal mounting

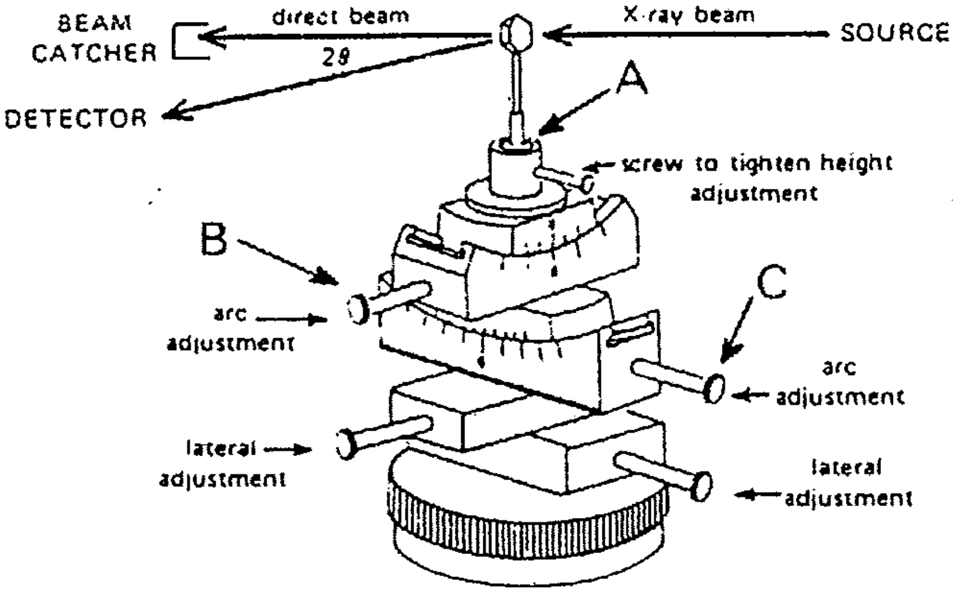

Figure 8 The goniometer head

## 2.6.2 Data collection

### 2.6.2.1 X-ray photography

The Enraf Nonius FR550 Weissenberg camera was performed, 2 methods of X-ray photography have been used :

(1) Oscillation methods

A crystal is oscillated range 10 - 20° but without moving a film. Usually an exposure of 1 - 2 h. is enough. After exposure the film is developed, fixed, and washed.

Oscillation photographs are generally used to align crystals and to measure the cell edge along the axis of rotation.

(2) Weissenberg methods

The film holder is engaged on the worm screw that leads from the motor to the crystal mounting and is moved in strict coincidence with the crystal rotation. At either end of its travel the film holder (or an adjustable stop) strikes a reversing switch, which changes the direction of the crystal rotation and sends the film back the other way. The usual free translation of the film carriage is 100 - 110 mm, corresponding to an oscillation range of 200 - 220°. An exposure is about 24 - 28 h. After exposure the film is developed, fixed, and washed.

Weissenberg photographs can be used for improving alignment, measuring cell constants ($a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$) and determining the space group.

The picture of Weissenberg camera and X-ray photography are shown in Figure 9 - 11.

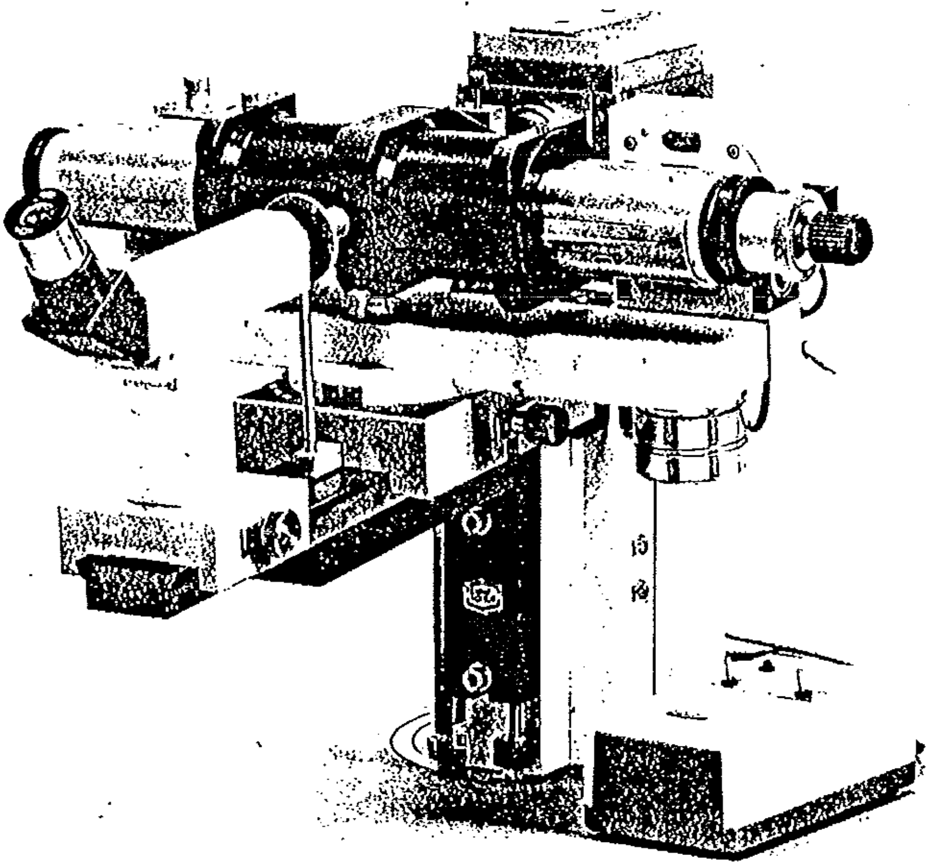

Figure 9 The Weissenberg camera

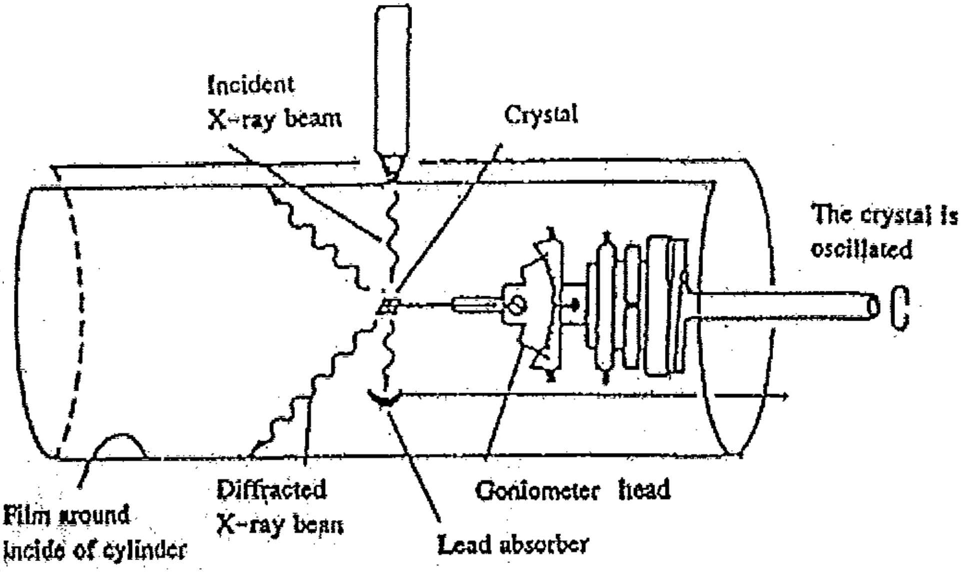

Figure 10 Schematic view of X-ray photography

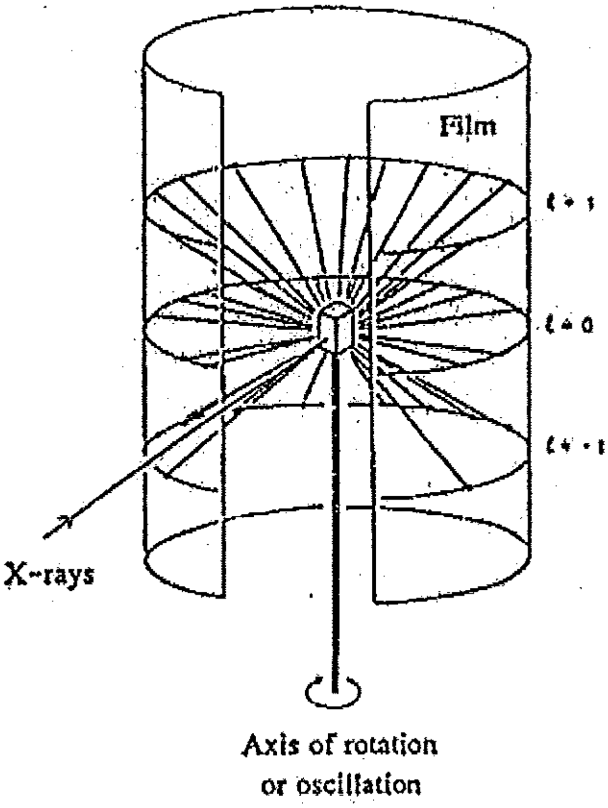

Figure 11 X-ray diffraction on a film

### 2.6.2.2 X-ray diffractometry

The crystallographic data of $[Ag(atu)_2]NO_3$ , $[Cu_4(ettu)_6 I_4].H_2O$ and $[Ag_2(etu)_6](ClO_4)_2$ were collected using the P4 diffractometer at Universiti Sains Malaysia by Prof. Dr. Hoong Kun Fun. The crystallographic data of $[Ag(etu)_4Br_2]$, $[Cu_2(etu)_6SO_4]$ and $(C_6H_5NH)_2CO$ were collected using SMART CCD detector system at University of Western Australia, Australia by Prof. Dr. Allan H. White.

With a four-circle diffractometer, the intensities of individual reflection can be measured. For each one, the detector must be moved round one axis (usually vertical) to the correct $2\theta$ angle. Because the detector can see only reflections which occur in the horizontal plane, more than one axis of rotation is needed for the crystal. The most widely used type of diffractometer has three rotation axes for the crystal (conventionally called $\phi, \chi, \omega$) and one for the detector ($2\theta$)., giving more than enough freedom, so that there is even a choice of settings possible for many of the reflections (Figure 12). With one of these four-circle diffractometers reflections (positions and intensities) are observed one at a time, the crystal and detector being moved under computer control from each one to the next in sequence.

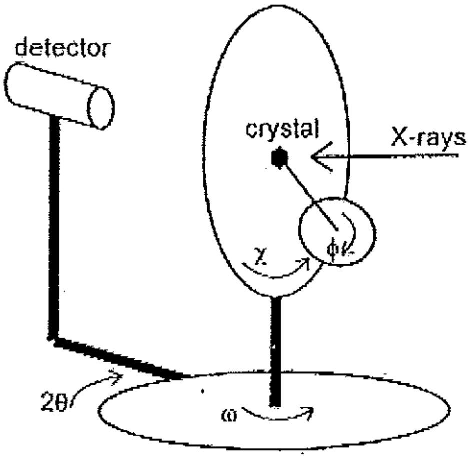

Figure 12 Schematic representation of a four-circle diffractometer

(1) Obtaining unit cell geometry and symmetry

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

(2) The measurement of intensities

A conventional four-circle diffractometer measures intensities one at a time in an automatic, computer-controlled process. For each reflection the crystal and detector are driven to the appropriate positions to satisfy the Bragg condition and bring the diffracted beam into the detector in the horizontal plane, and the total integrated intensity is measured while the crystal is rotated through a small angle from one side of the Bragg equation to the other.

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

(3) Data reduction

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

The various corrections for the intensities are applied also to their s.u.'s. The result of this whole process, which usually takes only a matter of minutes on a computer, is list of reflection as $h, k, l, |F_o|, \sigma(|F_o|)$ [or $h, k, l, |F_o|^2, \sigma(|F_o|^2)$].

### 2.6.3 Solving structure by Xtal system version 3.5, 3.6

The structures were solved from diffraction data by using the program Xtal 3.5, 3.6 (Hall, et. al. 1995 ; Hall, et. al. 1999) on Unix workstation computer at Department of Chemistry, Faculty of Science, Prince of Songkla University.

Most Xtal calculations are initiated, and controlled, from an input line file usually known as the .dat file. The results of a calculation are output to files and a screen device (as in graphics applications). Xtal calculations use various files to store intermediate and archival data. This strong dependence on files means that Xtal is considered a file-driven archival system, rather than an interactive menu-driven system.

The convention for filename construction for all Xtal files is normally <compid>.<ext> where compid is the compound identification code (maximum of six characters), and ext is the extension code (three characters). The compid code is defined by the user at the start of the input commands with the line "compid". This is the method step by step of solving :

(1) Getting started

This step is making binary data files, that are used extensively as working files (ie. intermediate files for exchanging within, and between, calculations), and to archive certain types of data. The used subprograms are

STARTX : Create initial archive file

DIFDAT : Process diffractometer data

SORTRF : Sort and merge reflection data

ADDREF : Add reflection data

(2) Solving the structure

There are 2 methods, that were used to solve the structures :

(a) Heavy atom methods

The methods involve solving structure of compounds that have heavy atoms. The used subprograms are

GENEV : Normalized structure factors (E values)

FOURR VECT : Patterson fourier map

PEKPIK : Search for peaks in map

(b) Direct methods

The methods involve solving structure of compounds that have no heavy atoms. The used subprograms are

GENEV

GENSIN : Generate triplets and quartets

GENTAN (or SIMPEL) : Tangent phasing

FOURR EMAP

PEKPIK

CRISP : Crystal Iterative Solution Program (only version 3.6)

GENSIN, GENTAN and FOURR EMAP' can be replaced by CRISP.

(3) Refining the structure

Once all atoms have been found, the model structure needs to be refined. This means varying the numerical parameters describing the structure to produce the best agreement. Anisotropic thermal parameters are used for all non-hydrogen atoms. Hydrogen atoms were located in difference-Fourier analyses and included with coordinations refined.

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

$$\sum w\,(|F_o| - |F_c|)^2$$

$w$ = Reflection weights

= $[\sigma^2|F_o|^2 + 0.005|F_o|^2]^{-1}$

$F_o$ = Observed structure factors

$F_c$ = Calculated structure factors ;

$$F_c(hkl) = \Sigma f_j \exp[2\pi i\,(hx_j + ky_j + lz_j)]\,.$$
$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} +$$
$$2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

Anisotropic temperature factors ($U_{ij}$) and atomic thermal parameters are in the form $1000U_{ij}$ Å$^2$.

The used subprograms are

ADDATM : Load atom parameters

CRYLSQ : Structure factor least-squares refinement

(4) Checking geometry

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

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

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

For a correct and complete crystal structure determination from well measured data, $R$ is typically around $0.02 - 0.05$ or $2 - 5\ \%$. Values of $R_w$ based on $|F|^2$ are generally higher than those base on $|F|$ values. The used subprograms are

CRYLSQ

BONDLA : Bond lengths and angles

(5) Preparing for publication

This step is showing the result by pictures and numerical parameters for report and publishing. The used subprograms are

LISTFC : List formatted reflection data

LSQPL : Least-squares planes & lines

ORTEP : Molecular plot

PLOTX : Interface plot devices

ATABLE : Tabulate atomic parameters

# Chapter 3

# RESULTS

## 3.1 Preparation of Complexes

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

Table 2 The condition of preparation compounds.

| Reactants | Mole ratio | Solvent | Temperature (°C) | Compound |
|---|---|---|---|---|
| $AgNO_3$ : atu | 1 : 5 | Ethanol | room | $[Ag(atu)_2]NO_3$ |
| CuI : ettu | 1 : 2.5 | ethanol | 60 | $[Cu_4(ettu)_6\,I_4].H_2O$ |
| $AgClO_4$ : etu | 1 : 5 | ethanol | room | $[Ag_2(etu)_6](ClO_4)_2$ |
| AgBr : etu | 1 : 3 | water | 70 | $[Ag_2(etu)_4Br_2]$ |
| $(CuSO_4).1/2H_2O$ : etu | 1 : 3 | water | 70 | $[Cu(etu)_3]_2SO_4$ |
| $Cu(NO_3)_2.2½H_2O$ : dptu | 1 : 3 | acetonitrile | 60 | $(C_6H_5NH)_2CO$ |

Table 3 The physical properties of ligands and compounds.

| Compounds | Physical properties | | | |
|---|---|---|---|---|
| | Appearance | Colour | Melting point (°C) | Solubility |
| ligand atu | powder | white | 165 - 168 | soluble* |
| $[Ag(atu)_2]NO_3$ | prism | light brown | 141 (d) | acetonitrile |
| ligand ettu | powder | white | 108 - 110 | soluble* |
| $[Cu_4(ettu)_6 I_4].H_2O$ | needle | colorless | 124 - 126 | insoluble** |
| ligand etu | powder | white | 198 - 200 | soluble* |
| $[Ag_2(etu)_6](ClO_4)_2$ | prism | colorless | 118 - 119 | ethanol |
| $[Ag_2(etu)_4Br_2]$ | needle | colorless | 151 - 152 | insoluble** |
| $[Cu(etu)_3]_2SO_4$ | prism | colorless | 248 - 250 (mwd) | water |
| ligand dptu | powder | white | 150 - 153 | soluble*** |
| $(C_6H_5NH)_2CO$ | prism | light brown | 238 - 240 | soluble**** |

d = decompose

mwd = melt with decompose

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

insoluble** = insoluble in ethanol, acetone, acetonitrile and water

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

soluble**** = soluble in acetone and acetonitrile

### 3.2 X-ray Fluorescence Spectrometry

The X-ray fluorescence spectrum of the compounds are shown in Figure 13 – 18.

### 3.3 Infrared Spectroscopy

The infrared spectrum of the ligands and compounds are shown in Figure 19 - 28.

