

## 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

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### Abstract

In present investigation, three cobalt [Co(II)] complexes were synthesized using various ligands of nitroaniline dithiocarbamate. The synthesized Co(II) complexes were studied for different 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, all the cobalt complexes synthesized and studied showed higher value for K-absorption edge ( $E_k$ ) than Co metal. Similarly, all the cobalt complexes synthesized and studied showed higher value for Absorption maxima ( $E_A$ ) than Co metal. The Chemical shift ( $\Delta E_K$ ) value for Co(II) complexes were ranged 1.07-2.71 eV. The Shift of principal absorption maxima ( $\Delta E_A$ ) value for Co(II) complexes were ranged 1.88-3.33 eV. The Edge width of three different complexes of cobalt [Co(II)] synthesized with ligands of nitroaniline dithiocarbamate ranged 11.04-12.95 eV. The bond length calculated by LSS method ranged 1.64-2.30 Å for different complexes whereas the bond length calculated by FT method ranged 1.14-2.33 Å. The Lytle's method and Levy's method gives the bond length ranged 2.00-2.98 Å and 3.22-3.31 Å, respectively for studied complexes.

**Keywords:** xanes, exafs, absorption maxima, bond length, k-absorption edge, chemical shift, nitroaniline dithiocarbamate, co(ii) complex, ligands

### Introduction

X-rays are electromagnetic radiations, which lie between ultraviolet and gamma rays in the electromagnetic spectrum. 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) <sup>[5]</sup>. X-rays have been used as powerful tools in analytical, physical, chemical, biological and structural characterization of matter (Attwood and Sakdinawat, 2017) <sup>[3]</sup>. X-rays are high-energy photons that are produced when electrons make transitions from one atomic orbit to another (Chang *et al.*, 1997) <sup>[5]</sup>. 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) <sup>[36]</sup>. 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 X-ray absorption fine structure (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) <sup>[36, 1]</sup>.

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) <sup>[36]</sup>. XAFS can be used in a variety of systems and bulk physical environment. XAFS is routinely used in a wide range of scientific fields, including biology, environmental science, catalysts research, and material science.

The features about 10-5 eV above  $E_0$  are referred to as XANES 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 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) [17]. The X-ray absorption near edge structure (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. Sharma *et al.* (2019) [38] studied the structural characteristics of the copper complexes using the X-ray spectroscopy and determined various parameters using XRD and EXAFS techniques. 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) [25] studied the copper complex geometries adsorbed on natural illite by combining EXAFS and ab initio study. Mishra and Patil (2016) [17] carried out synthesis of Cu-doped MnBi materials and studied their properties using XRD and XANES techniques. Mishra *et al.* (2014a) [29] conducted comparative study of experimental and theoretical analysis of EXAFS data of copper complexes using FT method. Mishra *et al.* (2014b) [28] synthesized cobalt complexes with amino pyrazole dicarboxylate ligand and studied the characteristics using XRD, IR and XAFS techniques. Ninama (2013) [34] applied IFEFFIT method for studying copper complexes using X-Ray k absorption near edge structure (XANES) and extended X-Ray absorption fine structure (EXAFS). In this study both theoretical and experimental approach were studied.

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

In present investigation nitroaniline dithiocarbamate ligands were synthesized and used as complexing agent for Co(II). The ligands were prepared by adding 0.01 M of nitroaniline 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-1	Co(o-Nitroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>
Co-2	Co(p-Nitroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>
Co-3	Co(m-Nitroaniline dithiocarbamate) <sub>2</sub>	Co(C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>

### Synthesis of Co (II) complexes

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 nitroaniline 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 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 appropriate software applications. In present study, Athena and Origin 6.0 software were used for interpretation of results.

### Calibration of the beamline

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].

