4. Discussion

4.1 Preparation of Complexes

The series of copper(I) halides (CuX, X = Cl, Br, I) with *N*-phenylthiourea (ptu) complexes; $[Cu(ptu)_4]Cl$, $[Cu_4(ptu)_6Br_4]_2$ and $[Cu_4(ptu)_6I_4]_2$ were synthesized by the reaction between copper(I) halides and ptu in acetonitrile solution. The system was heated about 60 ^oC and stirred for all reactions. This work sets out to study the structure of Cu(I) with *N*-phenylthiourea complexes by single crystal X-ray diffraction method. The complexes to be studied must be single crystals. The experimental condition for preparing the complexes could not be expected for each reaction, however in this research most mole ratios of ligand and Cu(I) salt were higher than 2 : 1, could give the complexes, whereas whose ratios lower than 2 : 1 gave the crystals of ligand. Additionally, most reactions could form more complexes at warm temperature because reactants could be more soluble in solvents, especially Cu(I) salts. The formation of crystals depends on both the solubility of compound (a thermodynamic property) and an nucleation and growth rates (kinetic property). 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 single crystal X-ray diffraction studies, most solvents were organic solvent and the crystallization of these complexes were obtained by slow evaporation.

4.2   X-ray Fluorescence Spectrometry

This techniques provides one of the simplest, most accurate and economic analytical methods for the determination of the chemical composition of many types of materials such as Cu, S and halides (Cl, Br and I). It is non-destructive and reliable, requires no, or very little sample preparation and is suitable for solid, liquid and powdered samples.

The Cu, Cl, Br and I are presented for copper(I) salts, the K_α spectrum of Cu, Cl, Br and I appear at 8.04, 2.63 , 11.92 and 28.54 keV, respectively. In addition, S atom is represented for substituted thiourea, ptu. The K_α spectrum of sulfur appears at 2.31 keV.

4.3   Elemental Analysis

This technique was utilized to indicate the quantitative composition C, H, N and S in complexes. The accepted experimental results must be closed to the calculated data. In practise, the experimental data are usually slightly different from the calculated data because of the impurity, the moisture and how sensitive of samples to the air. These effect the higher or lower quantitative values of the results. Thus these factors must not be negligible. The experimental and calculated data are compared in Table 4 (Chapter 3).

4.4   Infrared Spectroscopy

Infrared spectroscopy technique is a good indicator of coordination of metal ion and ligands into the complex systems. IR spectra were recorded on KBr discs in the region $4000 - 400$ cm^{-1} on Perkin – Elmer Spectrum GX FT-IR Spectrometer

providing the information of the coordination mode of ligands. The infrared spectrum of molecule is determined by arrangement of atoms in space and by the forces between atoms.

N-phenylthiourea(ptu) ligand consists of the NHC=S group, which may adopt either the thione form (H-N-C=S) or the thiol form (N=C-S-H) as shown in the following equation.

Thione   Thiol
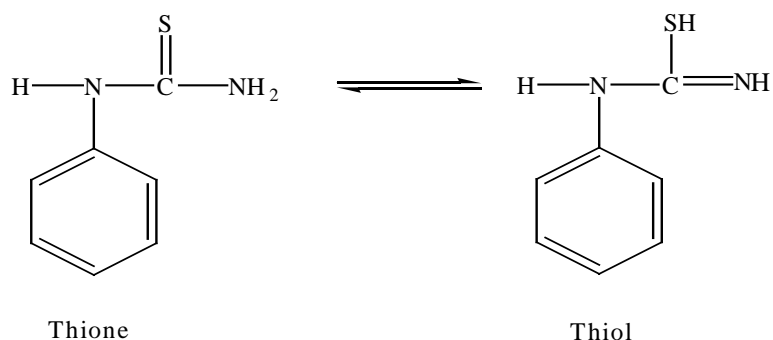
Therefore, sulfur atom or nitrogen atom can coordinate with copper(I) atom but from the experiment found that the ligand ptu adopt thione form in the free state and in their complexes. This is evident by the absence of the ν(S-H) band in the region 2500 cm^{-1} and by the presence of ν(N-H) in the range 2890-3310 cm^{-1} (Singh and Dikshit, 1995).

