

## EXAFS and XANES study of cobalt complexes synthesized with ligands of chloroaniline and fluoroaniline dithiocarbamate

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### Abstract

The cobalt [Co(II)] complexes (03 nos) were synthesized using various ligands of chloroaniline and fluoroaniline dithiocarbamate. The synthesized Co(II) complexes were studied for different physical, structural and chemical parameters using XANES and EXAFS conducted on DXAFS beamline BL-8, Indus 2, Synchrotron source. The EXAFS spectra recorded for Co(II) complexes were used for computation of the bond length, chemical shift, effective nuclear charge, principal absorption maxima and edge width using Athena and Origin 6.0 software. The results of the study revealed that, the synthesized cobalt complexes showed higher value for K-absorption edge ( $E_k$ ) and Absorption maxima ( $E_A$ ) than Co metal. The Chemical shift ( $\Delta E_k$ ) value for Co(II) complexes were ranged 1.17-4.52 eV. The Shift of principal absorption maxima ( $\Delta E_A$ ) value for Co(II) complexes were ranged 0.65-4.18 eV. The Edge width of three different complexes of cobalt [Co(II)] synthesized with ligands of chloroaniline/fluoroaniline dithiocarbamate ranged 6.60-11.14 eV. The bond length calculated by LSS method ranged 1.41-2.20 Å for different complexes whereas the bond length calculated by FT method ranged 1.26-3.06 Å. The Lytle's method and Levy's method gives the bond length ranged 2.44-3.08 Å and 1.97-2.58 Å, respectively for studied complexes.

**Keywords:** XANES, EXAFS, absorption maxima, bond length, k-absorption edge, chemical shift, chloroaniline, fluoroaniline, dithiocarbamate, co (ii) complex, ligands

### Introduction

X-rays are high-energy photons that are produced when electrons make transitions from one atomic orbit to another (Chang *et al.*, 1997) [5]. X-rays have been used as powerful tools in analytical, physical, chemical, biological and structural characterization of matter (Attwood and Sakdinawat, 2017) [3]. X-rays are characterized by the relatively short wavelengths of 0.01 Å to 100 Å with hard X-rays on one end and soft X-rays on the other they are conventionally produced by either the conversion of the kinetic energy of charged particles into radiation or the excitation of atoms in a target upon which fast moving electrons impinge (Chang *et al.*, 1997) [5]. X-ray Absorption Fine Structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. XAFS can be applied not only to crystals, but also to materials that possess little or no long-range translational order: amorphous systems, glasses, quasicrystals, disordered films, membranes, solutions, liquids, metalloproteins – even molecular gases. This versatility allows it to be used in a wide variety of disciplines: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology (Reich *et al.*, 2007) [38]. X-ray absorption spectroscopy (XAS) has been extensively used in the recent past to obtain information about molecular structure *viz.*, the valency, bond type, ionic charges, coordination stoichiometry etc. in inorganic compounds and complexes. The studies on XAFS, which ultimately yields information regarding the nearest

neighbours of the central metal ions, i.e., bond length etc., in an inorganic compound and complex has shown great promise (Reich *et al.*, 2007; Alain *et al.*, 2009) [38, 1]. Specifically, XAFS is the modulation of an atom's X-ray absorption probability due to the chemical and physical state of the atom. XAFS spectra are especially sensitive to the formal oxidation state, coordination chemistry, and the distances, coordination number and species of the atoms immediately surrounding the selected element. Because of this dependence, XAFS provides a practical, and relatively simple, way to determine the chemical state and local atomic structure for a selected atomic species (Reich *et al.*, 2007) [38].

The X-ray absorption near edge structure (XANES) constitutes 10-5 eV above  $E_0$  in the absorption spectrum. In this region, multiple scattering of the photoelectron with the first and even higher co-ordination shells dominates. These features also arise from transition of the bound electron to empty states of high density in the conduction band or to the available ant bonding orbital of appropriate symmetry (Koningsberger and Prins, 1988) [20]. The XANES is the part of the absorption spectrum near an absorption edge, ranging from approximately 0 to 50 eV relative to the edge energy. The shape of the absorption edge is related to the density of states available for the excitation of the photoelectron. Therefore, the binding geometry and the oxidation state of the atom affect the XANES part of the

absorption spectrum. This absorption edge has the properties that it is linear and smooth below the absorption edge, increases sharply at the edge (like a step), and then oscillates above the edge. The application of X-ray spectroscopy in structural investigation of metal complexes is widely used. The transition metal complexes were also addressed and number of researchers has studied the X-ray absorption spectra at the K-edge of these metals. Recent studies showed the effectiveness of XRD, EXAFS and XANES to study the copper and cobalt complexes (Geete *et al.*, 2020a; Geete *et al.*, 2020b; Geete *et al.*, 2021) [12, 13, 11].

Uchikoshi and Shinoda (2019) [40] determined the structures of Co(II) complexes formed with chlorine in hydrochloric acid solutions using X-ray absorption spectroscopy. Martins *et al.* (2018) [28] studied the copper complex geometries adsorbed on natural illite by combining EXAFS and ab initio study. Mishra and Patil (2016) [30] carried out synthesis of Cu-doped MnBi materials and studied their properties using XRD and XANES techniques. Mishra *et al.* (2014a) [32] conducted comparative study of experimental and theoretical analysis of EXAFS data of copper complexes using FT method. Mishra *et al.* (2014b) [31] synthesized cobalt complexes with amino pyrazole dicarboxylate ligand and studied the characteristics using XRD, IR and XAFS techniques.

Cobalt is a chemical element is a weakly reducing metal that is protected from oxidation by a passivating oxide film. The molecular compounds and polyatomic ions of cobalt are classified as coordination complexes, that is, molecules or ions that contain cobalt linked to several ligands. As the cobalt lying between s and p block elements of the periodic table are known as transition elements. Transition metal complexes consist of a transition metal coordinated or bonded with one or more ligand like natural or anionic nonmetal species. Transitional metal complexes are important in catalysis, material synthesis. Photochemistry and biological systems and possess diverse chemical, optical and magnetic properties. Transition metal ions usually form complexes with well- defined number of ligand. Considering the importance of cobalt and its properties to form complexes, present investigation was carried out. The metal complexes of cobalt has been synthesised by chemical method and studied using XANES and EXAFS techniques to explore the potential application of these metals in various fields.