### Recording the EXAFS spectra and study of XANES parameters

The EXAFS spectra of synthesized cobalt [Co(II)] complexes were recorded on DXAFS beamline BL-8, Indus 2, Synchrotron source at RRCAT, Indore. The EXAFS spectra viz. absorption ( $\mu E$ ) against incident energy ( $E$ );  $K^2 \chi(K)$  against  $K$ ;  $n$  against  $K$ ; FT of  $K^2 \chi(K)$  against  $R$ ; and  $E$  against  $Q$  were 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 as follows:

### K-absorption Edge (EK)

The K-absorption edge (eV) for Co metal and its different complexes synthesized with ligands of nitroaniline dithiocarbamate were determined directly (Gurman *et al.*, 1984)<sup>[12]</sup>.

### Absorption maxima (EA)

The Absorption maxima ( $E_A$ ) for Co metal and its different complexes synthesized with ligands of nitroaniline dithiocarbamate were determined directly from EXAFS spectra (Maeda, 1987)<sup>[23]</sup>.

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

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)<sup>[18]</sup>.

$$\text{Chemical shift } (\Delta EK) = E_{Complex} - E_{Metal}$$

### Effective nuclear charge (ENC)

The Effective nuclear charge (ENC) for different complexes of Co(II) synthesized with ligands of nitroaniline dithiocarbamate were obtained from EXAFS spectra (Joshi *et al.*, 2007)<sup>[14]</sup>.

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

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)<sup>[14]</sup>.

### Edge width (EA- EK)

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)<sup>[20]</sup>.

### 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 nitroaniline dithiocarbamate ligands was obtained from EXAFS spectra (Joshi *et al.*, 2000)<sup>[15]</sup>. 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)<sup>[22]</sup>, FT (Mishra *et al.*, 2011)<sup>[26]</sup>, Lytle (Lytle, 1965)<sup>[21]</sup> and Levy (Levy, 1965)<sup>[19]</sup>.

### Determination of 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.

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

Lytle, Sayer and Stern in 1975<sup>[22]</sup> (Lytle *et al.*, 1975)<sup>[22]</sup> introduced the method for determining the bond length. In this method, K values are plotted against n for various maxima and minima such as  $n= 0,2,4,..$  and  $n=1,3,5,..$ , respectively. It gives the straight line. From the slope of the line, the  $R_1$  (Phase uncorrected bond length) can be calculated as follows:

$$M = 2(R_1 - \alpha_1)/\pi$$

The values of  $\alpha$  can be calculate from the standard known sample. In a chemically similar environment, the value of  $\alpha$  remains same, thus the  $R_1$  for unknown can be calculated.

### Fourier Transform (FT) method

In this method, the bond length is calculated from the position of the first peak in the Fourier transform. The first peak in FT represents the radius of first coordination sphere i.e. it is the distance between absorbing atom and its neighbor atom. 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 (Mishra *et al.*, 2011)<sup>[26]</sup>.

### Lytle method

In Lytle method, the bond length is calculated as follows (Lytle *et al.*, 1965)<sup>[21]</sup>:

$$E = (h^2/mR_s^2)Q$$

Where,

E- Absorption maxima,

h- Plank's constant

m - mass of electron,

$R_s$ - Bond length

Q - zero roots of the half-order Bessel function

The curve E Vs Q gives the slope of the line. The bond length ( $R_s$ ) were determined from the slope by following the relationship:

$$R_s = (37.60/M)^{1/2}$$

### Levy method

Levy introduced the method of determining the bond length in 1965 (Levy, 1965)<sup>[19]</sup>. In this method, the bond length is calculated by using following equation:

$$R_1 = (151/\Delta E)^{1/2}$$

Where,

$R_1$  is the radius of first coordination sphere in  $\text{\AA}$

$\Delta E$  is energy difference of EXAFS maxima and minima i.e. B and  $\beta$ , respectively (eV)

The bond length obtained by following the above equation i.e. by Levy's method. The Levy method is the crude method for determining the bond length based upon mere  $\Delta E$  which encounters the errors.