The electronic structure of ligand ptu may be represented by a resonance hybrid of structures I and II with each contributing roughly an equal amount:

I   II
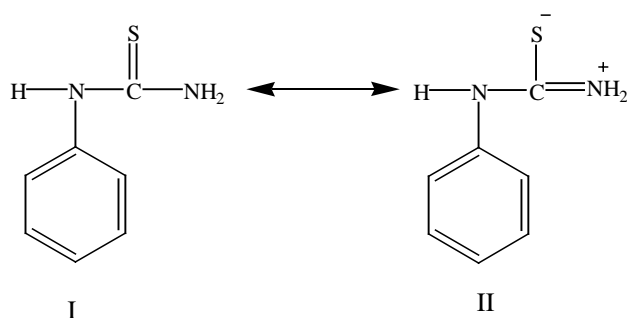
If coordination occurs through nitrogen, the contributions of structures II will decrease. This results in an increase of the ν(CS) with a decrease in the ν(CN). The ν(N-H) in this case may fall in the same range as the value for the amido complexes. If coordination occurs through sulfur, the contribution of structure I will decrease. This may result in a decrease of the ν(CS) but no appreciable change in the ν(N-H). From infrared studies on thiourea [(NH$_2$)$_2$CS] complexes, Yamaguchi, *et al.* found that all the metals studied (Pt, Pd, Zn and Ni) form M-S bonds, since the ν(CN) increases and the ν(CS) decreases upon coordination, without an appreciable change in the ν(N-H). On the basis of the same criterion, thiourea complexes of Cu(I) were shown to be S-bonded.

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

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

Band	Region	Mode of vibration
I	3350 cm^{-1}	ν(N-H)
II	1600 cm^{-1}	δ (NH$_2$)
III	1500 cm^{-1}	ν_s (C-N)
IV	1100 cm^{-1}	ν (C-S)
V	700 cm^{-1}	ν_s (C-N) + ν(C=S)

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

Creighton (Creighton, *et al.*, 1985) studied structures and properties of copper (I)halides with 1,3-dimethylimidazoline-2-thione(dmimtH). They assigned the absorption at 750 cm^{-1} as ν_s(C=S)+ ν_{as}(C=S)

Singh (Singh and Dikshit, 1995) 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 assigned four characteristic thioamide bands:

Band	Region (cm^{-1})	Mode of vibration
I	1500	ν(C-N) + δ (N-H)
II	1300	ν(C=S)+ν(C=N)+ ν(C-H)
III	1000	ν(C-N) +ν(C-S)
IV	800	ν(C-S)

The thioamide bands II have contributions from ν(C=S) and ν(C=N) vibrations but ν(C=S) contributes more than ν(C=N), therefore band II can be utilized to decide the coordination site.

Pettinari (Pettinari, *et al.*, 1999) studied structures and properties of derivatives of copper(I) with *N*- and *S*-donor ligands. The vibrational absorptions at approximately 770 and 740 cm^{-1}, exhibit a slight shift by $\pm$ 15 cm^{-1}, were assigned to ν(C=S) vibrations.

The infrared spectra of Cu(I) complexes with ligands containing nitrogen and sulfur atoms have four interesting regions.

Band	Region	Mode of vibration
I	1500 cm^{-1}	ν(C-N)+δ((N-H)
II	1300 cm^{-1}	ν(C=S)+ν(C=N)+ ν(C-H)
III	1000 cm^{-1}	ν(C-N)+ ν(C-S)
IV	800 cm^{-1}	ν(C-S)

IR Spectroscopy of ptu and its complexes

The infrared spectra of the ligand ptu and its complexes in this research are summarized in Table 15.