## Material and Methods

### Preparation of ligands and cobalt [Co (II)] complexes

In present investigation chloro/fluoroaniline dithiocarbamate ligands were synthesized and used as complexing agent for Co (II). The ligands were prepared by adding 0.01 M of chloro/fluoroaniline to 0.016 M solution of NaOH in 15 ml distilled water with continuous stirring. The mixture was refluxed for two hours and further it was cooled in ice. The ligands were precipitated by drop wise addition of carbon disulphide. The formed ligands were extracted by ether, filtered, washed with acetone and dried in vacuum.

**Table 1:** Details of Cobalt [Co(II)] mixed ligand complexes

Abbreviation	Complex name	Molecular formula
Co-Cl-o	Co(o-Chloroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> S <sub>2</sub> NCl) <sub>2</sub>
Co-Cl-p	Co(p-Chloroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> S <sub>2</sub> NCl) <sub>2</sub>
Co-F-p	Co(p-Fluoroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> S <sub>2</sub> NF) <sub>2</sub>

The cobalt [Co(II)] complexes with synthesized ligands were prepared by mixing 1:2 molar quantities of metal salt and ligand. The cobalt chloride salt (CoCl<sub>2</sub>) was dissolved in distilled water and ligand chloro/fluoroaniline dithiocarbamate was dissolved in ethanol. The 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 product was dried in vacuum. The fine powder of the formed complexes was used for further analytical studies (Table 1).

### XANES and EXAFS study of cobalt complexes

The EXAFS studies of the synthesized cobalt [Co(II)] complexes were carried out at RRCAT, UGC-DAE Consortium for Scientific Research, Indore (M.P.). The EXAFS spectra *viz.* absorption ( $\mu E$ ) against incident energy ( $E$ );  $K^2 \chi(K)$  against  $K$ ;  $n$  against  $K$ ; FT of  $K^2 \chi(K)$  against  $R$ ; and  $E$  against  $Q$  were recorded on DXAFS beamline BL-8, Indus 2, Synchrotron source. The recorded EXAFS spectra of complexes under study were used for XANES studies using Athena and Origin 6.0 software for result interpretation. The beam line was calibrated before recording the spectra for the Co metal and its synthesized complexes following the standard method as outlined by Gaur *et al.* (2011) [8]. The EXAFS spectra recorded for Co(II) complexes were used for computation of the bond length, chemical shift, effective nuclear charge, principal absorption maxima and edge width as follows:

The K-absorption edge (eV) for Co metal and its different complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate were determined directly (Gurman *et al.*, 1984) [15]. The Absorption maxima ( $E_A$ ) for Co metal and its different complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate were determined directly from EXAFS spectra (Maeda, 1987) [26]. The Chemical shift ( $\Delta EK$ ) is the difference in energy between complex ( $E_{Complex}$ ) and metal ( $E_{Metal}$ ). As the energy absorbed by the complex is more than energy absorbed by pure metal, the Chemical shift was calculated by subtracting  $E_{Metal}$  from  $E_{Complex}$  and expressed in eV (Lee *et al.*, 1977) [21]. The Effective nuclear charge (ENC) for different complexes of Co(II) synthesized with ligands of chloro/fluoroaniline dithiocarbamate were obtained from EXAFS spectra (Joshi *et al.*, 2007) [17]. The Shift of principal absorption maxima ( $\Delta EA$ ) is the difference in absorption maxima between complex ( $EA_{Complex}$ ) and metal ( $EA_{Metal}$ ). As the absorption maxima of the complex is more than pure metal, the Shift of principal absorption maxima ( $\Delta EA$ ) can be calculated by subtracting  $EA_{Metal}$  from  $EA_{Complex}$  and expressed in eV (Joshi *et al.*, 2007) [17]. The Edge width is the difference in absorption maxima ( $EA$ ) and K-absorption edge ( $EK$ ). As the absorption maxima of the complex is more than K-absorption edge ( $EK$ ). Therefore, the Edge width of a complex can be calculated by subtracting  $EK$  from  $EA$  and expressed in eV (Lu and Stern, 1983) [23]. The wave vector  $K$  values obtained from the EXAFS maxima and minima of K-absorption edge at corresponding  $n$  values for various cobalt [Co(II)] complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate ligands was obtained from EXAFS spectra (Joshi *et al.*, 2000) [18]. The values of Energy ( $E$ ) and  $Q$  were used to compute the graph and to determine the bond length of the cobalt complexes. From

the values of the K at corresponding n and energy (E) at different Q, the bond lengths of the complexes were determined by various methods *viz.* LSS (Lytle *et al.*, 1975), FT (Mishra *et al.*, 2011)<sup>[29, 34]</sup>, Lytle (Lytle, 1965)<sup>[24]</sup> and Levy (Levy, 1965)<sup>[22]</sup>.

## Results and Discussion

The EXAFS spectra of synthesized cobalt [Co(II)] complexes with ligands of chloro/fluoroaniline dithiocarbamate were recorded on DXAFS beamline BL-8, Indus 2, Synchrotron source at RRCAT, Indore. The EXAFS spectra *viz.* absorption ( $\mu E$ ) against incident energy (E) (Fig. 1);  $k^2 \chi(k)$  against k (Fig. 2); n against k (Fig. 3); FT of  $K^2 \chi(k)$  against R (Fig. 4); and E against Q (Fig. 5) were recorded and plotted. Similarly, the EXAFS spectra *viz.* absorption ( $\mu E$ ) against incident energy (E) (Fig. 1);  $k^2 \chi(k)$  against k (Fig. 2) and FT of  $K^2 \chi(k)$  against R (Fig. 4) for cobalt [Co(II)] metal also recorded and plotted. The EXAFS spectra recorded for Co(II) complexes were used for computation of the bond length, chemical shift, effective nuclear charge, principal absorption maxima and edge width. Each parameter determined are presented in Table 2 and described in detail as follows:

### K-absorption Edge ( $E_k$ )

The K-absorption edge (eV) for Co metal and its three different complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate are presented in Table 2. The results showed that, all the cobalt complexes synthesized and studied showed higher value for K-absorption edge ( $E_k$ ) than Co metal. The K-absorption edge value for Co metal was recorded 7709.4 eV. The K-absorption edge value for Co(II) complexes were ranged 7710.6-7713.9 eV. The Co(II) complex synthesized with the ligand of p-chloroaniline dithiocarbamate (Co-Cl-p) showed highest value for K-absorption edge followed by the cobalt complex [Co(II)] synthesized with ligand of o-chloroaniline dithiocarbamate (Co-Cl-o) and p-fluoroaniline dithiocarbamate (Co-F-p). The higher values of the K-absorption edge of Co(II) complexes than Co metal are attributed to the change in the structure and formation of the bonds with the ligands. Similar observations were reported by many researchers while studying the various metal complexes (Geete *et al.*, 2021; Geete *et al.*, 2019; Uchikoshi and Shinoda, 2019)<sup>[11, 10, 40]</sup>.