### Results and Discussion

The EXAFS spectra of synthesized cobalt [Co(II)] complexes 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 seven different complexes synthesized with ligands of nitroaniline dithiocarbamate is presented in Table 2. The results showed that, all the cobalt complexes synthesized and studied showed higher value for K-absorption edge ( $E_k$ ). The K-absorption edge value for Co metal was recorded 7709.4 eV. The K-absorption edge value for Co(II) complexes were ranged 7710.7-7712.1 eV. The Co(II) complex synthesized with the ligand of m-nitroaniline dithiocarbamate (Co-3) showed highest value for K-absorption edge followed by the cobalt complex [Co(II)] synthesized with ligand of o-nitroaniline dithiocarbamate (Co-1) and p-nitroaniline dithiocarbamate. The cobalt [Co(II)] complexes showed following trend with respect to the K-absorption edge values:

$$\text{Co-3} > \text{Co-1} > \text{Co-2}$$

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.*, 2019; Uchikoshi and Shinoda, 2019) [10, 40].

### Absorption maxima ( $E_A$ )

The Absorption maxima ( $E_A$ ) for Co metal and its three different complexes synthesized with ligands of nitroaniline dithiocarbamate is 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 7721.-7723.2 eV. The Co(II) complex synthesized with the ligand of m-nitroaniline dithiocarbamate (Co-3) showed highest value for Absorption maxima ( $E_A$ ) followed by p-nitroaniline dithiocarbamate (Co-2) and o-nitroaniline dithiocarbamate (Co-1). 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) [24].

**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-1	7710.7	7721.7	1.31	-	1.88	11.04
Co-2	7709.8	7722.7	1.07	-	2.85	12.95
Co-3	7712.1	7723.2	2.71	-	3.33	11.09

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

The Chemical shift ( $\Delta EK$ ) of three different complexes of cobalt [Co(II)] synthesized with ligands of nitroaniline dithiocarbamate is presented in Table 2. The results showed that, the Chemical shift ( $\Delta EK$ ) value for Co(II) complexes were ranged 1.07-2.71 eV. The Co(II) complex synthesized with the ligand of m-nitroaniline dithiocarbamate (Co-3) showed highest value for Chemical shift ( $\Delta EK$ ). Whereas the cobalt complex [Co(II)] synthesized with ligand of p-Nitroaniline dithiocarbamate (Co-2) 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 (Roux *et al.*, 1996; Bianconi *et al.*, 2012) [37].

### Effective nuclear charge (ENC)

No effective nuclear charge (ENC) for three different complexes of Co(II) synthesized with ligands of nitroaniline 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 nitroaniline 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 1.88-3.33 eV. The Co(II) complex synthesized with the ligand of m-nitroaniline dithiocarbamate (Co-3) showed highest value for Shift of principal absorption maxima ( $\Delta E_A$ ). The cobalt complex [Co(II)] synthesized with ligand of o-nitroaniline dithiocarbamate (Co-1) 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) [32, 13].

