4. Discussion

4.1 Preparation of Complexes

The purpose of this research is, to study the crystal structure of copper oxyainon substituted thiourea complexes by single crystal X - ray diffraction methods. The complexes in this study must be single crystals, then, the conditions in preparation of complexes and crystallization must be significant. In preparation process of copper oxyanion substituted thiourea complexes have been to get on using a number of methods such as varying reactants, ratios of reactants, solvents, reaction temperation time. In any cases, the four complexes were suitable for studying the structure, their conditions of preparation are shown in Table 1. Although the compound, S_8, is not a complex but it was interesting to solve the structure to establish to product of the reaction. $[Cu(etu)_3]_2SO_4$, $[Cu_2(detu)_6](NO_3)_2$, $[Cu(detu)_3]_2SO_3$ and $[Cu_2(detu)_6](ClO_4)_2$ were obtained by reduction of copper(II) salts in the presence of the ligands .

The reaction between copper salts and substituted thioureas invariably produce complexes which are unpredictable with respect to stoichiometry, stereochemistry and metal oxidation state. Clearly, reaction between copper salts and substituted thioureas ligand is capable of producing a variety of products whose composition is dependent on the nature of the solvent, the coordinating properties of the counterion as well as the molar ratios of the reactants and the reaction time employed. However, most mole ratio of copper salt and ligand which gave complexes are 1 : 3. In addition, most reaction could form more complexes at temperature in the range of 50 - 80 $^{\circ}C$ because reactants could be more soluble in solvents especially copper salts. Apart from solubility of reactants, crystallization in solvent was referred. This process occurs in two steps - nucleation and growth. In general, the faces of the crystal which grow most rapidly are those to which the crystallizing particles are bound most securely. These rapidly growing faces are usually the smaller, less well developed faces. The larger faces are usually associated with directions in the crystal where there are only weak intermolecular interactions. Good crystals usually have smooth flat faces, sharp edges, no inclusions, no striations and obvious dislocations.

4.2 X - ray Fluorescence Spectrometry

This technique was used to investigate the element of copper and sulfur in synthesized complexes. The K_α spectrum of copper atom is 8.04 keV and sulfur atom is 2.31 and 2.32 keV approximately, furthermore, the K_β spectrum of sulfur atom is about 2.465 keV. However this method was only preliminary quality analyses for complexes which copper was representative for copper salts and sulfur was representative for substituted thioureas as shown in Figure 46. - 53. $[Cu(etu)_3]_2SO_4$, $[Cu_2(detu)_6](NO_3)_2$, $[Cu(detu)_3]_2SO_3$ and $[Cu_2(detu)_6](ClO_4)_2$ show the peaks of both copper and sulfur.

4.3 Infrared Spectrophotometry

Because of substituted thioureas consist of the SCNH group as shown in Figure 2. , which may be available either the thione form (S = C – N – H) or the thiol form (H – S – C = N). From the study of infrared spectroscopy as shown in Figure 54. - 59. , indicated the ligands etu and detu available only the thione form in both free state and their complexes. This is distinct by the absence of the ν(S – H) band in the region of 2,600 - 2,550 cm^{-1} and by the presence of the ν(N – H) band in the region of 3,100 - 3,400 cm^{-1}.

Yamaguchi, *et al.* assigned the infrared absorption bands for some metal thiourea complexes such as tetrakis(thiuorea)platinum(II) chloride, tetrakis(thiourea) palladium(II) chloride, dichlorobis(thiourea)zinc(II), dithiocyanatobis(thiourea)nickel(II), dichlorobis(thiourea)platinum(II). The present investigation was undertaken to assign the infrared absorption bands for metal thiourea complexes based on the normal vibration calculation of the thiourea molecule. (Yamaguchi, *et al.* 1958) :

Band	Region	Assignment
I	1,600 cm^{-1}	$\delta(N-H)$
II	1,500 cm^{-1}	$\nu(C-N)$
III	1,400 cm^{-1}	$\nu(N-H) + \nu(C=S)$
IV	1,100 cm^{-1}	$\nu(C-N) + \nu(C=S)$
V	700 cm^{-1}	$\nu(C=S)$