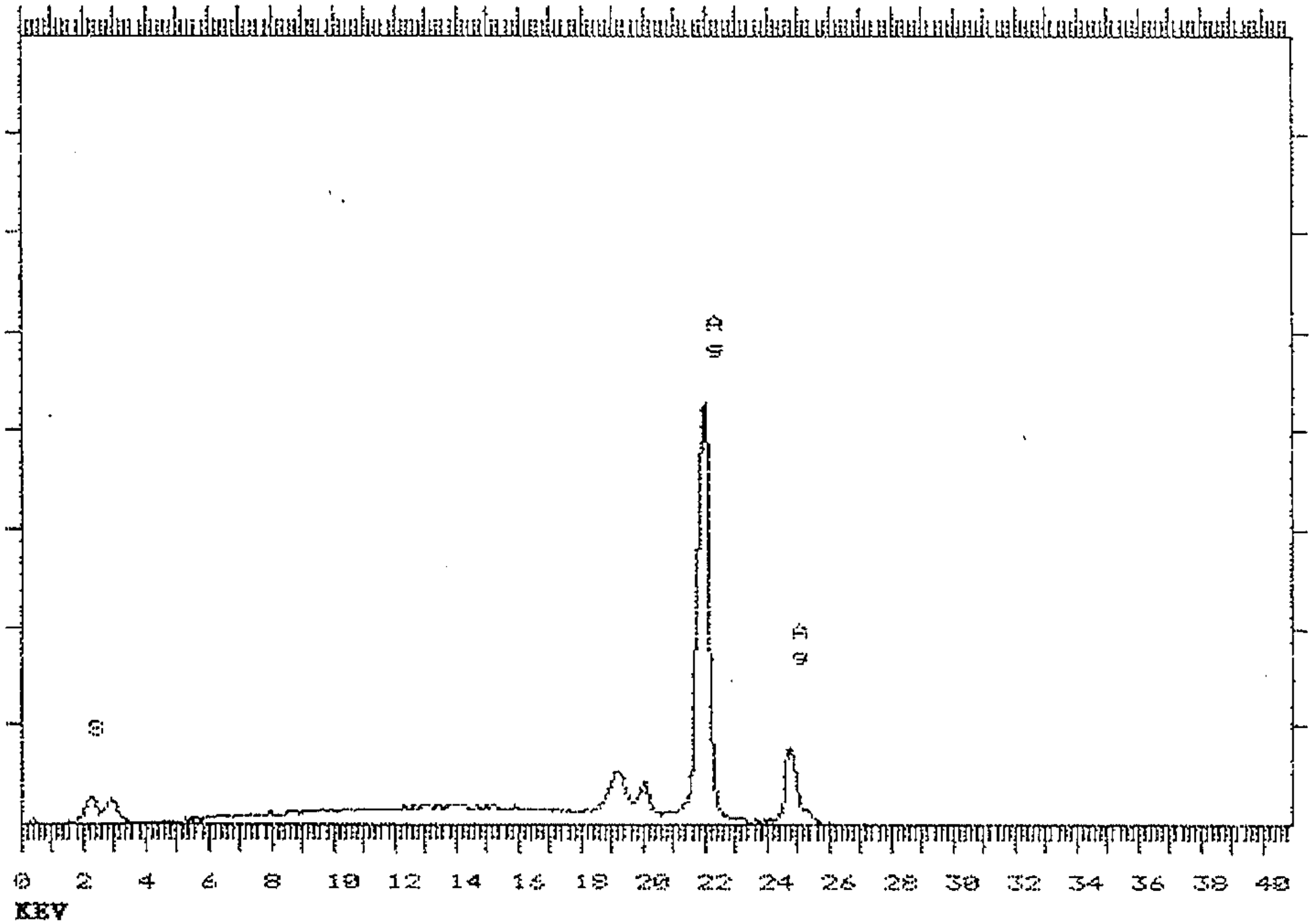

Figure 13 The X-ray fluorescence spectrum of $[Ag(atu)_2]NO_3$

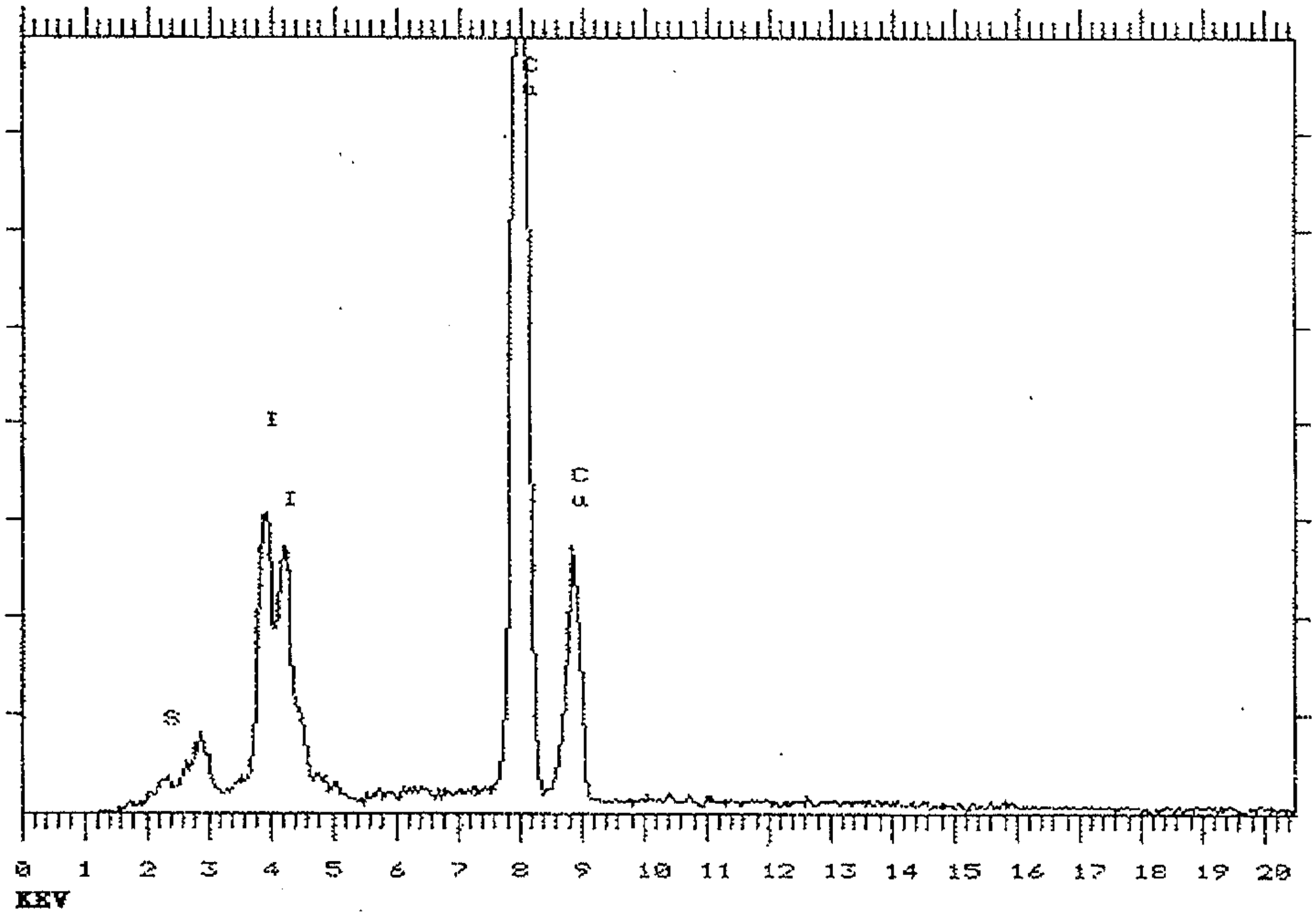

Figure 14 The X-ray fluorescence spectrum of $[Cu_4(ettu)_6I_4].H_2O$

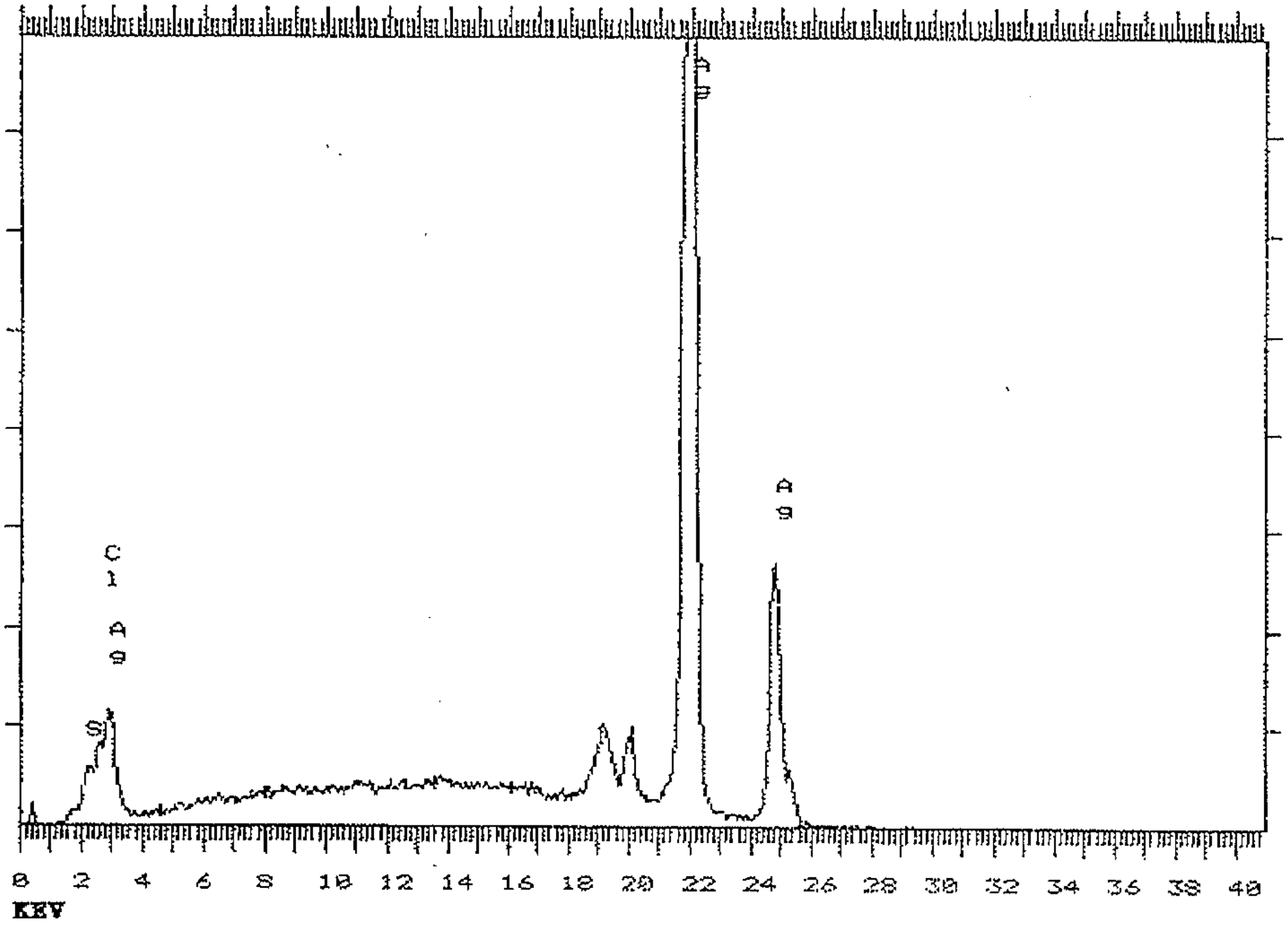

Figure 15 The X-ray fluorescence spectrum of $[Ag_2(etu)_6](ClO_4)_2$

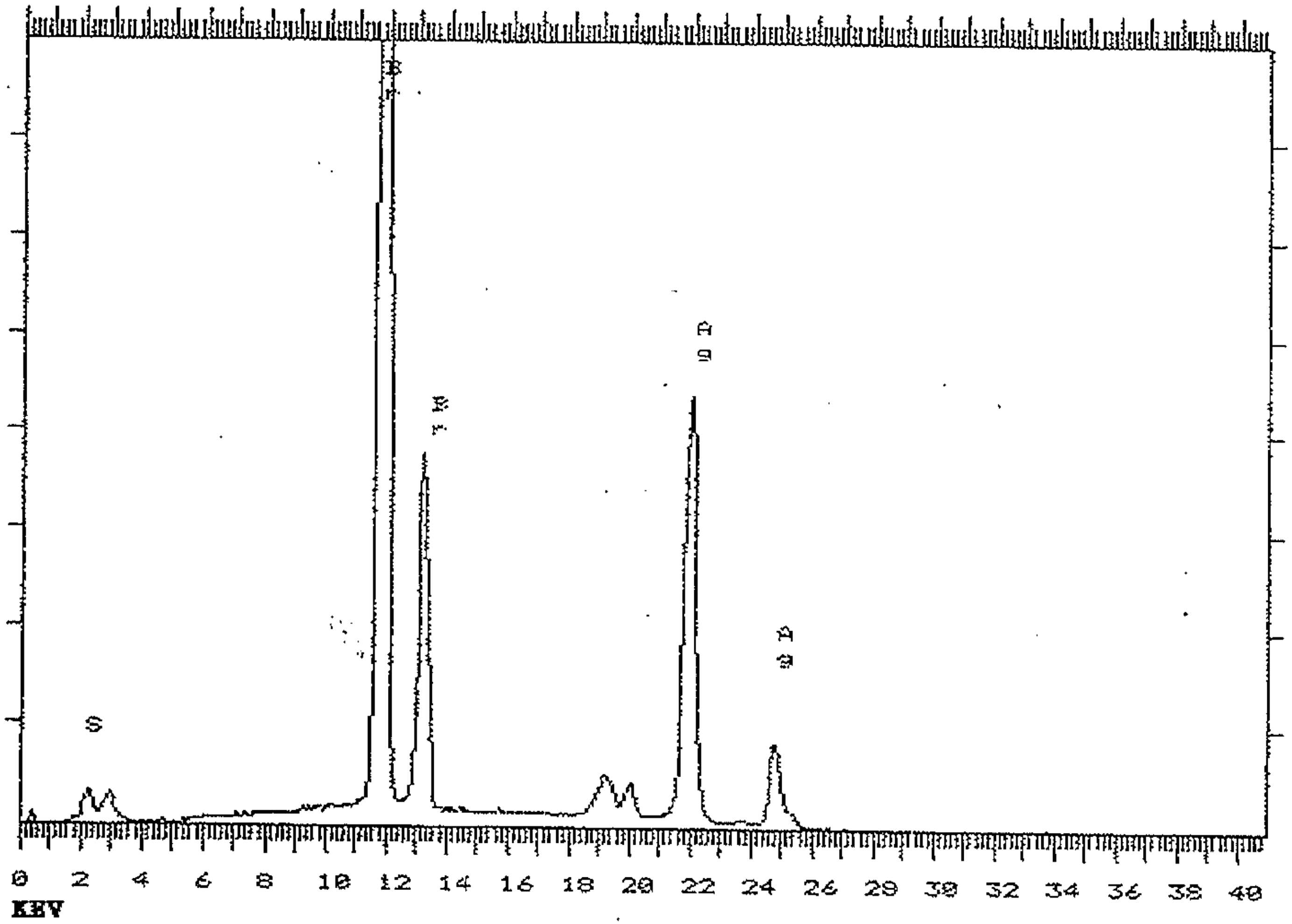

Figure 16 The X-ray fluorescence spectrum of $[Ag_2(etu)_4Br_2]$

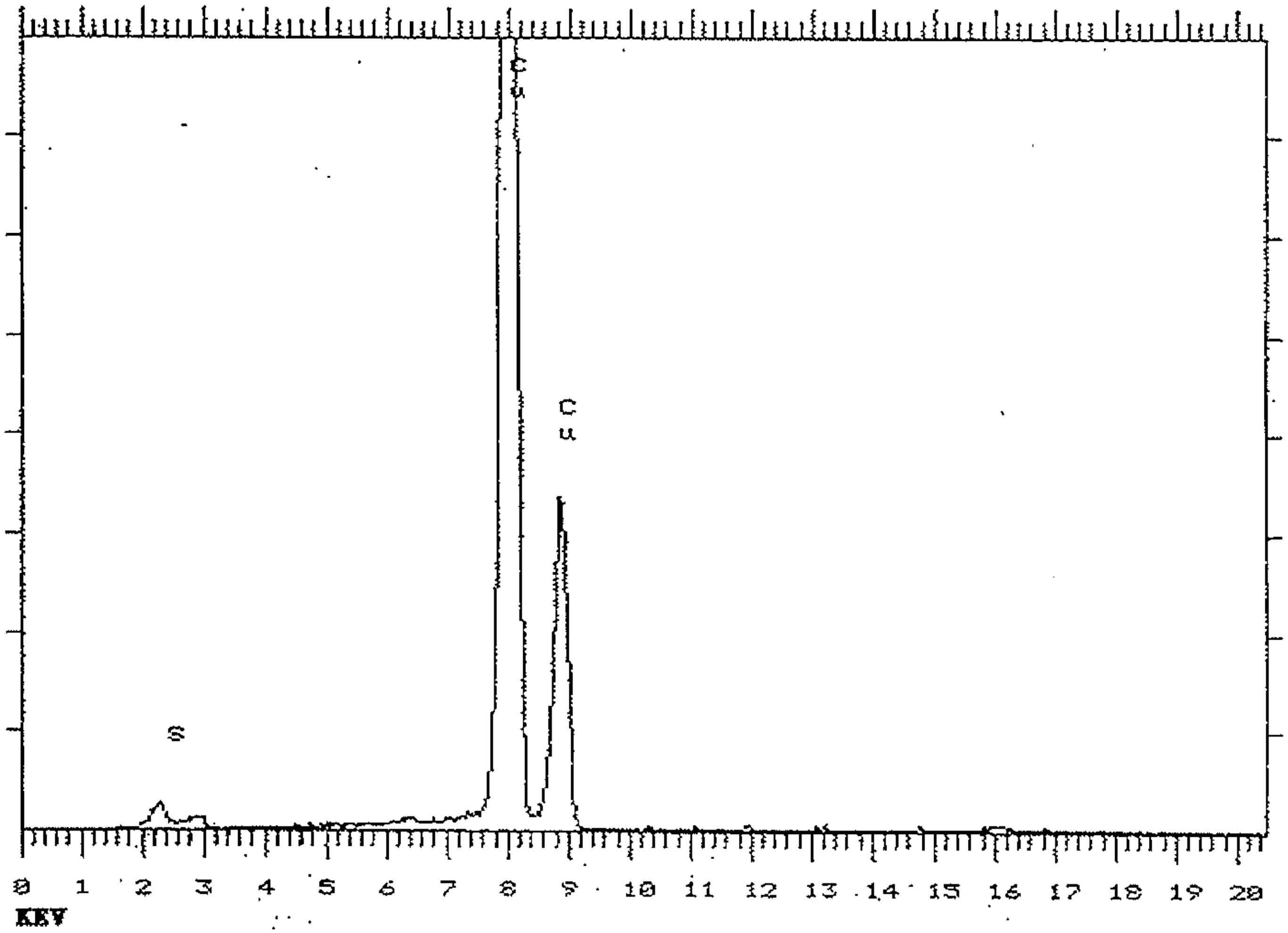

Figure 17 The X-ray fluorescense spectrum of $[Cu(etu)_3]_2SO_4$

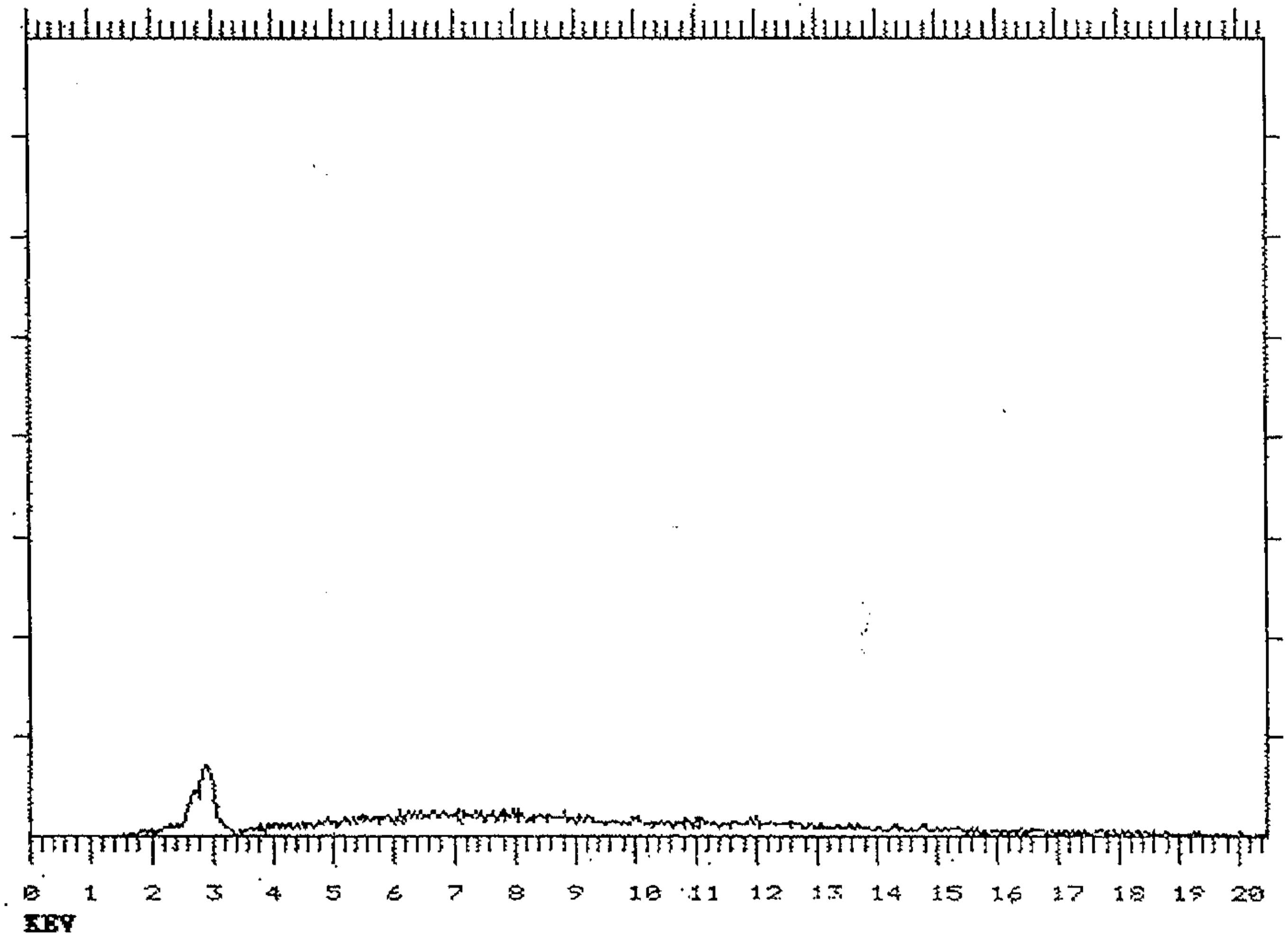

Figure 18 The X-ray fluorescense spectrum of $(C_6H_5NH)_2CO$

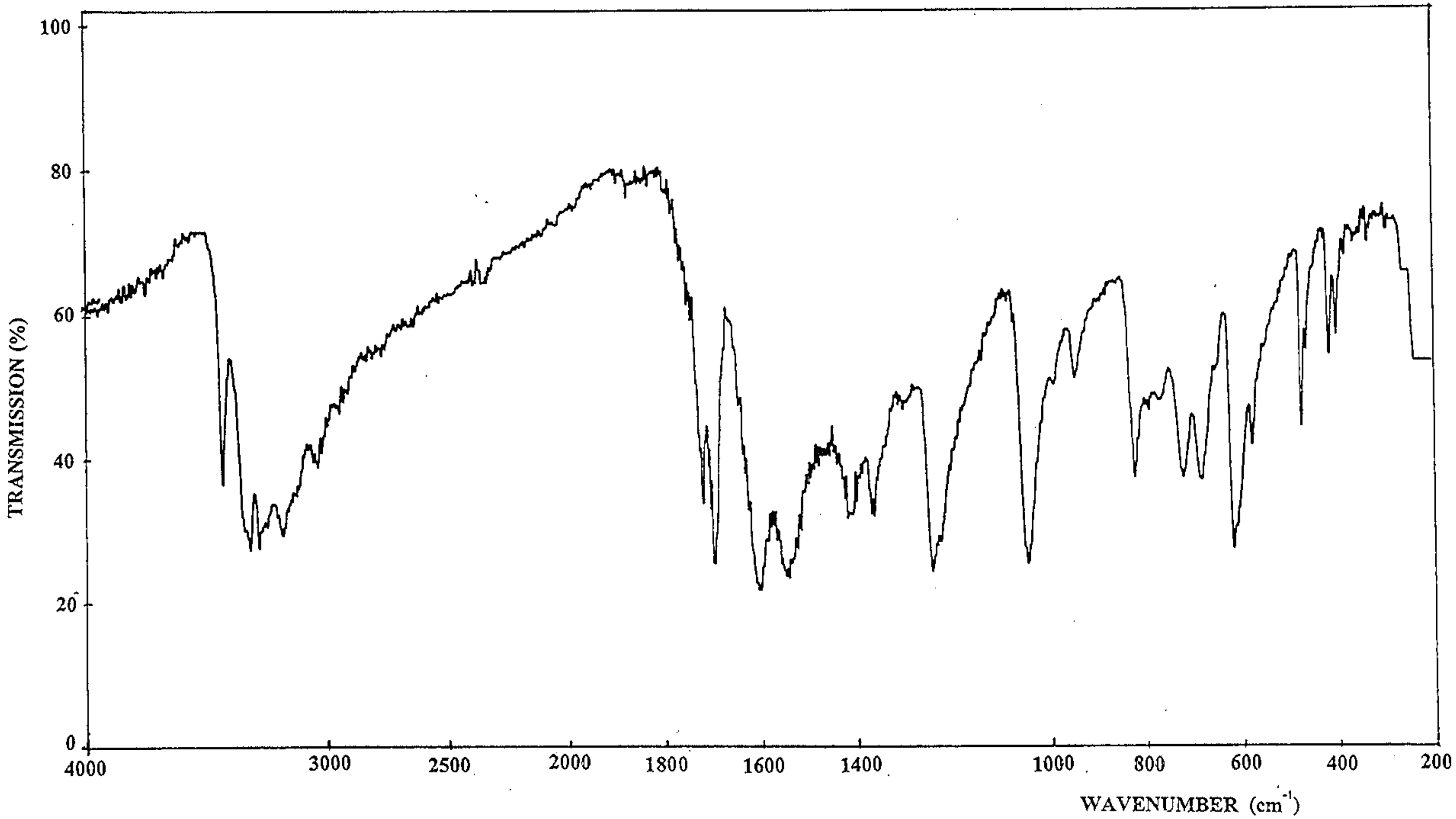

Figure 19 The infrared spectrum of ligand atu

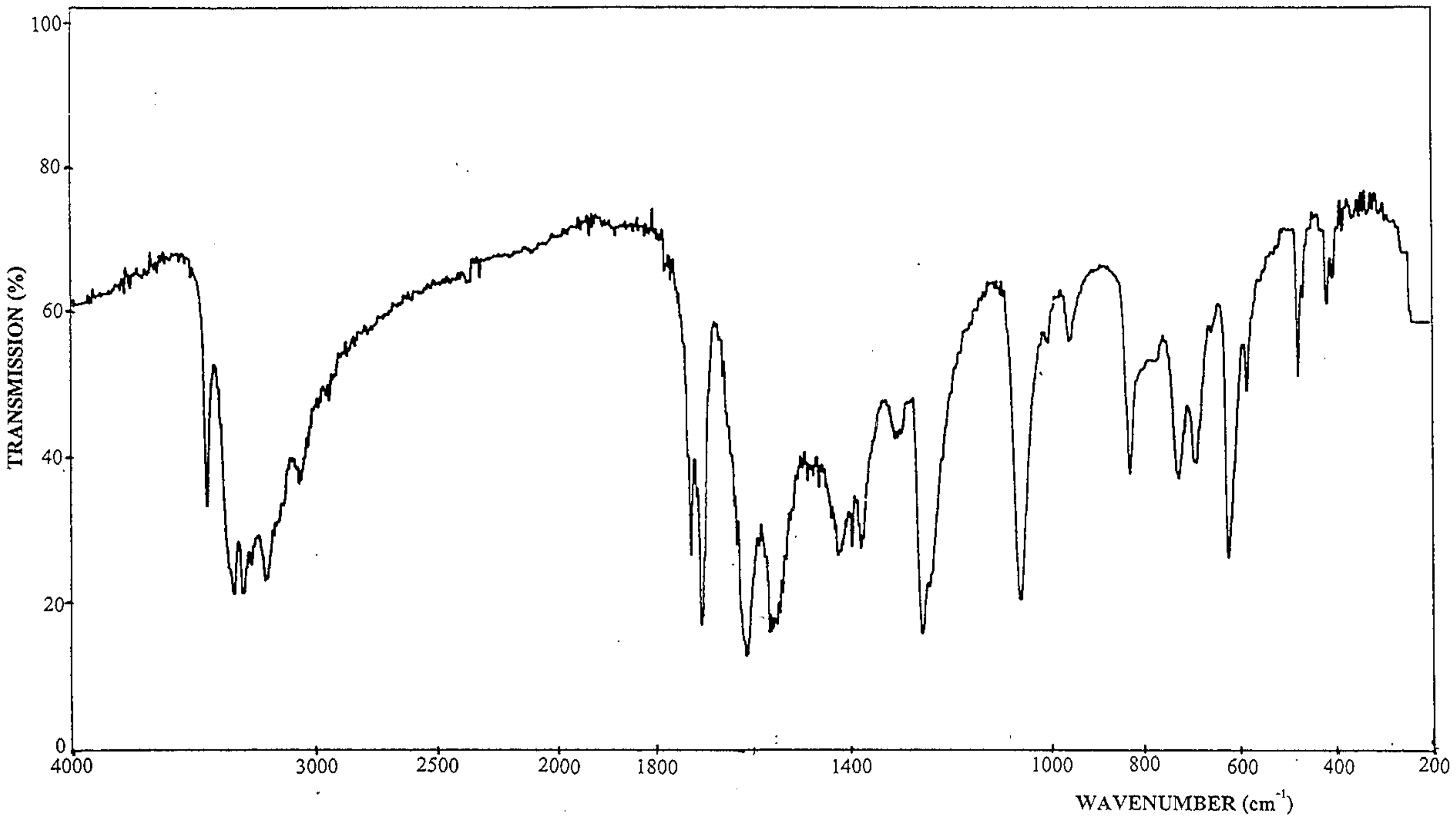

Figure 20 The infrared spectrum of $[Ag(atu)_2]NO_3$

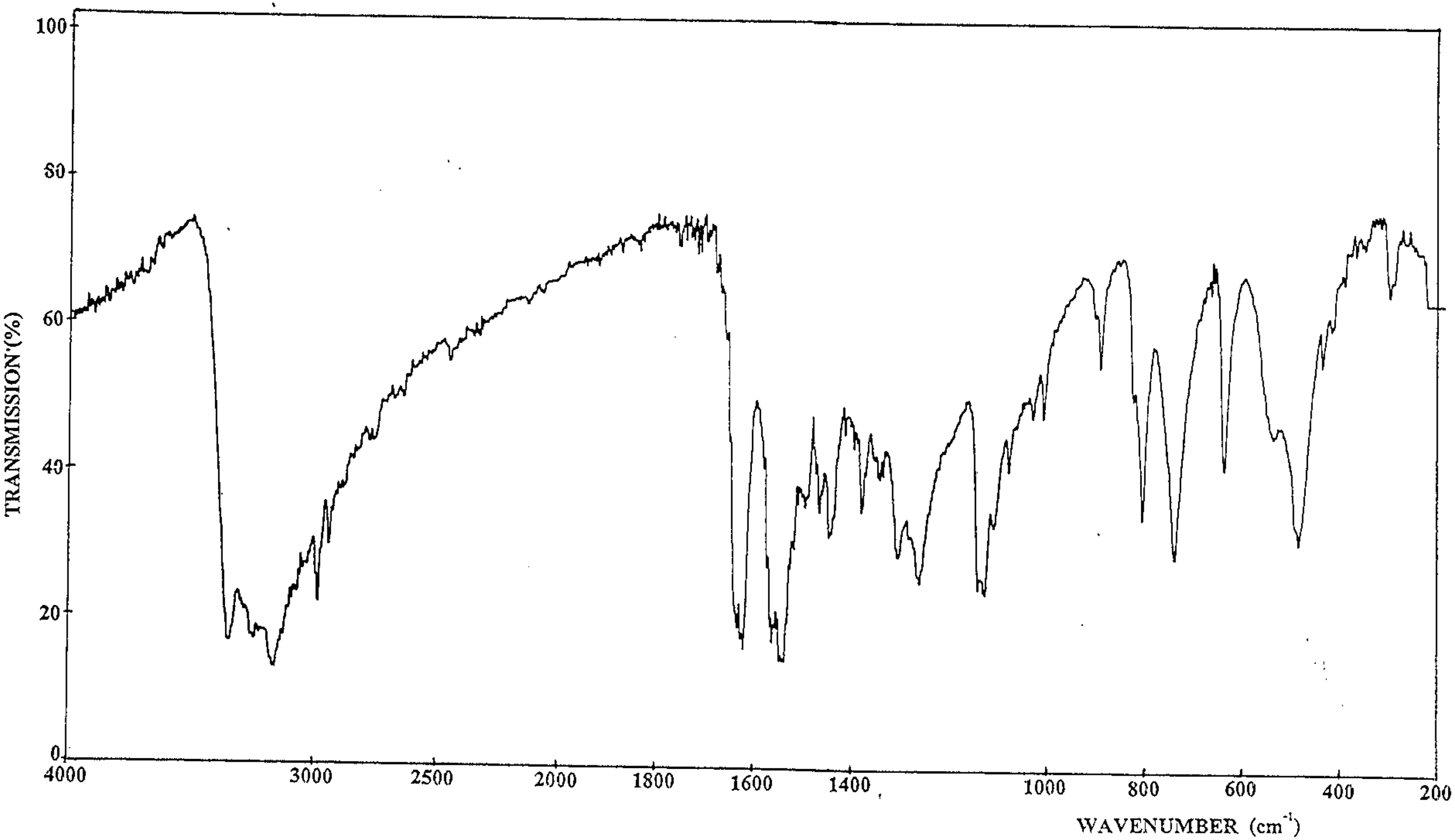

Figure 21 The infrared spectrum of ligand ettu

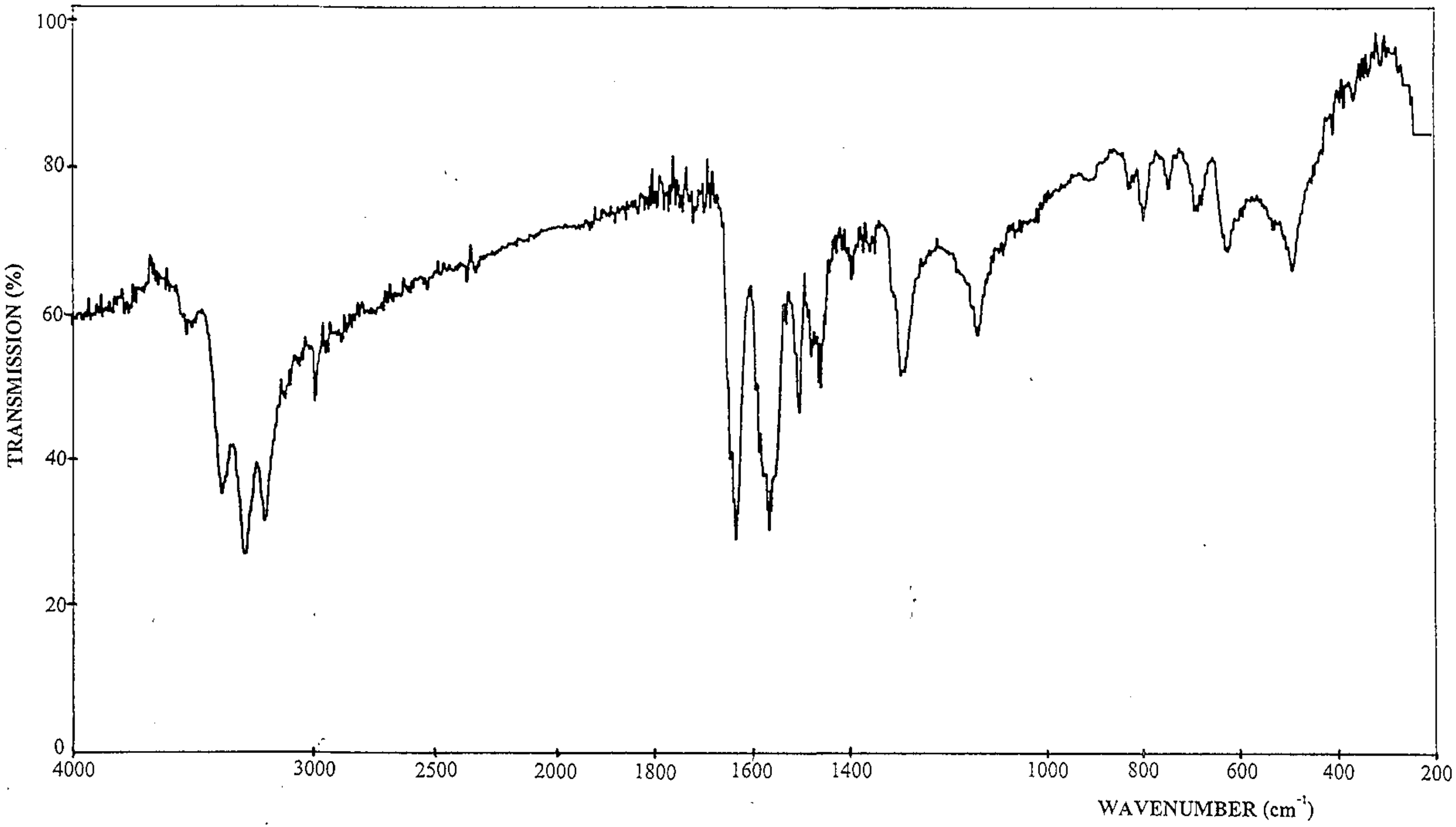

Figure 22 The infrared spectrum of $[Cu_4(ettu)_6 I_4].H_2O$

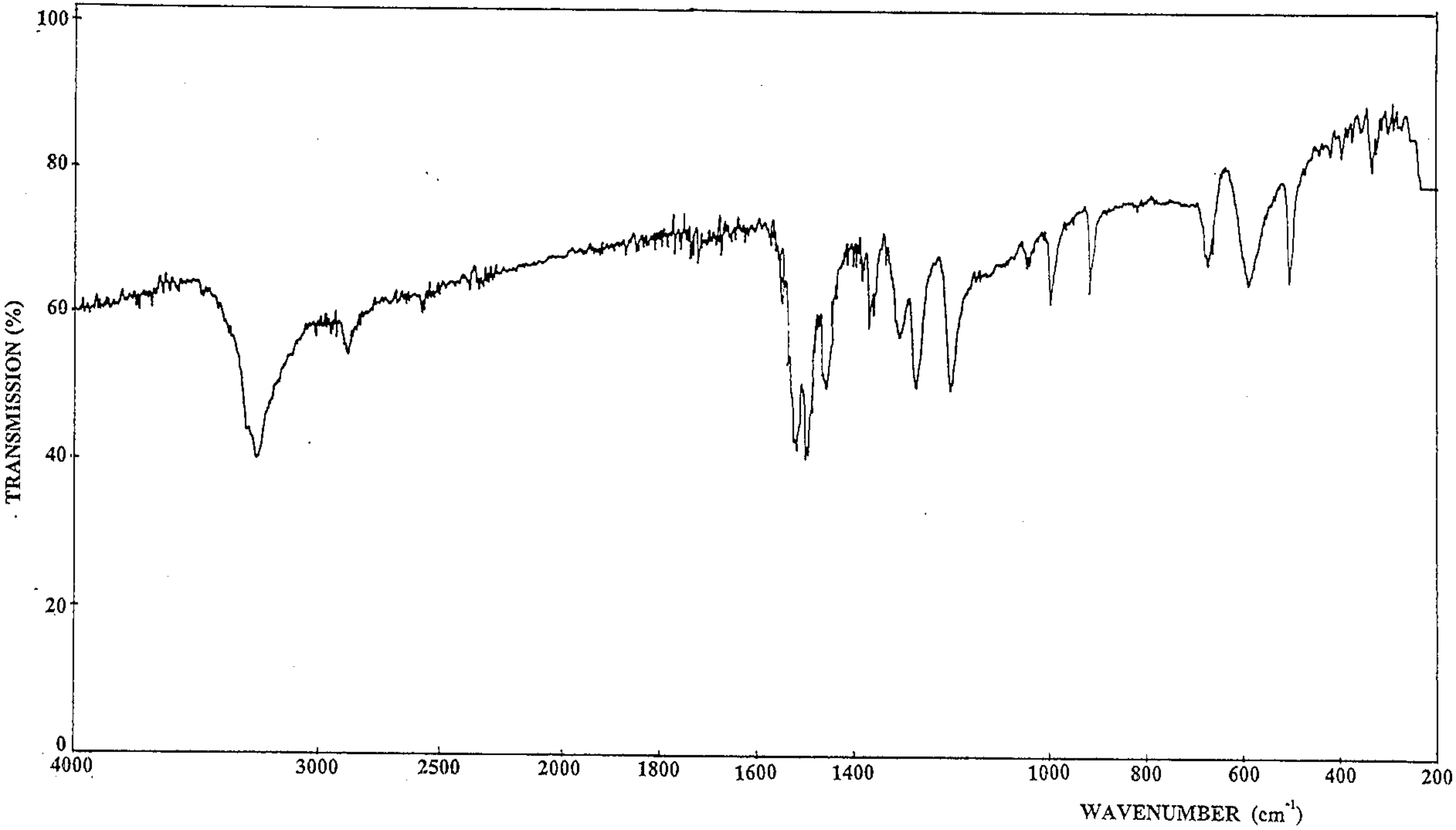

Figure 23 The infrared spectrum of ligand etu

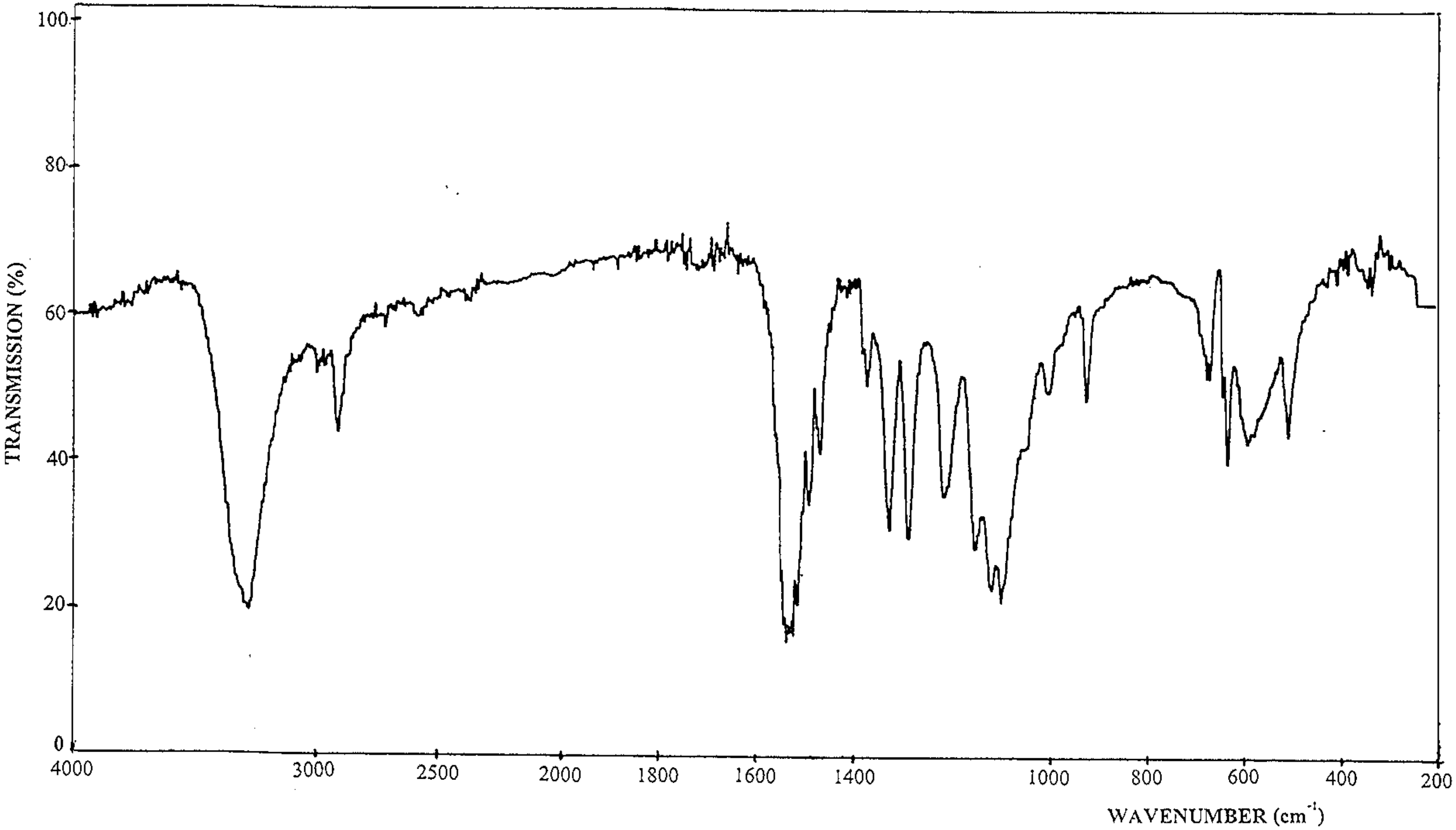

Figure 24 The infrared spectrum of $[Ag_2(etu)_6](ClO_4)_2$

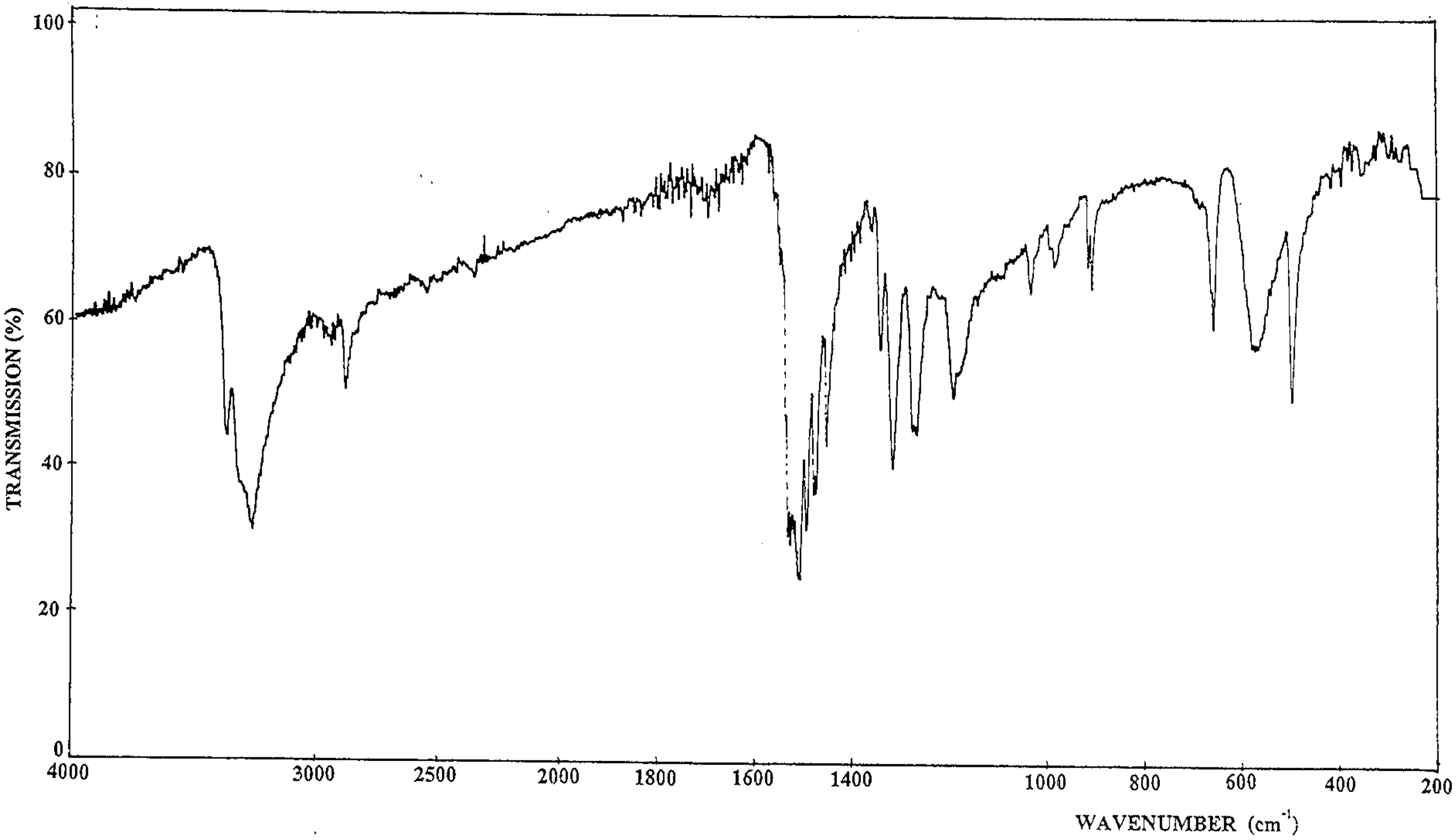

Figure 25 The infrared spectrum of [$Ag_2(ctu)_4Br_2$]

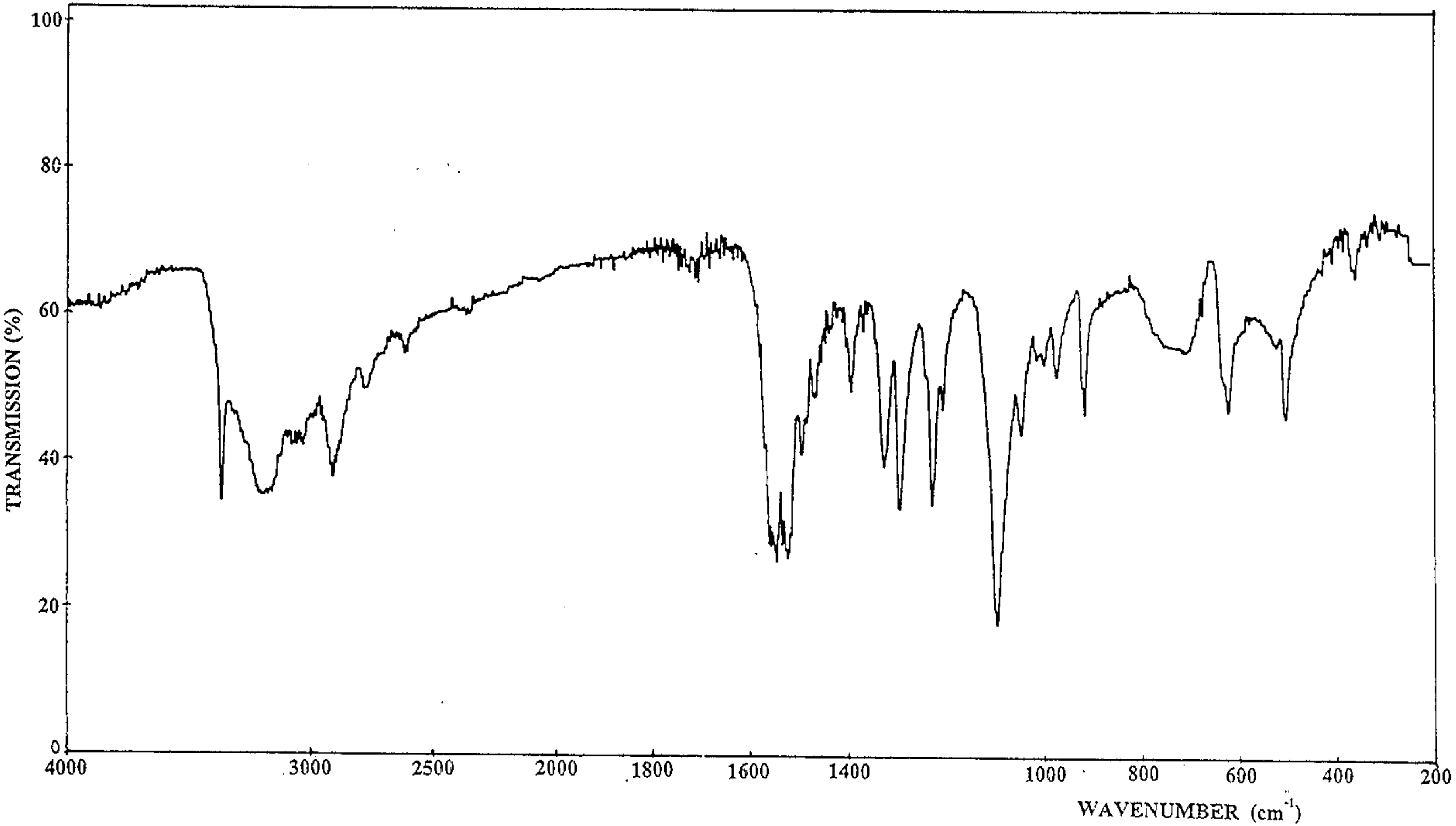

Figure 26 The infrared spectrum of $[Cu(etu)_3]_2SO_4$

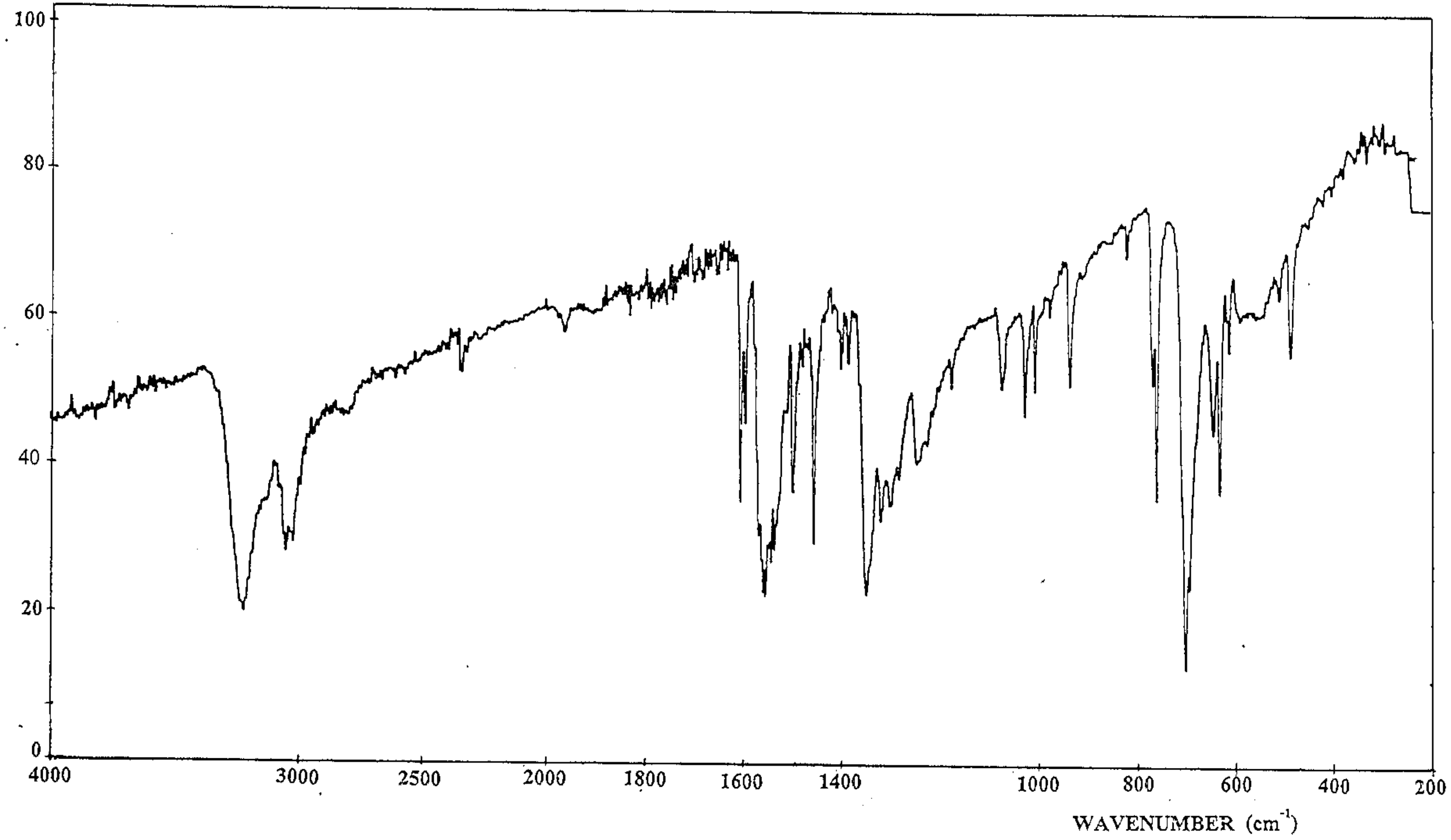

Figure 27 The infrared spectrum of ligand dptu

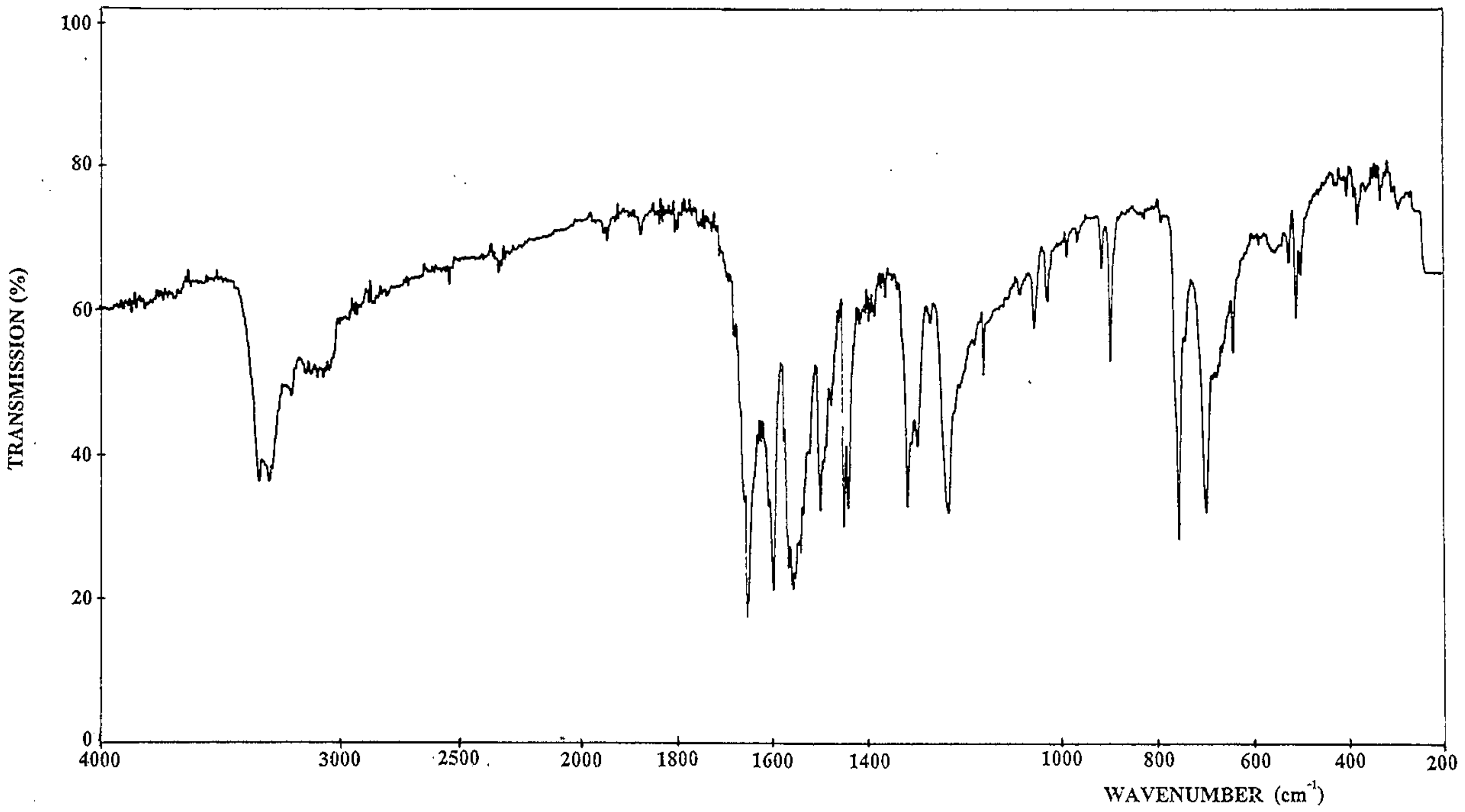

Figure 28 The infrared spectrum of $(C_6H_5NH)_2CO$

## 3.4 Crystal Structure Determination

### 3.4.1 X-ray Photography

$[Ag_2(etu)_4Br_2]$ and $(C_6H_5NH)_2CO$ were studied. The oscillation photographs are shown in Figure 29 – 30.

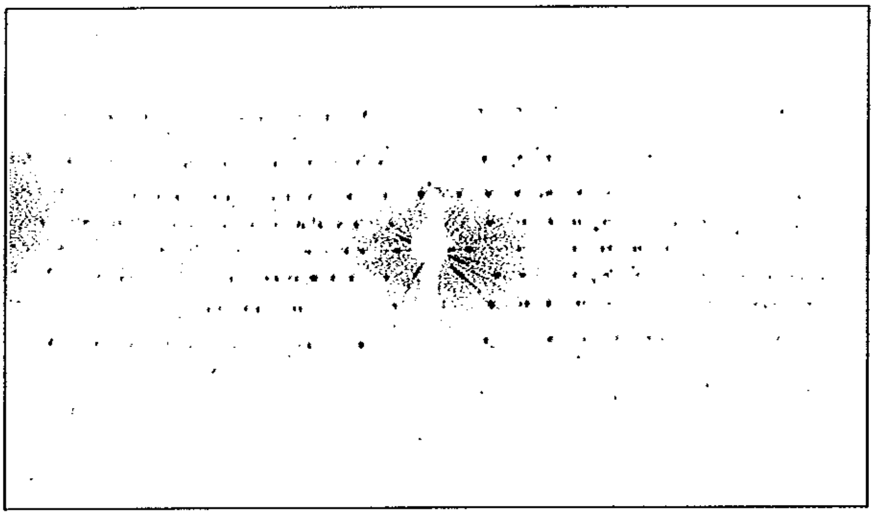

Figure 29 The oscillation photograph of $[Ag_2(etu)_4Br_2]$

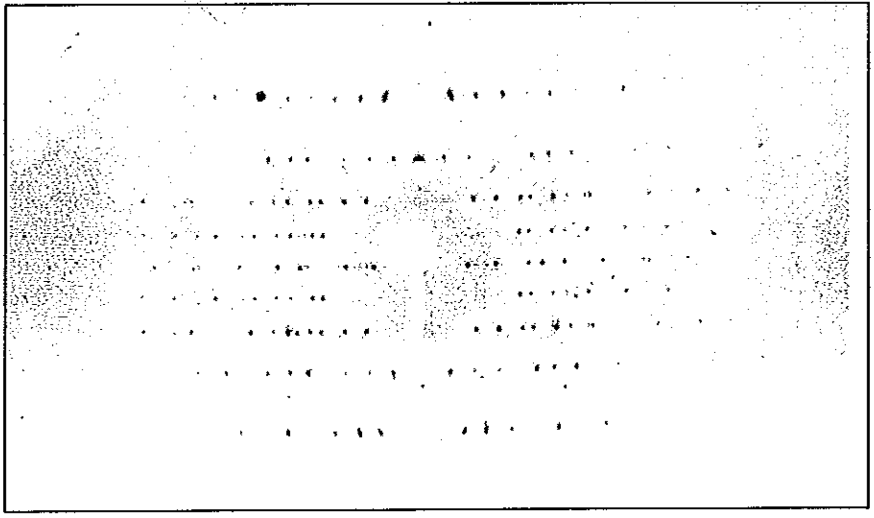

Figure 30 The oscillation photograph of $(C_6H_5NH)_2CO$

### 3.2.2 Crystal Structure

The results from crystal structure determination using Xtal 3.5 and 3.6 program system are shown in Table 4 – 21, Figure 31 – 43 and Appendix C.

Table 4 The crystallographic data for $[Ag(atu)_2]NO_3$

| | |
|---|---|
| Identification code | Agatno |
| Empirical formula | $C_6H_{12}AgN_5O_5S_2$ |
| Formula weight | 406.19 |
| Measured temperature (K) | 293 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 12.0680(6) |
