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X-ray diffraction study of copper and cobalt complexes of chloroaniline dithiocarbamate

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Abstract
Considering the importance of copper and cobalt and its properties to form complexes having diverse applications, present investigation was carried out. The complexes of copper and cobalt were synthesized using chloroaniline (Ortho and para) dithiocarbamate by chemical method and their properties were studied using XRD technique. The results revealed that the particle size of copper and cobalt complexes was found 69.4 nm and 125.3 nm; and 59.1 nm and 117.3 nm, respectively. The particle size of p-chloroanilinne complex was found higher as compared to the o-chloroaniline complex of both copper and cobalt. Further, the lattice constant of copper and cobalt were found 4.76 Å and 6.74 Å; and 8.67 Å and 8.28 Å, respectively. It has been observed that the lattice constant of p-chloroanilinne complex was found higher as compared to the o-chloroaniline complex for copper whereas higher lattice constant was recorded for o-chloroaniline cobalt complex. The investigation further showed that all the synthesized complexes are crystalline in nature, electrically neutral and thermally stable.

Keywords: X-ray diffraction, XRD, copper, cobalt, chloroaniline, dithiocarbamate

Introduction
Copper and cobalt elements lie between s and p block elements of the periodic table and are known as transition elements (Bradberry, 2016) [3]. A transition metal complexes consist of a transition metal (such as cobalt and copper) coordinated or bonded with one or more ligand like natural or anionic nonmetal species. Transitional metal complexes are important in catalysis, material synthesis (Rafique *et al*., 2010; Abu-Dief and Mohamed, 2015) [10, 1]. Photochemistry and biological systems and possess diverse chemical, optical and magnetic properties. Transition metal ions usually form complexes with well- defined number of ligands. The complexes exhibit many important properties and has wider applications. Before application it is essential to study the properties of such metal complexes with X-ray diffraction (XRD) technique. XRD is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample (Dang *et al*., 2011) [4]. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. 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-spacing 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. X-ray diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology (Al-Jaroudi *et al*., 2007) [2].
Considering the importance of copper and cobalt and its properties to form complexes having diverse applications, present investigation was carried out. In present study, copper and cobalt complexes were synthesized using chloroaniline (Ortho and para) dithiocarbamate by chemical method and their properties were studied using XRD technique.

Materials and Methods

Study site

The experiment was conducted at the Department of Physics, Devi Ahilya University, Indore (MP) which lies at 22.716°N and 75.871°E coordinates.

Synthesis of copper and cobalt metal complexes

The copper and cobalt complexes were prepared with the ligands of Chloroaniline. Aniline is an organic compound having a phenyl group attached to an amino group. The dithiocarbamate is a functional group and is the analog of a carbamate in which both oxygen atoms are replaced by sulfur atoms. The ligands of chloroaniline were prepared by adding 0.01 M of chloroaniline to solution of 0.016 M NaOH in 15 ml distilled water with continuous stirring. The mixture was refluxed for about 2 hours. The resultant mixture was cooled in ice. Then 0.01 M carbon disulphide was added dropwise. The formed precipitate was filtered off, washed with acetone and dried in vacuum. The Cu/Co complexes were prepared with ligands of Chloroaniline dithiocarbamate. The Cu/Co complexes with ligands were prepared by mixing 1:2 molar quantities of respective metal salt and ligand. These two solutions were mixed with continuous stirring. The complex produced in the form of precipitate was filtered off, washed with acetone and water in equal quantities (1: 1). The products were dried in vacuum oven. By following this process a total four complexes (2 each of copper and cobalt with o-Chloroaniline and p-Chloroaniline) were synthesized (Table 1). The synthesized products were used for XRD studies.

Table 1: Chloroaniline dithiocarbamate complexes of copper and cobalt

Cu(II)/Co(II) complex of Chloroaniline dithiocarbamate	Molecular formula
Cu (o-Chloroaniline dithiocarbamate)$_2$	Cu $(C_7H_4S_2NCl)_2$
Cu (p-Chloroaniline dithiocarbamate)$_2$	Cu $(C_7H_4S_2NCl)_2$
Co (o-Chloroaniline dithiocarbamate)$_2$	Co $(C_7H_4S_2NCl)_2$
Co (p-Chloroaniline dithiocarbamate)$_2$	Co $(C_7H_4S_2NCl)_2$

XRD study of copper and cobalt complexes

The four synthesized complexes were studied and characterized at room temperature. For this purpose the Cu and Co Kα radiation was used during XRD investigation. The XRD pattern of 2θ ranging between 10° and 60° were recorded. The XRD measurements were carried out on Bruker D-8 Advance X-ray diffractometer. The indexing of the XRD pattern was carried out using the Joint Committee for Powder diffraction optical phenomenon computer code (JCPDF). The lattice constants of synthesized complexes were determined using Bragg's equation. The particle size of all the complexes were also determined using the Scherrer's equation.