The infrared spectra of ptu complexs are essentially restricted to the "thioamide band". The bands observed in the frequency region 3000 - 3500 cm^{-1} undoubtedly can be assigned to the N-H stretching vibrations. Complex 2 and 3 occur at the lower frequencies than the free ligand but complex 1 occurs at the higher frequencies than the ligand. These may be due to the hydrogen bonding in complexes, so N-H stretching is somewhat difficult to vibrate in complex 2 and 3.

These bands are shown as follows :

Compound	ν(N-H) (cm^{-1})
ptu	3425, 3175, 3000
[Cu(ptu)$_4$]Cl	3430, 3241, 3124, 3086
[Cu$_4$(ptu)$_6$Br$_4$]	3420, 3267, 3178
[Cu$_4$(ptu)$_6$I$_4$]	3390, 3260, 3170

The bands near 1600 cm^{-1} can be assigned to NH_2 bending vibration. These absorptions are shown as follows :

Compound	δ(N-H) (cm^{-1})
ptu	1610, 1589
[Cu(ptu)$_4$]Cl	1620, 1591
[Cu$_4$(ptu)$_6$Br$_4$]	1615
[Cu$_4$(ptu)$_6$I$_4$]	1610

The strong band observed in the 1445 cm^{-1} in free ligand (ptu) can be explained as C-N stretching vibration. In complex 1, 2 and 3 observed at the position, 1448, 1449 and 1449 cm^{-1}, respectively. This is probably due to the increasing double bond character of C-N in complexes. These absorptions are shown as follow :

Compound	ν(C-N) (cm^{-1})
ptu	1445
[Cu(ptu)$_4$]Cl	1448
[Cu$_4$(ptu)$_6$Br$_4$]	1449
[Cu$_4$(ptu)$_6$I$_4$]	1449

Moreover, the bands observed at the region 1515 – 1535 cm^{-1} can be explained as thioamide band I, N-H bending plus C-N asymmetric stretching. The band in free ligand appears at 1520 cm^{-1}. There are slightly decreased about 5 cm^{-1} in complex 1, 1515 cm^{-1}; nevertheless there are slightly increased about 5-15 cm^{-1} in complex 2 and 3, 1535 and 1525 cm^{-1}. The increasing frequency in complex 2 and 3, involving the bridging of sulfur atom bonded to adjacent two copper atoms. In contrast to

complex 1, the sulfur atoms in molecule are not bridging between two copper atoms. The thioamide band I of compounds are given as follows:

Compound	Thioamide band I (cm^{-1})
ptu	1520
[Cu(ptu)$_4$]Cl	1515
[Cu$_4$(ptu)$_6$Br$_4$]	1535
[Cu$_4$(ptu)$_6$I$_4$]	1525

The frequencies found at the region 1325-1250 cm^{-1} have contributed to thioamide band II which supporting to C=S stretching and C=N stretching vibration but C=S stretching contributes more than C=N stretching. For free ligand, the frequencies appear at 1325, 1300, 1275, 1230 cm^{-1}. For all complexes, there are significantly decreased about 5-10 cm^{-1}. This is owing to the decrease of double bond character in carbon-to-sulfur bond and the increase of double bond character in carbon-to-nitrogen bond. The thioamide band II of compounds are given as follows:

Compound	Thioamide band II (cm^{-1})
ptu	1325, 1300, 1295, 1230
[Cu(ptu)$_4$]Cl	1315, 1295, 1250
[Cu$_4$(ptu)$_6$Br$_4$]	1320, 1300, 1265
[Cu$_4$(ptu)$_6$I$_4$]	1320, 1295, 1265

The bands illustrated at region 1060 cm^{-1} can be indicated to the C-N stretching plus C-S stretching refering to thioamide band III but C-S stretching dominates more than C-N stretching. This observation can be explained by

considerably change in the nature of the nitrogen-to-carbon bond and the C=S bond on coordination of complexes. All studied compounds appeared at 1065 cm^{-1} that can be compared to the bands at 1060 cm^{-1} of free ptu. The thioamide band III of compounds are given as follows:

Compound	Thioamide band III (cm^{-1})
ptu	1060
[Cu(ptu)$_4$]Cl	1065
[Cu$_4$(ptu)$_6$Br$_4$]	1065
[Cu$_4$(ptu)$_6$I$_4$]	1065

Finally, the vibration spectra assigned at about 800 cm^{-1}, attributed to C-S stretching refer to thioamide band IV. It is appeared 810 cm^{-1} in free ligand ptu but there are slightly shift into lower frequencies, 800, 795, 745 cm^{-1} for Complex 1, 2 and 3, respectively. The result of lower shift can be described as the reducing of C=S.