| $b$ (Å) | 6.8056(5) |
| $c$ (Å) | 17.6552(9) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 108.147(4) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1377.9(1) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 1.958 |
| $R$ | 0.036 |
| $R_w$ | 0.038 |
| $F(000)$ | 808 |
| Measured reflections | 4185 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 2841 |

Table 5 Non-hydrogen interatomic distances of $[Ag(atu)_2]NO_3$

| Atom | Distance (Å) |
|---|---|
| Ag - S(1) | 2.4548(9) |
| Ag - S(1') | 2.724(1) |
| Ag - S(2) | 2.4262(8) |
| S(1) - Ag'' | 2.724(1) |
| S(1) - C(11) | 1.711(3) |
| C(11) - N(11) | 1.368(4) |
| C(11) - N(12) | 1.291(6) |
| C(12) - C(13) | 1.500(6) |
| C(12) - N(11) | 1.381(4) |
| C(12) - O(12) | 1.214(5) |
| S(2) - C(21) | 1.697(4) |
| N(21) - C(21) | 1.380(4) |
| N(21) - C(22) | 1.378(5) |
| O(22) - C(22) | 1.218(4) |
| C(21) - N(22) | 1.301(4) |
| C(22) - C(23) | 1.488(5) |
| N(1) - O(1) | 1.232(4) |
| N(1) - O(2) | 1.266(4) |
| N(1) - O(3) | 1.218(5) |

Table 5 (continued)

| Atom | Distance (Å) |
|---|---|
| Hydrogen bonds | |
| O(1) --- H(21) (½+x, ½-y, ½+z) | 2.05(4) |
| O(2) --- H(22A) | 2.02(4) |
| O(2) --- H(12B) | 2.11(5) |
| O(3) --- H(23C) (½+x, ½-y, ½+z) | 2.32(6) |
| O(12) --- H(12A) | 2.37(5) |
| O(22) --- H(22B) | 2.06(5) |
| O(22) --- H(11) (x-½, ½-y, ½+z) | 2.29(4) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = ½-x, y-½, ½-z

" = ½ - x, ½ - y, ½ - z

Table 6 Non-hydrogen interbond angles of $[Ag(atu)_2]NO_3$

| Atom | Angle (°) |
|---|---|
| S(1) - Ag - S(2) | 152.98(4) |
| S(1) - Ag - S(1') | 94.00(3) |
| S(2) - Ag - S(1') | 108.11(3) |
| Ag - S(1) - Ag" | 122.54(4) |
| Ag - S(1) - C(11) | 112.7(1) |
| Ag" - S(1) - C(11) | 106.2(1) |
| S(1) - C(11) - N(11) | 117.0(3) |
| S(1) - C(11) - N(12) | 123.5(3) |
| N(11) - C(11) - N(12) | 119.5(3) |
| C(13) - C(12) - N(11) | 114.9(4) |
| C(13) - C(12) - O(12) | 123.3(4) |
| N(11) - C(12) - O(12) | 121.8(4) |
| Ag - S(2) - C(21) | 110.7(1) |
| C(21) - N(21) - C(22) | 127.5(3) |
| S(2) - C(21) - N(21) | 117.0(2) |
| S(2) - C(21) - N(22) | 124.9(3) |
| N(21) - C(21) - N(22) | 118.1(4) |
| N(21) - C(22) - O(22) | 121.9(3) |
| N(21) - C(22) - C(23) | 114.9(3) |
| O(22) - C(22) - C(23) | 123.2(4) |

Table 6 (continued)

| Atom | Angle (°) |
|---|---|
| O(1) - N(1) - O(2) | 118.0(3) |
| O(1) - N(1) - O(3) | 122.4(4) |
| O(2) - N(1) - O(3) | 119.6(3) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = ½ - x, y - ½, ½ - z