Lane, *et al.* reported infrared absorption spectra for some metal thiourea complexes, tetrakis(methylthiourea)copper(I) chloride, tetrakis(methylthiourea)platinum (II) chloride, tetrakis(methylthiourea)pallidium(II) chloride, dichlorobis(methylthiourea) cadmium(II), dichlorobis(methylthiourea)zinc(II). (Lane, *et al.* 1959) :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	2,900 cm^{-1}	$\nu(C-H)$
III	1,600 cm^{-1}	$\delta(N-H)$
IV	1,500 cm^{-1}	$\nu(N-H) + \nu_{as}(C-N)$
V	1,000 cm^{-1}	$\nu(C-N) + \nu(N-H) + \nu(C=S)$
VI	700 cm^{-1}	$\nu(C=S) + \nu(C-N)$

Ferrari, *et al.* assigned the infrared spectra for copper(I) 1-phenyl-3-(2-pyridyl)-2-thiourea complexes. (Ferrari, *et al.* 1985) :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	1,500 cm^{-1}	$\nu(C-N)$
III	1,400 cm^{-1}	$\nu(C=S)+\nu(C-N)$
IV	700 cm^{-1}	$\nu(C-N)+\nu(N-H)+\nu(C=S)$

Crieghton, *et al.* studied the infrared spectra for copper(I) complexes of imidazole thiones ligands, monochloro bis(1-methylimidazoline-2-thione) copper(I), (Crieghton, *et al.* 1985) :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	1,400 cm^{-1}	$\nu(C-N)+\delta(C-H)$
III	1,200 cm^{-1}	$\nu(C=S)+\nu(C-N)+\delta(C-H)$
IV	1,000 cm^{-1}	$\nu(C-N)+\nu(C=S)$
V	700 cm^{-1}	$\nu_s(C=S)+\nu_{as}(C-N)$

Sigh, *et al.* studied the vibration spectroscopic of some copper(I) complexes containing halides, triphenylphosphine and N,N'-dimethyl-N'-phenylthiourea(dmptH), $Cu(PPh_3)_2$ (dmptH)Cl, (Sign, *et al.* 1995) :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	1,500 cm^{-1}	$\nu(C-N)+\delta(N-H)$
III	1,300 cm^{-1}	$\nu(C=S)+\nu(C=N)+\nu(C-H)$
IV	1,000 cm^{-1}	$\nu(C-N)+\nu(C-S)$
V	800 cm^{-1}	$\nu(C-S)$

Bott, *et al.* studied the vibration spectroscopic of some copper(I) thiourea complexes such as hexakis(thiourea)dicopper(I) sulfate hydrate, pentakis(thiourea) dicopper(I) sulfate trihydrate, heptakis(thiourea)tetracopper(I) disulfate hydrate, hexakis (thiourea)tetracopper(I) tetranitrate tetrahydrate, nanokis(thiourea)tetracopper(I) tetranitrate tetrahydrate (Bott, *et al.* 1998) :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	1,600 cm^{-1}	$\delta(N-H)$
III	1,500 cm^{-1}	$\nu(C-N)$
IV	1,400 cm^{-1}	$\delta(N-H)+\nu(C-N)+\nu(C-S)$
V	1,000 cm^{-1}	$\nu(C-N)+\delta(N-H)$
VI	700 cm^{-1}	$\nu(C-S)$

The other bands useful for identification of donor atoms are $\nu(N-H)$ and $\nu(C=S)$ (Singh and Dikshit, 1995). The mode of ligand bonding is decided on the basis of shifts of $\nu(N-H)$, $\nu(C=S)$ and four thioamide bands on complexation. The thioamide band II and III have contributions from $\nu(C-N)$ and $\nu(C=S)$ vibrations but $\nu(C=S)$ contributes more than $\nu(C-N)$ to the thioamide band II (Singh and Dikshit, 1995), therefore, thioamide band II can be utilized to decide the coordination site but it is difficult to decide the coordination site on the basis of shifts of thioamide band III.