As can be seen above, the spectra of the metal complexes measured in this work can be concluded that the coordination takes place through sulfur atoms. As results from infrared spectrum, it can be supported by the structures which give rise from the single-crystal X-ray diffraction technique.

4.5   X-ray Structure Determination.

The X-ray diffraction analyses for complex [Cu(ptu)$_4$]Cl and [Cu$_4$(ptu)$_6$I$_4$] were performed at room temperature on SMART 1000 CCD diffractometer and for complex [Cu$_4$(ptu)$_6$Br$_4$] was performed at low temperature on SMART APEX CCD

Table 14 The infrared spectra of the ligands ptu and the studied compounds.

Compound	ν(N-H)	δ(N-H)	ν(C-N)	Band			
				I	II	III	IV
Ligand ptu	3425	1610	1445	1520	1325	1060	810
	3280	1589			1300		
	3182				1295		
	3001				1230		
1. [Cu(ptu)$_4$]Cl	3428	1620	1448	1515	1315	1065	800
	3241	1591			1295		
	3124				1250		
	3086						
2. [Cu$_4$(ptu)$_6$Br$_4$]	3427	1615	1449	1535	1320	1065	795
	3267				1300		
	3178				1265		
3. [Cu$_4$(ptu)$_6$I$_4$]	3427	1610	1449	1527	1320	1065	745
	3394				1295		
	3264				1265		
	3175				1231		

diffractometer with graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å). The structures were solved and refined by using Xtal program system.

The structures were solved by direct methods and heavy atom or Patterson methods and refined by full-matrix least squares. The remaining non-hydrogen atoms were found by difference Fourier maps. The final refinements were performed for data having $F > 4\sigma(F)$ and included anisotropic thermal parameters for all non-hydrogen atoms. Reliability factors are defined as $R = \Sigma(|F_0 - F_c)|/\Sigma|F_0|$ and $R_w = \{\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2\}^{1/2}$. All crystallographic computations were performed on a UNIX and PC computer by using the Xtal program system.

4.5.1   Structure of [Cu(ptu)₄]Cl

Copper atom is coordinated tetrahedrally by four sulfur atoms from four ptu ligands. The monomeric ionic complex [Cu(ptu)₄]Cl crystallizes in a tetragonal system, space group $I\bar{4}$, with unit cell dimensions $a = b = 11.5084(2)$ Å, $c = 12.8895(3)$ Å, and $Z = 2$. The structure is an ionic structure consisting of discrete [Cu(ptu)₄]$^+$ cation and Cl$^-$ anion. The [Cu(ptu)₄]$^+$ cation possesses a crystallographic symmetry, so that the copper atom is on four-fold inversion axis; $\bar{4}$ (Figure 41). The four Cu-S distances are equal; 2.334(1) Å, but the four angles of S-Cu-S are not equal; 105.72(4) – 117.27(3)°. As can be seen in Figure 42 these two angular distortion is due to the major sterical hindrance of the phenyl groups in ligand ptu and mainly to the intramolecular hydrogen bonds between the thioamide nitrogen atoms.