### Absorption maxima ( $E_A$ )

The Absorption maxima ( $E_A$ ) for Co metal and its three different complexes synthesized with ligands of nitroaniline dithiocarbamate are presented in Table 2. The results showed that, all the cobalt complexes synthesized and studied showed higher value for Absorption maxima ( $E_A$ ) as compared to the Co metal. The Absorption maxima ( $E_A$ ) value for Co metal was recorded 7719.9 eV. The Absorption maxima ( $E_A$ ) value for Co(II) complexes were ranged 7720.5-7724.1 eV. The Co(II) complex synthesized with the ligand of o-chloroaniline dithiocarbamate (Co-Cl-o) showed highest value for Absorption maxima ( $E_A$ ) followed by p-fluoroaniline dithiocarbamate (Co-F-p) and p-chloroaniline dithiocarbamate (Co-Cl-p). The higher values of

the Absorption maxima ( $E_A$ ) of Co(II) complexes than Co metal are attributed to the change in the structure and formation of the bonds with the ligands. Similar observations were reported by many researchers while studying the various metal complexes (Magini, 2018; Geete *et al.*, 2021)<sup>[27, 11]</sup>.

**Table 2:** XANES data for the K-absorption edge of cobalt mixed ligand complexes.

Complex	EK1(eV)	E <sub>A</sub> (eV)	ΔEK(eV)	ENC	ΔE <sub>A</sub> (eV)	Edge-width(eV)
Co metal	7709.4	7719.9	-	-	-	10.47
Co-Cl-o	7712.9	7724.1	3.51	-	4.18	11.14
Co-Cl-p	7713.9	7720.5	4.52	-	0.65	6.61
Co-F-p	7710.1	7721.5	1.17	-	1.66	10.91

### Chemical shift ( $\Delta EK$ )

The Chemical shift ( $\Delta EK$ ) of three different complexes of cobalt [Co(II)] synthesized with ligands of chloro/fluoroaniline dithiocarbamate is presented in Table 2. The results showed that, the Chemical shift ( $\Delta EK$ ) value for Co(II) complexes were ranged 1.17-4.52 eV. The Co(II) complex synthesized with the ligand of p-chloroaniline dithiocarbamate (Co-Cl-p) showed highest value for Chemical shift ( $\Delta EK$ ). Whereas the cobalt complex [Co(II)] synthesized with ligand of p-fluoroaniline dithiocarbamate (Co-F-p) showed lowest value of Chemical shift ( $\Delta EK$ ). The variation in values of the Chemical shift ( $\Delta EK$ ) for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Chemical shift ( $\Delta EK$ ) values for same metal in complexation with different and similar ligands (Bianconi *et al.*, 2012; Geete *et al.*, 2021)<sup>[4, 11]</sup>.

### Effective nuclear charge (ENC)

No effective nuclear charge (ENC) for three different complexes of Co(II) synthesized with ligands of chloro/fluoroaniline dithiocarbamate was detected (Table 2).

### Shift of principal absorption maxima ( $\Delta E_A$ )

The Shift of principal absorption maxima ( $\Delta E_A$ ) of three different complexes of cobalt [Co(II)] synthesized with ligands of chloro/fluoroaniline dithiocarbamate is presented in Table 2. The results showed that, the Shift of principal absorption maxima ( $\Delta E_A$ ) value for Co(II) complexes were ranged 0.65-4.18 eV. The Co(II) complex synthesized with the ligand of o-chloroaniline dithiocarbamate (Co-Cl-o) showed highest value for Shift of principal absorption maxima ( $\Delta E_A$ ). The cobalt complex [Co(II)] synthesized with ligand of p-chloroaniline dithiocarbamate (Co-Cl-p) showed lowest value of Shift of principal absorption maxima ( $\Delta E_A$ ). The variation in values of the Shift of principal absorption maxima ( $\Delta E_A$ ) for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Shift of principal absorption maxima ( $\Delta E_A$ ) values for same metal in complexation with

different and similar ligands (Mishra *et al.*, 2012c; Jiang *et al.*, 2019; Geete *et al.*, 2021) [35, 16, 11].