" = ½ - x, ½ - y, ½ - z

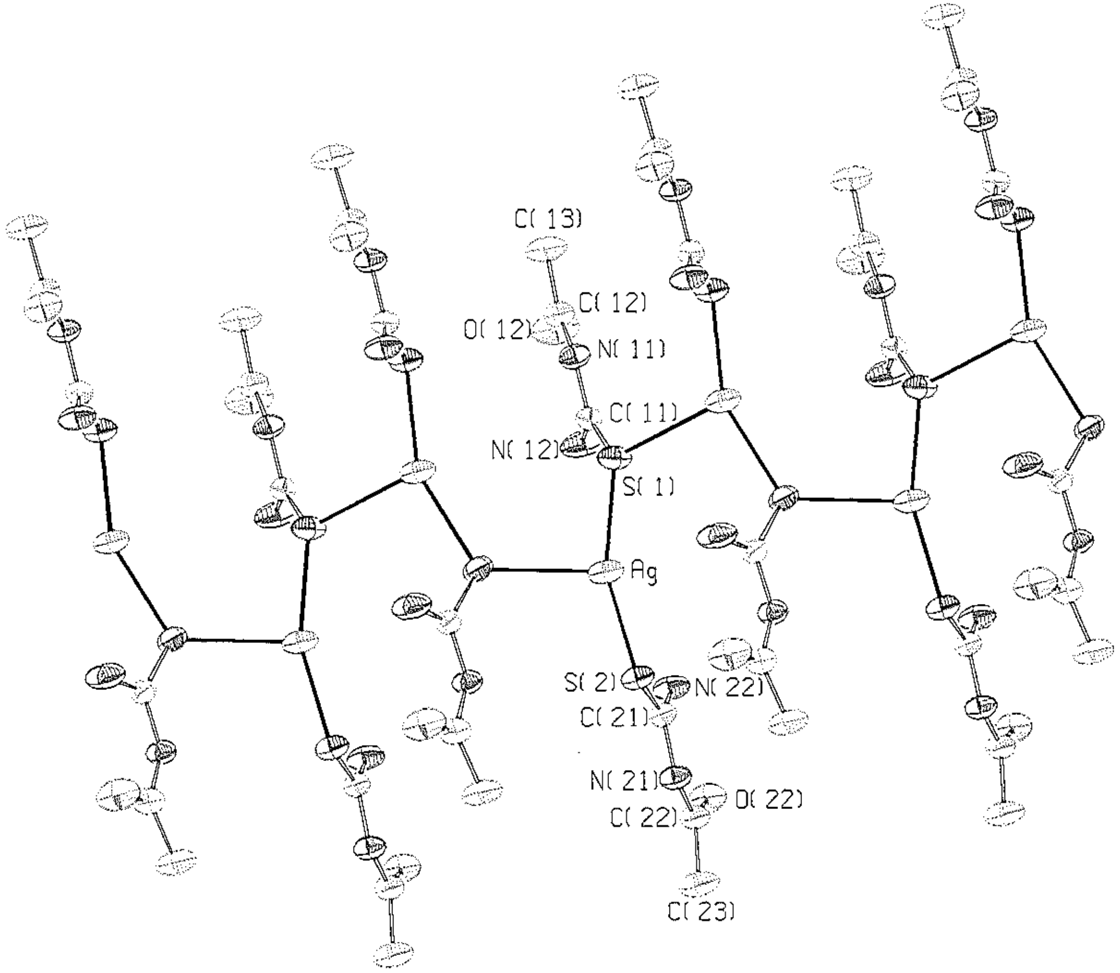

Figure 31 The polymer structure of $[Ag(atu)_2]^+_\infty$

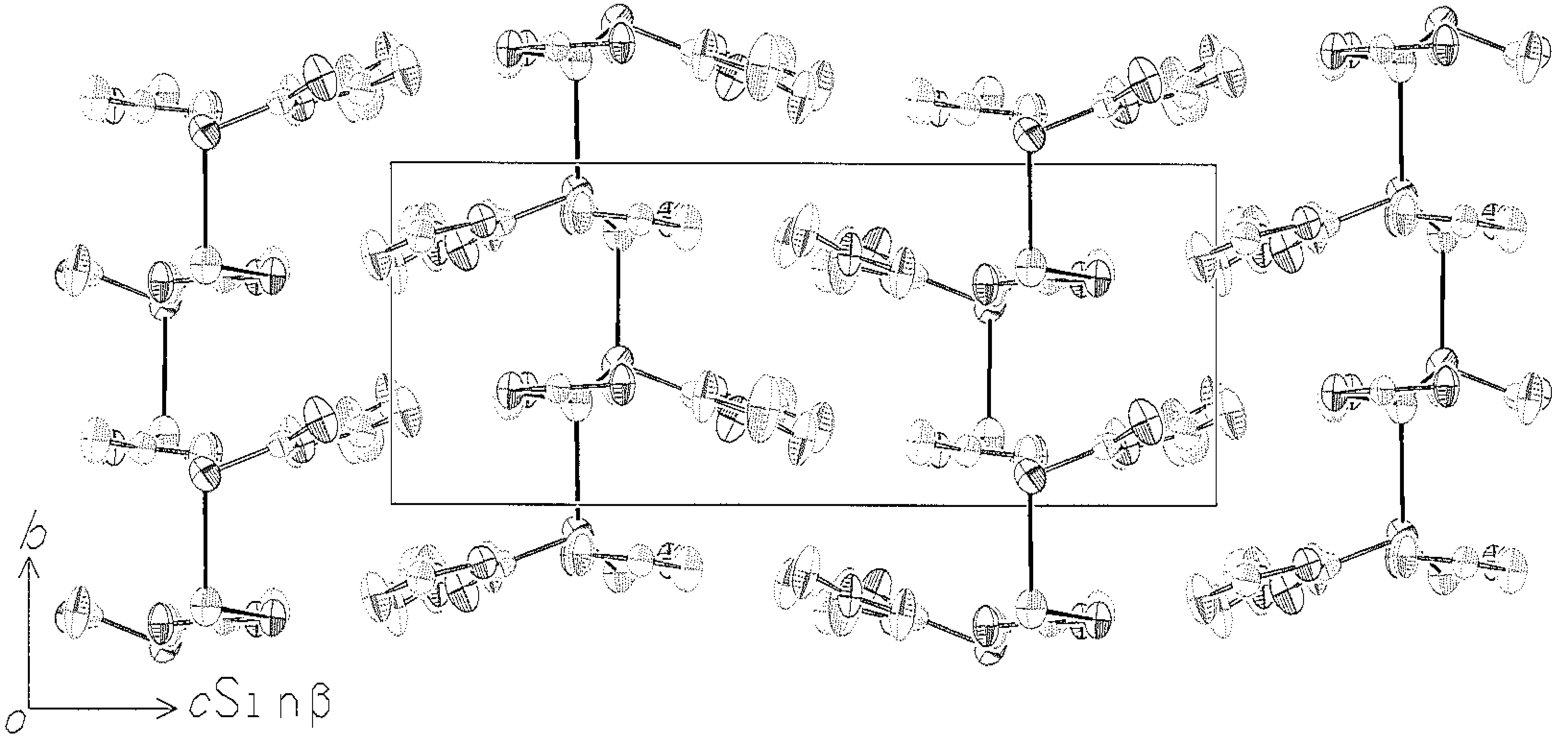

Figure 32 Unit cell contents of $[Ag(atu)_2]NO_3$ projected down *a*

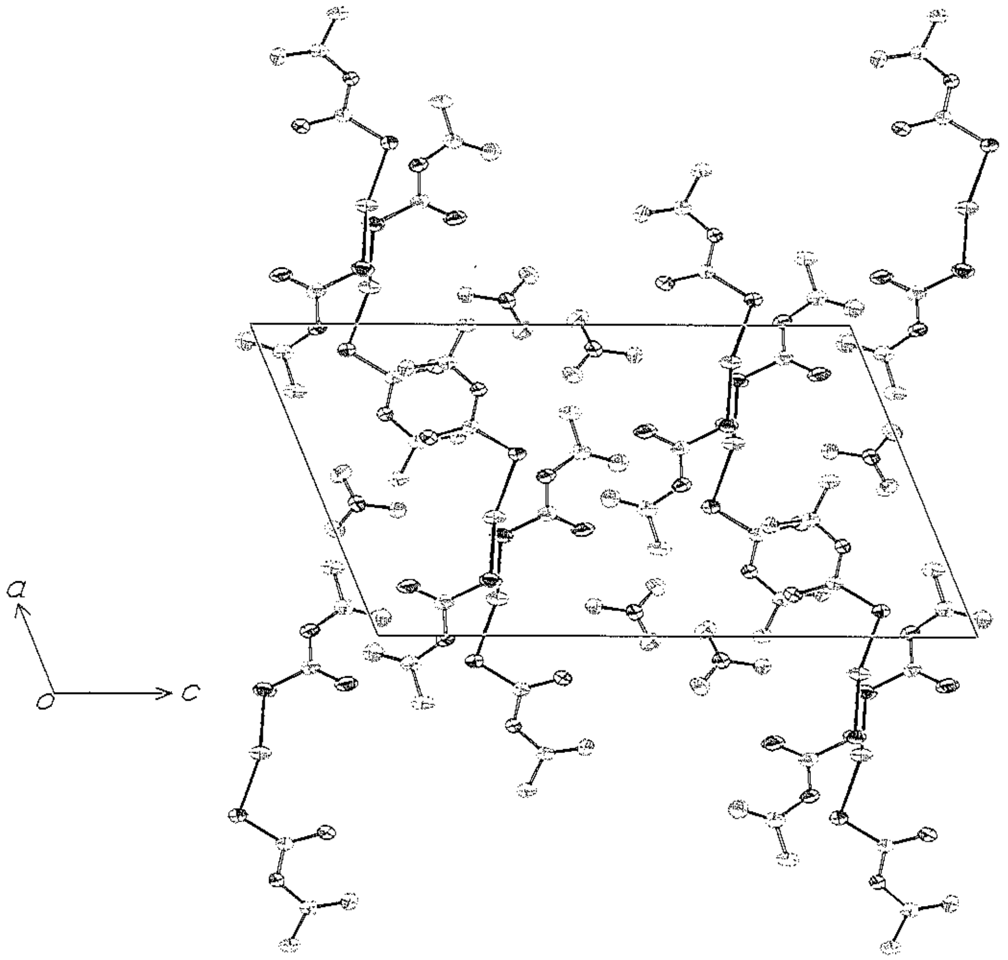

Figure 33 Unit cell contents of $[Ag(atu)_2]NO_3$ projected down *b*

Table 7 The crystallographic data for $[Cu_4(ettu)_6 I_4].H_2O$

| | |
|---|---|
| Identification code | Cuettu |
| Empirical formula | $C_{18}H_{50}Cu_4I_4N_{12}OS_6$ |
| Formula weight | 1404.84 |
| Measured temperature (K) | 293 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$ (Å) | 11.179(1) |
| $b$ (Å) | 18.505(2) |
| $c$ (Å) | 22.409(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 4635.7(8) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 2.010 |
| $R$ | 0.059 |
| $R_w$ | 0.040 |
| $F(000)$ | 2696 |
| Measured reflections | 7124 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 4180 |

Table 8 Non-hydrogen interatomic distances of $[Cu_4(ettu)_6 I_4].H_2O$

| Atom | Distance (Å) |
|---|---|
| I(1) - Cu(1) | 2.679(2) |
| I(2) - Cu(2) | 2.768(2) |
| I(3) - Cu(3) | 3.083(2) |
| I(4) - Cu(4) | 2.623(2) |
| Cu(1) - S(1) | 2.358(4) |
| Cu(1) - S(4) | 2.265(6) |
| Cu(1) - S(5) | 2.351(4) |
| Cu(2) - S(1) | 2.308(4) |
| Cu(2) - S(2) | 2.342(4) |
| Cu(2) - S(6) | 2.331(5) |
| Cu(3) - S(2) | 2.273(4) |
| Cu(3) - S(3) | 2.258(4) |
| Cu(3) - S(5) | 2.273(4) |
| Cu(4) - S(3) | 2.388(4) |
| Cu(4) - S(4) | 2.344(6) |
| Cu(4) - S(6) | 2.302(5) |
| S(1) - C(11) | 1.70(2) |
| S(2) - C(21) | 1.74(2) |
| S(3) - C(31) | 1.71(2) |
| S(4) - C(41) | 1.69(1) |
| S(5) - C(51) | 1.74(2) |
| S(6) - C(61) | 1.70(1) |

Table 8 (continued)

| Atom | Distance (Å) |
|---|---|
| N(12) - C(11) | 1.33(2) |
| N(13) - C(11) | 1.34(2) |
| N(13) - C(14) | 1.45(3) |
| N(22) - C(21) | 1.31(2) |
| N(23) - C(21) | 1.30(2) |
| N(23) - C(24) | 1.46(2) |
| N(32) - C(31) | 1.33(2) |
| N(33) - C(31) | 1.31(2) |
| N(33) - C(34) | 1.47(2) |
| N(42) - C(41) | 1.29(2) |
| N(43) - C(41) | 1.33(2) |
| N(43) - C(44) | 1.46(2) |
| N(52) - C(51) | 1.32(2) |
| N(53) - C(51) | 1.32(2) |
| N(53) - C(54) | 1.51(2) |
| N(62) - C(61) | 1.33(2) |
| N(63) - C(61) | 1.31(2) |
| N(63) - C(64) | 1.49(2) |
| C(14) - C(15) | 1.47(3) |
| C(24) - C(25A) | 1.34(5) |
| C(24) - C(25B) | 1.53(7) |
| C(25A) - C(25B) | 1.15(8) |

Table 8 (continued)

| Atom | Distance (Å) |
|---|---|
| C(34) - C(35) | 1.51(3) |
| C(44) - C(45) | 1.43(3) |
| C(54) - C(55A) | 1.36(5) |
| C(54) - C(55B) | 1.42(5) |
| C(55A) - C(55B) | 1.18(7) |
| C(64) - C(65) | 1.35(3) |
| Hydrogen bonds | |
| I(1) --- H(12B) | 2.925(1) |
| I(1) --- H(42B) | 2.787(1) |
| I(1) --- H(52B) | 2.878(1) |
| I(1) --- H(62A) (-x-1, ½+y, ½-z) | 3.005(1) |
| I(2) --- H(42A) (-x, y-½, ½-z) | 2.963(1) |
| I(2) --- H(62B) | 2.782(1) |
| I(3) --- H(12A) (-x, y-½, ½-z) | 3.008(1) |
| I(3) --- H(22A) (x-½, ½-y, 1-z) | 3.017(1) |
| I(3) --- H(22B) | 2.867(1) |
| I(3) --- H(33) | 2.985(1) |
| I(3) --- H(53) | 2.950(1) |
| I(4) --- H(32B) | 2.905(1) |
| I(4) --- H(43) | 2.852(1) |
| I(4) --- H(63) | 2.848(1) |
| O(1) --- H(32A) (½+x, 3/2 – y, 1-z) | 2.274(1) |
| O(1) --- H(52A) (-x, ½+y, ½-z) | 2.218(1) |

Table 9 Non-hydrogen interbond angles of $[Cu_4(ettu)_6 I_4].H_2O$

| Atom | Angle (°) |
|---|---|
| I(1) - Cu(1) - S(1) | 108.7(1) |
| I(1) - Cu(1) - S(4) | 119.0(1) |
| I(1) - Cu(1) - S(5) | 109.9(1) |
| S(1) - Cu(1) - S(4) | 106.3(2) |
| S(1) - Cu(1) - S(5) | 104.7(1) |
| S(4) - Cu(1) - S(5) | 107.2(1) |
| I(2) - Cu(2) - S(1) | 111.9(1) |
| I(2) - Cu(2) - S(2) | 108.68(9) |
| I(2) - Cu(2) - S(6) | 110.8(1) |
| S(1) - Cu(2) - S(2) | 107.4(1) |
| S(1) - Cu(2) - S(6) | 113.6(1) |
| S(2) - Cu(2) - S(6) | 103.9(1) |
| I(3) - Cu(3) - S(2) | 100.4(1) |
| I(3) - Cu(3) - S(3) | 103.7(1) |
| I(3) - Cu(3) - S(5) | 103.3(1) |
| S(2) - Cu(3) - S(3) | 114.0(1) |
| S(2) - Cu(3) - S(5) | 114.8(1) |
| S(3) - Cu(3) - S(5) | 117.6(1) |
| I(4) - Cu(4) - S(3) | 112.7(1) |
| I(4) - Cu(4) - S(4) | 115.4(1) |
| I(4) - Cu(4) - S(6) | 118.8(1) |

Table 9 (continued)

| Atom | Angle (°) |
|---|---|
| S(3) - Cu(4) - S(4) | 101.3(1) |
| S(3) - Cu(4) - S(6) | 99.1(1) |
| S(4) - Cu(4) - S(6) | 107.1(2) |
| Cu(1) - S(1) - Cu(2) | 113.3(1) |
| Cu(1) - S(1) - C(11) | 110.4(5) |
| Cu(2) - S(1) - C(11) | 109.0(5) |
| Cu(2) - S(2) - Cu(3) | 101.7(1) |
| Cu(2) - S(2) - C(21) | 105.3(4) |
| Cu(3) - S(2) - C(21) | 105.0(5) |
| Cu(3) - S(3) - Cu(4) | 108.0(1) |
| Cu(3) - S(3) - C(31) | 107.6(5) |
| Cu(4) - S(3) - C(31) | 106.8(4) |
| Cu(1) - S(4) - Cu(4) | 123.0(2) |
| Cu(1) - S(4) - C(41) | 116.7(5) |
| Cu(4) - S(4) - C(41) | 119.3(5) |
| Cu(1) - S(5) - Cu(3) | 103.2(1) |
| Cu(1) - S(5) - C(51) | 105.2(4) |
| Cu(3) - S(5) - C(51) | 106.1(4) |
| Cu(2) - S(6) - Cu(4) | 117.2(2) |
| Cu(2) - S(6) - C(61) | 121.1(5) |
| Cu(4) - S(6) - C(61) | 116.1(5) |

Table 9 (continued)

| Atom | Angle (°) |
|---|---|
| C(11) - N(13) - C(14) | 129(1) |
| C(21) - N(23) - C(24) | 128(1) |
| C(31) - N(33) - C(34) | 126(1) |
| C(41) - N(43) - C(44) | 128(1) |
| C(51) - N(53) - C(54) | 123(1) |
| C(61) - N(63) - C(64) | 126(1) |
| S(1) - C(11) - N(12) | 121(1) |
| S(1) - C(11) - N(13) | 121(1) |
| N(12) - C(11) - N(13) | 118(1) |
| N(13) - C(14) - C(15) | 111(2) |
| S(2) - C(21) - N(22) | 121.5(9) |
| S(2) - C(21) - N(23) | 119(1) |
| N(22) - C(21) - N(23) | 119(1) |
| N(23) - C(24) - C(25A) | 111(2) |
| N(23) - C(24) - C(25B) | 107(2) |
| C(25A) - C(24) - C(25B) | 47(3) |
| C(24) - C(25A) - C(25B) | 74(3) |
| C(24) - C(25B) - C(25A) | 60(3) |
| S(3) - C(31) - N(32) | 120(1) |
| S(3) - C(31) - N(33) | 121.1(9) |
| N(32) - C(31) - N(33) | 119(1) |
| N(33) - C(34) - C(35) | 111(1) |

Table 9 (continued)

| Atom | Angle (°) |
|---|---|
| S(4) - C(41) - N(42) | 119.1(9) |
| S(4) - C(41) - N(43) | 122.6(9) |
| N(42) - C(41) - N(43) | 118(1) |
| N(43) - C(44) - C(45) | 114(1) |
| S(5) - C(51) - N(52) | 120.1(9) |
| S(5) - C(51) - N(53) | 119(1) |
| N(52) - C(51) - N(53) | 121(1) |
| N(53) - C(54) - C(55A) | 116(2) |
| N(53) - C(54) - C(55B) | 117(2) |
| C(55A) - C(54) - C(55B) | 47(3) |
| C(54) - C(55A) - C(55B) | 71(3) |
| C(54) - C(55B) - C(55A) | 62(3) |
| S(6) - C(61) - N(62) | 119(1) |
| S(6) - C(61) - N(63) | 120(1) |
| N(62) - C(61) - N(63) | 121(1) |
| N(63) - C(64) - C(65) | 115(2) |

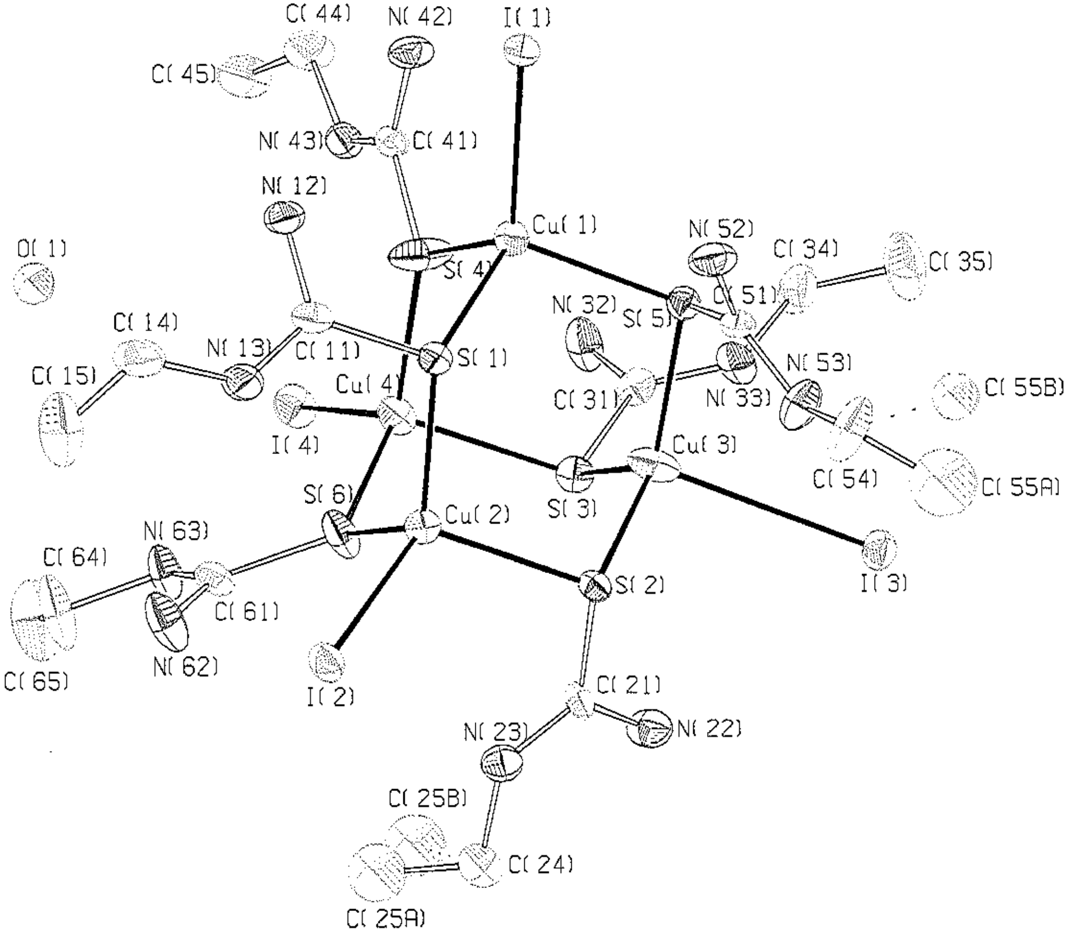

Figure 34 The structure of $[Cu_4(ettu)_6I_4].H_2O$ (H-atoms omitted)

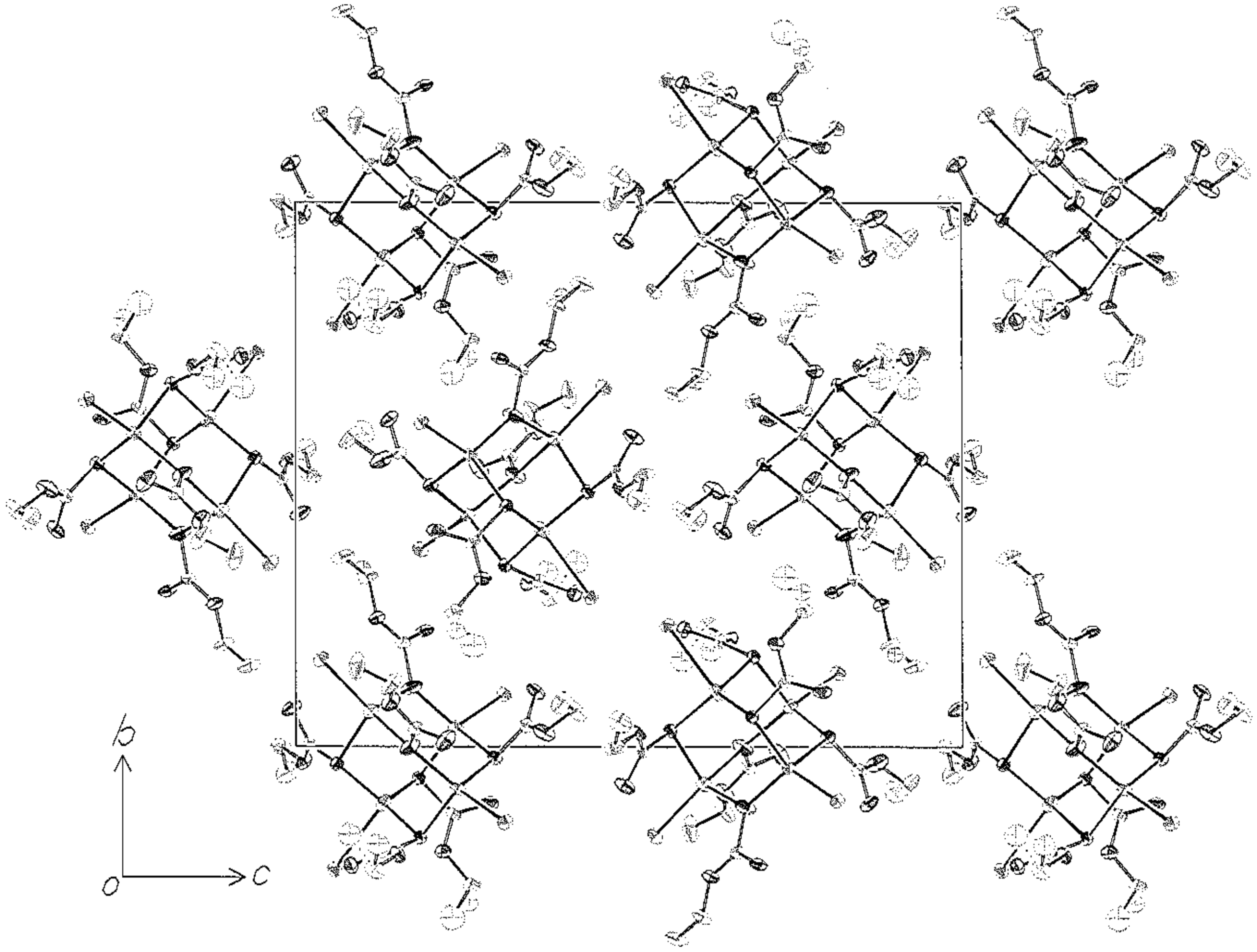

Figure 35 Unit cell contents of $[Cu_4(ettu)_6I_4].H_2O$ projected down *a*

Table 10 The crystallographic data for $[Ag_2(etu)_6](ClO_4)_2$

| | |
|---|---|
| Identification code | Ageclo |
| Empirical formula | $AgC_9H_{18}N_6O_4S_2$ |
| Formula weight | 495.66 |
| Measured temperature (K) | 293 |
| Wavelength | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 6.329(1) |
| $b$ (Å) | 24.262(2) |
| $c$ (Å) | 12.119(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 92.67(1) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1858.9(5) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 1.836 |
| $R$ | 0.041 |
| $R_w$ | 0.046 |
| $F(000)$ | 840 |
| Measured reflections | 5627 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 3697 |

Table 11 Non-hydrogen interatomic distahces of $[Ag_2(etu)_6](ClO_4)_2$

| Atom | Distance ( Å ) |
|---|---|
| Ag - S(1) | 2.598(1) |
| Ag - S(2) | 2.556(1) |
| Ag - S(3) | 2.566(1) |
| Ag - S(3') | 2.681(1) |
| S(1) - C(1) | 1.694(4) |
| S(2) - C(4) | 1.693(4) |
| S(3) - C(7) | 1.723(4) |
| N(1) - C(1) | 1.327(8) |
| N(1) - C(2) | 1.45(1) |
| N(2) - C(1) | 1.337(6) |
| N(2) - C(3) | 1.459(8) |
| N(3) - C(4) | 1.320(8) |
| N(3) - C(5) | 1.44(1) |
| N(4) - C(4) | 1.334(7) |
| N(4) - C(6) | 1.466(9) |
| N(5) - C(7) | 1.303(6) |
| N(5) - C(8) | 1.445(8) |
| N(6) - C(7) | 1.321(6) |
| N(6) - C(9) | 1.459(8) |
| C(2) - C(3) | 1.53(1) |
| C(5) - C(6) | 1.47(2) |

Table 11 (continued)

| Atom | Distance (Å) |
|---|---|
| C(8) - C(9) | 1.535(8) |
| Cl - O(1) | 1.411(5) |
| Cl - O(2) | 1.417(7) |
| Cl - O(3) | 1.399(5) |
| Cl - O(4) | 1.397(4) |
| Hydrogen bonds | |
| O(1) --- H(21) | 2.513(5) |
| O(1) --- H(81) | 2.717(5) |
| O(1) --- H(92) (+x, 3/2-y, z-½) | 2.791(4) |
| O(1) --- H(1N6) (+x, 3/2-y, z-½) | 2.690(5) |
| O(2) --- H(31) (+x, ½-y, z+½) | 2.634(6) |
| O(3) --- H(61) (1-x, ½+y, ½-z) | 2.751(5) |
| O(3) --- H(1N6) (+x, 3/2-y, z-½) | 2.158(5) |
| O(4) --- H(22) (1+x, 3/2-y, z+½) | 2.663(4) |
| O(4) --- H(92) | 2.738(5) |
| O(4) --- H(1N2) (+x, 3/2-y, z+½) | 2.112(5) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = 1-x, 1-y, 1-z

Table 12 Non-hydrogen interbond angles of $[Ag_2(etu)_6](ClO_4)_2$

| Atom | Angle °) |
|---|---|
| S(1) - Ag - S(2) | 109.18(4) |
| S(1) - Ag - S(3) | 115.23(4) |
| S(1) - Ag - S(3') | 109.95(4) |
| S(2) - Ag - S(3) | 111.20(4) |
| S(2) - Ag - S(3') | 102.83(4) |
| S(3) - Ag - S(3') | 107.71(3) |
| Ag - S(3) - Ag' | 72.29(3) |
| Ag - S(1) - C(1) | 100.4(1) |
| Ag - S(2) - C(4) | 103.1(2) |
| Ag - S(3) - C(7) | 106.1(1) |
| Ag' - S(3) - C(7) | 100.1(1) |
| C(1) - N(1) - C(2) | 113.5(6) |
| C(1) - N(2) - C(3) | 112.5(4) |
| C(4) - N(3) - C(5) | 112.9(7) |
| C(4)- N(4) - C(6) | 111.0(6) |
| C(7) - N(5) - C(8) | 112.7(4) |
| C(7) - N(6) - C(9) | 112.1(4) |
| S(1) - C(1) - N(1) | 127.5(4) |
| S(1) - C(1) - N(2) | 124.3(3) |
| N(1) - C(1) - N(2) | 108.1(5) |
| N(1) - C(2) - C(3) | 102.2(5) |
| N(2) - C(3) - C(2) | 102.1(5) |

Table 12 (continued)

| Atom | Angle (°) |
|---|---|
| S(2) - C(4) - N(3) | 125.0(4) |
| S(2) - C(4) - N(4) | 126.2(4) |
| N(3) - C(4) - N(4) | 108.8(5) |
| N(3) - C(5) - C(6) | 103.4(8) |
| N(4) - C(6) - C(5) | 103.9(7) |
| S(3) - C(7) - N(5) | 126.9(3) |
| S(3) - C(7) - N(6) | 122.7(3) |
| N(5) - C(7) - N(6) | 110.4(4) |
| N(5) - C(8) - C(9) | 102.8(4) |
| N(6) - C(9) - C(8) | 101.7(4) |
| O(1) - Cl - O(2) | 109.9(3) |
| O(1) - Cl - O(3) | 109.4(3) |
| O(1) - Cl - O(4) | 112.0(3) |
| O(2) - Cl - O(3) | 110.4(4) |
| O(2) - Cl - O(4) | 107.1(3) |
| O(3) - Cl - O(4) | 107.9(3) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

$^{i}$ = 1-x, 1-y, 1-z

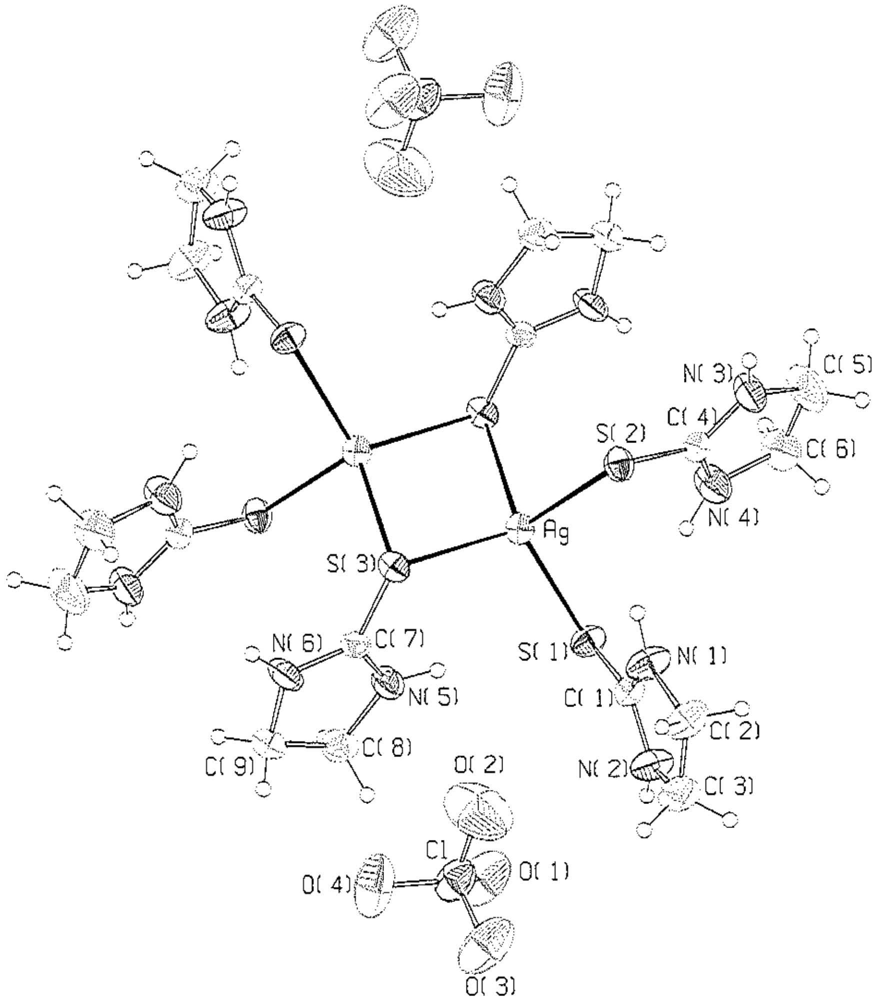

Figure 36 The structure of [$Ag_2(etu)_6$]($(ClO_4)_2$)