**Edge width (EA- EK)**

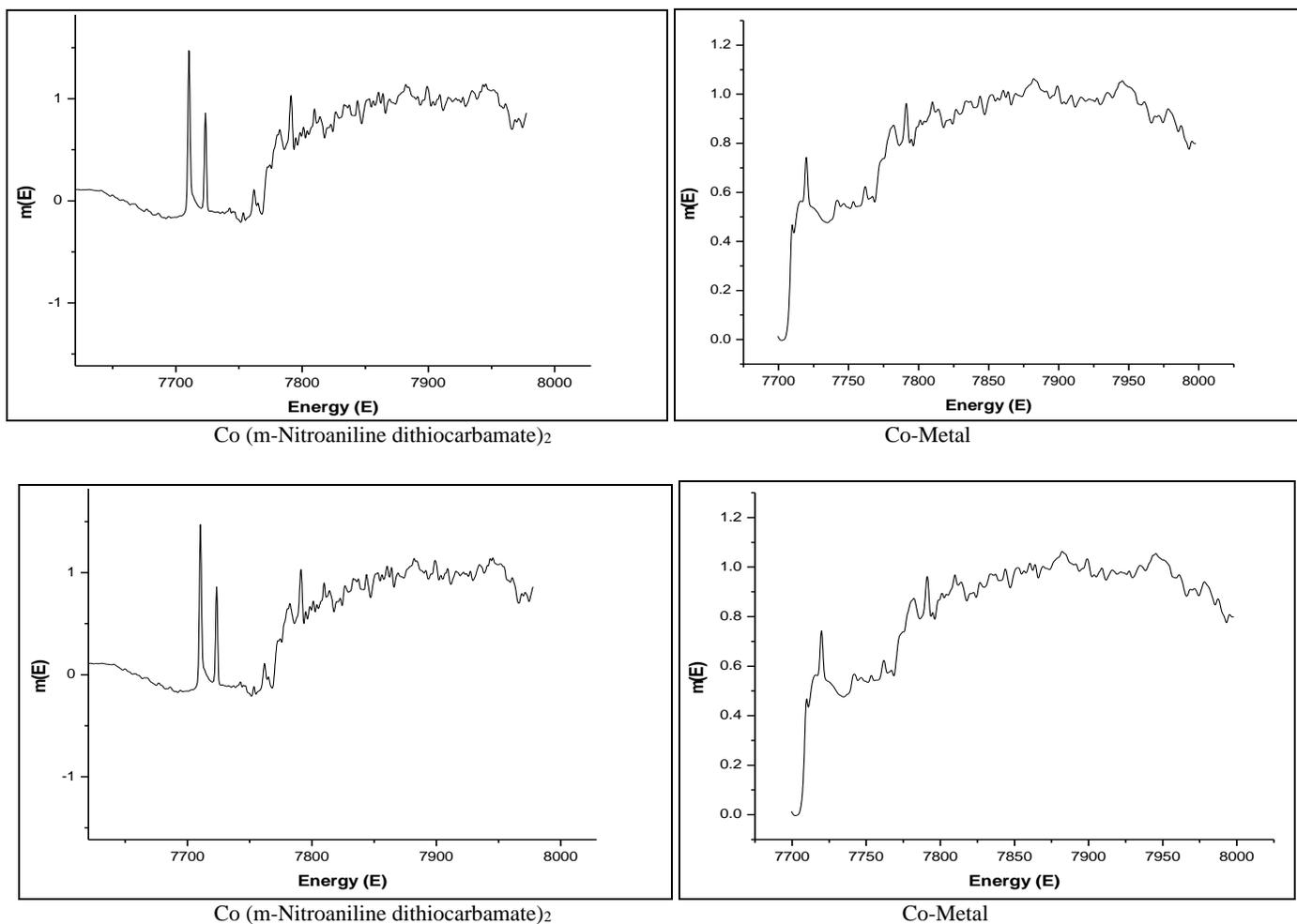
The Edge width of different complexes of cobalt [Co (II)] synthesized with ligands of nitroaniline dithiocarbamate is presented in Table 2. The results showed that, the Edge width value for Co (II) complexes were ranged 11.04-12.95 eV. The Co (II) complex synthesized with the ligand of p-Nitroaniline dithiocarbamate (Co-2) showed highest value for Edge width. Whereas, the cobalt complex [Co (II)] synthesized with ligand of o-nitroaniline dithiocarbamate (Co-1) 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) [35, 2, 7, 26].

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

n	K (Å)		
	Co-1	Co-2	Co-3
0	3.35	1.70	2.25
1	3.85	1.80	2.70
2	4.30	3.35	4.90
3	4.45	3.85	5.65
4	4.90	4.90	6.35
5	5.65	5.65	6.80
6	6.50	6.35	
7	6.80	6.80	

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

Structure	Q	Co-1	Co-2	Co-3
A	2.0	42.7	11.0	47.9
$\alpha$		56.4	12.8	56.4
B	6.0	70.3	42.7	98.9
$\beta$		75.3	56.4	104.8
C	12.0	91.3	91.3	121.4
$\gamma$		121.4	121.4	150.9
D	20.0	160.6	153.3	40.3
$\delta$		175.8	175.8	205.4