Similar ligand of CuCl/ptu has been already reported for $Cu_2(PTU)_4Cl_2$ where as PTU is *N'*-2-propenoylthiourea (Cernak, *et al.,* 1991). The unit cell of $Cu_2(PTU)_4Cl_2$ contains two different centrosymmetrical dimer molecules (denoted as A and B) of the complex with a different coordination sphere of Cu(I) atoms. In dimeric structure of molecule A (Figure 43a) contain two copper atoms, each copper atom is tetrahedrally coordinated by two terminal ptu ligands through the sulfur atoms and bridged by two chloride atoms to give $\mu\mu$-dichlorobridged dimer $(PTU)CuCl_2Cu$ (PTU). In dimer molecule B (Figure 43b), each copper atom is tetrahedrally bridged by two sulfur atoms from 2 molecules of ptu and terminally bonded by one ptu molecule and an Cl atom to give disulfur-bridged dimer $(PTU)ClCu(S- PTU)_2CuCl$ (PTU). The structure of CuCl/ptu complex in this work is different from the reported structure of CuCl/PTU as mentioned above. Moreover, the preparation and recrystallization solvents are different. The complex in this research prepared by reaction between CuCl and ptu in acetonitrile and the crystals were obtained by slow evaporation, whereas the reported complexes prepared by reaction between $CuCl_2.2H_2O$ and PTU in ethanol and the crystals were obtained by recrystallization from a $CHCl_3$-CH_3OH mixture (Cernak, *et al.,* 1991).

Similar structures have been reported for $[Cu(etu)_4]NO_3$ (etu = Ethylthiourea) with in structure coordination around copper atom is tetrahedral and involves the sulfur atoms of four independent etu molecules. (Battaglia, L.P., *et al.* 1976). The Cu-S distances of the synthesized structure in this research are in good agreement with this found in Cu(I) thiourea tetrahedral complexes. The selected bond distances and bond angle is shown in Table 15 – 16.
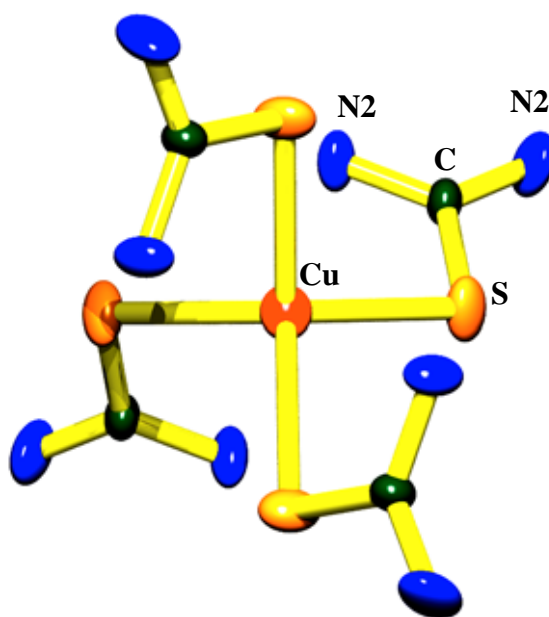
Figure 41 A projection of [Cu(ptu)$_4$]$^+$ down the $\bar{4}$ axis.

