

5. Conclusion

Copper oxyanions form complexes by substituted thioureas with various stoichiometries and structure types in which ionic complexes have been obtained. In this research, four copper oxyanion substituted thiourea complexes have been prepared. These complexes are $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$, $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$, $[\text{Cu}(\text{detu})_3]_2\text{SO}_3$ and $[\text{Cu}_2(\text{detu})_6](\text{ClO}_4)_2$. These complexes were prepared by direct reaction of copper(II) salts (CH_3COO^- , NO_3^- , ClO_4^-) with substituted thiourea ligands (etu, detu). In so far as the research involving copper oxyanion complexes with N,N' -ethylenethiourea and N,N' -diethylthiourea ligand. Therefore, S_8 was isolated from the reaction between copper(II) perchlorate hexahydrate and N,N' -diethylthiourea before the complex of $[\text{Cu}_2(\text{detu})_6](\text{ClO}_4)_2$ was produced. Then the structure of S_8 was also determined in this research although it is not a copper(I) N,N' -diethylthiourea complex as expected.

The complex of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ crystallized in trigonal cell ; $a = 12.7753(1)$, $c = 35.7052(4)$ Å, space group $R3c$, $Z = 6$, $R = 0.0201$ from 1574 observed reflections. The structure is an ionic noncentrosymmetric consisting of two $\text{Cu}(\text{etu})_3$ cations and one SO_4^{2-} anion. Each copper atom lies on a threefold axis so that each copper and only one ligand is crystallographically independent. The sulfate counter anion 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 complex of $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$ crystallized in triclinic cell ; $a = 9.099(2)$, $b = 11.688(2)$, $c = 13.201(3)$ Å, $\alpha = 111.34(3)$, $\beta = 104.52(3)$, $\gamma = 97.35(3)^\circ$, space group $P\bar{1}$; $Z = 2$, $R = 0.0353$ from 9869 observed reflections. The structure is an ionic centrosymmetric dimer consisting of $[\text{Cu}_2(\text{detu})_6]^{2+}$ cations and two NO_3^- anions. Each copper atom is pseudo - tetrahedrally coordinated by pairs of terminal thione - sulfur and asymmetric bridging detu ligands. Each copper is trans - related to its partner across crystallographic symmetry centres. Consequently each copper(I) atom has an identical S_4 donor set.

The complex of $[\text{Cu}(\text{detu})_3]_2\text{SO}_3$ crystallized in trigonal cell ; $a = 12.335(1)$, $c = 27.919(5)$ Å, space group $R\bar{3}$, $Z = 3$, $R = 0.0662$ from 1530 observed reflections. The structure is an ionic noncentrosymmetric consisting of two independent $\text{Cu}(\text{detu})_3^+$ cations and one SO_3^{2-} anion. Each copper atom lies on a threefold axis so that each copper and only one ligand is crystallographically independent. The sulfite counter anion is disposed with one of the S – O bonds lying on a crystallographic threefold axis, the S – O bond is approaching the copper atom normal to the planar CuS_3 array.

The complex of $[\text{Cu}_2(\text{detu})_6](\text{ClO}_4)_2$ crystallized in triclinic cell ; $a = 9.2936(8)$, $b = 12.3218(9)$, $c = 13.6225(9)$ Å, $\alpha = 113.504(1)$, $\beta = 105.180(1)$, $\gamma = 95.007(1)^\circ$, space group $P\bar{1}$; $Z = 2$, $R = 0.0601$ from 3229 observed reflections. The structure is an ionic centrosymmetric dimer consisting of $[\text{Cu}_2(\text{detu})_6]^{2+}$ cations and two ClO_4^- anions. Each copper atom is pseudo - tetrahedrally coordinated by pairs of terminal thione - S and asymmetric bridging detu ligands. Each copper is trans - related to its partner across crystallographic symmetry centres. Consequently each copper(I) atom has an identical S_4 donor set all the same the structure of $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$.

The structure of S_8 crystallized in orthorhombic cell ; $a = 10.460(1)$, $b = 12.865(1)$, $c = 24.486(9)$ Å, space group $Fddd$; $Z = 16$, $R = 0.0303$ from 978 observed reflections. The molecule adopts a crownlike structure known as cyclo - S_8 , consists of two interconnected layers of four sulfur atoms each.

Furthermore, the complexes have been studied by X - ray Fluorescence Spectrometry, Infrared Spectroscopy and Elemental Analysis to support the structures. These results were interrupted with the structures.

The experimental results are shown different structure types of complexes which prepared by copper salts with substituted thioureas. The reactions between these reactants generated a variety of complexes which have unpredictable stoichiometry and stereochemistry. The copper(I) coordinations are distorted trigonal planar or distorted tetrahedral in such a manner as to minimize steric interactions either monomer or dimer. The substituted thiourea ligands coordinate to the copper atom through the sulfur atom as terminal ligands and bridging ligands.

Copper oxyanions substituted thiourea complexes and another complexes of coinage metals have been increased to study by X - ray diffraction method. Because of the great advantage of X - ray analysis as a method of chemical structure analysis which its competence to bring out some totally unexpected and surprising beautiful structure. The preliminary structure of any complexes which have been studied is one of the fundamental objectives of chemistry and is essential for a proper understanding of the physical and chemical properties of the materials.