**Edge width (EA- EK)**

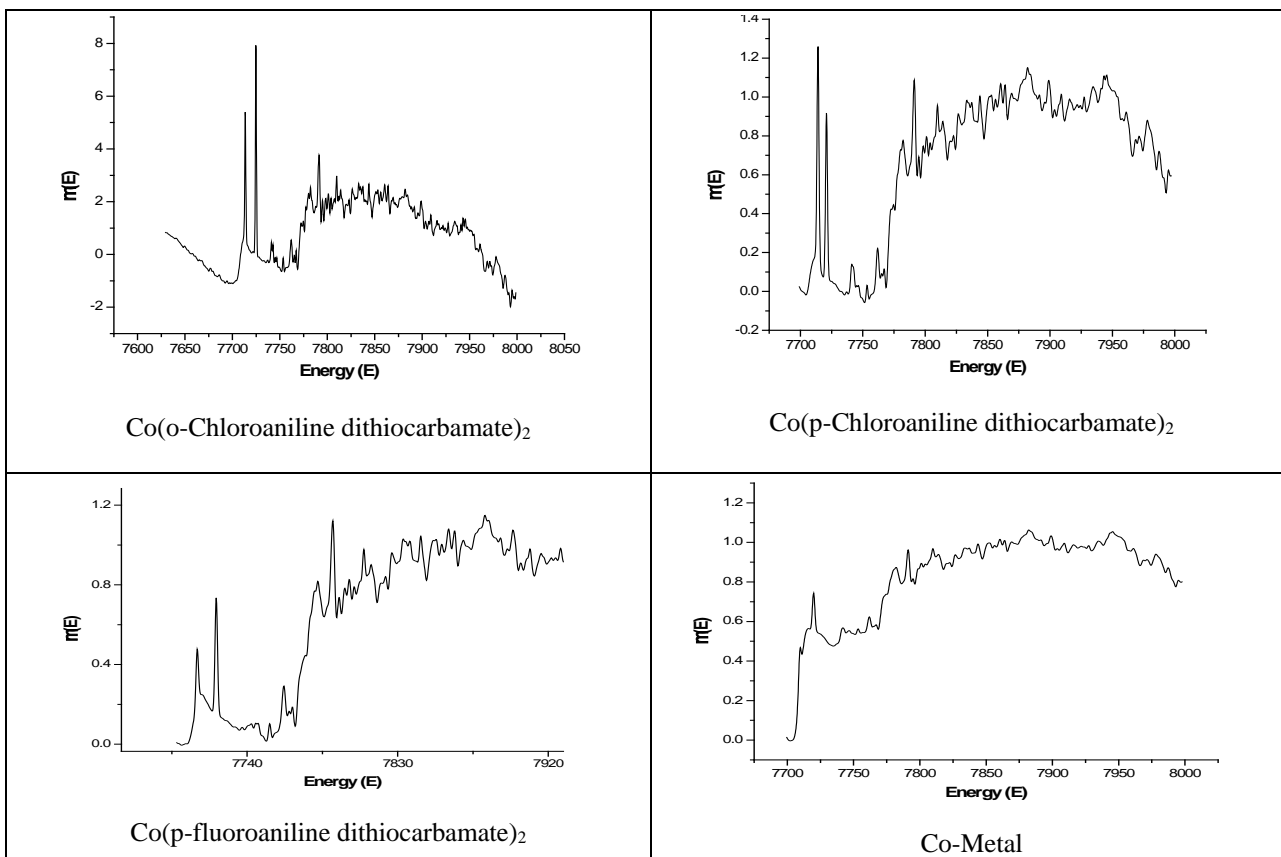
The Edge width of different complexes of cobalt [Co(II)] synthesized with ligands of chloro/fluoroaniline dithiocarbamate is presented in Table 2. The results showed that, the Edge width value for Co(II) complexes were ranged 6.61-11.14 eV. The Co(II) complex synthesized with the ligand of o-Chloroaniline dithiocarbamate (Co-Cl-o) showed highest value for Edge width. Whereas, the cobalt complex [Co(II)] synthesized with ligand of p-chloroaniline dithiocarbamate (Co-Cl-p) showed lowest value of Edge width. The variation in values of the Edge width for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Edge width values for same metal in complexation with different and similar ligands (Parsai and Mishra, 2014; Alvarez-Puebla *et al.*, 2004; Figueiredo *et al.*, 2012; Mishra and Mishra, 2011; Geete *et al.*, 2021) [37,2, 7, 29, 34, 11].

**Table 3:** Wave vector k values for corresponding n of cobalt [Co(II)] complexes.

n	K (Å)		
	Co-Cl-o	Co-Cl-p	Co-F-p
0	3.55	2.55	1.75
1	3.85	2.80	3.55
2	5.10	3.85	5.10
3	5.25	4.35	5.30
4	5.66	5.25	6.75
5	6.30	5.65	7.15
6	6.95		
7	7.35		

**Table 4:** Energy (eV) for EXAFS maxima and minima of cobalt (II) complexes at corresponding level of Q.

Structure	Q	Co-Cl-o	Co-Cl-p	Co-F-p
A	2.0	19.2	24.7	11.6
$\alpha$		27.7	29.8	47.9
B	6.0	24.0	14.8	98.9
$\beta$		31.92	18.9	106.80
C	12.0	153.3	27.5	173.2
$\gamma$		175.8	121.4	194.4