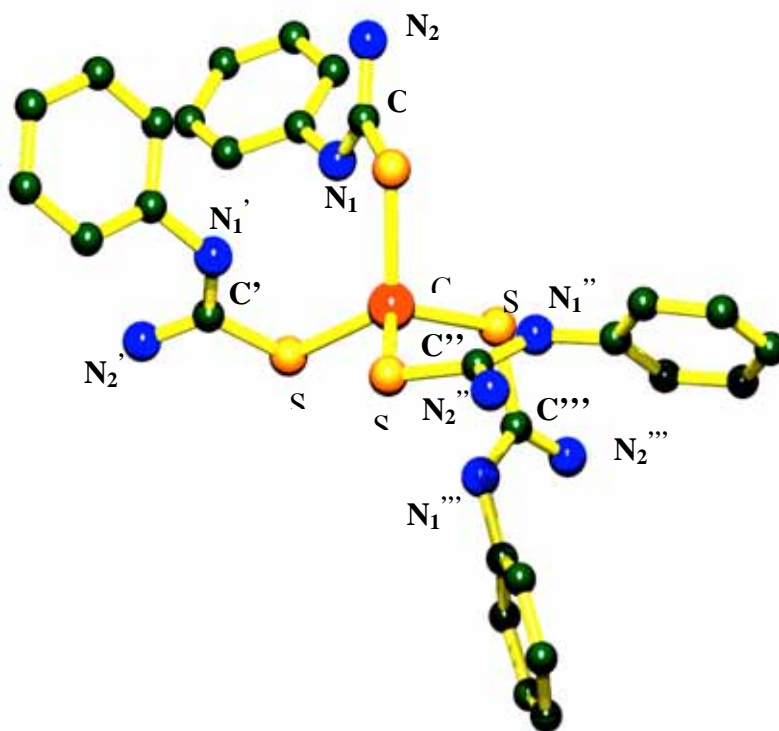Figure 42 The cation of [Cu(ptu)$_4$].
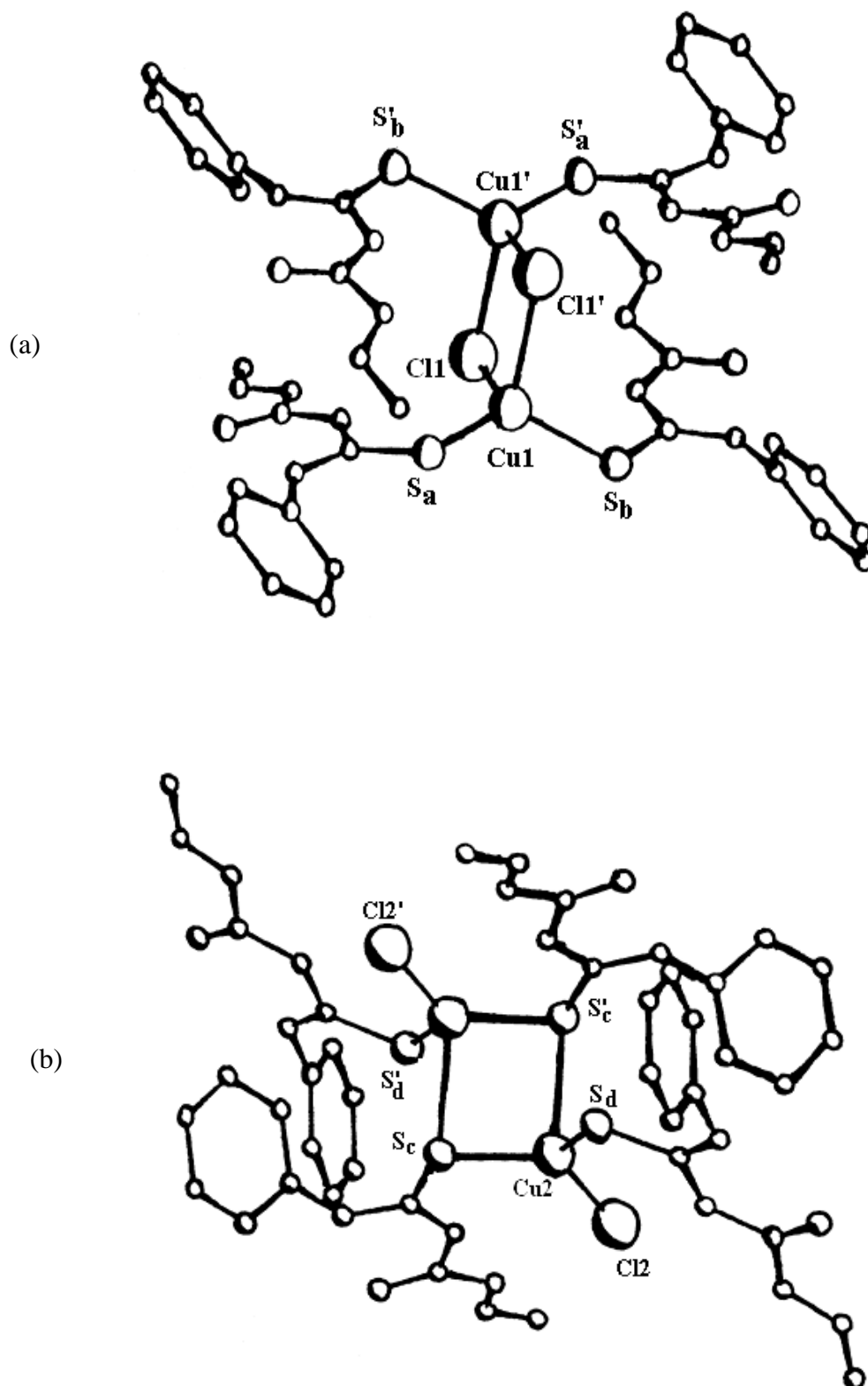
Figure 43 (a) The dimeric structure of molecule A of $Cu_2(PTU)_4Cl_2$.