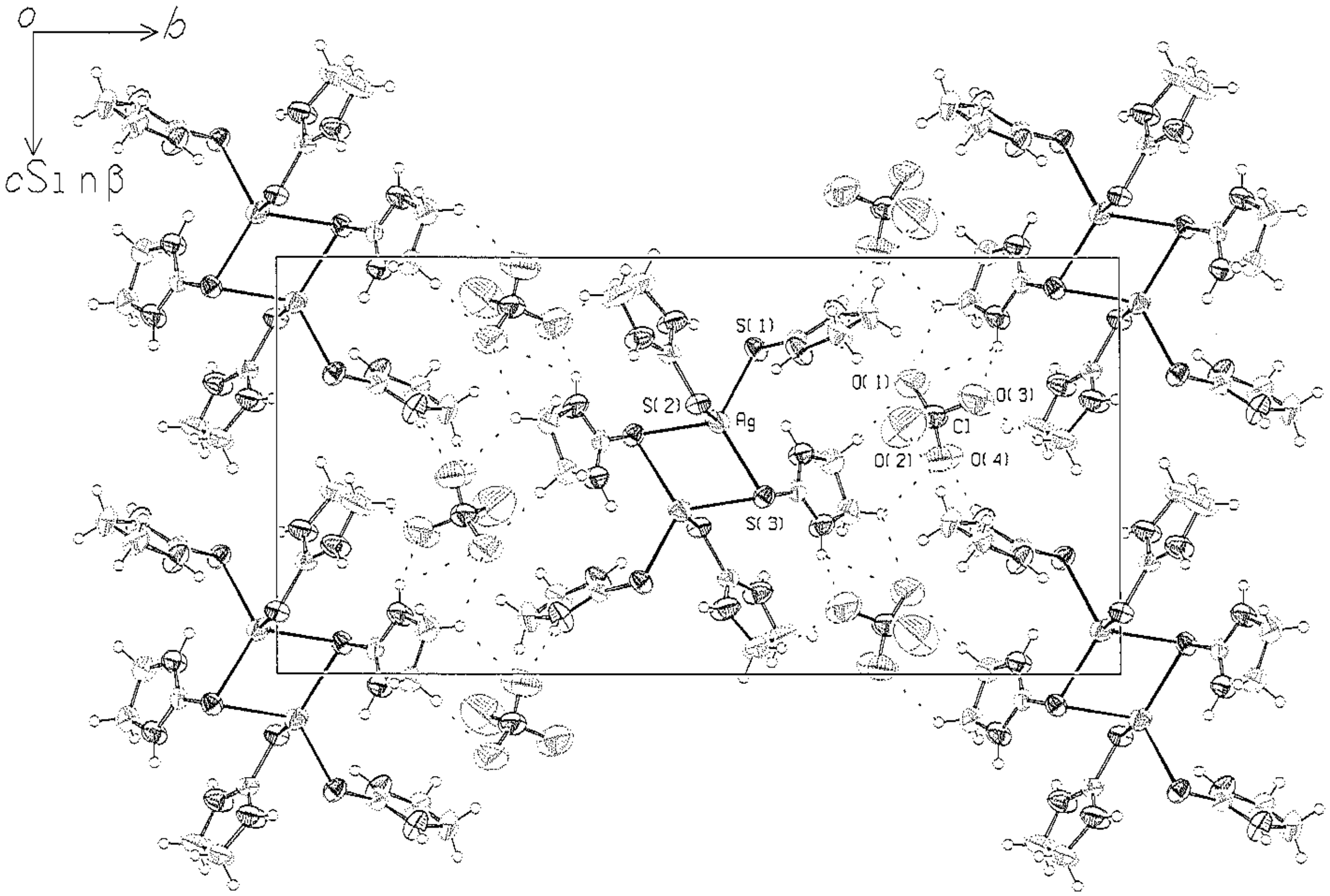

Figure 37 Unit cell contents of $[Ag_2(etu)_6](ClO_4)_2$ projected down *a*

Table 13 The crystallographic data for [$Ag_2(etu)_4Br_2$]

| | |
|---|---|
| Identification code | Agetbr |
| Empirical formula | $C_6H_{12}AgBrN_4S_2$ |
| Formula weight | 392.09 |
| Measured temperature (K) | 153 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 8.975(2) |
| $b$ (Å) | 10.457(2) |
| $c$ (Å) | 13.158(3) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 103.42(3) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1201.2(4) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 2.168 |
| $R$ | 0.022 |
| $R_w$ | 0.024 |
| $F(000)$ | 760 |
| Measured reflections | 2968 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 2763 |

Table 14 Non-hydrogen interatomic distances of [$Ag_2(etu)_4Br_2$]

| Atom | Distance ( Å ) |
|---|---|
| Ag - Br | 2.7997(6) |
| Ag' - Br | 2.8320(5) |
| Ag - S(1) | 2.483(1) |
| Ag - S(2) | 2.483(1) |
| S(1) - C(11) | 1.698(4) |
| N(12) - C(11) | 1.332(5) |
| N(12) - C(13) | 1.460(5) |
| N(15) - C(11) | 1.333(4) |
| N(15) - C(14) | 1.458(6) |
| C(13) - C(14) | 1.533(6) |
| S(2) - C(21) | 1.694(3) |
| N(22) - C(21) | 1.318(5) |
| N(22) - C(23) | 1.455(5) |
| C(21) - N(25) | 1.337(5) |
| N(25) - C(24) | 1.455(5) |
| C(24) - C(23) | 1.515(7) |
| Hydrogen bonds | |
| Br --- H(12) | 2.69(3) |
| Br --- H(22) | 2.92(4) |
| Br --- H(15) (½-x, ½+y, ½-z) | 2.64(3) |
| Br --- H(25) (x-½, 3/2-y, ½+z) | 2.94(4) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z : ' = -x, 1-y,

Table 15 Non-hydrogen interbond angles of [$Ag_2(etu)_4Br_2$]

| Atoms | Angle (°) |
|---|---|
| Ag - Br - Ag' | 92.28(2) |
| Br - Ag - Br' | 87.72(2) |
| S(1) - Ag - Br | 114.60(3) |
| S(1) - Ag - Br' | 105.38(3) |
| S(2) - Ag - Br | 110.16(3) |
| S(2) - Ag - Br' | 108.82(3) |
| S(1) - Ag - S(2) | 123.70(4) |
| Ag - S(1) - C(11) | 108.7(1) |
| C(13) - N(12) - C(11) | 111.8(3) |
| C(11) - N(15) - C(14) | 112.6(3) |
| N(12) - C(13) - C(14) | 102.6(3) |
| S(1) - C(11) - N(12) | 126.7(3) |
| S(1) - C(11) - N(15) | 124.3(3) |
| N(12) - C(11) - N(15) | 109.1(3) |
| N(15) - C(14) - C(13) | 101.3(3) |
| Ag - S(2) - C(21) | 106.1(1) |
| C(21) - N(22) - C(23) | 113.2(4) |
| S(2) - C(21) - N(22) | 127.4(3) |
| S(2) - C(21) - N(25) | 123.7(3) |

Table 15 (continued)

| Atom | Angle (°) |
|---|---|
| N(22) - C(21) - N(25) | 108.8(3) |
| C(21) - N(25) - C(24) | 112.4(3) |
| N(25) - C(24) - C(23) | 102.9(3) |
| N(22) - C(23) - C(24) | 102.7(3) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = -x, 1-y, -z

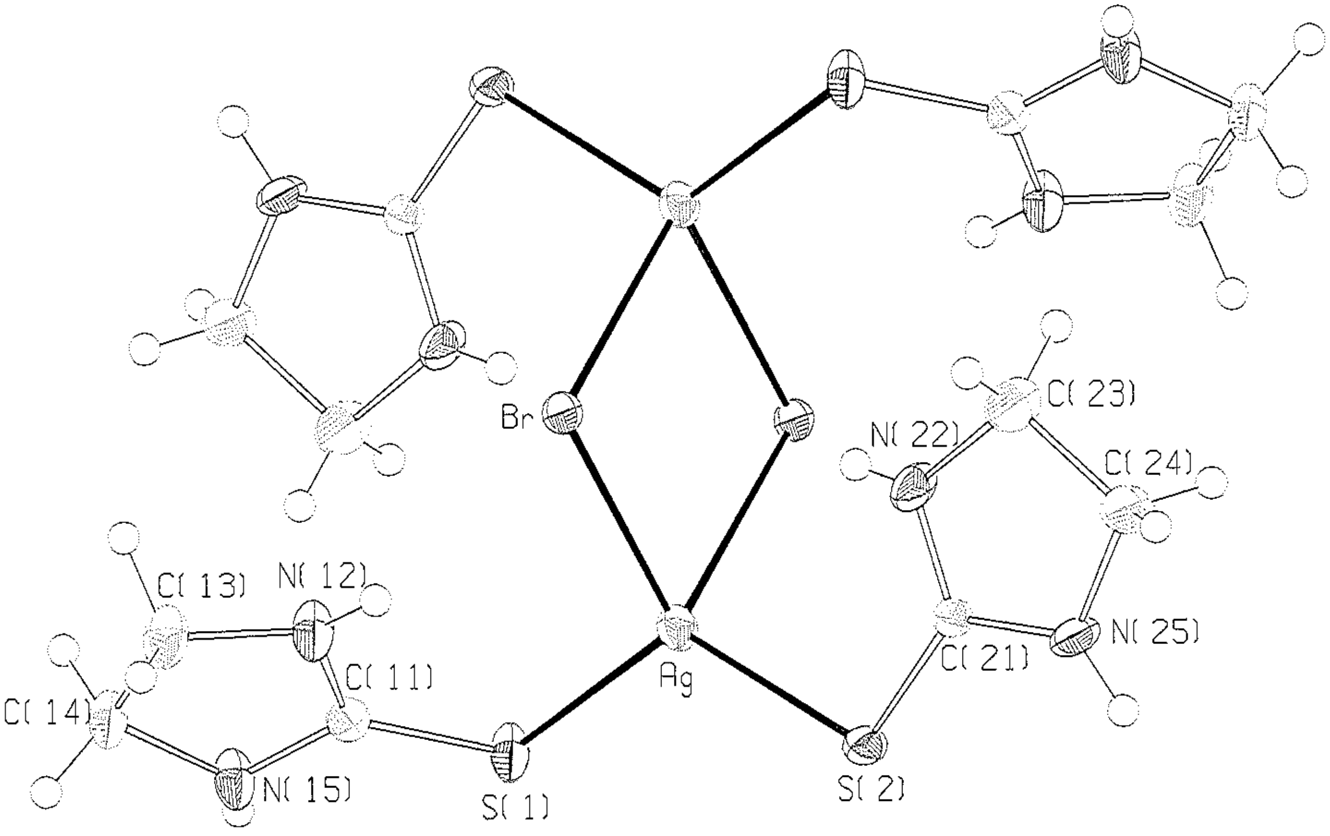

Figure 38 The structure of $[Ag_2(etu)_4Br_2]$

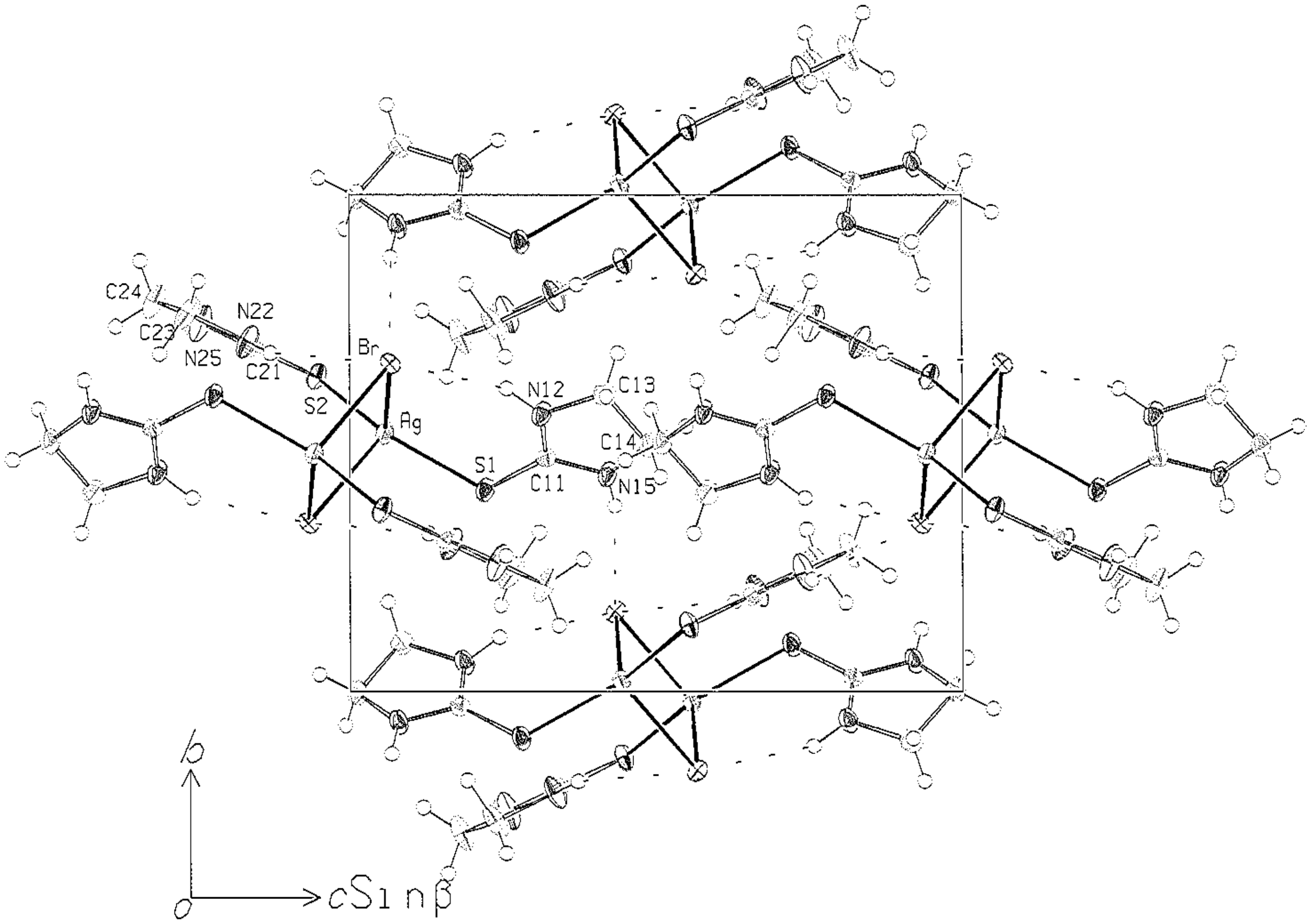

Figure 39 Unit cell contents of [$Ag_2(etu)_4Br_2$] projected down *a*

Table 16 The crystallographic data for $[Cu(etu)_3]_2SO_4$

| | |
|---|---|
| Identification code | Cuetso |
| Empirical formula | $C_{18}H_{36}Cu_2N_{12}O_4S_7$ |
| Formula weight | 836.12 |
| Measured temperature (K) | 153 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Trigonal |
| Space group | *R*3*c* |
| $a$ (Å) | 12.750(2) |
| $b$ (Å) | 12.750(2) |
| $c$ (Å) | 35.083(7) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 120 |
| $V$ (Å$^3$) | 4939(2) |
| $Z$ | 6 |
| $D_c$ (g/cm$^3$) | 1.686 |
| $R$ | 0.017 |
| $R_w$ | 0.019 |
| *F(000)* | 2580 |
| Measured reflections | 1393 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 1393 |

Table 17 Non-hydrogen interatomic distances of $[Cu(etu)_3]_2SO_4$

| Atom | Distance ( Å ) |
|---|---|
| Cu(1) - S(1) | 2.2457(8) |
| Cu(1) - S(1') | 2.2468(9) |
| Cu(1) - S(1") | 2.2456(8) |
| Cu(2) - S(2) | 2.2704(8) |
| Cu(2) - S(2"') | 2.2696(8) |
| Cu(2) - S(2"") | 2.2691(8) |
| Cu(2) - O(1) | 2.782(2) |
| S(1) - C(11) | 1.719(3) |
| S(2) - C(21) | 1.708(3) |
| C(11) - N(12) | 1.314(4) |
| C(11) - N(15) | 1.326(4) |
| N(12) - C(13) | 1.460(5) |
| C(13) - C(14) | 1.535(5) |
| C(14) - N(15) | 1.467(5) |
| C(21) - N(22) | 1.322(4) |
| C(21) - N(25) | 1.336(4) |
| N(22) - C(23) | 1.472(4) |
| C(23) - C(24) | 1.536(5) |
| C(24) - N(25) | 1.464(5) |

Table 17 (continued)

| Atom | Distance ( Å ) |
|---|---|
| S - O (1) | 1.469(4) |
| S - O(2) | 1.482(2) |
| S - O(2''''') | 1.482(2) |
| S - O(2'''''') | 1.483(2) |
| Hydrogen bonds | |
| O(1) --- H(22) | 2.13(3) |
| O(2) --- H(22) | 2.73(3) |
| O(1) --- H(22) (1-x-y, 1-x, +z) | 2.13(6) |
| O(1) --- H(22) (1-y, +x-y, +z) | 2.13(4) |
| O(2) --- H(25) (4/3-y, 2/3-x, 1/6+z) | 1.98(3) |
| O(2'''''') --- H(12) (1-x-y, 1-x, +z) | 1.95(4) |
| O(2'''''') --- H(22) (1-x-y, 1-x, +z) | 2.75(3) |
| O(2'''''') --- H(25) (4/3-y, 2/3-x, ½+z) | 1.98(4) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = 1-y, 1+x-y, +z
'' = -x+y, 1-x, +z
''' = -y, +x-y, +z
'''' = -x+y, -x, +z
''''' = 1-y, +x-y, +z
'''''' = 1-x-y, 1-x, +z

Table 18 Non-hydrogen interbond angles of $[Cu(etu)_3]_2SO_4$

| Atom | Angle (°) |
|---|---|
| S(1) - Cu(1) - S(1') | 119.98(3) |
| S(1) - Cu(1) - S(1") | 120.03(3) |
| S(1') - Cu(1) - S(1") | 119.98(4) |
| S(2) - Cu(2) - S(2"') | 119.80(3) |
| S(2) - Cu(2) - S(2"") | 119.82(4) |
| S(2"') - Cu(2) - S(2"") | 119.86(3) |
| Cu(1) - S(1) - C(11) | 107.2(1) |
| Cu(2) - S(2) - C(21) | 105.1(1) |
| S(1) - C(11) - N(12) | 122.9(3) |
| S(1) - C(11) - N(15) | 126.9(3) |
| N(12) - C(11) - N(15) | 110.3(3) |
| C(11) - N(12) - C(13) | 112.7(3) |
| N(12) - C(13) - C(14) | 102.4(3) |
| C(13) - C(14) - N(15) | 102.4(3) |
| C(11) - N(15) - C(14) | 111.9(4) |
| S(2) - C(21) - N(22) | 125.6(2) |
| S(2) - C(21) - N(25) | 124.3(3) |
| N(22) - C(21) - N(25) | 110.1(3) |
| C(21) - N(22) - C(23) | 112.7(3) |
| N(22) - C(23) - C(24) | 102.1(3) |
| C(23) - C(24) - N(25) | 103.1(3) |

Table 18 (continued)

| Atom | Angle (°) |
|---|---|
| C(21) - N(25) - C(24) | 112.0(3) |
| O(1) - S - O(2) | 109.5(1) |
| O(1) - S - O(2''''') | 109.5(1) |
| O(1) - S - O(2'''''') | 109.5(1) |
| O(2) - S - O(2''''') | 109.5(1) |
| O(2) - S - O(2'''''') | 109.4(1) |
| O(2''''') - S - O(2'''''') | 109.5(1) |

Superscript refers to the following symmetry operations, relative to the reference asymmetric unit at x, y, z :

' = 1-y, 1+x-y, +z
'' = -x+y, 1-x, +z
''' = -y, +x-y, +z
'''' = -x+y, -x, +z
''''' = 1-y, +x-y, +z
'''''' = 1-x-y, 1-x, +z

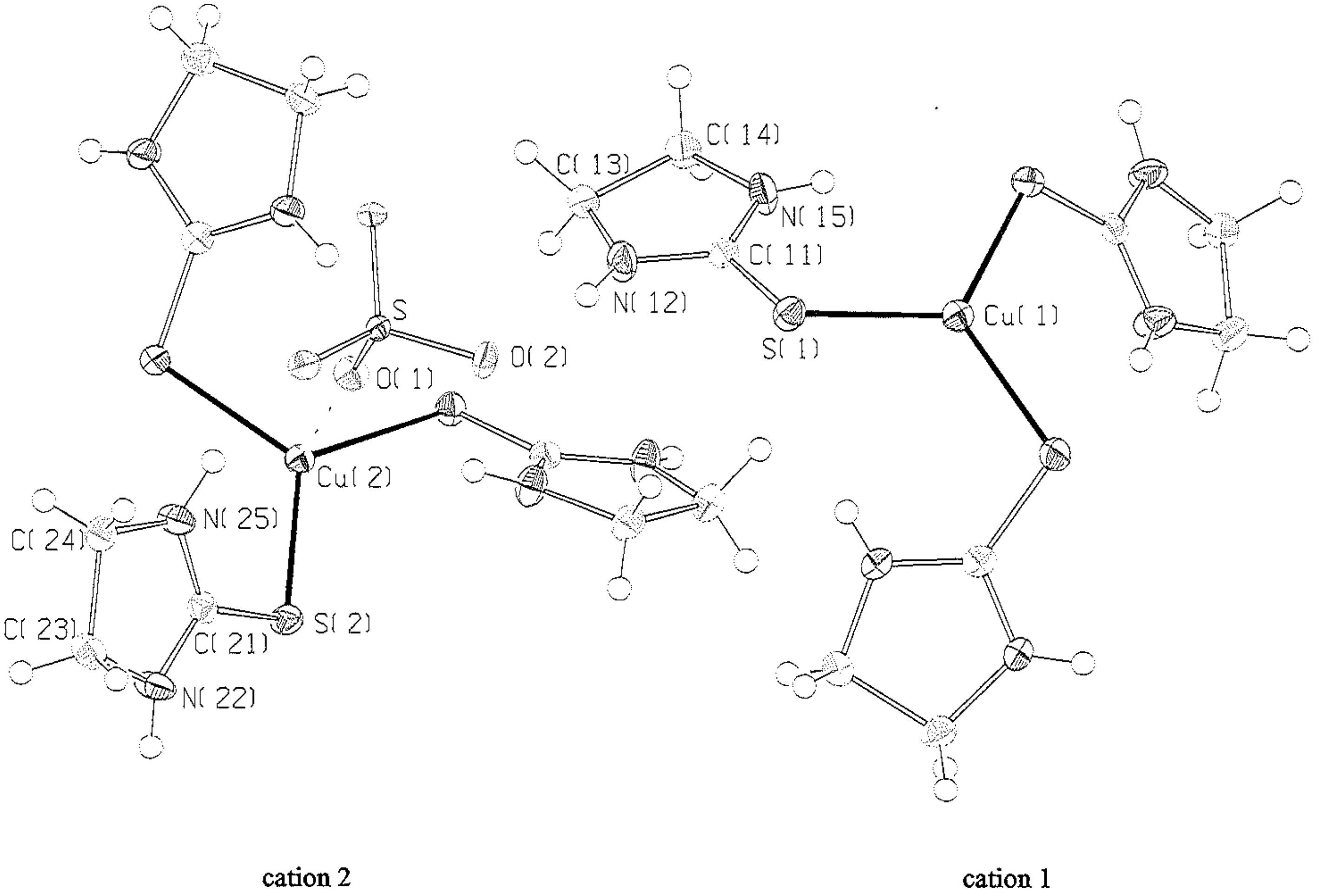

Figure 40 The structure of $[Cu(etu)_3]_2SO_4$

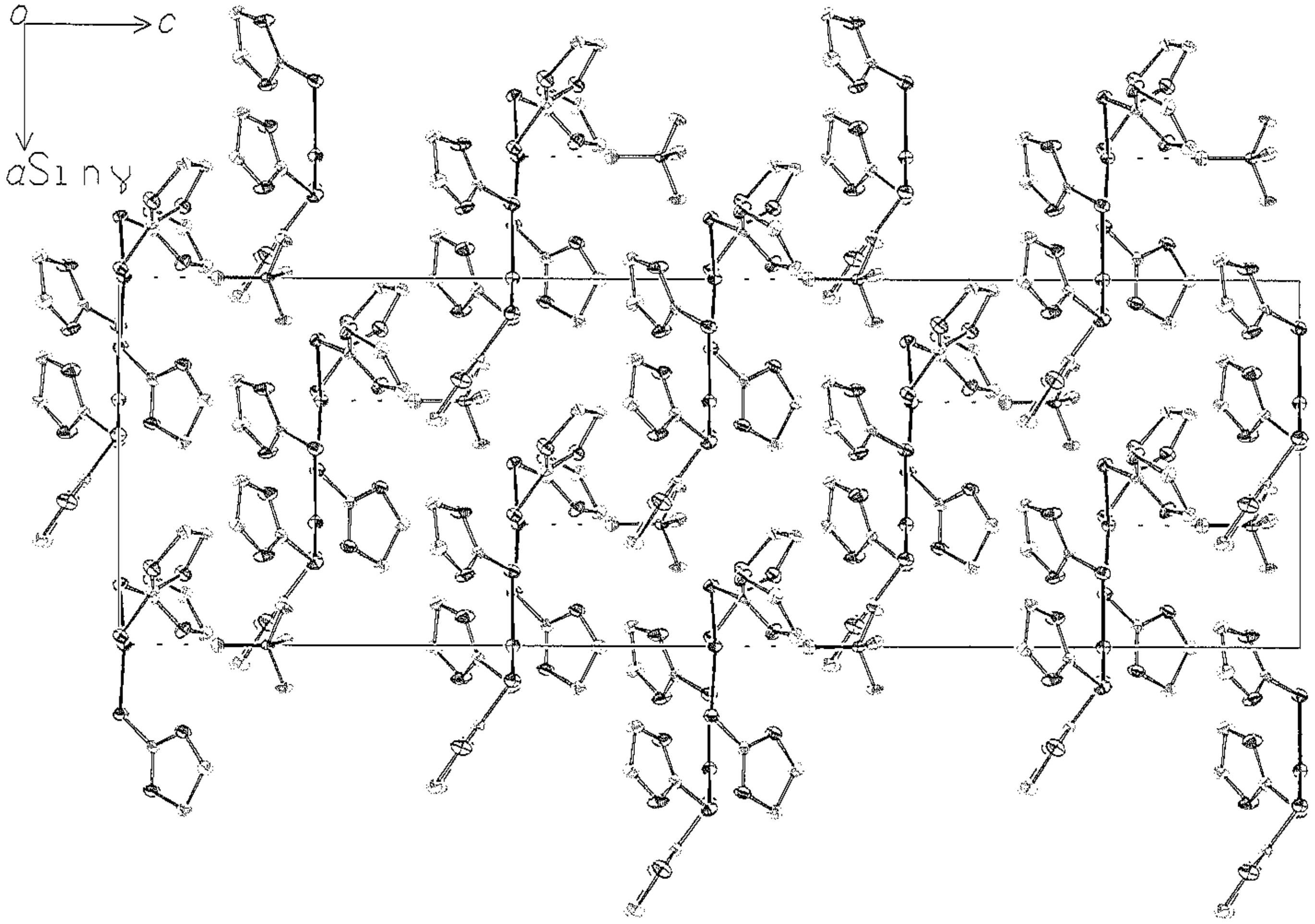

Figure 41 Unit cell contents of $[Cu(etu)_3]_2SO_4$ projected down *b*

Table 19 The crystallographic data for $(C_6H_5NH)_2CO$

| | |
|---|---|
| Identification code | Cudpno |
| Empirical formula | $C_{13}H_{12}N_2O$ |
| Formula weight | 212.25 |
| Measured temperature (K) | 153 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | $Pna2_1$ |
| $a$ (Å) | 9.089(2) |
| $b$ (Å) | 11.795(2) |
| $c$ (Å) | 10.401(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 1115.0(4) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 1.264 |
| $R$ | 0.019 |
| $R_w$ | 0.018 |
| $F(000)$ | 448 |
| Measured reflections | 1498 |
| Condition for observed reflections | $F > 4\sigma(F)$ |
| Observed reflections | 1364 |