**Fig 1:** Normalized  $\mu(E)$  versus E spectra of cobalt complexes

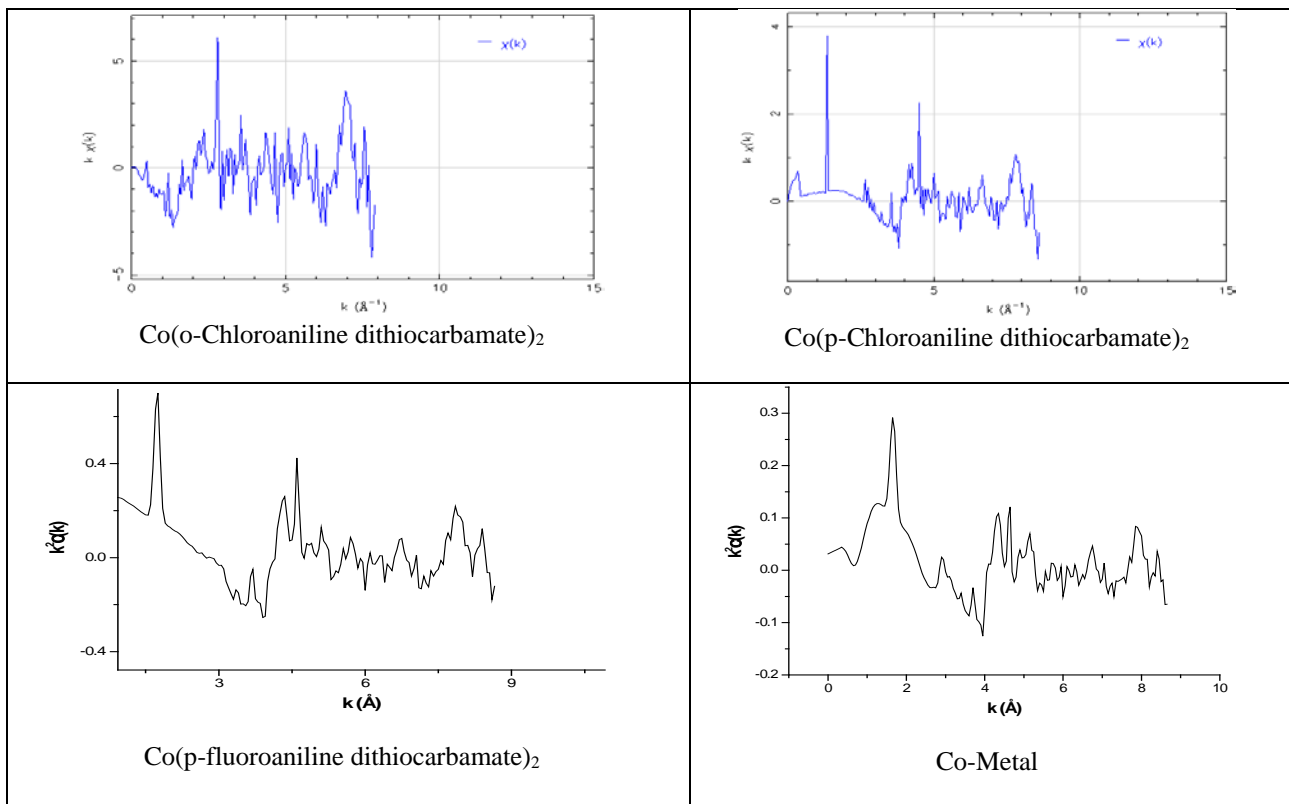
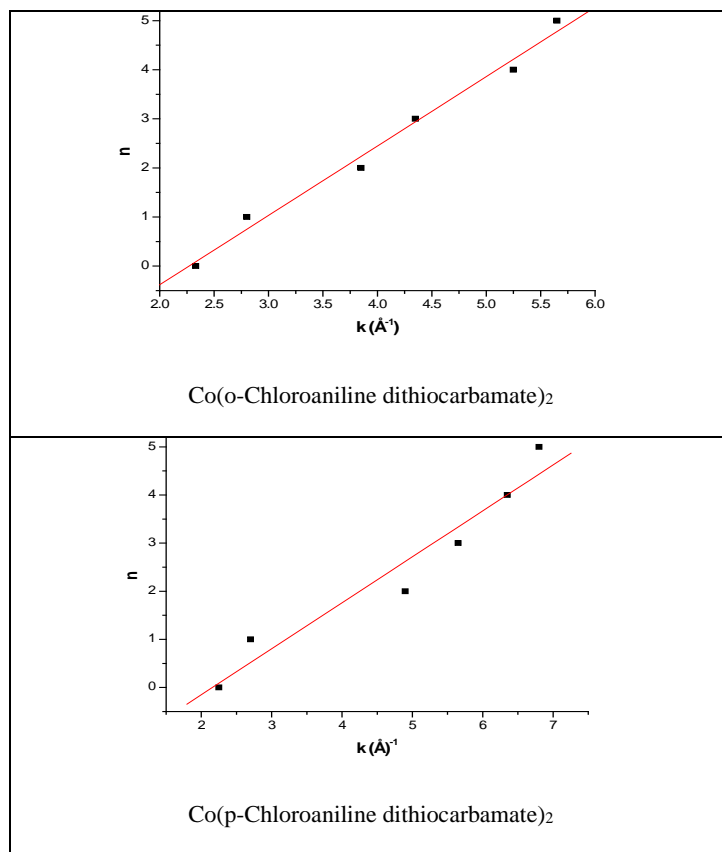
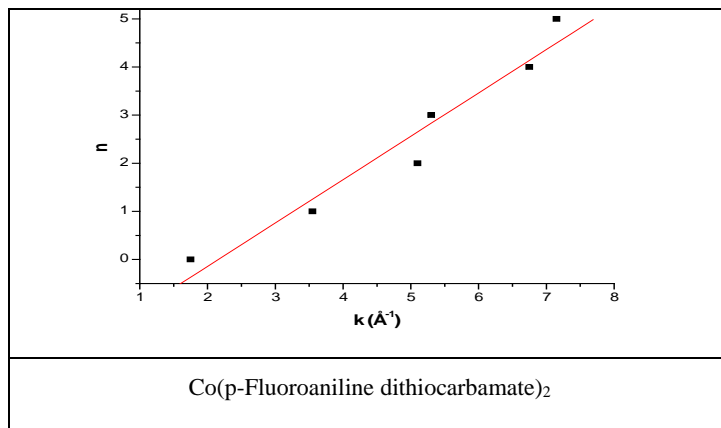
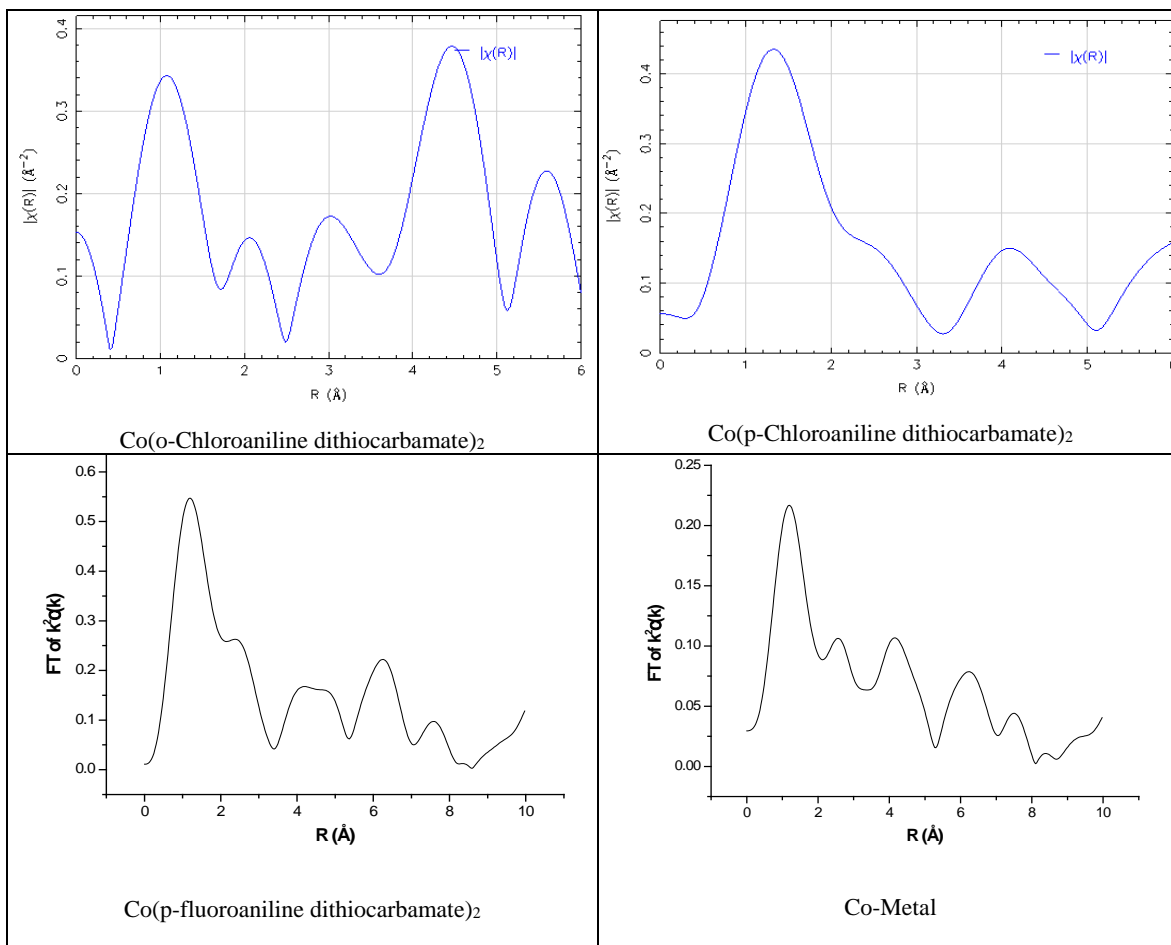