(b) The dimeric structure of molecule B of $Cu_2(PTU)_4Cl_2$.

4.5.2 Structures of [Cu$_4$(ptu)$_6$Br$_4$] and [Cu$_4$(ptu)$_6$I$_4$]

The two complexes crystallize in the triclinic system, space group $P\bar{1}$, with unit cell dimensions $a = 11.987(1)$, $b = 19.891(2)$, $c = 25.213(2)$ Å, $\alpha = 11.58(1)$, $\beta = 98.91(1)$, $\gamma = 97.45(1)°$, $Z = 4$ for [Cu$_4$(ptu)$_6$Br$_4$] and $a = 12.1943(1)$, $b = 20.8855(4)$, $c = 23.5722(4)$ Å, $\alpha = 82.121(1)$, $\beta = 89.217(1)$, $\gamma = 84.367(1)°$, $Z = 4$ for [Cu$_4$(ptu)$_6$I$_4$]. Each structures consists of two independent [Cu$_4$(ptu)$_6$X$_4$] units (X = Br or I) with above stoichiometry, comprises asymmetric unit. Copper atom in each molecule is coordinated tetrahedrally by three sulfur atoms and a Br or an I atom, respectively. Four such tetrahedra are held together by corner sharing at sulfur position to form a tetrahedral array. This arrangement defines four six-membered Cu$_3$S$_3$ rings, all adopting a chair conformation. In these rings, the substitiuent Br (or I) atom occupy equatorial positions and of the three C(NH$_2$)(NHC$_6$H$_5$) substituents, one is in an axial position and the remaining two are in equatorial positions. The Cu – Br and Cu – I distances vary from 2.478(6) to 2.496(8)Å and 2.627(1) to 2.746(1)Å, respectively. The Cu – S distances range from 2.262(1) to 2.352(1) Å. The overall complex has an adamantane-type cluster structure with S atom from ptu as bridging and Br, I as terminal ligands. As can be seen in Figure 44 and Table 17. In both structures, the two independent molecules in each structure (adamantine-like structure) are similar; there are, however, crystallographic significant differences in cell parameters between the two structures, then the two structures are not isomorphous. Similar adamantane structures have been reported for Cu$_4$(ettu)$_6$I$_4$.H$_2$O with tetrahedral Cu atoms (Pakawatchai *et. al.*, 1998), Cu$_4$(tu)$_6$(NO$_3$)$_4$.4H$_2$O and Cu$_4$(tu)$_9$(NO$_3$)$_4$.4H$_2$O, with trigonal planar Cu atoms in the former, but with three