To support the crystal structures of 4 complexes, the 5 bands were considered :

Band	Region	Assignment
I	3,000 cm^{-1}	$\nu(N-H)$
II	1,500 cm^{-1}	$\nu(C-N)$
III	1,400 cm^{-1}	$\nu(C=S)+\nu(C-N)+\delta(N-H)$
IV	1,100 cm^{-1}	$\nu(C-N)+\nu(C=S)$
V	700 cm^{-1}	$\nu(C-S)$

The infrared spectra of the ligands etu, detu and 4 complexes are summerized in Table 19.

Table 19. The infrared spectra of the ligand etu, detu and the studied complexes.

Compound	Band				
	I	II	III	IV	V
ligand etu	3234	1499	1459	1045 1001	679
$[Cu(etu)_3]_2SO_4$	3250	1523	1461	1030	682 619
ligand detu	3235 2972	1555 1523	1449	1165 1138	797
$[Cu_2(detu)_6](NO_3)_2$	3260 2975	1577 1516	1449	1161 1137	794
$[Cu(detu)_3]_2SO_3$	3235 2974	1558 1515	1451	1164 1138	795
$[Cu_2(detu)_6](ClO_4)_2$	3246 2976	1567 1508	1450	1086	795 741

The high frequency N – H absorption bands in the spectrum of etu and detu ligands were not shifted to lower frequencies on the formation of the metal - substituted thioureas complexes. This indicates that nitrogen to metal bonds are not present therefore the bonding in these complexes must be between the sulfur and metal atoms. The formation of S → Cu bonds is expected to increase the contribution of the highly polar structure to the substituted thioureas molecule, resulting in a greater double bond character for the nitrogen to carbon bond and a greater single bond character for the carbon to sulfur bond. The N – H stretching vibrations [ν(N – H)] bands of the etu and detu ligands are observed as medium band in the 2,900 - 3,300 cm^{-1} region. The slight shift of these bands and the appearance of a new medium band at higher frequency in the spectra of copper(I) complexes suggest the participation of secondary nitrogen atoms in hydrogen bonding. The infrared absorption bands observed at about 1,500 cm^{-1} assigned to N – C – N stretching vibration, [ν(C – N)]. The increase in frequency observed for the complexes can be explained as resulting from the greater double bond character of the carbon to nitrogen bond on the complex formation. Moreover, the bands at about 1,400 cm^{-1} assigned to the NH_2 rocking vibration and N – C – N and C = S stretching vibrations, [ν(C = S) + ν(C – N) + δ(N – H)]. The nature of the vibration is changed slightly on coordination through the sulfur atoms. A conspicuous difference in the spectra of both ligands and its metal complexes appears in the region at about 1,100 cm^{-1}. A strong absorption band is extremely weakened or disappears on complex formation. This observation can be explained by the considerable change in nature of the N – C bond as well as the C = S bond on coordination of ligand through the sulfur atom, in these complexes the N – C – N stretching frequency, [ν(C – N)] , and the C =S stretching frequency, [ν(C = S)], is decreased. Therefore, in coordination complexes, the contribution of the ν(C = S) band is decrease and the intensity of this band is reduced. Finally, the bands observed at about 700 cm^{-1} in the spectra of the complexes assigned to C = S stretching vibrations, [ν(C = S)]. The lowering of frequency can be attributed to the reduced double bond character of the C = S bond. The absorption bands in the spectra of the copper substituted thiourea complexes which have been assigned to the particular vibrations indicated the presence of sulfur to metal bonds in the copper complexes.

4.4 Elemental Analysis

This technique was used to determine the elemental composition percentage in the complexes. The calculated percentage of carbon, hydrogen, nitrogen and sulfur in the complexes are nearly close to the values which can be found experimentally as shown in Table 3.

4.5 Single crystal X - ray diffractometry

4.5.1 X - ray photography

The use of film methods for recording X - ray diffraction patterns have declined in recent decades as diffractometers have become more widespread but it is still an excellent teaching tool. The oscillation photographs are generally used to allign crystals and to measure the cell adge along the axis of rotation. One unit cell axis is aligned in a particular direction normal to the incident X - ray beam and this produces a regular pattern of spots on the film, to which indices can easily be assigned by counting along rows. With regard to intepreting oscillation photographs shows that distance between the zero- and the nth levels of reciprocal lattice points

$$d_1^* = d_1^*/1 = d_2^*/2 = d_3^*/3 = \ldots = d_n^*/\mathrm{n}$$

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

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

when λ is wavelength of radiation which in this research equal to 1.542 Å.