Fig 2:  $k^2\chi(k)$  versus  $k$  spectra of cobalt complexes





**Fig 3:** n Vs K curve for cobalt complexes



**Fig 4:** FT of K2 Vs R curve for cobalt complexes



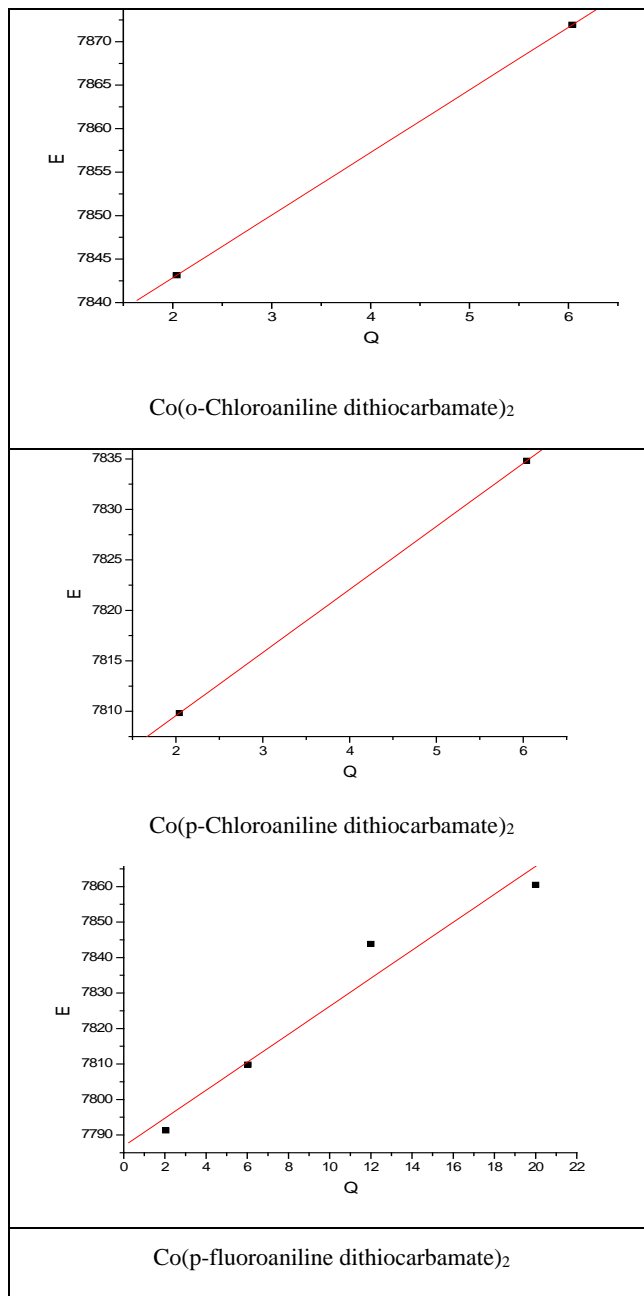


Fig 5: E Vs Q curve for cobalt complexes

### Wave vector $k$ and Energy level $Q$ for K-absorption edge for EXAFS maxima and minima

The wave vector  $k$  values obtained from the EXAFS maxima and minima of K-absorption edge at corresponding  $n$  values for various cobalt [Co(II)] complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate ligands is presented in Table 3. The  $k$  and  $n$  values were plotted and used for determination of the bond length using Athena and Origin 6.0 software. The  $K$  Vs  $n$  graphs are presented in Fig. 3 for various Co(II) complexes. Similarly, the Energy  $E$  (eV) for EXAFS maxima and minima at the K-absorption edge of cobalt (II) complexes with their corresponding values of energy level  $Q$  are presented in Table 4. The values of Energy ( $E$ ) and  $Q$  are used to compute the graph and to determine the bond length of the cobalt [Co(II)] complexes (Fig. 5). From the values of the  $k$  at

corresponding  $n$  and energy ( $E$ ) at different  $Q$ , the bond lengths of the complexes were determined by various methods *viz.* LSS, FT, Lytle and Levy.

### Bond length ( $\text{\AA}$ )

The bond length of first shell was calculated using LSS (Lytle, Sayer and Stern), FT (Fourier Transform), Lytle and Levy methods for cobalt (II) complexes. The obtained bond lengths are presented in Table 5.

### LSS (Lytle, Sayer and Stern) method

The phase uncorrected bond length ( $R_1$ ) data for different Co(II) complexes is presented in Table 5. The bond length calculated by LSS method ranged 1.41-2.20  $\text{\AA}$  for different complexes of cobalt [Co(II)] synthesized with various ligands of chloro/fluoroaniline

dithiocarbamate. The highest bond length was recorded for the Co(II) complex formed with the ligand of o-chloroaniline dithiocarbamate (Co-Cl-o) whereas the lowest bond length was observed for p-fluoroaniline dithiocarbamate (Co-F-p). The variation in values of the bond length calculated by LSS method for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Edge width values for same metal in complexation with different and similar ligands (Gaur *et al.*, 2018; Geete *et al.*, 2021) [9, 11].

### Fourier Transform (FT) method

The bond length of various cobalt complexes under study calculated from the FT method is presented in Table 5. The method generally underestimates the actual bond length. In order to reduce the errors in bond length, generally the obtained bond lengths are determined by using appropriate theoretical models. The bond length calculated by FT method ranged 1.26-3.06 Å for different complexes of cobalt [Co(II)] synthesized with various ligands of chloro/fluoroaniline dithiocarbamate. The highest bond length was recorded for the Co(II) complex formed with the ligand of o-chloroaniline dithiocarbamate (Co-Cl-o) whereas the lowest bond length was observed for p-fluoroaniline dithiocarbamate (Co-F-p). The variation in values of the bond length calculated by FT method for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Edge width values for same metal in complexation with different and similar ligands (Karvonen *et al.*, 2009; Mishra *et al.*, 2016; Geete *et al.*, 2021) [19, 30, 36, 11].

