X-Ray diffraction and Fourier transformation infrared spectroscopy studies of copper (II) thiourea chloro and sulphate complexes

Ashutosh Mishra[1], Jagrati Dwivedi[1], Kritika Shukla[1], Pramod Malviya[2]
[1]School of Physics, Devi Ahilya University, Indore-452001, India
[2]Physics Department, Govt. P. G. College, Nagda, India

Email: amishra1960@yahoo.co.in, hemu.dwi@gmail.com

Abstract. Copper (II) thiourea complexes were synthesized by chemical route method. To analyze the samples, X-Ray diffraction and Fourier transformation infrared spectroscopy method have been used. XRD analysis shows that sample is crystalline in nature and having particle size in the range of nanometres. FTIR spectroscopy shows the organic and inorganic compounds present in the sample. The X-ray diffraction pattern (XRD) using Bruker D-8 advance instrument and Infrared spectra of the complexes were obtained by KBr disc technique by using VERTEX 70 (Bruker).

1. Introduction

The aim of this paper is to determine the crystal structure and lattice parameter by X-ray diffraction technique. Complexes prepared for this experiment are $Cu(NH_2CSNH_2)_2Cl_2$ and $Cu(NH_2CSNH_2)_2(SO_4)_2$. Thiourea, having a considerably wide range of applications, is a functional organic compound similar to urea, except that the oxygen atom is replaced by a sulfur atom. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen. Thiourea ligands and their metal complexes exhibit a wide range of biological activity including anticancer, antimicrobial, antibacterial, antifungal, antimalarial and antituberculosis.[1-2]

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials or sample. For diffraction, only short wavelength X-rays in the range of few angstroms to 0.1 angstrom are used because the wavelength of X-rays is comparable to the size of atoms. The energetic X-rays can penetrate the materials and provide information about the crystal structure. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. [3] In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through the sample (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. It can identify unknown materials, it can determine the quality or consistency of a sample, and it can determine the amount of components in a mixture.[4]

2. Experimental

2.1. Powder method for XRD

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. [5-6]

2.2. Synthesis of the ligands

Stirred solution of Urea /Thiourea and $CuCl_2$.and $CuSO_4$ in methanol (10 mL) was added drop wise to Malonic acid in methanol. After the addition was completed, the stirring was continued for 12 hour. The precipitate was filtered and washed with methanol, then dried in air. [7]

$$CuCl_2 + 2(NH_2CSNH_2) \rightarrow Cu(NH_2CSNH_2)_2Cl_2$$
$$Cu(SO_4)_2 + 2(NH_2CSNH_2) \rightarrow Cu(NH_2CSNH_2)_2(SO_4)_2$$

2.3. Physical measurement

The X-ray diffraction pattern (XRD) using Bruker D-8 advance (IUC, Indore), X-ray powder diffractometer was obtained with Ni-filtered Cu Kα radiation (λ=1.54A°) having voltage 40kV and current 100mA. The X-ray was detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector.1).

Infrared spectra of the complexes were obtained by KBr disc technique by using VERTEX 70 (Bruker) (IUC, Indore) in the range of 4000-400 cm-1. Its innovative design results in the highest flexibility and highest performance. This advanced DigiTect technology prevents external signal disturbance and guarantees the highest signal-to-noise ratio.

3. Results and discussion

The diffraction pattern of complexes recorded between 2θ ranging from 10° to 80°. The crystalline size of the samples is estimated using the Scherrer's formula. According to Scherrer's equation [2], the particle size is given by $t = 0.9\ \lambda/B\ Cos\theta$, where t is the crystal thickness (same units as λ), B is half width (in radians) of the diffraction the line, θ is the Bragg angle and λ is the wavelength. Lattice parameter for simple cubic crystal structure is determined by $a^2 = \lambda^2(h^2+k^2+l^2)/4\sin\theta$. The determined particle size and lattice parameter are shown in table 1 and XRD pattern shown in figure 1.

Table 1. Particle size and Lattice parameter of copper (II) thiourea complexes

S. No.	Complexes	Particle size t (nm)	Lattice parameter a (Å)
1.	$[Cu(II)(NH_2CSNH_2)]Cl_2$	20.83	8.02
2.	$[Cu(II)(NH_2CSNH_2)](SO_4)_2$	07.43	14.35