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

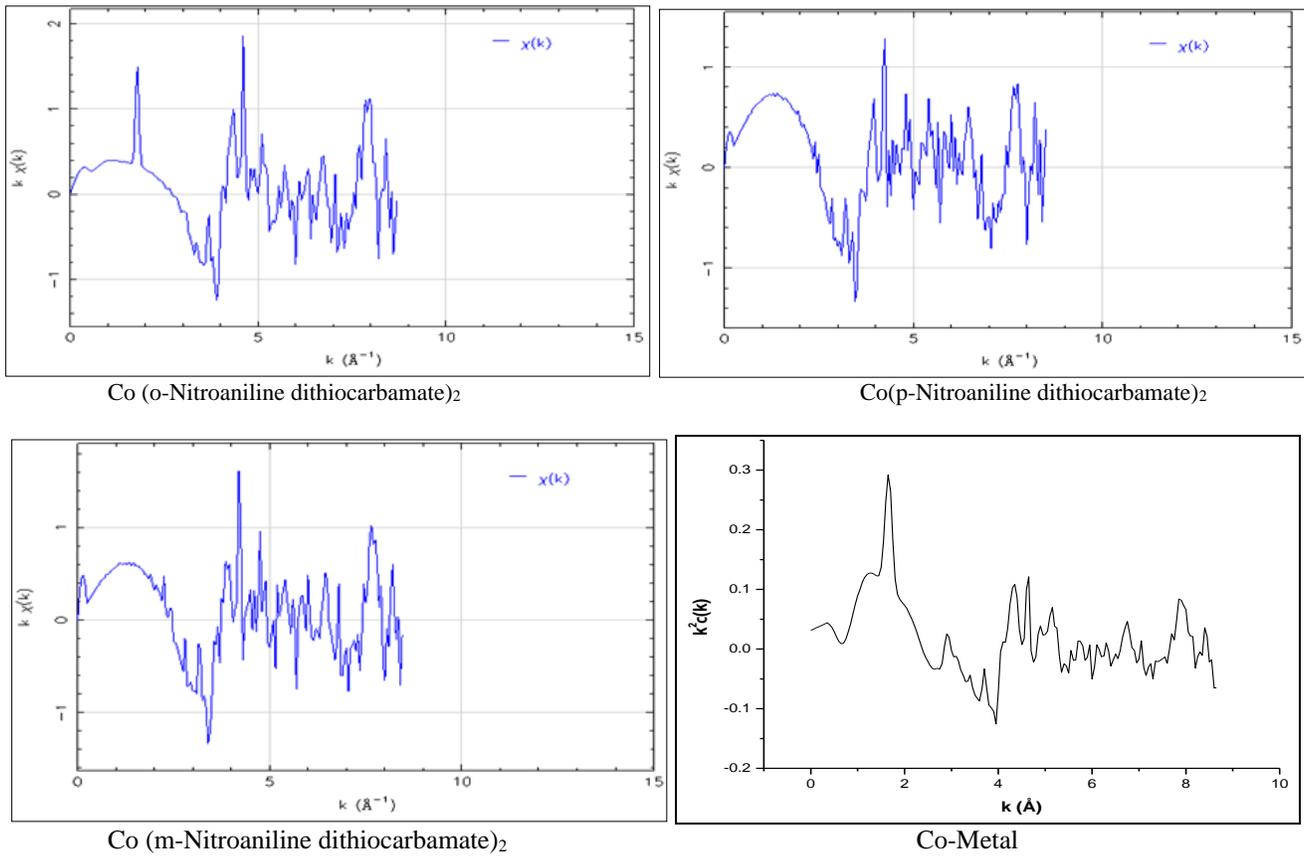


Fig 2:  $k\chi(k)$  versus K spectra of cobalt complexes

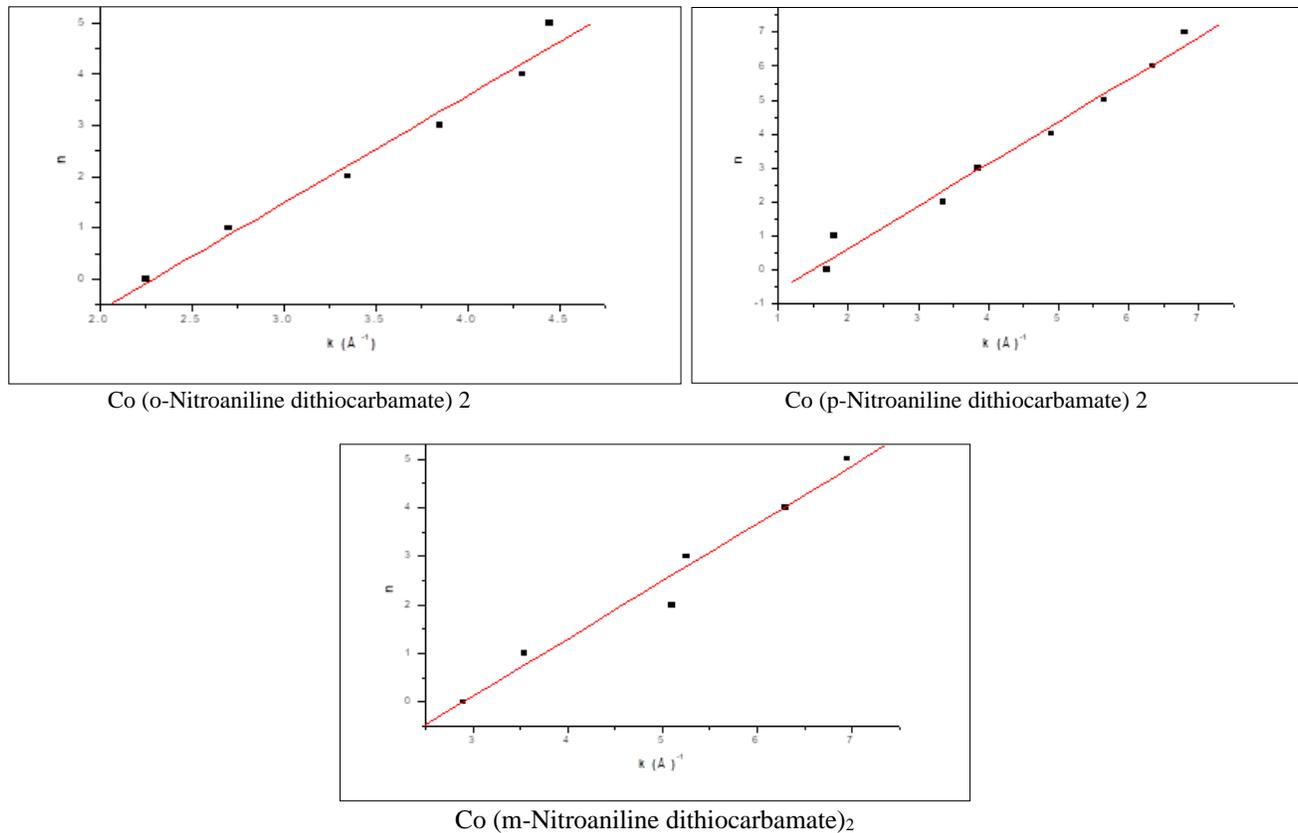


Fig 3: n Vs K curve for cobalt complexes

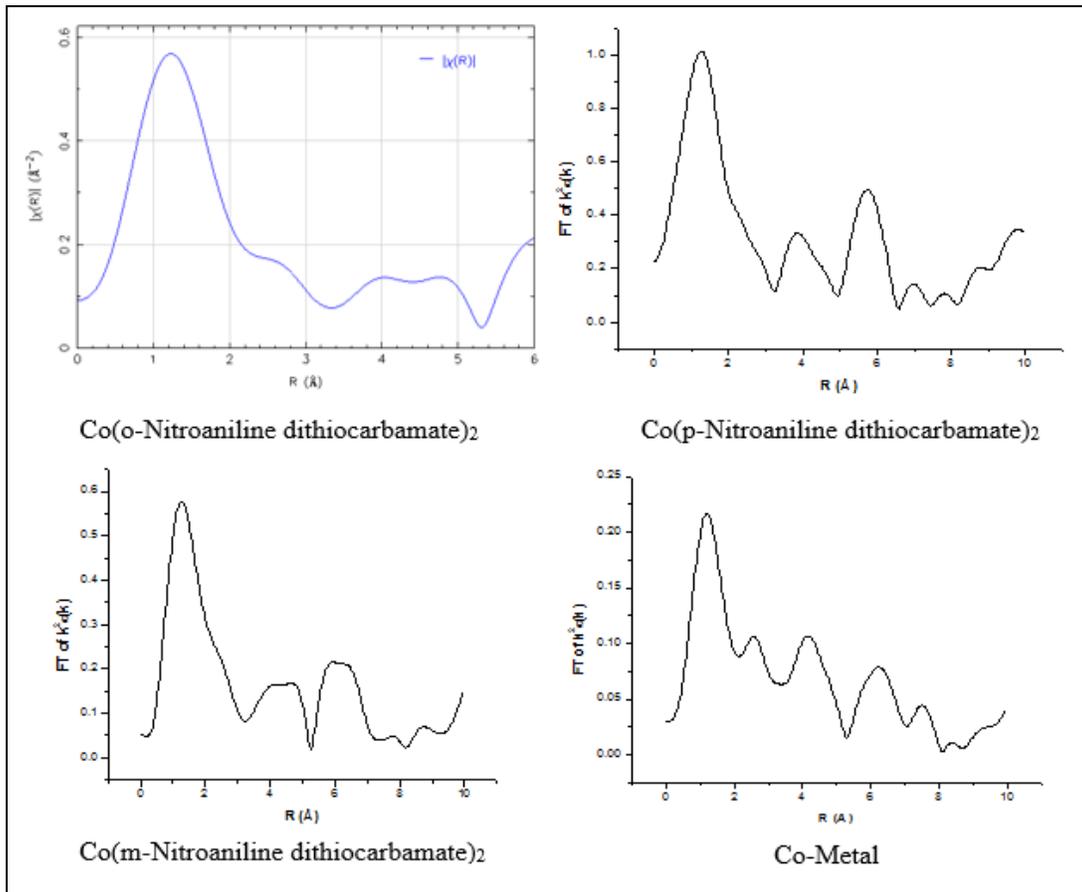


Fig 4: FT of  $K_2$  Vs  $R$  curve for cobalt complexes

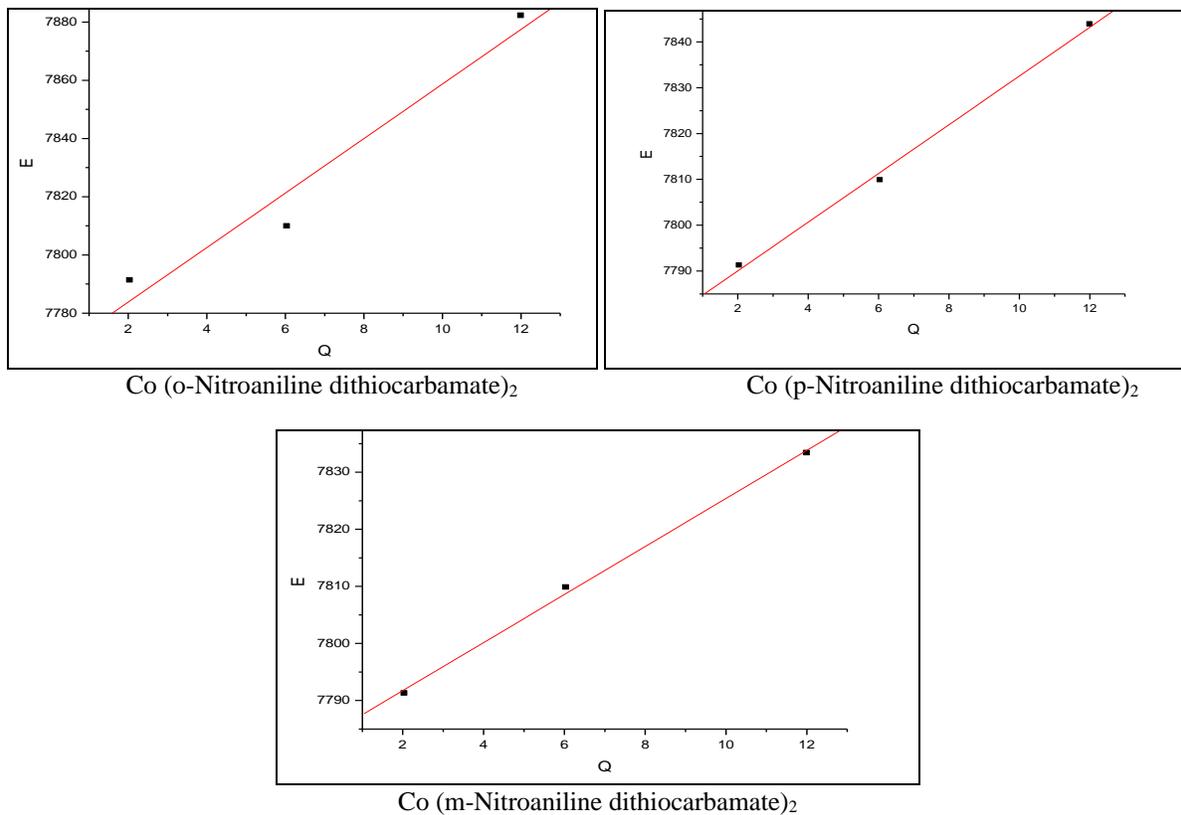


Fig 5:  $E$  Vs  $Q$  curve for cobalt complexes

### 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 nitroaniline 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 1.64-2.30  $\text{\AA}$  for different complexes of cobalt [Co (II)] synthesized with various ligands of nitroaniline dithiocarbamate. The highest bond length was recorded for the Co (II) complex formed with the ligand of o-nitroaniline dithiocarbamate (Co-1) whereas the lowest bond length was observed for p-Nitroaniline dithiocarbamate (Co-2). 