tetrahedral and one trigonal planar Cu atoms in the latter (Griffith, *et al.*, 1976). The selected bond distances and bond angle are shown in Table 16 –17.
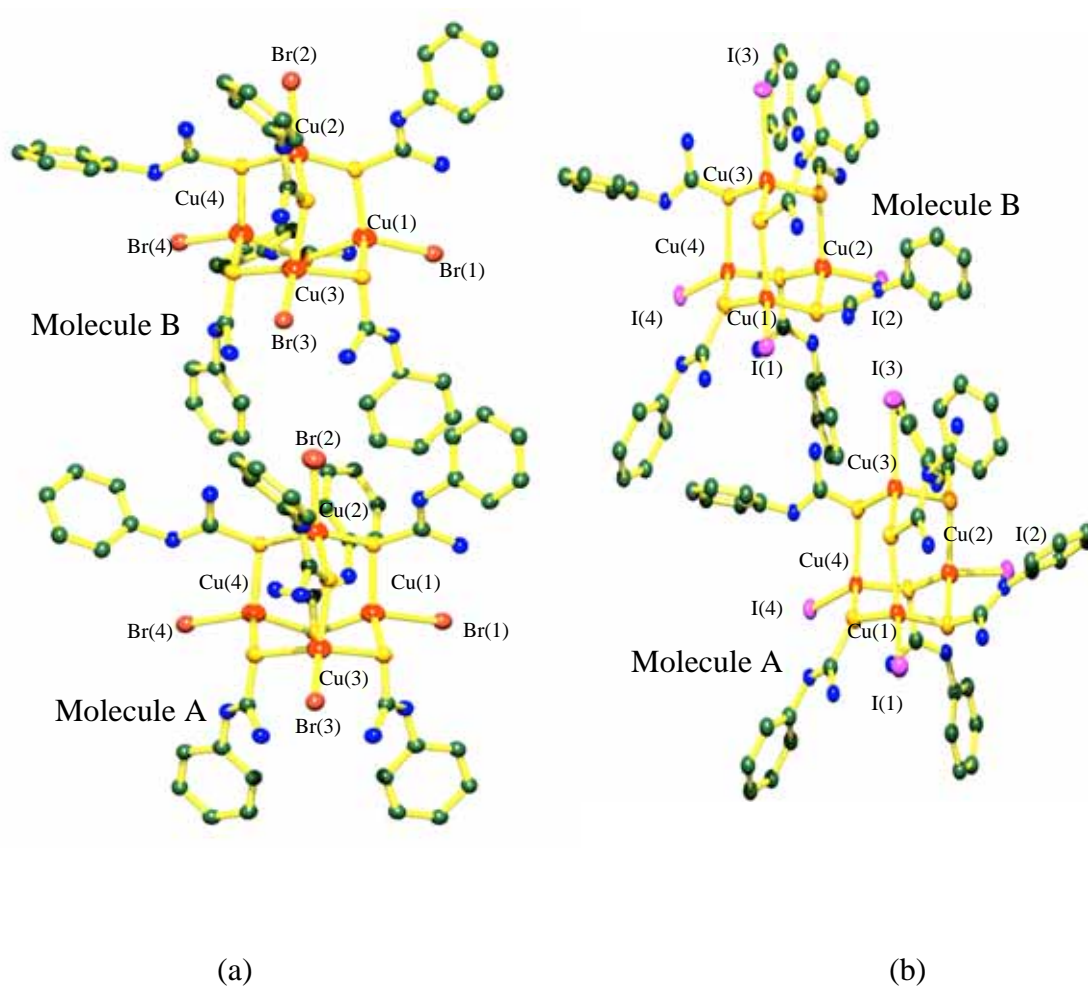

(a)   (b)

Figure 44 The two independent molecule of (a) $[Cu_4(ptu)_6Br_4]_2$ and (b) $[Cu_4(ptu)_6I_4]_2$.

Table 15 The selected bond distances of the studied compounds.

Compound	Cu – S (Å)	Cu – X (Å)	C – S (Å)
[Cu(ptu)$_4$]Cl	2.334	-	1.711
[Cu$_4$(ptu)$_6$Br$_4$]	2.262-2.352	2.478-2.496	1.720-1.732
[Cu$_4$(ptu)$_6$I$_4$]	2.283-2.423	2.627-2.746	1.720-1.739

Table 16 The selected bond angles of the studied compounds.

Compound	S – Cu – S (angle)	S – Cu – X (X=Br and I) (angle)
[Cu(ptu)$_4$]Cl	105.70-117.30	-
[Cu$_4$(ptu)$_6$Br$_4$]$_2$	95.46-115.37	106.66-120.76
[Cu$_4$(ptu)$_6$I$_4$]$_2$	96.30-109.46	108.24-119.07