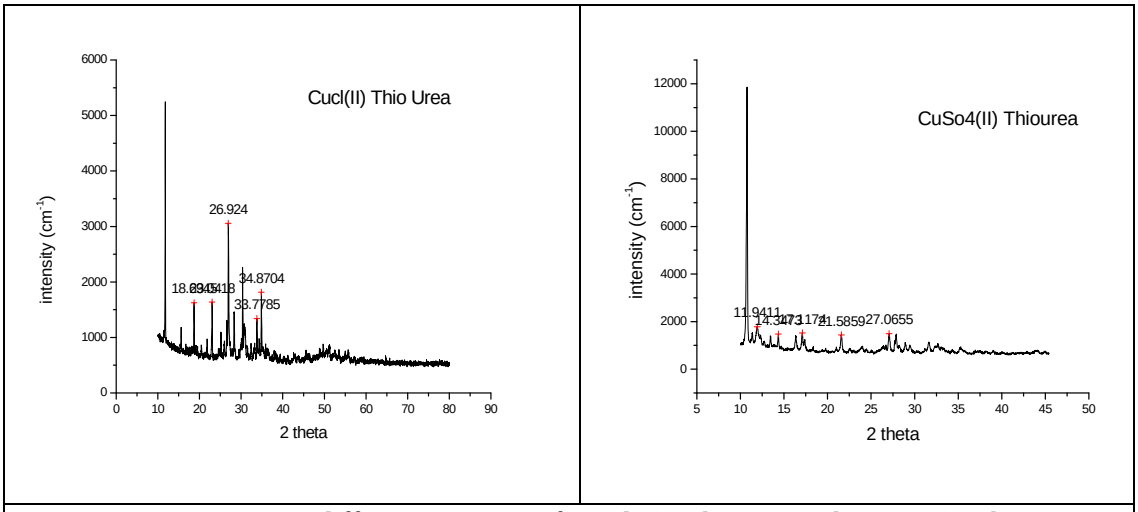

Figure 1. X-Ray diffraction pattern of $CuCl_2$ (II) thiourea and $CuSO_4$ (II) thiourea.

Figure 2 represents selected Infra red absorption bands of thiourea and its Cu(II) complexes, The infra red spectra of free legend, i.e., thiourea and its complexes are complicated as a number of vibrations are observed. The assignments of the important vibrational band have been made by analogy to other reported complexes. In table 2, the data of copper complexes have been reported.

Table 2. Selected Infra red absorption bands of thiourea and its complexes with Cu

Thiourea		**$CuCl_2$+ Thiourea**		**$CuSO_4$+ Thiourea**	
Band intensity	**assignment**	**Band intensity**	**assignment**	**Band intensity**	**assignment**
3364	(N-H)	3282	(N-H)	3303	(N-H)
3163	(C-H)	2767	(C-H)	2781	(C-H)
1605	(C=N)	1541	(C=N)	1564	(C=N)
729	(C-O)	1631	(C-O)	1633	(C-O)
593	(C-N)	1622	(Cu-O)	1627	(Cu-O)
		1174	(C=S)	1085	(C=S)

4. Conclusion

On the basis of the above discussion, table 3.1 Figure 3.1 shows the suggested structure for copper (II) complexes are cubic and crystalline in nature. Range of particle size is 7.43 to 20.83nm and range of lattice parameter is 8.02 to 14.35Å. FTIR clearly showing in thiourea (N-H), (C-H), (C=N) and (C-O) groups are present .The wavelength lie between 3364 to 593cm^{-1}. In $CuCl_2$+thiourea (N-H), (C-H), (C=N), (C-O), (Cu-O) and (C=S) groups are present. The wavelengths lie between 3382 to 1174 cm^{-1}. Also FTIR showing in $CuSO_4$+thiourea (N-H), (C-H), (C=N), (C-O), (Cu-O) and (C=S) groups are present. The wavelengths lie between 3303 to 1085 cm^{-1}.

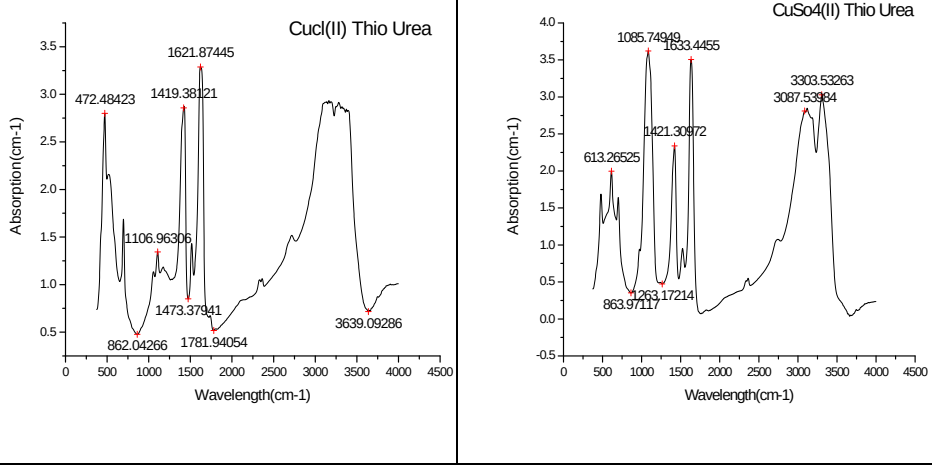

Figure 2. FTIR representation of $CuCl_2$ (II) Thiourea and $CuSO_4$ (II) Thiourea.

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