**Table 5:** Bond lengths of cobalt (II) complexes calculated by various methods.

Complex	Phase uncorrected first shell radial distance R (in Å)		Phase corrected first shell radial distance R (in Å)	
	LSS method	Fourier Transform method	Lytle Method	Levy Method
Co-Cl-o	2.20	3.06	2.60	2.58
Co-Cl-p	1.50	2.00	2.44	1.97
Co-F-p	1.41	1.26	3.08	2.24

### Lytle method

The bond lengths of various Co(II) complexes determined using Lytle's method are presented in Table 5. The bond length calculated by this method ranged 2.44-3.08 Å for different complexes of cobalt [Co(II)] synthesized with various ligands of chloro/fluoroaniline dithiocarbamate. The highest bond length was recorded for the Co(II) complex formed with the ligand of p-fluoroaniline dithiocarbamate (Co-F-p) whereas the lowest bond length was observed for p-Chloroaniline dithiocarbamate (Co-Cl-p). The variation in values of the bond length calculated by Lytle's method for Co(II) complexes are attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Edge width values for same metal

in complexation with different and similar ligands (Shrivastava, 2012; Geete *et al.*, 2019; Geete *et al.*, 2021) [39, 10, 11].

**Table 6:** Binding energies of 1s electrons of cobalt atom in different oxidation states.

Oxidation state	Electronic configuration	B.E. of 1s electrons (Å)	Shift in B.E. (Å)	Shift in B.E. (in eV)
0	3d <sup>7</sup> 4s <sup>2</sup>	283.06587	-	-
+1	3d <sup>8</sup> 4s <sup>0</sup>	283.15239	0.08652	2.354
+2	3d <sup>7</sup> 4s <sup>0</sup>	283.74624	0.68037	18.513
+3	3d <sup>6</sup> 4s <sup>0</sup>	284.50437	1.43850	39.143
+4	3d <sup>5</sup> 4s <sup>0</sup>	285.36147	2.29560	62.466

$$*1 \text{ \AA} = 2r_y = 27.2116$$

The above value has been fitted to the polynomial curve

$$y = A + B_1x + B_2x^2 + B_3x^3 + B_4x^4$$

**Table 7:** The parameters are given below

Parameter	Value	Error
A	-6.39488E-14	0
B <sub>1</sub>	-9.54883	0
B <sub>2</sub>	15.03267	0
B <sub>3</sub>	-3.44467	0
B <sub>4</sub>	0.31483	0

### Levy method

The bond length for cobalt complexes under study obtained by Levy's method are presented in Table 5. The data showed that the bond length ranged 1.97-2.58 Å for different Co(II) complexes. The highest and lowest bond length was recorded for the Co(II) complex formed with the ligand of p-Chloroaniline dithiocarbamate (Co-Cl-p) and o-chloroaniline dithiocarbamate (Co-Cl-o), respectively. The Levy method is the crude method for determining the bond length based upon mere ΔE which encounters the errors. However, the trend exhibited in bond lengths by the Levy's method for Co(II) complexes are more or less similar with other methods. The fluctuation in the bond length is attributed to the nature of functional group in complex and relative position of the functional group in the complex *viz.* ortho, para and meta positions. Earlier researchers also found similar observations with respect to the variation in Edge width values for same metal in complexation with different and similar ligands (Dumond *et al.*, 2007; Mishra *et al.*, 2010; Goel *et al.*, 2018; Geete *et al.*, 2021) [6, 33, 14, 11].

### Conclusions

Based on the XANES and EXAFS study of cobalt [Co(II)] complexes synthesized with ligands of chloro/fluoroaniline dithiocarbamate, it is concluded that all the cobalt complexes synthesized and studied showed higher value for K-absorption edge (E<sub>k</sub>) and Absorption maxima (E<sub>A</sub>) than Co metal. The bond lengths determined by LSS, FT, Lytle's and Levy's methods exhibited more or less similar trend for Co(II) complexes. Further studies may be carried out to explore the potential application of the synthesized complexes.