Table 20 Interatomic distances of $(C_6H_5NH)_2CO$

| Atom | Distance ( Å ) |
|---|---|
| O(1) - C(1) | 1.239(4) |
| N(1) - C(1) | 1.392(9) |
| N(1) - C(11) | 1.42(1) |
| N(1) - H(1) | 0.98(5) |
| N(2) - C(1) | 1.356(9) |
| N(2) - C(21) | 1.44(1) |
| N(2) - H(2) | 0.96(5) |
| C(11) - C(12) | 1.388(6) |
| C(11) - C(16) | 1.40(1) |
| C(12) - C(13) | 1.40(1) |
| C(12) - H(12) | 1.04(4) |
| C(13) - C(14) | 1.41(1) |
| C(13) - H(13) | 1.03(4) |
| C(14) - C(15) | 1.377(7) |
| C(14) - H(14) | 1.07(5) |
| C(15) - C(16) | 1.41(1) |
| C(15) - H(15) | 0.98(5) |
| C(16) - H(16) | 1.10(4) |
| C(21) - C(22) | 1.389(8) |
| C(21) - C(26) | 1.383(7) |
| C(22) - C(23) | 1.40(1) |
| C(22) - H(22) | 0.94(4) |

Table 20 (continued)

| Atom | Distance (Å) |
|---|---|
| C(23) - C(24) | 1.395(8) |
| C(23) - H(23) | 1.12(5) |
| C(24) - C(25) | 1.372(9) |
| C(24) - H(24) | 0.90(6) |
| C(25) - C(26) | 1.42(1) |
| C(25) - H(25) | 1.19(6) |
| C(26) - H(26) | 0.98(7) |
| Hydrogen bonds | |
| N(1) --- H(2) | 2.41(9) |
| N(2) --- H(1) | 2.37(4) |
| O(1) --- H(1) (x-½, +y, ½-z) | 2.02(4) |
| O(1) --- H(2) (x-½, +y, ½-z) | 1.88(5) |
| O(1) --- H(25) (1-x, ½+y, +z) | 2.54(6) |

Table 21 Interbond angles of $(C_6H_5NH)_2CO$

| Atom | Angle (°) |
|---|---|
| C(1) - N(1) - C(11) | 123.8(4) |
| C(1) - N(1) - H(1) | 114(3) |
| C(11) - N(1) - H(1) | 119(3) |
| C(1) - N(2) - C(21) | 124.5(4) |
| C(1) - N(2) - H(2) | 119(3) |
| C(21) - N(2) - H(2) | 116(3) |
| O(1) - C(1) - N(1) | 122.3(6) |
| O(1) - C(1) - N(2) | 124.5(6) |
| N(1) - C(1) - N(2) | 113.1(4) |
| N(1) - C(11) - C(12) | 122.9(6) |
| N(1) - C(11) - C(16) | 117.1(4) |
| C(12) - C(11) - C(16) | 119.9(6) |
| C(11) - C(12) - C(13) | 120.2(6) |
| C(11) - C(12) - H(12) | 121(2) |
| C(13) - C(12) - H(12) | 119(2) |
| C(12) - C(13) - C(14) | 120.1(4) |
| C(12) - C(13) - H(13) | 120(2) |
| C(14) - C(13) - H(13) | 120(2) |
| C(13) - C(14) - C(15) | 119.2(6) |
| C(13) - C(14) - H(14) | 119(3) |
| C(15) - C(14) - H(14) | 121(3) |
| C(14) - C(15) - C(16) | 121.2(6) |
| C(14) - C(15) - H(15) | 129(3) |

Table 21 (continued)

| Atom | Angle (°) |
|---|---|
| C(16) - C(15) - H(15) | 110(3) |
| C(11) - C(16) - C(15) | 119.3(5) |
| C(11) - C(16) - H(16) | 119(2) |
| C(15) - C(16) - H(16) | 121(2) |
| N(2) - C(21) - C(22) | 121.3(5) |
| N(2) - C(21) - C(26) | 117.3(5) |
| C(22) - C(21) - C(26) | 121.4(6) |
| C(21) - C(22) - C(23) | 119.2(5) |
| C(21) - C(22) - H(22) | 129(2) |
| C(23) - C(22) - H(22) | 112(2) |
| C(22) - C(23) - C(24) | 119.5(5) |
| C(22) - C(23) - H(23) | 114(2) |
| C(24) - C(23) - H(23) | 126(2) |
| C(23) - C(24) - C(25) | 121.3(7) |
| C(23) - C(24) - H(24) | 118(4) |
| C(25) - C(24) - H(24) | 121(4) |
| C(24) - C(25) - C(26) | 119.4(6) |
| C(24) - C(25) - H(25) | 122(2) |
| C(26) - C(25) - H(25) | 118(2) |
| C(21) - C(26) - C(25) | 119.2(5) |
| C(21) - C(26) - H(26) | 124(7) |
| C(25) - C(26) - H(26) | 116(7) |

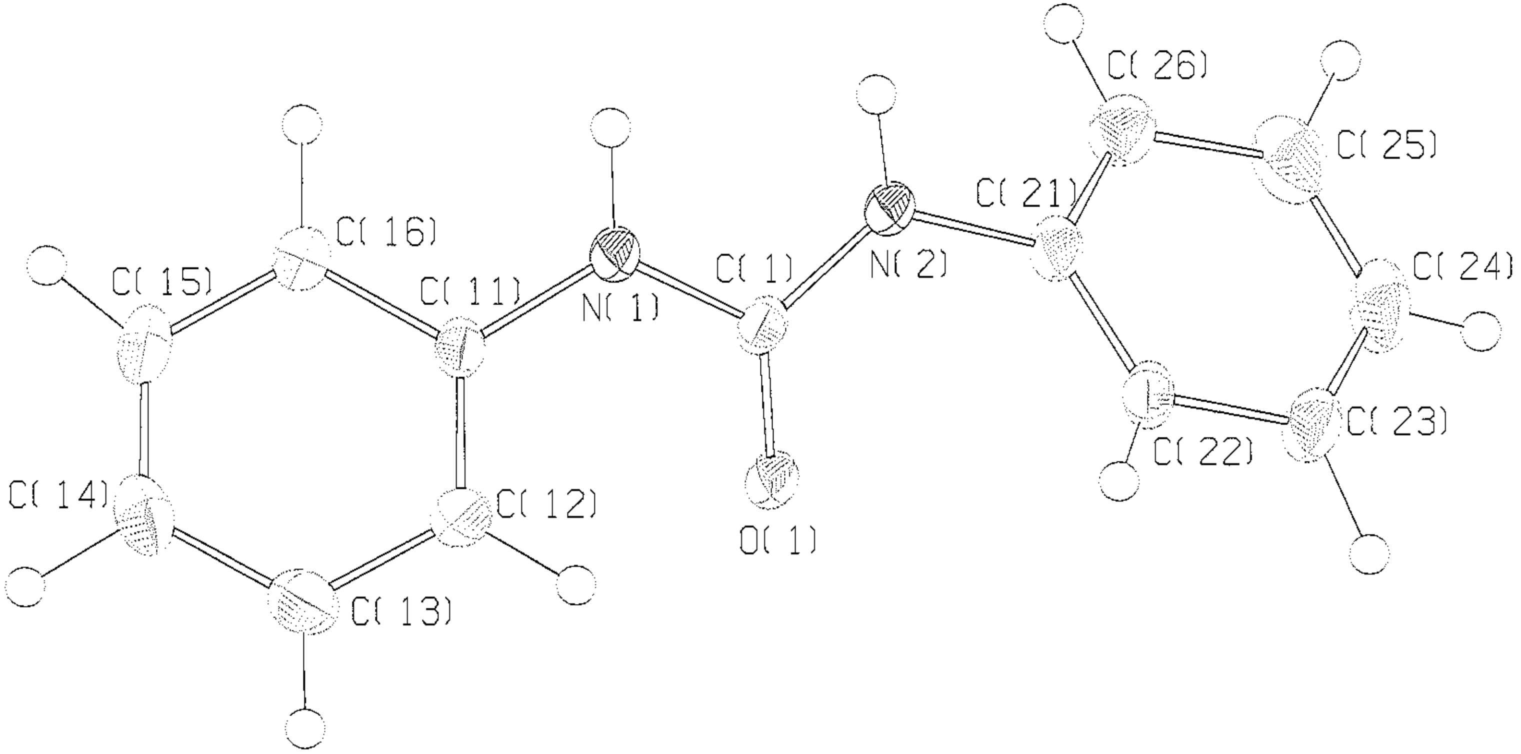

Figure 42 The structure of $(C_6H_5NH)_2CO$

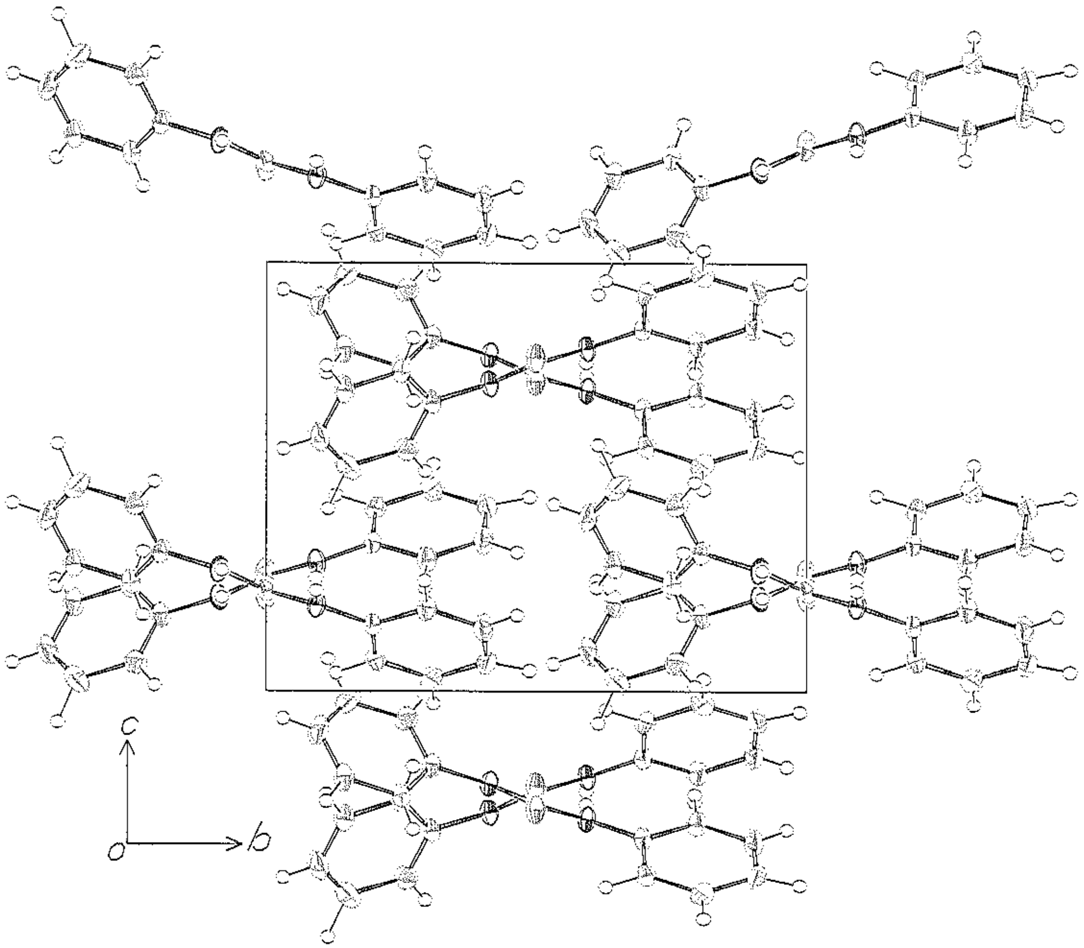

Figure 43 Unit cell contents of $(C_6H_5NH)_2CO$ projected down *a*

## Chapter 4

# DISCUSSION

### 4.1 Preparation of Complexes

The research set out to study the structure of Cu(I) and Ag(I) substituted thiourea complexes by X-ray diffraction methods. The complexes to be studied must be single crystals. Hence the conditions of preparation must be suitable for this purpose. Preparations of Cu(I) and Ag(I) substituted thiourea complexes have been carried out using a number of methods; varying reactants, mole ratios of reactants, solvents and reaction temperature. However the 6 compounds were suitable for studying the structures, their conditions of preparation are shown in Table 2. Although the compound $(C_6H_5NH)_2CO$ is not a complex but it was interesting to solve the structure to establish the product of the reaction. $[Ag(atu)_2]NO_3$, $[Cu_4(ettu)_6 I_4].H_2O$, $[Ag_2(etu)_6](ClO_4)_2$ and $[Ag_2(etu)_4Br_2]$ were obtained by direct interaction of ligands with Cu(I) or Ag(I) salts, but $[Cu(etu)_3]_2SO_4$ and $(C_6H_5NH)_2CO$ were obtained by reduction of Cu(II) salts in the presence of the ligands.

The experimental condition could not be expected for each reaction, however most mole ratio of Cu(I) or Ag(I) salt and ligand were higher than 1 : 2, which gave complexes. Most lower 1 : 2 mole ratios gave crystals of ligand. Additionally, most reactions could form more complexes at warm temperature (~60 - 70 °C) because reactants could be more soluble in solvents, especially Cu(I) and Ag(I) salts. Apart from solubility of reactants, crystallization in solvent was referred. The formation of crystals depends both on the solubility of compound (a thermodynamic property) and an nucleation and growth rates (kinetic properties). There are many factors involved in the growth of large, well-define crystals. In practical, the experiment is usually most effective if crystallization occurs over a period of one to several days (Glusker, Lewis and Rossi, 1994 : 40-49). To obtain crystals suitable for X-ray diffraction studies, most solvents were organic solvent and the crystallization of these complexes were obtained by slow solvent evaporation.

## 4.2 X-ray Fluorescence Spectrometry

This method was used to check prevalence of Cu or Ag and S in synthesized compounds. The $K_\alpha$ spectrum of Cu atom is about 8.04 keV, Ag atom is about 22.1 keV and S atom is about 2.31 keV. However the method was only preliminary quality analyses for complexes, which Cu or Ag was representative for Cu(I) or Ag(I) salts and S was representative for substituted thioureas. As shown in Figure 13 - 18, $[Ag(atu)_2]NO_3$, $[Cu_4(ettu)_6 I_4].H_2O$, $[Ag_2(etu)_6](ClO_4)_2$, $[Ag_2(etu)_4Br_2]$ and $[Cu(etu)_3]_2SO_4$ show the peaks of Cu or Ag and S but $(C_6H_5NH)_2CO$ shows the absence of these peaks.

## 4.3 Infrared Spectrophotometry

Substituted thioureas contain the NHCS group (Figure 1), which may adopt either the thione form (H – N – C = S) or the thiol form (N = C – S – H). The ligands atu, ettu, etu and dptu adopt the thione form in the free state and in their complexes (Figure 19 - 27). This is evident by the absence of the

$V$(SH) band in the region 2500 $cm^{-1}$ and by the presence of $V$(NH) in the range 2890 - 3310 $cm^{-1}$ (Singh and Dikshit, 1995).

Yamaguchi, *et al.* assigned the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule (Yamaguchi, *et al.*, 1958) :

| Band | Region | Mode of vibration |
|---|---|---|
| I | 3350 $cm^{-1}$ | $V(N-H)$ |
| II | 1600 $cm^{-1}$ | $\delta(NH_2)$ |
| III | 1500 $cm^{-1}$ | $V_s(C-N)$ |
| IV | 700 $cm^{-1}$ | $V_s(C-N) + V(C=S)$ |

Swaminathan and Irving attributed the band near 750 $cm^{-1}$ as C – S stretching with small contribution of symmetric C – N stretching vibrations (Swaminathan and Irving, 1964)

Singh and Dikshit studied the structures and infrared spectra of mixed ligand Cu(I) complexes containing halides, triphenylarsine and *N,N*-dimethyl-*N′*-phenylthiourea (dmptu), *N,N*-dibutyl- *N′*-phenylthiourea (dbptH) or 1,3-thiazolidine-2-thione (tzdtH) and assiged four characteristic thioamide bands :

| Band | Region | Mode of vibration |
|---|---|---|
| I | 1500 $cm^{-1}$ | $V(C-N) + \delta(N-H)$ |
| II | 1300 $cm^{-1}$ | $V(C=S) + V(C=N) + V(C-H)$ |
| III | 1000 $cm^{-1}$ | $V(C-N) + V(C-S)$ |
| IV | 750 $cm^{-1}$ | $V(C-S)$ |

The other bands useful for identication of donor atoms are $V$(NH) and $V$(C = S) (Singh and Dikshit, 1995). The thioamide bands II and III have contributions from $V$(CN) and $V$(CS) vibrations but $V$(CS) contributes more than $V$(CN) to the thioamide band II (Devillannova, *et al.*, 1979, quoted in Singh and Dikshit, 1995) ; therefore band II can be utilized to decide the coordination site but it is difficult to decide the coordination site on the basis of shift of band III.

To support the crystal structures of compounds, the 5 bands were considered :

| Band | Region | Mode of vibration |
|---|---|---|
| I | 3000 $cm^{-1}$ | $V(N-H)$ |
| II | 1500 $cm^{-1}$ | $V(C-N) + \delta(N-H)$ |
| III | 1400 $cm^{-1}$ | $V(C-N)$ |
| IV | 1300 $cm^{-1}$ | $V(C=S)$ |
| V | 1000 $cm^{-1}$ | $V(C-N) + V(C-S)$ |

The infrared spectra of the ligands atu, ettu, etu, dptu and the studied compounds are summaried in Table 22.

Table 22 The infrared spectra of the ligands atu, ettu, etu, dptu and the studied compounds

| Compound | Band | | | | |
|---|---|---|---|---|---|
| | I | II | III | IV | V |
| ligand atu | 3435 | 1540 | 1415 | 1320 | 1050 |
| | 3320 | | 1370 | | |
| | 3285 | | | | |
| | 3190 | | | | |
| 1. $[Ag(atu)_2]NO_3$ | 3440 | 1565 | | 1310 | 1045 |
| | 3330 | | 1425 | | |
| | 3290 | | 1400 | | |
| | 3200 | | 1380 | | |
| ligand ettu | 3345 | 1560 | 1465 | 1305 | 1030 |
| | 3240 | 1540 | 1445 | 1260 | 1010 |
| | 3160 | | | | |
| 2. $[Cu_4(ettu)_6 I_4].H_2O$ | 3390 | 1565 | 1480 | 1295 | - |
| | 3300 | | 1460 | | |
| | 3215 | | | | |
| ligand etu | 3250 | 1520 | 1460 | 1370 | 1045 |
| | | 1500 | | 1360 | |
| 3. $[Ag_2(etu)_6](ClO_4)_2$ | 3280 | 1530 | 1470 | 1330 | 1005 |
| | | 1515 | | 1290 | |
| 4. $[Ag_2(etu)_4Br_2]$ | 3360 | 1530 | 1475 | 1345 | 1035 |
| | 3260 | 1510 | 1455 | 1320 | |
| 5. $[Cu(etu)_3]_2SO_4$ | 3370 | 1550 | 1500 | 1330 | 1020 |
| | 3200 | 1525 | 1470 | 1300 | 1010 |

Table 22 (continued)

| Compound | Band | | | | |
|---|---|---|---|---|---|
| | I | II | III | IV | V |
| ligand dptu | 3210 | 1560 | 1460 | 1350 | 1030 |
| | 3060 | | | 1320 | 1010 |
| | 3020 | | | 1300 | |
| 6. $(C_6H_5NH)_2CO$ | 3340 | 1560 | 1450 | - | 1060 |
| | 3300 | | 1445 | | 1030 |
| | 3200 | | | | |

The bands observed in the frequency region higher than 3000 $cm^{-1}$ can be assigned to the N – H stretching [$V$ (N – H)] frequencies. All studied compounds (except compound 6) the frequencies are higher than the ligands. The $V$ (N – H) bands which shift to the higher region may be due to intramolecular hydrogen bonding in the complexes. The infrared absorption bands observed near 1500 $cm^{-1}$ are assigned to C – N antisymmetric stretching and N – H bending [$V$(C – N) + $\delta$(N – H)] vibrations. In case of complexes of ligands atu, ettu and etu, there are increment in frequency about 10 – 30 $cm^{-1}$ but in compound 6, the frequency is at the same position as the ligand dptu. Moreover, the bands region 1400 $cm^{-1}$ assigned to the C – N stretching [$V$(C – N)] vibrations, which are increasing in frequency about 10 – 30 $cm^{-1}$ for all compounds, except compound 6 is decreasing in frequency. These increasing frequencies observed for the complexes can be explained as resulting from the greater double bond character of the carbon – to – nitrogen bands on complex formation.

The band IV has contribution from C = S stretching [$V$(C = S)] undergo a red shift in which intense bands are observed in the lower frequency region (except compound 6). These shifts indicate the involvement of the C = S group in coordination. The bands observed in the frequency region higher than 1000 $cm^{-1}$ can be assigned to the C – N stretching and C – S stretching [$V$(C – N) + $V$ (C – S)] but $V$(C – S) contributes more than $V$(C – N). All studied compound (except compound 6) the frequencies are lower than the ligands. These shifts can be explained as resulting from the greater single bond character of carbon – to – sulfur bands on complex formation.

From the foregoing discussion it may be concluded that in all cases except that of compound 6, there are coordination with Cu(I) or Ag(I) through sulfur whereas in case of compound 6, the infrared spectra are different from the ligand dptu. The bands observed in the frequency region 1300 $cm^{-1}$ of compound 6 (1320 and 1300 $cm^{-1}$, Figure 28) can be explained as the C – O stretching [$V$(C – O)] but the bands in this region of dptu have contribute from C = S stretching [$V$ (C = S)]. Moreover, the band at 1650 $cm^{-1}$ of compound 6 has contribute from C = O stretching [$V$(C = O)] but the absence of the [$V$(C = O)] band in dptu.

## 4.4 Crystal Structure Determination

### 4.4.1 X-ray photography

The Weissenberg camera served for many years as the standard data-collecting device in X-ray crystallography. It has been largely supplanted by diffractometers in modern practice but is still an excellent teaching tool. Furthermore, an understanding of its principles provides a needed familiarity with the practical application of reciprocal lattice concept. (Stout and Jensen, 1989, 94)

Oscillation photographs are generally used to align crystals and to measure the cell edge along the axis of rotation. With regard to interpreting oscillation photographs shows that distance between the zero- and *n*th levels of reciprocal lattice points :

$$d_1^* = d_1^*/1 = d_2^*/2 = d_3^*/3 \quad \ldots = d_n^*/n$$

Because the direct axis, which is the axis of rotation, is perpendicular to the reciprocal lattice levels and thus parallel to $d^*$, the repeat distance $r$ along this axis is given by

$$r = \lambda / d_1^*$$

$\lambda$ = wavelength of radiation (this research, $\lambda = 1.542$ Å)

Weissenberg photographs give a view of an entire reciprocal lattice level, they can provide almost any desired information about that level. In particular they can be used for improving alignment, measuring cell constants, determining the space group, and measure intensities.

The experiment, the crystals of $[Ag_2(etu)_4Br_2]$ and $(C_6H_5NH)_2CO$ were studied by Oscillation methods using the PW 1720 X-ray Generator (Philips) and Enraf Nonius FR550 Weissenberg camera. With photographs (Figure 29 - 30), one unit cell axis of crystals were aligned in a particular direction relative to the incident X-ray beam and this produced a regular pattern of spots on the film. The study was to check for a cracked or twinned crystal and determine an axis length of crystal approximately. The results from X-ray photographs are shown in Table 23. The results show an axis length of each compound are slightly different from the diffractometry results. The error may occur from measurement.

Table 23 The results of X-ray photograph of $[Ag_2(etu)_4Br_2]$ and $(C_6H_5NH)_2CO$

| Distance (Å) | $[Ag_2(etu)_4Br_2]$ | $(C_6H_5NH)_2CO$ |
|---|---|---|
| $d_1^*/1$ | 0.17 | 0.17 |
| $d_2^*/2$ | 0.18 | 0.17 |
| $d_3^*/3$ | 0.17 | 0.17 |
| $d_4^*/4$ | 0.17 | 0.17 |
| $d_1^*$ | 0.172 | 0.17 |
| $r$ | 8.965 | 9.071 |

### 4.4.2 X-ray diffractometry

The diffraction data from X-ray diffractometer were preprocessed and the crystal structures were solved by Xtal system version 3.5, 3.6. The followings are the results from structure determination.

$[Ag(atu)_2]NO_3$

The structure consists of sulfur-bridged polymeric cation $Ag(atu)_2^+$ and $NO_3^-$ anions with only van der Waals and hydrogen bond forces superposed on ionic interactions. The structure is made up of distorted trigonal planar, silver atom bonded to a terminal sulfur atom and two bridging sulfur atoms and these bridging sulfur atoms shared with other trigonal planar silver atoms to form an infinite chain in the *b* direction (Figure 31, 32, 33). The Ag – S distances fall into the range 2.426(8) - 2.724(1) Å, the non-bridging sulfur (Ag – S(2) = 2.426(8) Å) is shorter than the bridging sulfurs, (Ag – S(1) = 2.4548(9), Ag – S(1') = 2.724(1) Å). The S – Ag – S angles are very interesting, the S(1) – Ag – S(2) angle (152.98(4) °) is much broader than the S(1) – Ag – S(1') and S(2) – Ag – S(1'), which are in the range 94.00(3) – 108.11(3)°, respectively). These are due to ligand – ligand interactions.

$[Cu_4(ettu)_6 I_4].H_2O$

The stoichiometric ratio of CuI and *N*-ethylthiourea in $[Cu_4(ettu)_6 I_4].H_2O$ is 1 : 1.5. Each Cu atom is coordinated tetrahedrally by three S atoms and an I atom. Four such tetrahedra are held together by corner sharing at sulfur positions to form a tetrahedral array (Figure 34). This arrangement defines four six-membered $Cu_3S_3$ rings, all adopting a chair conformation. In these rings, the substituent I atoms occupy equatorial positions and of the three $C(NH_2)(NHCH_2CH_3)$ substituents, one is in an axial position. The Cu – I distances vary from 2.623(2) to 3.083(2) Å and the Cu – S distances range from 2.258(4) to 2.388(4) Å. The overall complex has an adamantane-like cluster structure with *N*-ethylthiourea as bridging and I as terminal ligands. Similar adamantane structures have been reported for $Cu_4(tu)_6(NO_3)_4.4H_2O$ and $Cu_4(tu)_9(NO_3)_4.4H_2O$, with trigonal planar Cu atoms in the former, but with three tetrahedral and one trigonal planar Cu atom in the latter (Griffith, *et al.*, 1976). For the sulfate analogue, the structure of $[Cu_4(tu)_7](SO_4)_2.4H_2O$ has been reported (Bott, *et al.*, 1998). The ethyl C(25) and C(55) atoms of the ligand were found to be disordered. The unit cell of the complex consists of four $[Cu_4(ettu)_6 I_4].H_2O$ repeating units (Figure 35). The iodide significantly stabilized the cell through hydrogen bonds primarily with the $NH_2$ ends of the coordinated ettu ligands with in the $[Cu_4(ettu)_6 I_4]$ cages. Furthermore, the water molecule, which comes from the undried ethanol solvent is also hydrogen-bonded to $NH_2$ of ligand.

### $[Ag_2(etu)_6](ClO_4)_2$

The structure is isomorphous with the complex $[Cu_2(etu)_6](ClO_4)_2$, which has been studied by Raper, Wilson and Clegg (1992). The structure consists of isolated centrosymmetrically constrained dinuclear complex cations, $[Ag_2(etu)_6]^{2+}$, formed from two edge-sharing, $AgS_4$ tetrahedral and perchlorate anions. A perspective view of the structure with the atoms labeled is in Figure 36 and unit cell contents are in Figure 37. The silver(I) atoms in the dinuclear cation are coordinated by a combination of 2 terminal and 2 bridging etu ligands forming a planar $Ag_2S_2$ unit. Because of the imposed centrosymmetry in the cation the metal atoms have identical $S_4$ coordination with distorted tetrahedral geometry and angles ranging from 102.83(4) to 115.23(4)°. The $Ag_2S_2$ bridging core geometry is a planar lozenge shaped with alternating short and long Ag – S bridging distances (Ag – S(3) = 2.566(1) and Ag – S(3') = 2.681(1) Å). Terminal ligands form typical Ag – S – C angles (100.4(1) – 103.1(2)°).

### $[Ag_2(etu)_4Br_2]$

The crystal determinations establish the stoichiometry of siver(I) bromide : ethylenethiourea as 1 : 2. The complex molecule is a dimer of the form $(etu)_2AgBr_2Ag(etu)_2$ with a pair of four-coordinate distorted tetrahedral silver atoms bridged by a pair of bromine atoms, Figure 38. The Ag – S distances are equal (2.483(1) Å) and the Ag – Br distances are nearly same (Ag – Br = 2.7997(6) and Ag – Br' = 2.8320(5) Å). The dimeric complex is crystallographically constrained to occupy centres of symmetry in the unit cell (Figure 39). Consequently, both of the Ag(I) atoms in the dimer have identically distorted tetrahedral environments with angles at the metal ranging from 108.82(3) to 123.70(4)°. There are intramolecular hydrogen bondings in the structure, Br – H(12) = 2.69(3) and Br – H(22) = 2.92(4) Å. The dihedral angle between the planes C(11), N(12), C(13), C(14), N(15), and C(21), N(22), C(23), C(24), N(25) is 44.3(2)° in such a manner as to minimize steric interactions between ethylene groups. The structure is the same as the one that has been done by Battaglia, *et al.* (1984). However the preparation and temperature of collecting diffraction data are different. The temperature of present study (153 K) is lower than the previous study (293 K). Furthermore, the *R*-factor is lower than the previous study (present study, $R = 0.022$ ; previous study, $R = 0.038$), which means a new accurate analysis of crystal structure of this complex has been redetermined.

$[Cu(etu)_3]_2SO_4$

The structure consists of two independent $[Cu(etu)_3]^{2+}$ units, the symmetry imposed by space group *R*3*c* simplified the assignment of the asymmetric unit considerably (Figure 40, 41). Each cation is located with the copper atom on a threefold crystallographic axis so that each copper and only one ligand is crystallographically independent. There is only one sulfate counter ion, this is disposed with one of the S – O bonds lying on a crystallographic threefold axis common to one of the cations and with the axial oxygen atom approaching the silver atom at a relatively long distance (Cu(2) – O(1) = 2.782(2) Å). The interaction being insufficient to perturb the sulfate geometry from tetrahedral. Nevertheless, the cation geometry (cation 2) differs significantly from that of cation 1 and in a manner suggestive and supportive of some perturbation arising from the presence of the sulfate oxygen. In cation 1, the $CuS_3$ moiety is closely planar, with the angle between the sulfur atoms being about 120 °;

Cu(1) – S(1) is about 2.25(1) Å. In cation 2, the angle between the sulfurs is 119.8°, with Cu(2) – S(2) slightly but significantly longer about 2.27(1) Å.