Results

XRD study of copper complexes

The XRD patterns of the copper complexes synthesized with para and ortho chloroaniline dithiocarbamate is presented in Fig. 1 and Fig. 2. Similarly, The XRD patterns of the cobalt complexes synthesized with para and ortho chloroaniline dithiocarbamate is presented in Fig. 3 and Fig. 4.

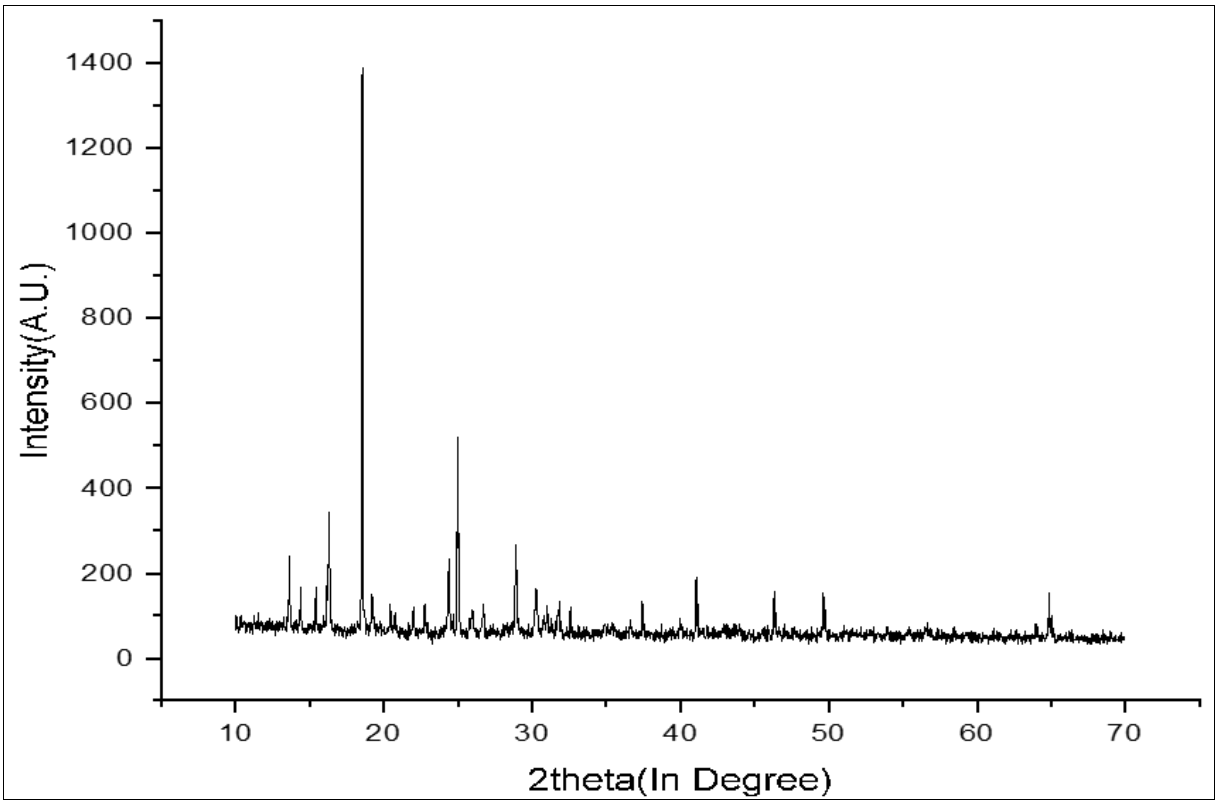

Fig 1: XRD Pattern of Cu(o-Chloroaniline dithiocarbamate)$_2$ complex

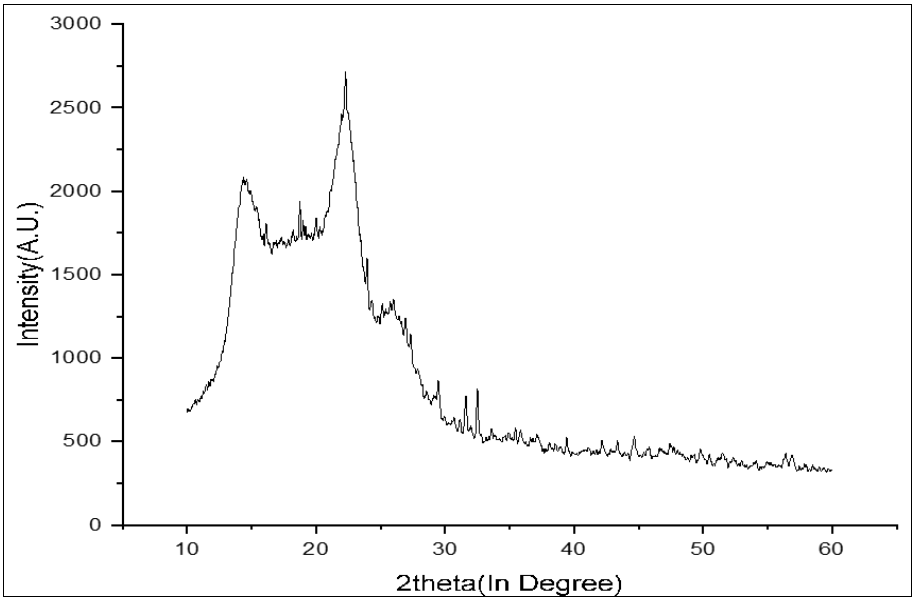

Fig 2: XRD Pattern of Cu(o-Chloroaniline dithiocarbamate)$_2$ complex

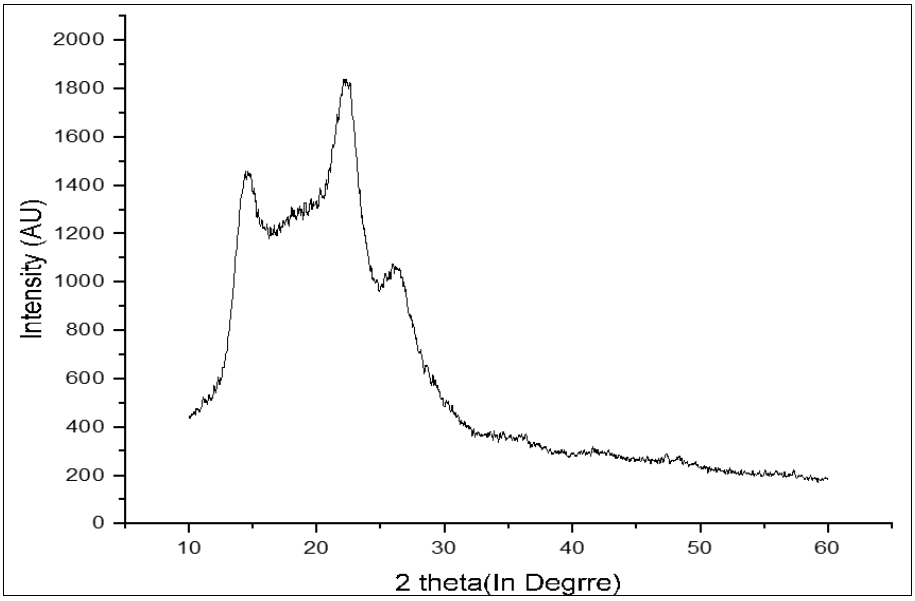

Fig 3: XRD Pattern of Co(o-Chloroaniline dithiocarbamate)$_2$ complex

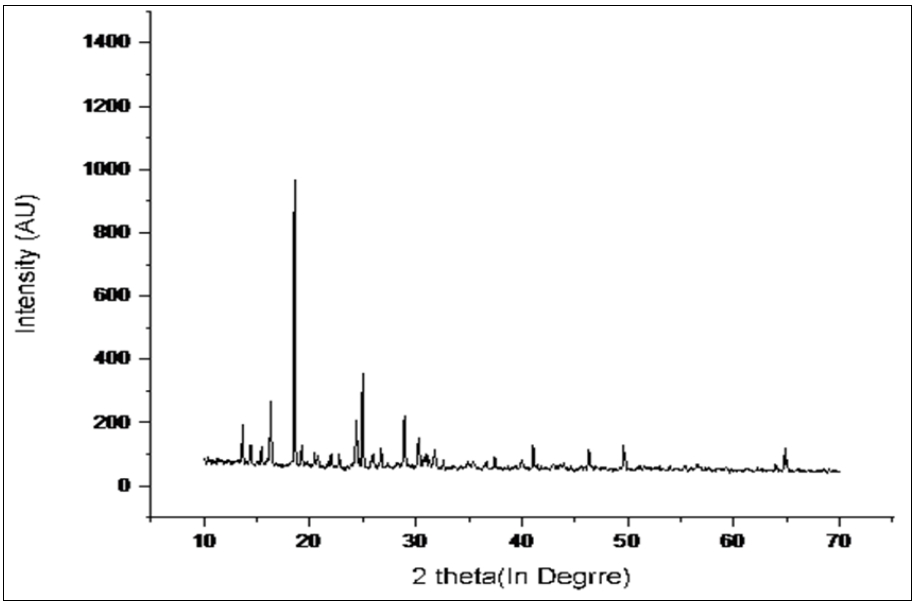

Fig 4: XRD Pattern of Co(p-Chloroaniline dithiocarbamate)$_2$ complex

Particle size of copper and cobalt complexes

The particle size of the synthesized copper and cobalt complexes under study is presented in Table 2. The particle size of Cu(II) complexes of o-Chloroaniline dithiocarbamate and p-Chloroaniline dithiocarbamate found 69.4 nm and 125.3 nm, respectively. The particle size of p-Chloroaniline dithiocarbamate found higher as compared to the o-Chloroaniline