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## References

- Alain M, Jacques M, Diane MB, Karine P. MAX: multiplatform applications for XAFS. In *Journal of Physics: Conference Series*. Iop Publishing,2009:190(1):012034.
- Alvarez-Puebla RA, Aisa C, Blasco J, Echeverria JC, Mosquera B, Garrido JJ *et al.* Copper heterogeneous nucleation on a palygorskitic clay: an XRD, EXAFS and molecular modeling study. *Applied clay science*,2004:25(1-2):103-110.
- Attwood D, Sakdinawat A. X-rays and extreme ultraviolet radiation: principles and applications. Cambridge university press,2017.
- Bianconi A, Inocchia L, Stipcich S. eds. 2012. EXAFS and Near Edge Structure: Proceedings of the International Conference Frascati, Italy. Springer Science & Business Media,1982,27.
- Chang Z, Rundquist A, Wang H, Murnane MM, Kapteyn HC. Generation of coherent soft X rays at 2.7 nm using high harmonics. *Physical Review Letters*,1997:79(16):2967.
- Dumond F, Marceau E, Che M. A Study of Cobalt Speciation in Co/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared from Solutions of Cobalt-Ethylenediamine Complexes. *The Journal of Physical Chemistry C*,2007:111(12):4780-4789.
- Figueiredo MO, Silva TP, Veiga JP. A XANES study of cobalt speciation state in blue-and-white glazes from 16th to 17th century Chinese porcelains. *Journal of Electron Spectroscopy and Related Phenomena*,2012:185(3-4):97-102.
- Gaur A, Johari A, Shrivastava BD, Gaur DC, Jha SN, Bhattacharyya D *et al.* On the method of calibration of the energy dispersive EXAFS beamline at Indus-2 and fitting theoretical model to the EXAFS spectrum. *Sadhana*,2011:36(3):339.
- Gaur A, Nair NN, Shrivastava BD, Das BK, Chakraborty M, Jha SN *et al.* Study of distorted octahedral structure in 3d transition metal complexes using XAFS. *Chemical Physics Letters*,2018:692:382-387.
- Geete A, Shrivastava BD, Mishra A, Parsai N. XAFS study at the K-edge of some copper mixed ligand complexes and determination of first shell radial distance. *International Journal of Scientific Research in Physics and Applied Sciences*,2019:7(5):1030-1037.
- Geete A, Shrivastava BD, Mishra A. X-ray absorption near edge structure and extended x-ray absorption fine structure study of cobalt [Co(II)] complexes synthesized with ligands of para, ortho and Meta Nitroaniline dithiocarbamate. *International Journal of Physics and Applications*,2021:3(1):08-17.
- Geete A, Shrivastava BD, Mishra A. Synthesis, XRD, EXAFS and XANES Study of Cu(II) Complexes of Aniline Dithiocarbamate. *Asian Journal of Chemistry*,2020a:32(3):627-633.
- Geete A, Shrivastava BD, Mishra A. XRD study of cobalt [Co(II)] complexes synthesized with ligands of aniline/toluidine dithiocarbamate. *Rasayan Journal of Chemistry*,2020b:13(3):1878-1884.
- Goel P, Kumar D, Chandra S, Kumar A. Synthesis and Spectroscopic Study of Biologically Active Tridentate Schiff's Base Ligand 2-Acetyl-5-methyl-furanthiosemicarbazone and its Mn (II), Co (II), Ni (II), and Cu (II) Complexes. *Iranian Journal of Science and Technology, Transactions A: Science*,2018:42(2):557-565.
- Gurman SJ, Binsted N, Ross I. A rapid, exact curved-wave theory for EXAFS calculations. *Journal of Physics C: Solid State Physics*,1984:17(1):143.
- Jiang K, Liu B, Luo M, Ning S, Peng M, Zhao Y *et al.* Single platinum atoms embedded in nanoporous cobalt selenide as electrocatalyst for accelerating hydrogen evolution reaction. *Nature communications*,2019:10(1):1743.
- Joshi SK, Hinge VK, Shrivastava BD. February. EXAFS Studies of Cobalt (II) Complexes with Amino Acids. In *AIP Conference Proceedings*. AIP,2007:882(1):337-339.
- Joshi SK, Mahajan NK, Shrivastava BD. EXAFS studies of cobalt (II) complexes with salicylic acids. *Indian Journal of Pure & Applied Physics*,2000:39A(4):442-445.
- Karvonen L, Valkeapää M, Liu RS, Chen JM, Yamauchi H, Karppinen M *et al.* O-K and Co-L XANES study on oxygen intercalation in perovskite SrCoO<sub>3-δ</sub>. *Chemistry of Materials*,2009:22(1):70-76.
- Koningsberger DC, Prins R. X-ray absorption: principles, applications, techniques of EXAFS, SEXAFS, and XANES,1988.
- Lee PA, Teo BK, Simons AL. EXAFS: A new parameterization of phase shifts. *Journal of the American Chemical Society*,1977:99(11):3856-3859.
- Levy RM. Bond Lengths from X-Ray Absorption-Edge Fine Structure. *The Journal of Chemical Physics*, 1965:43(5):1846-1847.
- Lu KQ, Stern EA. Size effect of powdered sample on EXAFS amplitude. *Nuclear Instruments and Methods in Physics Research*,1983:212(1-3):475-478.
- Lytle FW. Determination of interatomic distances from X-ray absorption fine structure. *Advances in X-ray Analysis*,1965:9:398-409.
- Lytle FW, Sayers DE, Stern EA. Extended X-ray-absorption fine-structure technique. II. Experimental practice and selected results. *Physical Review B*,1975:11(12):4825.
- Maeda H. Accurate bond length determination by EXAFS method. *Journal of the Physical Society of Japan*,1987:56(8):2777-2787.
- Magini M. X-ray diffraction of ions in aqueous solutions: Hydration and complex formation. CRC press,2018.
- Martins DM, Mirão JP, Göttlicher J, Molinari M, Steininger R, Parker SC *et al.* Combined EXAFS and ab initio study of copper complex geometries adsorbed on natural illite. *Applied Clay Science*,2018:152:73-82.
- Mishra A, Mishra N. Synthesis and Characterization of Cobalt and Copper Doped BaTiO<sub>3</sub>. In *AIP Conference Proceedings*,2011:1349(1):1037-1038.AIP.
- Mishra A, Patil H. XRD and XANES study of some Cu-doped MnBi materials. In *Journal of Physics: Conference Series*,2016:755(1):012017). IOP Publishing.
- Mishra A, Jain G, Patil H. XRD, IR and XAFS studies of cobalt complexes having amino pyrazole dicarboxylate (APD) as ligand. In *Journal of Physics: Conference Series*,2014b:534:1:012033. IOP Publishing.
- Mishra A, Mishra S, Kekre P, Choudhary P. Comparative study of experimental and theoretical analysis of EXAFS data of copper complexes using FT method. In *Journal of Physics: Conference Series*. IOP Publishing, 2014a:534(1):012028.

33. Mishra A, Parsai N, Dagaonkar N. Determination of Structural Parameters by EXAFS Analysis of Some Co Complexes. *Acta Physica Polonica A*,2010;117(3):490-492.
34. Mishra A, Parsai N, Shrivastava BD. Simplified analysis of EXAFS data and determination of bond lengths. *Indian Journal of Pure & Applied Physics*,2011;49(1):25-29.
35. Mishra A, Parsai N, Shrivastava BD. Analysis of K-absorption extended X-ray absorption fine structure data of some transition metals. *X-Ray Spectrometry*, 2012c;41(4):219-224.
36. Mishra A, Singh P, Ninama S. Characterization and EXAFS Studies of Cobalt Synthesized by sol-gel auto Combustion Method. In *Journal of Physics: Conference Series*. IOP Publishing,2016;755(1):012046.
37. Parsai N, Mishra A. X-ray K-absorption spectroscopic study, K-absorption spectroscopic studies of some copper and cobalt Complexes by theoretical and experimental approach. LAP LAMBERT Academic Publishing, Germany,2014. ISBN: 978-3-659-56376-8.2.
38. Reich T, Reich TY, Amayri S, Drebert J, Banik NL, Buda RA *et al.* February. Application of XAFS spectroscopy to actinide environmental science. In *AIP Conference Proceedings*. AIP,2007;882(1):179-183.
39. Shrivastava BD. X-ray absorption fine structure (XAFS) spectroscopy using synchrotron radiation. In *Journal of Physics: Conference Series*. IOP Publishing, 2012;365(1):012002.
40. Uchikoshi M, Shinoda K. Determination of structures of cobalt (II)-chloro complexes in hydrochloric acid solutions by X-ray absorption spectroscopy at 298 K. *Structural Chemistry*,2019;30(3):945-954.