In the experiment, the crystals of $[Cu(etu)_3]_2SO_4$ was studied by Oscillation method using the PW 1720 X - ray Generator (Philips) and Enraf Nonius FR 550 Weissenberg camera. With photograph in Figure 60., the study was to check for a cracked or twinned crystal and determine an axis length of crystal approximately. The result from X - ray photograph is shown in Table 23. The results show an axis length of $[Cu(etu)_3]_2SO_4$ complex (12.639 Å, Table 23.) is slightly different from diffractometry result (12.775 Å, Table 4.). The error may occur from measurement.

Table 23. The result of X - ray photograph of $[Cu(etu)_3]_2SO_4$.

Distance (Å)	$[Cu(etu)_3]_2SO_4$
$d_1^* / 1$	0.12
$d_2^* / 2$	0.12
$d_3^* / 3$	0.13
$d_4^* / 4$	0.12
d_1^*	0.122
r	12.639

4.5.2 X - ray diffractometry

The diffraction data from X - ray diffractometer were preprocessed and the crystal structures were solved by SHELXTL version 6.12 and Xtal system version 3.6. The followings are the results from structure determination.

$[Cu(etu)_3]_2SO_4$

The structure consists of two independent $Cu(etu)_3^+$ units and one SO_4^{2-} anion as shown in Figure 61. - 62. The two cations remain crystallogaphically distinct but each is located with the copper atom on a threefold crystallographic axis so that about each copper and only one ligand is crystallographically independent. While there are two independent cations, there is only one sulfate counter ion, this is also imposed with one of the S – O bonds lying on a crystallographic 3 axis common to only one of the cations and with this axis oxygen atom approaching the copper atom at a relatively long distance [Cu(2) – O(2) = 2.836(8) Å], the interaction being insufficient at the present level of precision to significant perturb the sulfate geometry from tetrahedral. Neverless, the geometry of cation 2 differs significantly from that of cation 1 and in a manner suggestive and supportive of some purturbation 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 120.00(2)° ; Cu(1) – S(1) is 2.2513(6) Å. In cation 2, the angle between the sulfurs is 119.75(3)° ; Cu(2) – S(2) is 2.2753 Å. In the anion, S(3) – O(1) and S(3) – O(2) are 1.478(3) and 1.468(8) Å ; O(1) – S(3) – O(2) and O(1) – S(3) – O(1') are 109.3(3) and 109.6(2)°, respectively. Furthermore, there are hydrogen bondings between oxygen - sulfate and hydrogen of nitrogen - etu molecules. The distances between O(1)- - H(N(12)), O(1) - - H(N(22)) and O(2) - - H(N(21)) are equal to 2.802(2), 2.845(2) and 3.000(2) Å, respectively as shown in Figure 71.

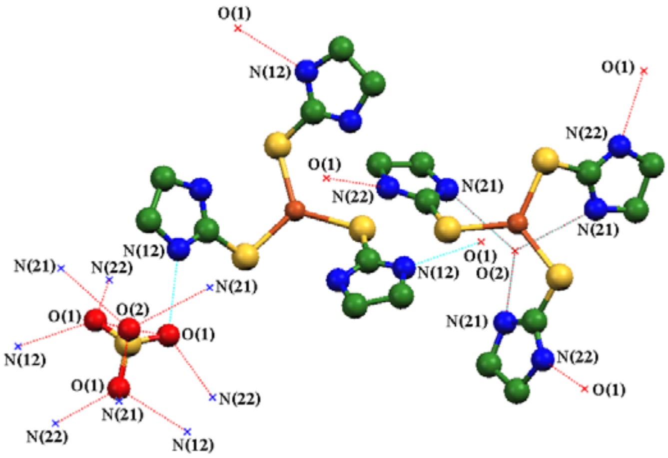

Figure 71. The hydrogen bonding in $[Cu(etu)_3]_2SO_4$.