dithiocarbamate. Similarly, the particle size of Co(II) complexes of o-Chloroaniline dithiocarbamate and p-Chloroaniline dithiocarbamate found 59.1 nm and 117.3 nm, respectively. The particle size of cobalt p-Chloroaniline dithiocarbamate complex was found higher as compared to the cobalt o-Chloroaniline dithiocarbamate. The synthesized copper complexes showed noticeable difference in particle size (Table 2). The earlier reported findings are found in line with the present results (Mishra *et al*., 2010; Mishra and Jain, 2013; Sharma *et al*., 2017; Sharma *et al*., 2019) [9, 7, 12, 11]. The results obtained by Malviya *et al*. (2014) [5] with respect to the particle size variation are inline with the present observations.

Table 2: Particle size and lattice constant of synthesized complexes copper and cobalt

Cu(II)/Co(II) complex of Chloroaniline dithiocarbamate	Particle size (nm)	Lattice constant (Å)
Cu-1	69.4	4.76
Cu-5	125.3	6.74
Co-4	59.1	8.67
Co-5	117.3	8.28

Lattice constant of copper and cobalt complexes

The Lattice constant for various copper and cobalt complexes under study is presented in Table 2. The Lattice constant of Cu(II) complexes for o-Chloroaniline dithiocarbamate and p-Chloroaniline dithiocarbamate found 4.76 Å and 6.74 Å, respectively. The lattice constant of copper p-Chloroaniline dithiocarbamate found higher as compared to the copper o-Chloroaniline dithiocarbamate. Similarly, the lattice cconstant of Co(II) complexes of o-Chloroaniline dithiocarbamate and p-Chloroaniline dithiocarbamate found 8.67 Å and 8.28 Å, respectively. The lattice constant of cobalt o-Chloroaniline dithiocarbamate complex was found higher as compared to the cobalt p-Chloroaniline dithiocarbamate. The synthesized copper and cobalt complexes showed noticeable difference in lattice constant. The synthesized copper complexes did not show noticeable difference in Lattice constant (Table 2). The earlier results are similar to the present findings (Mishra *et al*., 2010; Mishra and Jain, 2013; Sharma *et al*., 2017; Sharma *et al*., 2019) [9, 7, 12, 11]. However, the synthesized cobalt complexes showed noticeable difference in Lattice constant due to the nature and position of ligand and ligand forming group, respectively (Table 1). The earlier reported works are in conformity with present findings (Malviya *et al*., 2014) [5].