The structure is the same as the one that has been studied by Bowmaker, *et al.* (1994) but there are several significant and important differences. For example, the preparation and temperature of collecting diffraction data are different. The experimental temperature of collecting diffraction data (153 K) is lower than the previous study (295 K). Furthermore, the *R*-factor is lower than the previous study (present study, $R = 0.017$ ; previous study, $R = 0.029$).

$(C_6H_5NH)_2CO$

The structure has been determined by direct-methods, the space group is $Pna2_1$. The structure is not a complex as expected but it is the structure of *N,N′*-diphenylurea [$(C_6H_5NH)_2CO$], figure 42. However this structure has not been done by X-ray diffraction methods. There is no copper atom but the sulfur atom in dptu was substituted by the oxygen atom, with C(1) – O(1) distance is 1.239(4) Å. The C – N distances are in the range 1.354(9) - 1.44(1) Å and the C – C distances are in the range 1.383(7) - 1.41(1) Å. The dihedral angles between plane defined by C(1), O(1), N(1), N(2) and phenyl group 1 and 2 are 41.9(3) and 35.4(3) °, respectively. Moreover, the dihedral angle between phenyl groups is 27.5(3) ° in such a manner as to minimize steric interactions between phenyl groups. The unit cell of the complex consists of four $(C_6H_5NH)_2CO$ repeating units (Figure 43).

# Chapter 5

## CONCLUSION

Copper(I) and silver(I) form complexes with substituted thioureas with various stoichiometries and structure types in which neutral or ionic complexes may be obtained. In this work, 5 Cu(I) and Ag(I) substituted thiourea complexes have been prepared. These complexes are $[Ag(atu)_2]NO_3$, $[Cu_4(ettu)_6 I_4].H_2O$, $[Ag_2(etu)_6](ClO_4)_2$, $[Ag_2(etu)_4Br_2]$ and $[Cu(etu)_3]_2SO_4$, prepared by the reaction of Cu(I) or Ag(I) salts ($NO_3^-$, $ClO_4^-$, $SO_4^{2-}$, $Br^-$, $I^-$) with substituted thiourea ligands (atu, ettu, etu). In addition, in the course of the study involving Cu(I) and Ag(I) (substituted thiourea) complexes, the compound diphenylurea, $(C_6H_5NH)_2CO$ was isolated from the copper(II) nitrate and diphenylthiourea. Then the structure of this compound was also determined in this work although it is not a copper-diphenylthiourea complex as expected.

The crystal structure of $[Ag(atu)_2]NO_3$ consists of sulfur-bridged polymeric cation $Ag(atu)_2^+$ and $NO_3$ anions with only van der Waals and hydrogen bond forces superposed on ionic interactions. Unit cell-constants are : $a$ = 12.0680(6), $b$ = 6.8056(5), $c$ = 17.6552(9) Å, $\beta$ = 108.147(4)°. The structure consists of distorted trigonal planar Ag(I). The $R$-factor is 0.036 for 2841 observed reflections at 293 K.

The crystal structure of $[Cu_4(ettu)_6I_4].H_2O$ is a $[Cu_4(ettu)_6I_4]$ adamantane-like cluster. The X-ray structure is refined to residual $R$ = 0.059 for 4180 observed reflections. The copper atoms lie in a tetrahedral arrangement. Four such tetrahedra share corners to form a tetrahedral assembly. This cage structure results in the formation of four six-membered Cu – S – Cu – S – Cu – S rings all in the chair conformation, which strongly interact with the ettu ligands through hydrogen bonds.

The structure of $[Ag_2(etu)_6](ClO_4)_2$ crystallized in monoclinic cells ; $a$ = 6.329(1), $b$ = 24.262(2), $c$ = 12.119(2) Å, $\beta$ = 92.67°, space group $P2_1/c$ , $Z$ = 4, $R$ = 0.041 from 3697 observed reflections. The structure is an ionic centrosymmetric dimer consisting of $[Ag(etu)_6Ag]^{2+}$ cations and $ClO_4^-$ anions. Each silver atom is pseudo-tetrahedrally coordinated by pairs of terminal thione-$S$ and asymmetric bridging etu ligands. Each ligand is *trans*-related to its partner across crystallographic symmetry centres. Consequently each silver(I) atom has an identical $S_4$ donor set.

The dimeric structure $[Ag_2(etu)_4Br_2]$ crystallized in a monoclinic $P2_1/n$, $a$ = 8.975(2), $b$ = 10.457(2), $c$ = 13.158(3) Å, $\beta$ = 103.42(3)°, $Z$ = 4, $R$ = 0.022 from 2763 observed reflections at 153 K. The structure is a neutral dimer built by a centre of symmetry. The asymmetry unit consists of half of the dimer where the other half is generated by this centre of symmetry. The silver atom is bonded to two bridging bromine atoms and two terminal etu ligands.

The crystal structure of $[Cu(etu)_3]_2SO_4$ consists of two independent $[Cu(etu)_3]^{2+}$ units, in space group $R3c$, $Z$ = 6. Each copper atom lies on a threefold axis so that each copper and only one ligand is crystallographically independent. The sulfate counter ion is disposed with one of the S – O bonds lying on a crystallographic threefold axis common to one of the two cations, the S – O axial bond approaching the copper atom normal to the planar $CuS_3$ array. The $R$-factor is 0.019 for 1393 observed reflections at 153 K.

The crystal structure of *N,N′*-diphenylurea, $[(C_6H_5NH)_2CO]$, is not copper-sulfur complex as expected but it is the structure prepared by reaction between copper(II) and diphenylthiourea as described previously. The structure has also been determined by direct-methods to a final *R* of 0.019 from 1364 measured reflections at 153 K. The space group is $Pna2_1$ with four formular entities per cell.

Furthermore, the compounds have been studied by X-ray Fluorescence Spectrometry and Infrared Spectroscopy to support the structures. These results are consistent with the structures.

The experimental results show different structure types of compounds prepared from Cu(I) or Cu(II) or Ag(I) salts with substituted thioureas. Reactions between these reactants generate a variety of complexes which have unpredictable stoichiometry and stereochemistry. The Cu(I) and Ag(I) coordinations are distorted trigonal planar or distorted tetrahedral in such a manner as to minimize steric interactions. The substituted thiourea ligands coordinate to the Cu or Ag atom through the S atom as terminal ligands or bridging ligands or both.

Studies of Cu(I) and Ag(I) substituted thiourea complexes and other complexes by X-ray diffraction have been increased. A great advantage of X-ray analysis as a method of chemical structure analysis is its power to show some totally unexpected and surprising structure with concurrent complete certainty. A knowledge of the molecular structure is one of the fundamental aims of chemistry and is essential for a proper understanding of the physical and chemical properties of the materials.

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# Appendix

# Appendix A

## X-ray Crystal Structure Determination

X-rays lie in the electromagnetic spectrum between ultraviolet light and gamma radiation and give an approximate range of wavelengths of 0.1 – 100 Å, but the wavelength of about 1 Å is concerning to X-ray crystal structure determination. X-rays are usually produced by rapidly decelerating fast – moving electrons and converting their energy of motion into a quantum of radiation.

### Sources of X-rays

Two types of radiation are produced when the anode target is bombarded by fast – moving electrons. A continuum of radiation referred to as white radiation, is produced by simple collision between electrons and target. In addition to simple energy exchange on collision, metal atoms in the target may become ionized by the loss of an inner shell electron. An outer-shell electron then moves to an inner shell, and radiation of a wavelength specific to the target material is emitted (Figure 44). These X-rays produced are called characteristic X-rays because their nature is dependent on the atomic character of the material used to make the target. The characteristic radiation that is generally used for X-ray.

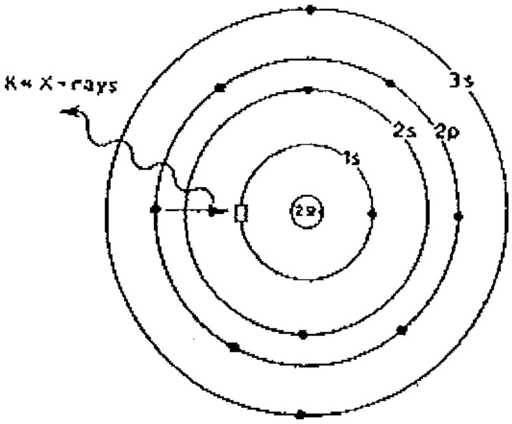

Figure 44 Occurrence of X-ray spectra

## X-ray Diffraction

In 1912 Max von Laue placed a crystal of copper (II) sulfate between a white X-ray Source and a photographic plate. The resulting photograph contained a central bright spot due to that part of the beam which passed straight through the crystal. Surrounding the central spot was a number of fuzzy spots arranged in a regular pattern. The fuzzy spots had been produced by diffracted beams .

The theory of diffraction of light by a ruled grating was well known. Laue derived equations extending the principles to a three dimensional grating. These equations expressed angles of diffraction in terms of interatomic distances and X-ray wavelength .

Laue's discovery of X-ray diffraction captured the interest of W.H. Bragg and his son W.L. Bragg who successfully applied X-ray diffraction to the determination of a number of crystal structures. Instead of considering X-ray diffraction in terms of a three dimensional grating, W.L. Bragg devised a simpler approach based on the reflection of X-rays by planes of atoms, Figure 45.

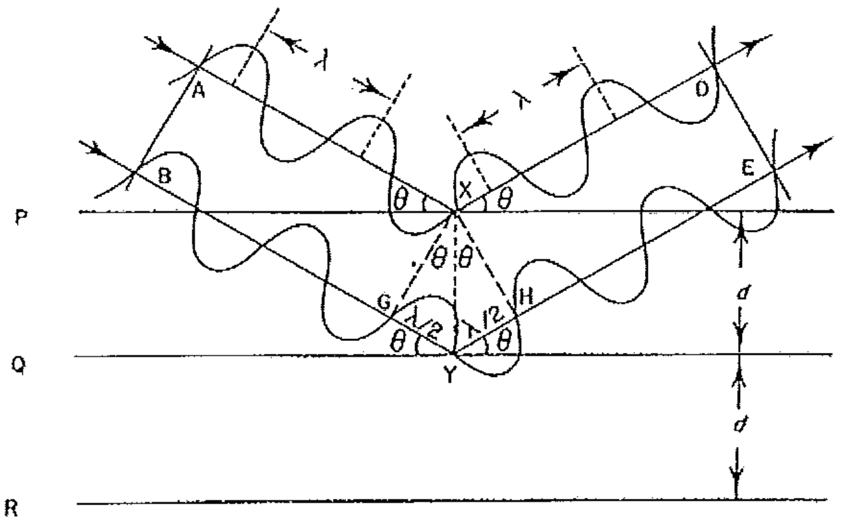

Figure 45 The Bragg condition

Since Q is lower than P, the beam path BYE is longer than AXD by the amount GY + YH, Figure 45. This is called the path difference. Now the two reflected rays, XD and YE, will constructively interfere when the path difference is equal to the wavelength ( $\lambda$ ) or a multiple of it. Thus the condition for X-ray diffraction is

$$2d\sin\theta = n\lambda \tag{1}$$

where $n$ is an integer (1 , 2 , 3 , etc) called the order of reflection. Equation (1) is known as the Bragg equation.

The most powerful application of X-ray diffraction is crystal structure determination and refinement. This is normally carried out using the intensities of literally thousands of reflections collected from a single crystal.

## Xtal System

Xtal is a package of over sixty crystallographic programs for calculations ranging from the reduction of raw diffraction intensities, to the solution, refinement and publication of crystal structures. These are applicable to X-ray, neutron and electron diffraction analyses, including charge density studies. The package contains interactive graphics tools and is available as execution modules for most common platforms.

Xtal program authors are from many different laboratories around the world. Their efforts are rewarded by citing Xtal and the programs used in producing results for publication. The experiment used Xtal 3.5, 3.6 which have been developed by Hall, S.R., du Boulay, D.J. and Olthof-Hazekamp, R., University of Western Australia.

# Appendix B

## Calculation of unit cell volume

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

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

## Calculation of number of molecules per unit cell (*Z*)

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

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

$V$ = Volume of unit cell (cm$^3$)

N = Avogadro number ($6.02 \times 10^{23}$ mol$^{-1}$)

Fw = Formula weight

# Appendix C

## The Crystallographic data

Table 24 Non-hydrogen atom coordinates and isotropic thermal parameters of $[Ag(atu)_2]NO_3$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| Ag | 0.11879(2) | 0.30057(5) | 0.22438(2) | * 0.0465(2) |
| S(1) | 0.32174(7) | 0.4141(2) | 0.27397(5) | * 0.0429(5) |
| N(11) | 0.5135(3) | 0.3311(5) | 0.3900(2) | * 0.035(2) |
| C(11) | 0.3944(3) | 0.3246(5) | 0.3667(2) | * 0.033(2) |
| C(12) | 0.5904(3) | 0.2863(6) | 0.4641(2) | * 0.040(2) |
| C(13) | 0.7168(4) | 0.309(1) | 0.4710(3) | * 0.056(3) |
| O(12) | 0.5569(3) | 0.2295(6) | 0.5184(2) | * 0.065(2) |
| N(12) | 0.3427(3) | 0.2524(7) | 0.4145(2) | * 0.056(3) |
| S(2) | -0.08379(7) | 0.3340(2) | 0.14378(5) | * 0.0377(5) |
| N(21) | -0.2906(2) | 0.3372(5) | 0.1639(2) | * 0.034(2) |
| C(21) | -0.172(3) | 0.3409(5) | 0.2022(2) | * 0.032(2) |
| C(22) | -0.3786(3) | 0.3383(6) | 0.1983(2) | * 0.036(2) |
| N(22) | -0.1360(3) | 0.3524(6) | 0.2795(2) | * 0.044(2) |
| C(23) | -0.4981(4) | 0.314(1) | 0.1415(3) | * 0.053(3) |
| O(22) | -0.3587(2) | 0.3553(5) | 0.2700(1) | * 0.047(2) |
| N(1) | 0.0776(3) | 0.2644(6) | 0.4441(2) | * 0.047(2) |
| O(1) | 0.1599(3) | 0.1948(6) | 0.4976(2) | * 0.068(2) |
| O(2) | 0.0961(2) | 0.3180(5) | 0.3804(1) | * 0.059(2) |
| O(3) | -0.0194(3) | 0.2826(7) | 0.4505(2) | * 0.093(3) |

Table 25 Hydrogen atom coordinates and isotropic thermal parameters of $[Ag(atu)_2]NO_3$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| H(11) | 0.537(3) | 0.357(6) | 0.359(2) | 0.04(1) |
| H(12A) | 0.385(4) | 0.216(7) | 0.454(3) | 0.07(2) |
| H(12B) | 0.276(4) | 0.266(7) | 0.398(3) | 0.06(2) |
| H(13A) | 0.735(6) | 0.42(1) | 0.453(4) | 0.15(3) |
| H(13B) | 0.751(6) | 0.20(1) | 0.444(4) | 0.15(3) |
| H(13C) | 0.759(5) | 0.319(9) | 0.509(3) | 0.09(2) |
| H(21) | -0.314(3) | 0.314(5) | 0.119(2) | 0.03(1) |
| H(22A) | -0.065(3) | 0.351(6) | 0.303(2) | 0.03(1) |
| H(22B) | -0.189(4) | 0.346(7) | 0.302(2) | 0.06(1) |
| H(23A) | -0.535(6) | 0.40(1) | 0.142(4) | 0.12(3) |
| H(23B) | -0.546(5) | 0.223(8) | 0.160(3) | 0.09(2) |
| H(23C) | -0.507(5) | 0.296(8) | 0.088(3) | 0.09(2) |

Table 26 Non-hydrogen thermal parameters of [Ag(atu)$_2$]NO$_3$

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| Ag | 0.0251(2) | 0.0671(3) | 0.0442(2) | -0.0010(1) | 0.0063(1) | 0.0006(1) |
| S(1) | 0.0288(4) | 0.0513(6) | 0.0437(4) | -0.0080(4) | 0.0043(4) | 0.0088(4) |
| C(11) | 0.029(2) | 0.032(2) | 0.039(2) | -0.002(1) | 0.011(1) | -0.003(1) |
| C(12) | 0.033(2) | 0.048(2) | 0.039(2) | -0.000(2) | 0.010(2) | -0.002(2) |
| C(13) | 0.027(2) | 0.088(4) | 0.048(2) | -0.002(2) | 0.005(2) | 0.001(3) |
| N(11) | 0.027(1) | 0.046(2) | 0.036(2) | 0.000(1) | 0.013(1) | 0.004(1) |
| O(12) | 0.047(2) | 0.108(3) | 0.040(1) | -0.004(2) | 0.015(1) | 0.020(2) |
| N(12) | 0.028(2) | 0.091(3) | 0.050(2) | -0.000(2) | 0.014(2) | 0.022(2) |
| S(2) | 0.0258(4) | 0.0570(6) | 0.0305(4) | 0.0019(4) | 0.0088(3) | 0.0019(4) |
| N(21) | 0.026(1) | 0.053(2) | 0.023(1) | 0.001(1) | 0.006(1) | -0.001(1) |
| O(22) | 0.040(1) | 0.074(2) | 0.030(1) | -0.001(1) | 0.016(1) | -0.003(1) |
| C(21) | 0.028(2) | 0.037(2) | 0.030(1) | 0.002(1) | 0.008(1) | 0.001(1) |
| C(22) | 0.029(2) | 0.045(2) | 0.033(2) | -0.001(2) | 0.009(1) | -0.002(2) |
| N(22) | 0.029(1) | 0.071(2) | 0.029(1) | 0.000(2) | 0.005(1) | -0.001(2) |
| C(23) | 0.028(2) | 0.088(4) | 0.041(2) | 0.001(2) | 0.010(2) | -0.005(2) |
| N(1) | 0.034(2) | 0.080(3) | 0.026(1) | -0.004(2) | 0.007(1) | 0.005(2) |
| O(1) | 0.044(2) | 0.123(3) | 0.034(1) | 0.011(2) | 0.006(1) | 0.023(2) |
| O(2) | 0.035(1) | 0.115(3) | 0.029(1) | -0.000(2) | 0.011(1) | 0.015(2) |
| O(3) | 0.044(2) | 0.194(5) | 0.048(2) | 0.023(2) | 0.025(2) | 0.024(2) |

Table 27 Non-hydrogen atom coordinates and isotropic thermal parameters of $[Cu_4(ettu)_6 I_4].H_2O$

| Atom | x/a | y/b | z/c | U(eq) A**2 | PP |
|---|---|---|---|---|---|
| I(1) | -0.25891(9) | 0.59699(5) | 0.18827(5) | * 0.0555(3) | |
| I(2) | 0.37274(9) | 0.36305(5) | 0.18657(5) | * 0.0599(4) | |
| I(3) | -0.1420(1) | 0.27552(6) | 0.44245(5) | * 0.0602(4) | |
| I(4) | 0.2463(1) | 0.66190(6) | 0.46233(5) | * 0.0687(4) | |
| Cu(1) | -0.0959(2) | 0.53755(9) | 0.26083(9) | * 0.0534(7) | |
| Cu(2) | 0.1986(2) | 0.4250(1) | 0.25789(9) | * 0.0586(7) | |
| Cu(3) | -0.0272(2) | 0.3980(1) | 0.36885(9) | * 0.0711(8) | |
| Cu(4) | 0.1562(2) | 0.5665(1) | 0.38836(9) | * 0.0612(7) | |
| S(1) | 0.0516(3) | 0.4807(2) | 0.2021(2) | * 0.051(1) | |
| S(2) | 0.1066(3) | 0.3337(2) | 0.3139(2) | * 0.044(1) | |
| S(3) | 0.0572(4) | 0.4697(2) | 0.4387(2) | * 0.053(1) | |
| S(4) | 0.0030(5) | 0.6092(2) | 0.3263(3) | * 0.100(2) | |
| S(5) | -0.1837(3) | 0.4435(2) | 0.3161(2) | * 0.046(1) | |
| S(6) | 0.2844(4) | 0.4999(2) | 0.3297(2) | * 0.077(2) | |
| N(12) | 0.062(1) | 0.6025(7) | 0.1404(6) | * 0.075(6) | |
| N(13) | 0.221(1) | 0.5275(8) | 0.1279(8) | * 0.096(7) | |
| N(22) | 0.185(1) | 0.2829(7) | 0.4181(6) | * 0.071(5) | |
| N(23) | 0.326(1) | 0.3029(7) | 0.3481(6) | * 0.068(5) | |
| N(32) | -0.040(1) | 0.5709(7) | 0.5068(7) | * 0.084(6) | |
| N(33) | -0.157(1) | 0.4734(7) | 0.4881(6) | * 0.064(5) | |
| N(42) | -0.145(1) | 0.7141(5) | 0.3069(6) | * 0.065(5) | |
| N(43) | -0.010(1) | 0.7371(6) | 0.3785(6) | * 0.055(4) | |

Table 27 (continued)

| Atom | x/a | y/b | z/c | U(eq) A**2 | PP |
|---|---|---|---|---|---|
| N(52) | -0.258(1) | 0.3972(6) | 0.2104(7) | * 0.076(5) | |
| N(53) | -0.211(1) | 0.3092(6) | 0.2797(6) | * 0.080(6) | |
| N(62) | 0.491(1) | 0.5124(9) | 0.2752(7) | * 0.097(7) | |
| N(63) | 0.467(1) | 0.5832(8) | 0.3580(7) | * 0.081(6) | |
| C(11) | 0.117(1) | 0.5410(8) | 0.1548(7) | * 0.060(6) | |
| C(21) | 0.215(1) | 0.3060(8) | 0.3647(8) | * 0.053(6) | |
| C(31) | -0.056(1) | 0.5073(8) | 0.4800(7) | * 0.054(6) | |
| C(41) | -0.056(1) | 0.6918(7) | 0.3387(7) | * 0.049(5) | |
| C(51) | -0.222(1) | 0.3777(7) | 0.2644(7) | * 0.056(6) | |
| C(61) | 0.424(1) | 0.5352(8) | 0.3205(8) | * 0.058(6) | |
| C(14) | 0.283(2) | 0.569(1) | 0.083(1) | * 0.14(1) | |
| C(15) | 0.407(2) | 0.582(1) | 0.102(1) | * 0.13(1) | |
| C(24) | 0.428(2) | 0.277(1) | 0.383(1) | * 0.101(9) | |
| C(25A) | 0.520(4) | 0.322(2) | 0.377(2) | 0.14(2) | 0.6000(-) |
| C(25B) | 0.473(7) | 0.340(4) | 0.421(3) | 0.15(3) | 0.4000(-) |
| C(34) | -0.260(2) | 0.5003(9) | 0.522(1) | * 0.099(8) | |
| C(35) | -0.370(2) | 0.453(1) | 0.514(1) | * 0.13(1) | |
| C(44) | -0.048(2) | 0.8112(8) | 0.3914(9) | * 0.082(8) | |
| C(45) | 0.033(2) | 0.8501(9) | 0.430(1) | * 0.101(9) | |
| C(54) | -0.241(2) | 0.2485(8) | 0.2371(9) | * 0.11(1) | |
| C(55A) | -0.274(6) | 0.187(3) | 0.266(2) | 0.18(2) | 0.5500(-) |
| C(55B) | -0.355(4) | 0.215(2) | 0.241(2) | 0.09(1) | 0.4500(-) |
| C(64) | 0.588(2) | 0.616(1) | 0.357(1) | * 0.12(1) | |
| C(65) | 0.620(2) | 0.649(2) | 0.408(1) | * 0.15(1) | |
| O(1) | 0.364(1) | 0.8286(5) | 0.3991(5) | 0.069(3) | |

Table 28 Hydrogen atom coordinates and isotropic thermal parameters of $[Cu_4(ettu)_6 I_4].H_2O$

| Atom | x/a | y/b | z/c | U(eq) A**2 | PP |
|---|---|---|---|---|---|
| H(12A) | 0.0931(-) | 0.6322(-) | 0.1159(-) | 0.089(-) | |
| H(12B) | -0.0061(-) | 0.6133(-) | 0.1575(-) | 0.089(-) | |
| H(13) | 0.2567(-) | 0.4888(-) | 0.1401(-) | 0.111(-) | |
| H(22A) | 0.2401(-) | 0.2674(-) | 0.4417(-) | 0.086(-) | |
| H(22B) | 0.1125(-) | 0.2848(-) | 0.4291(-) | 0.086(-) | |
| H(23) | 0.3427(-) | 0.3179(-) | 0.3121(-) | 0.080(-) | |
| H(32A) | -0.0952(-) | 0.5885(-) | 0.5289(-) | 0.100(-) | |
| H(32B) | 0.0261(-) | 0.5936(-) | 0.5018(-) | 0.100(-) | |
| H(33) | -0.1652(-) | 0.4325(-) | 0.4710(-) | 0.073(-) | |
| H(42A) | -0.1740(-) | 0.7572(-) | 0.3106(-) | 0.078(-) | |
| H(42B) | -0.1768(-) | 0.6858(-) | 0.2800(-) | 0.078(-) | |
| H(43) | 0.0495(-) | 0.7216(-) | 0.3981(-) | 0.069(-) | |
| H(52A) | -0.2773(-) | 0.3647(-) | 0.1848(-) | 0.085(-) | |
| H(52B) | -0.2640(-) | 0.4423(-) | 0.2013(-) | 0.085(-) | |
| H(53) | -0.1879(-) | 0.2999(-) | 0.3144(-) | 0.095(-) | |
| H(62A) | 0.5620(-) | 0.5277(-) | 0.2703(-) | 0.113(-) | |
| H(62B) | 0.4623(-) | 0.4797(-) | 0.2510(-) | 0.113(-) | |
| H(63) | 0.4201(-) | 0.5966(-) | 0.3866(-) | 0.099(-) | |
| H(14A) | 0.2453(-) | 0.6158(-) | 0.0795(-) | 0.159(-) | |
| H(14B) | 0.2835(-) | 0.5443(-) | 0.0471(-) | 0.159(-) | |
| H(15A) | 0.4488(-) | 0.6104(-) | 0.0717(-) | 0.205(-) | |
| H(15B) | 0.4498(-) | 0.5371(-) | 0.1068(-) | 0.205(-) | |
| H(15C) | 0.4117(-) | 0.6085(-) | 0.1392(-) | 0.205(-) | |

Table 28 (continued)

| Atom | x/a | y/b | z/c | U(eq) A**2 | PP |
|---|---|---|---|---|---|
| H(24A) | 0.4063(-) | 0.2720(-) | 0.4230(-) | 0.120(-) | 0.600(-) |
| H(24B) | 0.4517(-) | 0.2291(-) | 0.3668(-) | 0.120(-) | 0.600(-) |
| H(24C) | 0.4877(-) | 0.2557(-) | 0.3549(-) | 0.120(-) | 0.400(-) |
| H(24D) | 0.4017(-) | 0.2388(-) | 0.4085(-) | 0.120(-) | 0.400(-) |
| H(25AA) | 0.5928(-) | 0.3090(-) | 0.3974(-) | 0.204(-) | 0.600(-) |
| H(25AB) | 0.5017(-) | 0.3727(-) | 0.3896(-) | 0.204(-) | 0.600(-) |
| H(25AC) | 0.5469(-) | 0.3299(-) | 0.3336(-) | 0.204(-) | 0.600(-) |
| H(25BA) | 0.5433(-) | 0.3253(-) | 0.4401(-) | 0.175(-) | 0.400(-) |
| H(25BB) | 0.4142(-) | 0.3581(-) | 0.4429(-) | 0.175(-) | 0.400(-) |
| H(25BC) | 0.4996(-) | 0.3781(-) | 0.3899(-) | 0.175(-) | 0.400(-) |
| H(34A) | -0.2766(-) | 0.5507(-) | 0.5124(-) | 0.112(-) | |
| H(34B) | -0.2390(-) | 0.5000(-) | 0.5654(-) | 0.112(-) | |
| H(35A) | -0.4356(-) | 0.4730(-) | 0.5361(-) | 0.196(-) | |
| H(35B) | -0.3538(-) | 0.4057(-) | 0.5241(-) | 0.196(-) | |
| H(35C) | -0.3913(-) | 0.4563(-) | 0.4712(-) | 0.196(-) | |
| H(44A) | -0.0580(-) | 0.8363(-) | 0.3524(-) | 0.098(-) | |
| H(44B) | -0.1261(-) | 0.8091(-) | 0.4092(-) | 0.098(-) | |
| H(45A) | 0.0032(-) | 0.8983(-) | 0.4339(-) | 0.146(-) | |
| H(45B) | 0.1102(-) | 0.8534(-) | 0.4081(-) | 0.146(-) | |
| H(45C) | 0.0421(-) | 0.8261(-) | 0.4649(-) | 0.146(-) | |
| H(54A) | -0.3053(-) | 0.2643(-) | 0.2107(-) | 0.130(-) | 0.550(-) |
| H(54B) | -0.1722(-) | 0.2385(-) | 0.2130(-) | 0.130(-) | 0.550(-) |
| H(54C) | -0.2308(-) | 0.2662(-) | 0.1969(-) | 0.130(-) | 0.450(-) |
| H(54D) | -0.1824(-) | 0.2113(-) | 0.2437(-) | 0.130(-) | 0.450(-) |

Table 28 (continued)

| Atom | x/a | y/b | z/c | U(eq) A**2 | PP |
|---|---|---|---|---|---|
| H(55AA) | -0.2940(-) | 0.1505(-) | 0.2345(-) | 0.220(-) | 0.550(-) |
| H(55AB) | -0.3475(-) | 0.1953(-) | 0.2876(-) | 0.220(-) | 0.550(-) |
| H(55AC) | -0.2141(-) | 0.1693(-) | 0.2899(-) | 0.220(-) | 0.550(-) |
| H(55BA) | -0.3623(-) | 0.1786(-) | 0.2133(-) | 0.138(-) | 0.450(-) |
| H(55BB) | -0.4157(-) | 0.2523(-) | 0.2352(-) | 0.138(-) | 0.450(-) |
| H(55BC) | -0.3645(-) | 0.1970(-) | 0.2816(-) | 0.138(-) | 0.450(-) |
| H(64A) | 0.6435(-) | 0.5785(-) | 0.3457(-) | 0.143(-) | |
| H(64B) | 0.5869(-) | 0.6511(-) | 0.3234(-) | 0.143(-) | |
| H(65A) | 0.6971(-) | 0.6686(-) | 0.4022(-) | 0.235(-) | |
| H(66B) | 0.6193(-) | 0.6135(-) | 0.4385(-) | 0.235(-) | |
| H(65C) | 0.5627(-) | 0.6862(-) | 0.4161(-) | 0.235(-) | |