This structure is the same as the one that has been studied by Bowmaker, *et al.* (1994) but there are several significant and important differences such as reactants and conditions in preparation processes. In this research, $Cu(CH_3COO)_2{\cdot}H_2O$ and etu were used in this research but $CuSO_4$ and etu were used in previous study. In preparation process, this complex was prepared by direct reaction between $Cu(CH_3COO)_2{\cdot}H_2O$ and etu but the crystal structure, sulfate counter anion instead of acetate anion because of the over abundant of sulfur from etu molecules were produced and reacted with O_2 in air became to SO_2 which then converted to SO_3 by the exothermic reaction. The SO_3 then reacted with water to form sulfuric acid which contain conjugated acid of SO_4^{2-}. The reaction is shown in Scheme 1. (Gary, L.M. and Donald, A.T. 1999).

$$\begin{tikzcd}
S + O_2 \arrow[r] & SO_2 \arrow[r, "\frac{1}{2}O_2"] & SO_3 \arrow[d, "H_2O"] \\
& & H_2SO_4 \arrow[d, leftrightarrow] \\
& & 2H^+ + SO_4^{2-}
\end{tikzcd}$$

Scheme 1. Formation of SO_4^{2-} anion.

Furthermore, etu could reduce CH_3COOH to CH_3CH_2OH mixed with H_2O as solvent in reaction because etu not only act as ligands but also reducing agent in this reaction.

$[Cu_2(detu)_6](NO_3)_2$

The structure of this complex consists of discrete dinuclear $Cu_2(detu)_6^{2+}$ cations and two nitrate anions. A perspective view of the $[Cu_2(detu)_6](NO_3)_2$ with atomic labelling is given in Figure 63. and the unit cell contents are in Figure 64. The asymmetric unit consists of one half of the ionic dimer whereas the other half is generated by the center of symmetry. The dinuclear cation contains copper(I) atoms tetrahedrally coordinated by four terminal monodentate sulfur - donating detu ligands and two sulfur - bridging (μ_2) detu ligands. Consequently both copper(I) atoms have a S_4 - donor set and distorted tetrahedral environments with angles between the sulfur atoms ranging from 105.84(2) - 119.57(6) Å. Terminal, $Cu – S_t$ distances are in the range normally observed for tetrahedral CuS_4 systems, 2.2867(6) - 2.3419(6) Å, and are typically shorter than the bridging $Cu – S_{br}$ distances, 2.3384(5) - 2.4593(6) Å. The angles between Cu(1) – S – C for terminal ligands are 101.07(6) - 108.00(6)° and for bridging ligands are 100.96(5) - 111.10(5)° and Cu(1) – S(3) – Cu(1') is 74.79(3). For nitrate anions, the nitrate anion is nearly planar with the angles between the nitrogen atom ranging from 118.9(1) - 121.1(1)° and N(1) – O distances are 1.243(2) - 1.248(2) Å. In addition, there are three O - - H(N) distances which suggest weak hydrogen bonding between ligand amide groups and nitrate oxygen atoms. These involve O(1) and H(N(11)) at 2.975(1) Å, O(2) and H(N(21)) at 2.975(2), 3.042(2) Å and O(3) and H(N(32)) at 2.892(1) Å, as shown in Figure 72. The structure like this is similar to a previous studied, $Cu(tu)_3(ClO_4)$, (Hanic, et. al.1969).

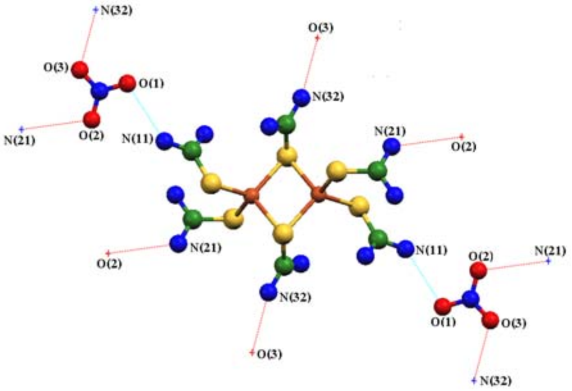

Figure 72. The hydrogen bonding in $[Cu(detu)_3]_2(NO_3)_2$.