Structures of synthesized copper [Cu(II)] and cobalt [Co(II)] complexes

Based on the X ray diffraction studies, particle size and lattice constant of the obtained Cu(II) and Co(II) complexes the structures for the same were suggested. Considering the chemistry of reactants, ligands and copper (II) / cobalt (II) ion and obtained results of complexes, the structures of the complexes are presented in Fig. 5 to Fig. 8. The structures reported earlier by Mishra Jain (2013) [9] and Sharma *et al*. (2019) [11] for copper complexes are in conformity with present findings. Similarly, the findings of Macro *et al*. (2000) [6], Mishra *et al*. (2012) [8] and Malviya *et al*. (2014) [5] for structures of copper complexes are in line with the findings of present investigation.

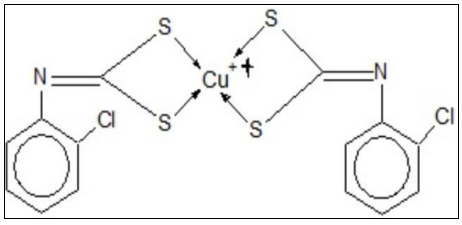

Fig 5: Suggested Structure of Cu(o-Chloroaniline dithiocarbamate)$_2$

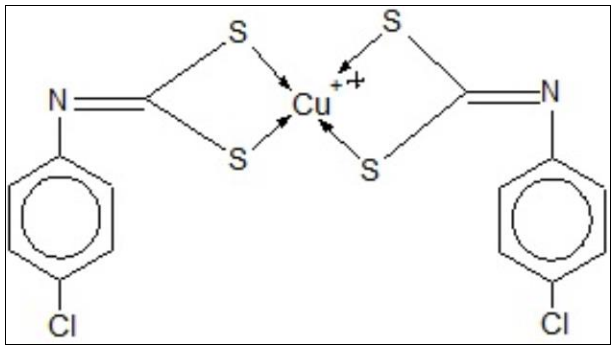

Fig 6: Suggested structure of Cu(p-Chloroaniline dithiocarbamate)$_2$

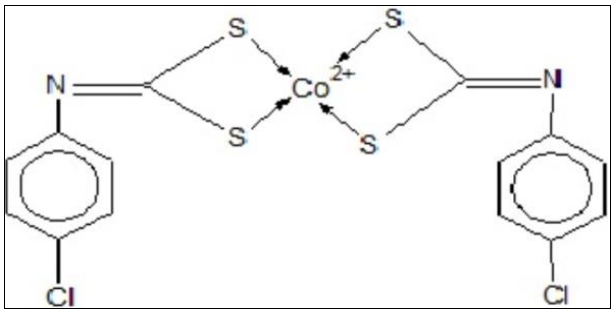

Fig 7: Suggested structure of Co(p-Chloroaniline dithiocarbamate)$_2$

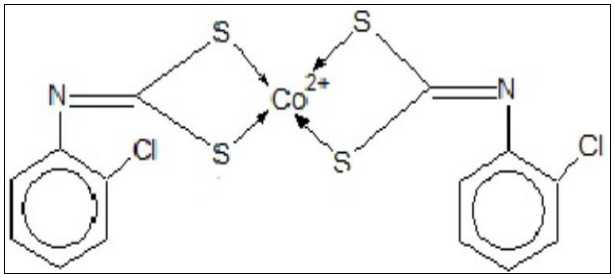

Fig 8: Suggested structure of Co(o-Chloroaniline dithiocarbamate)$_2$

The X-ray diffraction investigation revealed that the particle size of copper and cobalt complexes was found 69.4 nm and 125.3 nm; and 59.1 nm and 117.3 nm, respectively. The particle size of p-chloroanilinne complex was found higher as compared to the o-chloroaniline complex of both copper and cobalt. Further, the lattice constant of copper and cobalt were found 4.76 Å and 6.74 Å; and 8.67 Å and 8.28 Å, respectively. It has been observed that the lattice constant of p-chloroanilinne complex was found higher as compared to the o-chloroaniline complex for copper whereas higher lattice

constant was recorded for o-chloroaniline cobalt complex. The investigation further showed that all the synthesized complexes are crystalline in nature, electrically neutral and thermally stable. Thus, the applications of XRD technique for determination of particle size and lattice constant of coper and cobalt complexes synthesized with chloroaniline dithiocarbamate were found successful.