Table 29 Non-hydrogen thermal parameters of $[Cu_4(ettu)_6 I_4].H_2O$

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| I(1) | 0.0471(6) | 0.0577(5) | 0.0616(6) | 0.0033(5) | -0.0074(6) | 0.0085(6) |
| I(2) | 0.0468(6) | 0.0611(6) | 0.0717(7) | 0.0010(5) | 0.0159(6) | -0.0090(6) |
| I(3) | 0.0613(7) | 0.0586(6) | 0.0608(7) | -0.0043(6) | 0.0117(6) | 0.0066(6) |
| I(4) | 0.0620(7) | 0.0723(6) | 0.0716(7) | -0.0077(7) | -0.0131(7) | -0.0181(6) |
| Cu(1) | 0.050(1) | 0.050(1) | 0.060(1) | -0.0021(9) | -0.001(1) | -0.000(1) |
| Cu(2) | 0.054(1) | 0.057(1) | 0.065(1) | 0.004(1) | 0.000(1) | 0.009(1) |
| Cu(3) | 0.060(1) | 0.085(1) | 0.068(1) | 0.029(1) | -0.017(1) | -0.028(1) |
| Cu(4) | 0.050(1) | 0.065(1) | 0.069(1) | 0.001(1) | 0.001(1) | -0.012(1) |
| S(1) | 0.045(2) | 0.050(2) | 0.059(3) | 0.005(2) | 0.006(2) | 0.005(2) |
| S(2) | 0.037(2) | 0.051(2) | 0.044(2) | 0.003(2) | 0.002(2) | -0.000(2) |
| S(3) | 0.056(2) | 0.055(2) | 0.049(2) | 0.003(2) | 0.001(2) | -0.005(2) |
| S(4) | 0.117(4) | 0.056(3) | 0.126(5) | 0.031(3) | -0.079(4) | -0.030(3) |
| S(5) | 0.046(2) | 0.047(2) | 0.046(2) | -0.002(2) | -0.002(2) | 0.001(2) |
| S(6) | 0.043(2) | 0.076(3) | 0.111(4) | -0.016(2) | 0.018(3) | -0.039(3) |
| N(12) | 0.064(9) | 0.077(9) | 0.08(1) | 0.026(8) | 0.026(9) | 0.038(9) |
| N(13) | 0.07(1) | 0.09(1) | 0.14(1) | 0.032(9) | 0.05(1) | 0.04(1) |
| N(22) | 0.075(9) | 0.081(9) | 0.057(9) | 0.018(9) | 0.006(8) | 0.010(8) |
| N(23) | 0.061(9) | 0.08(1) | 0.064(9) | 0.003(8) | -0.013(8) | 0.021(8) |
| N(32) | 0.07(1) | 0.072(9) | 0.11(1) | -0.020(8) | 0.04(1) | -0.039(9) |
| N(33) | 0.053(8) | 0.065(8) | 0.07(1) | 0.005(7) | 0.024(8) | -0.028(8) |
| N(42) | 0.067(9) | 0.040(6) | 0.09(1) | 0.012(7) | -0.02(1) | -0.012(7) |
| N(43) | 0.050(7) | 0.044(7) | 0.071(9) | 0.002(6) | 0.003(7) | -0.013(7) |

Table 29 (continued)

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| N(52) | 0.08(1) | 0.052(7) | 0.10(1) | 0.018(8) | -0.02(1) | -0.004(8) |
| N(53) | 0.12(1) | 0.048(7) | 0.08(1) | -0.018(9) | 0.01(1) | -0.003(8) |
| N(62) | 0.058(9) | 0.13(1) | 0.11(1) | -0.03(1) | 0.02(1) | -0.05(1) |
| N(63) | 0.056(9) | 0.10(1) | 0.09(1) | -0.037(9) | 0.015(9) | -0.03(1) |
| C(11) | 0.05(1) | 0.06(1) | 0.06(1) | 0.013(9) | -0.01(1) | -0.000(9) |
| C(21) | 0.034(8) | 0.06(1) | 0.07(1) | -0.006(7) | 0.010(8) | 0.002(9) |
| C(31) | 0.07(1) | 0.06(1) | 0.034(9) | 0.007(9) | 0.010(9) | 0.000(8) |
| C(41) | 0.036(8) | 0.048(8) | 0.06(1) | 0.001(7) | -0.009(8) | 0.001(8) |
| C(51) | 0.042(9) | 0.054(9) | 0.07(1) | 0.005(7) | -0.013(9) | 0.017(9) |
| C(61) | 0.043(9) | 0.06(1) | 0.07(1) | 0.013(8) | 0.004(9) | -0.01(1) |
| C(14) | 0.10(2) | 0.16(2) | 0.16(2) | 0.07(2) | 0.08(2) | 0.11(2) |
| C(15) | 0.14(2) | 0.14(2) | 0.12(2) | -0.06(2) | 0.05(2) | -0.04(2) |
| C(24) | 0.07(1) | 0.11(2) | 0.13(2) | 0.00(1) | -0.00(1) | 0.03(2) |
| C(34) | 0.10(1) | 0.07(1) | 0.13(2) | 0.00(1) | 0.05(2) | 0.02(1) |
| C(35) | 0.11(2) | 0.14(2) | 0.15(2) | -0.03(2) | 0.07(2) | -0.03(2) |
| C(44) | 0.08(1) | 0.06(1) | 0.11(2) | 0.02(1) | 0.00(1) | -0.03(1) |
| C(45) | 0.09(1) | 0.06(1) | 0.16(2) | 0.00(1) | -0.04(2) | -0.04(1) |
| C(54) | 0.19(2) | 0.06(1) | 0.09(1) | -0.04(2) | 0.02(2) | -0.00(1) |
| C(64) | 0.08(1) | 0.16(2) | 0.11(2) | -0.08(1) | 0.05(1) | -0.08(2) |
| C(65) | 0.15(2) | 0.23(3) | 0.08(1) | -0.09(2) | -0.01(2) | -0.02(2) |

Table 30 Non-hydrogen atom coordinates and isotropic thermal parameters of $[Ag_2(etu)_6](ClO_4)_2$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| Ag | 0.38670(6) | 0.52238(1) | 0.39323(3) | * 0.0508(2) |
| S(1) | 0.5395(2) | 0.56840(5) | 0.22053(9) | * 0.0464(6) |
| S(2) | -0.0031(2) | 0.49946(5) | 0.35210(8) | * 0.0435(5) |
| S(3) | 0.4380(2) | 0.57720(4) | 0.57357(8) | * 0.0419(5) |
| N(1) | 0.157(1) | 0.6190(3) | 0.2231(6) | * 0.062(3) |
| N(2) | 0.3913(7) | 0.6638(2) | 0.1354(3) | * 0.060(2) |
| N(3) | -0.145(1) | 0.4298(3) | 0.1940(6) | * 0.063(3) |
| N(4) | 0.1481(8) | 0.4695(2) | 0.1558(3) | * 0.064(3) |
| N(5) | 0.7699(8) | 0.6221(2) | 0.4717(3) | * 0.051(2) |
| N(6) | 0.7492(9) | 0.6456(2) | 0.6422(3) | * 0.057(3) |
| C(1) | 0.3572(7) | 0.6185(2) | 0.1947(3) | * 0.039(2) |
| C(2) | 0.040(1) | 0.6669(3) | 0.1828(6) | * 0.062(4) |
| C(3) | 0.213(1) | 0.7020(2) | 0.1348(6) | * 0.066(4) |
| C(4) | -0.0002(7) | 0.4656(2) | 0.2301(3) | * 0.043(2) |
| C(5) | -0.096(2) | 0.4054(5) | 0.0894(7) | * 0.097(7) |
| C(6) | 0.105(2) | 0.4317(4) | 0.0632(5) | * 0.078(5) |
| C(7) | 0.6623(6) | 0.6164(2) | 0.5601(3) | * 0.039(2) |
| C(8) | 0.9507(9) | 0.6579(3) | 0.4888(5) | * 0.055(3) |
| C(9) | 0.9296(9) | 0.6778(2) | 0.6081(4) | * 0.059(3) |
| Cl | 0.5693(3) | 0.77821(6) | 0.38100(9) | * 0.0695(8) |
| O(1) | 0.6941(8) | 0.7531(2) | 0.3016(3) | * 0.107(3) |
| O(2) | 0.398(1) | 0.7432(3) | 0.4055(5) | * 0.169(6) |
| O(3) | 0.4938(8) | 0.8288(2) | 0.3404(3) | * 0.118(4) |
| O(4) | 0.6842(8) | 0.7881(2) | 0.4802(3) | * 0.112(4) |

Table 31 Hydrogen atom coordinates and isotropic thermal parameters of $[Ag_2(etu)_6](ClO_4)_2$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| H(21) | -0.03(2) | 0.692(4) | 0.242(5) | * 0.2(1) |
| H(22) | -0.055(7) | 0.653(3) | 0.139(6) | * 0.12(6) |
| H(31) | 0.164(8) | 0.707(2) | 0.056(5) | * 0.09(4) |
| H(32) | 0.23(1) | 0.720(3) | 0.204(7) | * 0.17(8) |
| H(51) | -0.17(1) | 0.401(4) | 0.055(6) | * 0.11(6) |
| H(52) | -0.09(2) | 0.326(6) | 0.136(9) | * 0.5(2) |
| H(61) | 0.223(8) | 0.404(2) | 0.070(5) | * 0.08(4) |
| H(62) | 0.11(1) | 0.442(3) | 0.008(5) | * 0.09(5) |
| H(81) | 0.93(1) | 0.694(4) | 0.432(5) | * 0.18(8) |
| H(82) | 1.07(1) | 0.653(3) | 0.459(5) | * 0.13(7) |
| H(91) | 1.060(7) | 0.682(3) | 0.659(4) | * 0.11(5) |
| H(92) | 0.881(7) | 0.721(2) | 0.611(4) | * 0.06(3) |
| H(1N6) | 0.706(8) | 0.652(2) | 0.702(4) | * 0.07(4) |
| H(1N5) | 0.778(7) | 0.602(2) | 0.413(4) | * 0.06(4) |
| H(1N2) | 0.563(9) | 0.673(2) | 0.087(9) | * 0.3(1) |
| H(1N1) | 0.12(1) | 0.598(3) | 0.251(5) | * 0.14(8) |
| H(1N4) | 0.261(9) | 0.487(2) | 0.177(4) | * 0.09(5) |
| H(1N3) | -0.21(1) | 0.435(4) | 0.219(6) | * 0.11(6) |

Table 32 Non-hydrogen thermal parameters of $[Ag_2(etu)_6](ClO_4)_2$

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| Ag | 0.0560(2) | 0.0496(2) | 0.0456(2) | -0.0093(2) | -0.0116(2) | 0.0066(1) |
| S(1) | 0.0431(6) | 0.0464(6) | 0.0502(6) | 0.0073(5) | 0.0060(5) | 0.0106(5) |
| S(2) | 0.0398(5) | 0.0524(6) | 0.0384(5) | -0.0010(5) | 0.0025(4) | -0.0057(4) |
| S(3) | 0.0396(5) | 0.0405(5) | 0.0457(5) | -0.0042(4) | 0.0042(4) | -0.0047(4) |
| N(1) | 0.052(3) | 0.060(3) | 0.075(4) | 0.015(2) | 0.018(2) | 0.023(2) |
| N(2) | 0.053(2) | 0.049(2) | 0.078(3) | 0.003(2) | 0.004(2) | 0.021(2) |
| N(3) | 0.063(4) | 0.077(4) | 0.049(3) | -0.026(3) | 0.004(2) | -0.015(2) |
| N(4) | 0.072(3) | 0.079(3) | 0.043(2) | -0.027(3) | 0.015(2) | -0.015(2) |
| N(5) | 0.051(2) | 0.055(3) | 0.049(2) | -0.015(2) | 0.007(2) | -0.008(2) |
| N(6) | 0.068(3) | 0.057(3) | 0.047(2) | -0.030(2) | 0.008(2) | -0.011(2) |
| C(1) | 0.043(2) | 0.041(2) | 0.034(2) | 0.006(2) | 0.003(2) | 0.002(2) |
| C(2) | 0.063(4) | 0.063(4) | 0.062(3) | 0.027(3) | 0.014(3) | 0.012(3) |
| C(3) | 0.073(4) | 0.046(3) | 0.078(4) | 0.018(3) | -0.001(4) | 0.015(3) |
| C(4) | 0.047(2) | 0.046(2) | 0.035(2) | -0.003(2) | -0.004(2) | 0.002(2) |
| C(5) | 0.120(9) | 0.118(6) | 0.055(3) | -0.059(6) | 0.016(4) | -0.040(4) |
| C(6) | 0.107(7) | 0.086(5) | 0.043(3) | -0.020(5) | 0.020(4) | -0.018(3) |
| C(7) | 0.042(2) | 0.028(2) | 0.045(2) | -0.002(2) | -0.001(2) | 0.001(2) |
| C(8) | 0.048(3) | 0.058(3) | 0.061(3) | -0.009(2) | 0.012(2) | 0.001(3) |
| C(9) | 0.066(3) | 0.050(3) | 0.061(3) | -0.022(3) | -0.004(3) | 0.001(2) |
| Cl | 0.093(1) | 0.0701(9) | 0.0460(6) | 0.0162(8) | 0.0141(7) | 0.0010(5) |
| O(1) | 0.153(4) | 0.101(3) | 0.069(2) | 0.051(3) | 0.039(3) | -0.002(2) |
| O(2) | 0.168(6) | 0.179(7) | 0.166(5) | -0.078(5) | 0.070(5) | -0.038(5) |
| O(3) | 0.153(5) | 0.117(4) | 0.085(3) | 0.069(4) | 0.032(3) | 0.024(3) |
| O(4) | 0.126(4) | 0.144(5) | 0.065(2) | 0.056(4) | -0.014(3) | -0.020(3) |

Table 33 Non-hydrogen atom coordinates and isotropic thermal parameters of $[Ag_2(etu)_4Br_2]$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| Br | -0.03324(4) | 0.66053(3) | 0.06704(2) | * 0.0178(1) |
| Ag | 0.22905(3) | 0.52054(3) | 0.05744(2) | * 0.02030(9) |
| S(1) | 0.3498(1) | 0.40567(9) | 0.22098(7) | * 0.0241(3) |
| N(12) | 0.1761(4) | 0.5588(3) | 0.3135(2) | * 0.026(1) |
| N(15) | 0.3357(4) | 0.4377(3) | 0.4210(2) | * 0.026(1) |
| C(11) | 0.2846(4) | 0.4701(3) | 0.3209(3) | * 0.019(1) |
| C(13) | 0.1581(5) | 0.5994(4) | 0.4162(3) | * 0.029(1) |
| C(14) | 0.2476(5) | 0.4968(4) | 0.4887(3) | * 0.026(1) |
| S(2) | 0.3762(1) | 0.63378(9) | -0.05335(6) | * 0.0215(3) |
| N(22) | 0.0959(4) | 0.7034(4) | -0.1657(3) | * 0.029(1) |
| N(25) | 0.2799(4) | 0.7409(4) | -0.2421(2) | * 0.033(1) |
| C(21) | 0.2448(4) | 0.6930(3) | -0.1564(2) | * 0.016(1) |
| C(23) | 0.0166(5) | 0.7608(5) | -0.2642(3) | * 0.035(2) |
| C(24) | 0.1455(5) | 0.7852(5) | -0.3185(3) | * 0.035(2) |

Table 34 Hydrogen atom coordinates and isotropic thermal parameters of $[Ag_2(etu)_4Br_2]$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| H(12) | 0.148(4) | 0.610(4) | 0.256(3) | 0.04(1) |
| H(13A) | 0.192(5) | 0.681(4) | 0.438(3) | 0.04(1) |
| H(13B) | 0.044(5) | 0.594(4) | 0.419(3) | 0.06(1) |
| H(14A) | 0.315(4) | 0.534(3) | 0.550(3) | 0.04(1) |
| H(14B) | 0.170(4) | 0.432(4) | 0.507(3) | 0.04(1) |
| H(15) | 0.375(4) | 0.374(3) | 0.432(2) | 0.005(9) |
| H(22) | 0.064(5) | 0.681(4) | -0.129(3) | 0.03(1) |
| H(23A) | -0.056(6) | 0.679(5) | -0.309(4) | 0.09(2) |
| H(23B) | -0.030(5) | 0.826(4) | -0.246(3) | 0.06(2) |
| H(24A) | 0.133(5) | 0.734(4) | -0.381(4) | 0.07(2) |
| H(24B) | 0.162(5) | 0.866(4) | -0.341(3) | 0.06(2) |
| H(25) | 0.369(4) | 0.726(3) | -0.255(2) | 0.02(1) |

Table 35 Non-hydrogen thermal parameters of [$Ag_2(etu)_4Br_2$]

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| Br | 0.0173(2) | 0.0187(2) | 0.0176(2) | -0.0011(1) | 0.0045(1) | -0.0049(1) |
| Ag | 0.0219(2) | 0.0231(2) | 0.0155(1) | -0.0014(1) | 0.0035(1) | 0.0031(1) |
| S(1) | 0.0321(6) | 0.0262(5) | 0.0158(4) | 0.0128(4) | 0.0091(4) | 0.0035(4) |
| N(12) | 0.034(2) | 0.028(2) | 0.018(2) | 0.017(2) | 0.009(1) | 0.006(1) |
| N(15) | 0.035(2) | 0.029(2) | 0.016(2) | 0.018(2) | 0.006(1) | 0.005(1) |
| C(11) | 0.021(2) | 0.017(2) | 0.019(2) | -0.002(2) | 0.005(1) | 0.001(1) |
| C(13) | 0.037(3) | 0.027(3) | 0.025(2) | 0.010(2) | 0.013(2) | 0.001(2) |
| C(14) | 0.033(2) | 0.028(2) | 0.019(2) | 0.004(2) | 0.011(2) | 0.000(2) |
| S(2) | 0.0152(5) | 0.0312(6) | 0.0177(4) | -0.0007(4) | 0.0028(4) | 0.0067(4) |
| N(22) | 0.020(2) | 0.048(2) | 0.023(2) | 0.007(2) | 0.010(2) | 0.017(2) |
| N(25) | 0.013(2) | 0.063(3) | 0.024(2) | 0.003(2) | 0.006(1) | 0.019(2) |
| C(21) | 0.015(2) | 0.016(2) | 0.016(2) | -0.001(1) | 0.004(1) | 0.002(1) |
| C(23) | 0.026(2) | 0.050(3) | 0.030(2) | 0.010(2) | 0.008(2) | 0.023(2) |
| C(24) | 0.022(2) | 0.057(3) | 0.024(2) | 0.002(2) | 0.002(2) | 0.020(2) |

Table 36 Non-hydrogen atom coordinates and isotropic thermal parameters of $[Cu(etu)_3]_2SO_4$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| Cu(1) | 1/3 | 2/3 | 0.50000(-) | * 0.0189(3) |
| Cu(2) | 2/3 | 1/3 | 0.3372(3) | * 0.0173(2) |
| S(1) | 0.44246(7) | 0.57258(7) | 0.4993(3) | * 0.0206(4) |
| S(2) | 0.18841(7) | 0.02341(7) | 0.50203(4) | * 0.0184(6) |
| C(11) | 0.3682(3) | 0.4469(3) | 0.47157(9) | * 0.017(2) |
| N(12) | 0.4212(3) | 0.3901(3) | 0.4572(1) | * 0.026(2) |
| C(13) | 0.3392(3) | 0.2851(3) | 0.4343(1) | * 0.021(3) |
| C(14) | 0.2190(3) | 0.2847(3) | 0.4378(1) | * 0.023(3) |
| N(15) | 0.2536(3) | 0.3942(3) | 0.46031(9) | * 0.025(2) |
| C(21) | 0.2763(3) | 0.1473(3) | 0.52961(9) | * 0.017(2) |
| N(22) | 0.2359(3) | 0.1949(3) | 0.55511(8) | * 0.022(2) |
| C(23) | 0.3341(3) | 0.3029(3) | 0.5737(1) | * 0.020(2) |
| C(24) | 0.4475(3) | 0.3095(3) | 0.5561(1) | * 0.022(3) |
| N(25) | 0.3972(3) | 0.2091(3) | 0.52881(9) | * 0.024(2) |
| S | 2/3 | 1/3 | 0.45984(4) | * 0.0134(6) |
| O(1) | 2/3 | 1/3 | 0.4180(1) | * 0.023(2) |
| O(2) | 0.6549(2) | 0.4366(2) | 0.47392(7) | * 0.019(2) |

Table 37 Hydrogen atom coordinates and isotropic thermal parameters of $[Cu(etu)_3]_2SO_4$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| H(23B) | 0.340(2) | 0.300(3) | 0.6018(9) | 0.007(8) |
| H(24A) | 0.498(3) | 0.382(3) | 0.5448(9) | 0.015(9) |
| H(12) | 0.488(3) | 0.409(3) | 0.463(1) | 0.02(1) |
| H(23A) | 0.323(3) | 0.365(3) | 0.5684(9) | 0.012(8) |
| H(14B) | 0.165(3) | 0.220(3) | 0.452(1) | 0.03(1) |
| H(13B) | 0.335(3) | 0.209(3) | 0.4433(9) | 0.017(8) |
| H(22) | 0.163(3) | 0.159(3) | 0.563(1) | 0.022(9) |
| H(24B) | 0.494(3) | 0.296(3) | 0.576(1) | 0.024(9) |
| H(13A) | 0.367(3) | 0.291(3) | 0.4095(9) | 0.019(9) |
| H(14A) | 0.181(4) | 0.289(3) | 0.411(1) | 0.05(1) |
| H(25) | 0.444(3) | 0.205(3) | 0.514(1) | 0.02(1) |
| H(15) | 0.217(4) | 0.422(4) | 0.468(1) | 0.05(1) |

Table 38 Non-hydrogen thermal parameters of $[Cu(etu)_3]_2SO_4$

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| Cu(1) | 2U12 | 2U12 | 0.0201(4) | 0.0092(1) | 0 | 0 |
| Cu(2) | 2U12 | 2U12 | 0.0190(4) | 0.0082(1) | 0 | 0 |
| S(1) | 0.0193(4) | 0.0190(4) | 0.0241(4) | 0.0101(4) | -0.0039(4) | -0.0010(4) |
| S(2) | 0.0165(4) | 0.0176(4) | 0.0209(4) | 0.0084(3) | -0.0005(3) | -0.0033(3) |
| C(11) | 0.019(2) | 0.017(2) | 0.016(2) | 0.010(1) | 0.002(1) | 0.005(1) |
| N(12) | 0.016(2) | 0.024(2) | 0.040(2) | 0.012(1) | -0.004(1) | -0.007(1) |
| C(13) | 0.022(2) | 0.021(2) | 0.023(2) | 0.012(2) | 0.005(1) | 0.001(1) |
| C(14) | 0.018(2) | 0.021(2) | 0.028(2) | 0.008(2) | -0.002(2) | -0.005(2) |
| N(15) | 0.017(2) | 0.028(2) | 0.034(2) | 0.015(1) | -0.003(1) | -0.009(1) |
| C(21) | 0.018(2) | 0.018(2) | 0.016(2) | 0.009(1) | 0.001(1) | 0.003(1) |
| N(22) | 0.015(1) | 0.022(2) | 0.023(2) | 0.006(1) | 0.004(1) | -0.005(1) |
| C(23) | 0.021(2) | 0.015(2) | 0.022(2) | 0.007(1) | 0.000(1) | -0.003(1) |
| C(24) | 0.019(2) | 0.020(2) | 0.021(2) | 0.006(2) | 0.002(1) | -0.001(1) |
| N(25) | 0.014(1) | 0.026(2) | 0.026(2) | 0.007(1) | 0.004(1) | -0.008(1) |
| S | 2U12 | 2U12 | 0.0171(7) | 0.0058(2) | 0 | 0 |
| O(1) | 2U12 | 2U12 | 0.013(2) | 0.0137(7) | 0 | 0 |
| O(2) | 0.019(1) | 0.014(1) | 0.029(1) | 0.010(1) | -0.006(1) | -0.008(1) |

Table 39 Non-hydrogen atom coordinates and isotropic thermal parameters of $(C_6H_5NH)_2CO$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| O(1) | 0.3756(3) | -0.0013(6) | 0.2772(3) | * 0.029(2) |
| N(1) | 0.5958(4) | 0.0937(6) | 0.2994(4) | * 0.024(2) |
| N(2) | 0.5922(4) | -0.0866(6) | 0.2171(4) | * 0.024(2) |
| C(1) | 0.5112(4) | -0.0000(7) | 0.2655(4) | * 0.022(2) |
| C(11) | 0.5357(4) | 0.1974(7) | 0.3450(4) | * 0.022(2) |
| C(12) | 0.4163(5) | 0.2022(6) | 0.4280(4) | * 0.027(2) |
| C(13) | 0.3631(5) | 0.3072(7) | 0.4708(4) | * 0.031(2) |
| C(14) | 0.4323(6) | 0.4082(6) | 0.4317(5) | * 0.032(3) |
| C(15) | 0.5529(6) | 0.4025(6) | 0.3518(5) | * 0.037(3) |
| C(16) | 0.6074(5) | 0.2978(6) | 0.3082(5) | * 0.030(2) |
| C(21) | 0.5322(4) | -0.1937(6) | 0.1752(4) | * 0.025(2) |
| C(22) | 0.4249(5) | -0.2495(7) | 0.2461(5) | * 0.026(2) |
| C(23) | 0.3733(5) | -0.3551(6) | 0.2035(5) | * 0.033(3) |
| C(24) | 0.4327(6) | -0.4029(6) | 0.0924(6) | * 0.041(3) |
| C(25) | 0.5408(6) | -0.3488(7) | 0.0239(5) | * 0.041(3) |
| C(26) | 0.5904(5) | -0.2407(7) | 0.0645(5) | * 0.031(3) |

Table 40 Hydrogen atom coordinates and isotropic thermal parameters of $(C_6H_5NH)_2CO$

| Atom | x/a | y/b | z/c | U(eq) A**2 |
|---|---|---|---|---|
| H(1) | 0.697(5) | 0.093(4) | 0.265(4) | 0.03(1) |
| H(12) | 0.362(5) | 0.129(3) | 0.457(4) | 0.03(1) |
| H(13) | 0.272(4) | 0.310(3) | 0.529(4) | 0.02(1) |
| H(14) | 0.380(5) | 0.488(4) | 0.452(5) | 0.04(1) |
| H(15) | 0.618(5) | 0.464(4) | 0.324(5) | 0.05(1) |
| H(16) | 0.702(4) | 0.293(3) | 0.242(4) | 0.03(1) |
| H(2) | 0.697(6) | -0.081(4) | 0.219(5) | 0.05(2) |
| H(22) | 0.380(4) | -0.228(3) | 0.323(4) | 0.02(1) |
| H(23) | 0.276(5) | -0.388(4) | 0.258(4) | 0.05(1) |
| H(24) | 0.393(6) | -0.468(5) | 0.064(7) | 0.08(2) |
| H(25) | 0.588(5) | -0.385(4) | -0.075(6) | 0.05(1) |
| H(26) | 0.669(4) | -0.21(1) | 0.013(4) | 0.03(1) |

Table 41 Non-hydrogen thermal parameters of $(C_6H_5NH)_2CO$

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| O(1) | 0.017(1) | 0.018(1) | 0.052(2) | -0.003(1) | -0.001(1) | 0.001(1) |
| N(1) | 0.016(2) | 0.016(2) | 0.041(2) | -0.002(1) | -0.001(2) | -0.003(2) |
| N(2) | 0.015(2) | 0.016(2) | 0.041(2) | -0.004(1) | -0.001(2) | -0.003(2) |
| C(1) | 0.019(2) | 0.017(2) | 0.031(2) | -0.003(2) | -0.002(2) | 0.005(2) |
| C(11) | 0.019(2) | 0.016(2) | 0.032(3) | -0.001(2) | -0.005(2) | 0.001(2) |
| C(12) | 0.023(2) | 0.024(2) | 0.033(3) | -0.001(2) | 0.002(2) | 0.004(2) |
| C(13) | 0.027(2) | 0.032(2) | 0.034(3) | 0.003(2) | 0.001(2) | -0.004(2) |
| C(14) | 0.038(3) | 0.022(3) | 0.037(3) | 0.004(2) | -0.006(2) | -0.005(2) |
| C(15) | 0.045(3) | 0.019(2) | 0.049(3) | -0.006(2) | 0.005(2) | 0.001(2) |
| C(16) | 0.028(2) | 0.022(2) | 0.042(3) | -0.003(2) | 0.006(2) | 0.000(2) |
| C(21) | 0.020(2) | 0.019(2) | 0.037(3) | -0.001(2) | -0.008(2) | -0.002(2) |
| C(22) | 0.024(2) | 0.017(2) | 0.037(3) | -0.001(2) | -0.004(2) | 0.001(2) |
| C(23) | 0.027(3) | 0.023(2) | 0.049(3) | -0.006(2) | -0.007(2) | 0.001(2) |
| C(24) | 0.047(3) | 0.023(3) | 0.054(4) | -0.005(2) | -0.015(3) | -0.009(2) |
| C(25) | 0.046(3) | 0.035(3) | 0.042(3) | 0.001(2) | -0.007(3) | -0.015(2) |
| C(26) | 0.030(3) | 0.029(2) | 0.034(3) | -0.004(2) | -0.002(2) | -0.002(2) |

# Vitae

**Name** Miss Suwaluk Pansook

**Birth date** 30 August 1974

**Educational Attainment**

| Degree | Name of Institution | Year of Graduation |
|---|---|---|
| Bachelor of Science<br>(Chemistry) | Prince of Songkla University | 1996 |

**Scholarship Awards during Enrolment**

University Development Comity (UDC) Scholarship for Outstanding Scholastic Achievement, Ministry of university Affairs, the Royal Thai Government