$[Cu(detu)_3]_2SO_3$

The structure of the complex consists of two independent $Cu(detu)_3^{2+}$ cations and one SO_3^{2-} counter anion. A perspective view of $[Cu(detu)_3]_2SO_3$ with the atomic labelling is given in Figure 65 and the unit cell contents are in Figure 66. The copper(I) atoms is clearly coordinated by three sulfur atoms from three detu molecules in a distorted trigonal configuration. Nevertheless, the geometry of cation 2 differs significantly from that of cation 1 in a manner suggestive and supportive of some purturbation arising from the presence of the sulfite oxygen. In cation 1, the CuS_3 moiety is closely planar, with the angle between the sulfur atoms being 119.3(4)° ; Cu(1) – S(1) is 2.254(7) Å. In cation 2, the angle between the sulfurs is 119.3(4)° ; Cu(2) – S(2) is 2.227(7) Å. In anion, S(3) – O(1) is 1.34(4) Å ; O – S(3) – O is 91.5(3)°. Cu(1) – S(1) – C(1) and Cu(2) – S(2) – C(2) are 108.2(6) and 107.4 (6)°, respectively for the two cations. Furthermore, there is one distance which suggests weak hydrogen bonding between ligand amide group and sulfite oxygen atom involving O(1)- - H(N(21)) at 2.979(1) Å as shown in Figure 73. The structure of this complex is similar to the previous studied structure, $Cu(detu)_3 \cdot 1/2SO_4$, (Kamara, et. al. 1982). It is deferent in anion, the previous studied containing sulfate anion but in this work, this involved sulfite anion.

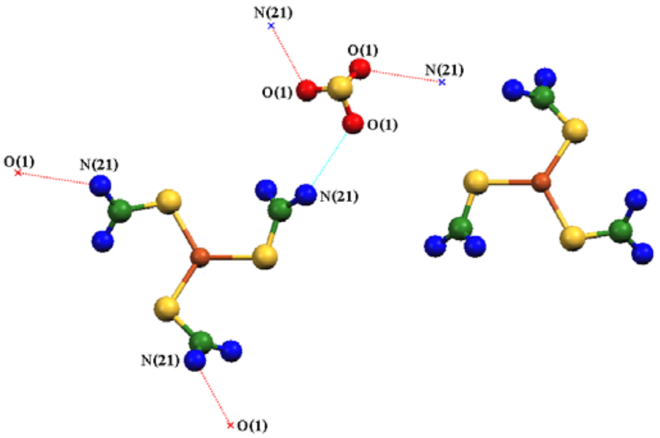

Figure 73. The hydrogen bonding in $[Cu(detu)_3]_2SO_3$.

In so far as preparation, this complex was prepared by reaction between $Cu(CH_3COO)_2{\cdot}H_2O$ and detu but the crystal structure consists of sulfite counter anion instead of acetate ion. Because the over abundant of S from detu molecules were produced and reacted with O_2 in air became to SO_2 then they were hydrolysed completely by water that used as solvent to sulfurous acid, conjugated acid of SO_3^{2-}. The reaction is shown in Scheme 2. (Gary, L.M. and Donald, A.T. 1999).

$$\begin{array}{ccccc} S + O_2 & \longrightarrow & SO_2 & \xrightarrow{H_2O} & H_2SO_3 \\ & & & & \updownarrow \\ & & & & 2H^+ + SO_3^{2-} \end{array}$$

Scheme 2. Formation of SO_3^{2-} anion.

For CH_3COO^-, because detu not only act as ligands but also reducing agent so detu could reduced CH_3COOH became to CH_3CH_2OH which mixed with H_2O as solvent in this reaction as same as $[Cu(etu)_3]_2SO_4$.