Conclusion

The present study focused on the synthesis and characterization of copper and cobalt complexes with chloroaniline dithiocarbamate ligands using X-ray diffraction (XRD) techniques. The synthesized complexes, including both ortho- and para-chloroaniline derivatives, demonstrated a range of structural properties:

1. **Particle Size Variations:** The XRD analysis revealed that the particle sizes of the copper and cobalt complexes varied between 59.1 nm to 125.3 nm. Specifically, the p-chloroaniline complexes exhibited larger particle sizes compared to their ortho-chloroaniline counterparts for both copper and cobalt. This suggests that the choice of ligand affects the crystallite size of the resulting complexes.
2. **Lattice Constants:** The lattice constants for copper and cobalt complexes ranged from 4.76 Å to 8.67 Å. Notably, the lattice constant for p-chloroaniline copper complexes was higher compared to the ortho-chloroaniline variants, while the opposite trend was observed for cobalt complexes. This variation in lattice constants indicates the influence of ligand orientation on the crystal structure.
3. **Crystalline Nature and Stability:** All synthesized complexes were found to be crystalline, electrically neutral, and thermally stable. This confirms their suitability for various applications where stability and defined crystalline structure are critical.

The XRD study successfully provided insights into the structural characteristics of the synthesized copper and cobalt complexes, demonstrating that ligand type and orientation significantly affect particle size and lattice constants. The study underscores the effectiveness of XRD in analyzing metal-ligand complex structures and highlights the importance of ligand selection in tailoring the properties of metal complexes for specific applications.

References

1. Abu-Dief AM, Mohamed IM. A review on versatile applications of transition metal complexes incorporating Schiff bases. Beni-Suef Univ J Basic Appl. Sci. 2015;4(2):119-133.
2. Al-Jaroudi SS, Ul-Hamid A, Mohammed ARI, Saner S. Use of X-ray powder diffraction for quantitative analysis of carbonate rock reservoir samples. Powder Technol. 2007;175(3):115-121.
3. Bradberry SM. Metals (Cobalt, copper, lead, mercury). Medicine. 2016;44(3):182-184.
4. Dang Z, Le Song X, Qing Guo X, Yun Du F, Yang J, Yang J, *et al*. Applications of powder X-ray diffraction to inclusion complexes of cyclodextrins. Curr Org Chem. 2011;15(6):848-861.
5. Malviya PK, Sharma P, Mishra A. XRD and X-ray, K-absorption Near Edge Studies of cobalt, nickel ferrites. Int J Sci. Res Phys Appl. Sci. 2014;2(1):1-4.
6. Marco JF, Gancedo JR, Gracia M, Gautier JL, Rios E, Berry FJ, *et al*. Characterization of the nickel cobaltite, NiCo2O4, prepared by several methods: an XRD, XANES, EXAFS, and XPS study. J Solid State Chem. 2000;153(1):74-81.
7. Mishra A, Jain G. XRD and XANES studies of copper complexes using (diethyl 4-amino-1-phenyl-1H-pyrazole-3,5-dicarboxylate) as ligand. In: AIP Conference Proceedings. 2013 Jun;1536(1):811-812.
8. Mishra A, Ninama S, Mishra N. XRD, SEM and EXAFS investigation of cobalt (II) macrocyclic complexes. In: AIP Conference Proceedings. 2012 Jun;1447(1):163-164.
9. Mishra A, Samrath Ninama K, Sura. XRD studies of copper macrocyclic complexes. Search Res. 2010;1:1.
10. Rafique S, Idrees M, Nasim A, Akbar H, Athar A. Transition metal complexes as potential therapeutic agents. Biotechnol. Mol. Biol Rev. 2010;5(2):38-45.
11. Sharma M, Tripathi J, Yadav AK, Jha SN, Mishra A, Shrivastava BD, *et al*. Structural characterizations of copper complex using X-ray diffraction and X-ray absorption fine structure spectroscopy. In: AIP Conference Proceedings. 2019 Jul;2115(1):030418.
12. Sharma PK, Mishra A, Malviya V, Kame R, Malviya PK. X-ray diffraction and X-ray K absorption near edge studies of copper (II) complexes with amino acids. In: Journal of Physics: Conference Series. 2017;836(1):012039.