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)<sup>[9]</sup>.

### 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 1.14-2.33  $\text{\AA}$  for different complexes of cobalt [Co(II)] synthesized with various ligands of nitroaniline dithiocarbamate. The highest bond length was recorded for the Co(II) complex formed with the ligand of o-nitroaniline dithiocarbamate (Co-1) whereas the lowest bond length was observed for m-Nitroaniline dithiocarbamate (Co-3). 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)<sup>[16, 17]</sup>

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

Complex	Phase uncorrected first shell radial distance R (in $\text{\AA}$ )		Phase corrected first shell radial distance R (in $\text{\AA}$ )	
	LSS method	Fourier Transform method	Lytle Method	Levy Method
Co-1	2.30	2.33	2.00	3.31
Co-2	1.64	2.30	2.66	3.22
Co-3	1.85	1.14	2.98	3.30

### 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 2.00-2.98  $\text{\AA}$  for different complexes of cobalt [Co(II)] synthesized with various ligands of nitroaniline dithiocarbamate. The highest bond length was recorded for the Co(II) complex formed with the ligand of m-nitroaniline dithiocarbamate (Co-3) whereas the lowest bond length was observed for o-Nitroaniline dithiocarbamate (Co-1). 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 (Geete *et al.*, 2019; Shrivastava, 2012)<sup>[10, 39]</sup>.

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

Oxidation state	Electronic configuration	B.E. of 1s electrons ( $\text{\AA}$ )	Shift in B.E. ( $\text{\AA}$ )	Shift in B.E. (in eV)
0	$3d^7 4s^2$	283.06587	-	-
+1	$3d^8 4s^0$	283.15239	0.08652	2.354
+2	$3d^7 4s^0$	283.74624	0.68037	18.513
+3	$3d^6 4s^0$	284.50437	1.43850	39.143
+4	$3d^5 4s^0$	285.36147	2.29560	62.466

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

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 3.22-3.31 Å for different Co(II) complexes. The highest and lowest bond length was recorded for the Co(II) complex formed with the ligand of o-Nitroaniline dithiocarbamate (Co-1) and p-nitroaniline dithiocarbamate (Co-2), respectively. The Levy method is the crude method for determining the bond length based upon mere  $\Delta E$  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)<sup>[6, 11]</sup>.

### Conclusions

Based on the XANES and EXAFS study of cobalt [Co (II)] complexes synthesized with ligands of nitroaniline dithiocarbamate, it is concluded that all the cobalt complexes synthesized and studied showed higher value for K-absorption edge ( $E_K$ ) and Absorption maxima ( $E_A$ ) 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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