$[Cu_2(detu)_6](ClO_4)_2$

The structure of the complex consists of distorted dinuclear $Cu_2(detu)_6^+$ cations and two perchlorate anions. A perspective view of the $[Cu_2(detu)_6](ClO_4)_2$ with atomic labelling is given in Figure 64. and the unit cell contents are in Figure 65. The dinuclear cation contains copper(I) atoms tetrahedrally coordinated by four terminal monodentate sulfur - donating detu ligands and two sulfur - bridging (μ_2) detu ligands. Consequently both copper(I) atoms have a S_4 - donor set and distorted tetrahedral environments with angles between the sulfur atoms ranging from 102.74(6) – 118.73(6) Å. Terminal, $Cu – S_t$ distances are in the range normally observed for tetrahedral CuS_4 systems, 2.283(2) - 2.344(2) Å, and are typically shorter than the bridging $Cu – S_{br}$ distances, 2.364(1) - 2.447(1) Å. The angles between Cu(1) – S – C for terminal ligands are 102.5(3) – 107.3(3)° and for bridging ligands are 102.9(2) - 111.3(2)° and Cu(1) – S(3) – Cu(1') is 74.22(4)°. For perchlorate anions, the perchlorate anion has the tetrahedral arrangement with the Cl – O distances are 1.26(1) - 1.35(1) Å and with O – Cl – O bond angles 99.2(8) -123.6(9)°. In addition, there are two O - - H(N) distances which suggest weak hydrogen bonding between ligand amide groups and perchlorate oxygen atoms. These involve O(1)- - H(N(22)) at 3.002(1) Å and O(2) - - H(N(12)) at 3.033(1) Å, as shown in Figure 74. The structure like this is similar to a previous studied, $Cu(tu)_3ClO_4$, but different in ligands (Hanic, et. al. 1969).

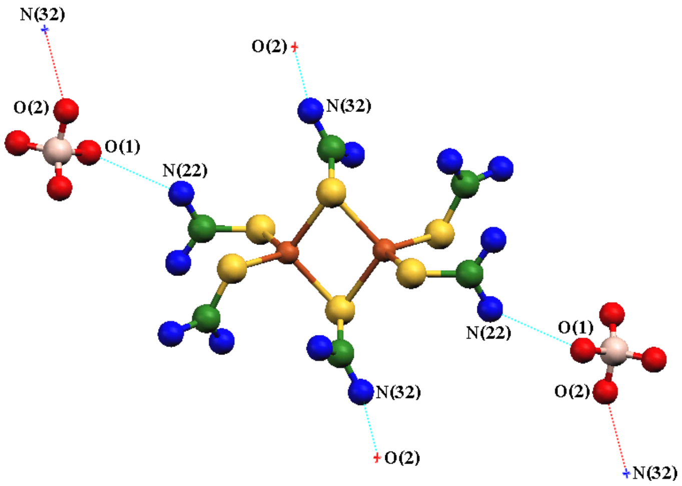

Figure 74. The hydrogen bonding in $[Cu(detu)_3]_2(ClO_4)_2$.

S_8

Sulfur exits in a number of allotropic modifications. Solid allotropes include rhombic sulfur and monoclinic sulfur, so named from the type of crystal formed in each case. Both are yellow solids. The rhombic modification is the stable form at room temperature, and changes into the monoclinic variety at 95.6 °C. However, the rate of conversion is quite slow and if heating is sufficiently rapid rhombic sulfur can be raised to its melting point (112.8°C) without very much transformation to the monoclinic form (m.p. 119°C) (Brown, D.A.,1988). In this work, X - ray studies have shown that rhombic sulfur contain 8 - membered puckered rings. The molecule adopts a crownlike structre known as cyclo - S_8, consists of two interconnected layers of four sulfur atoms each as shown in Figure 69. The S – S bond distances are 2.042(2) - 2.051(3) Å and S – S – S bond angles are 107.31(5)-108.97(5) ° and the unit cell contents are in Figure 70. This form of sulfur is obtained by decomposition of copper(II) perchlorate in *N,N'*- diethylthiourea. The form of sulfur like this has been occurred in the previous studied by decomposition of copper(I) ethyl xanthate in pyridine (Cotton, F.A., 1988).