

Comparative XAFS studies of some Cobalt complexes of (3-N-phenyl -thiourea-pentanone-2)

Namrata soni¹, Neetu Parsai¹, Ashutosh Mishra²

¹Shri Vaishnav Institute of Management, Indore

²School of Physics DAVV, Indore

E-mail: namrata.123soni@gmail.com

Abstract. XAFS spectroscopy is a useful method for determining the local structure around a specific atom in disordered systems. XAFS study of some cobalt complexes of (3-N-phenylethiourea-pentanone-2) is carried out using the latest XAFS analysis software *Demeter with Strawberry Perl*. The same study is also carried out theoretically using *Mathcad* software. It is found that the thiourea has significant influence in the spectra and the results obtained experimentally and theoretically are in agreement. Fourier transform of the experimental and theoretically generated XAFS have been taken to obtain first shell radial distance. The values so obtained are in agreement with each other.

1. Introduction

EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum. It allows determining the chemical environment of a single element in terms of the number and type of its neighbors, inter-atomic distances and structural disorders. XAFS spectroscopy is a useful method for determining the local structure around a specific atom in disordered systems. XAFS study of some cobalt complexes of (3-N-phenylethiourea-pentanone-2) is carried out using the latest XAFS analysis software *Demeter with Strawberry Perl*. The same study is also carried out theoretically using *Mathcad* software using method given by N Parsai et al [1, 2]. It is found that the thiourea has significant influence in the spectra and the results obtained experimentally and theoretically are in agreement. Fourier transform of the experimental and theoretically generated XAFS have been taken to obtain first shell radial distance. The values so obtained are in agreement with each other.

The five cobalt complexes are:

S. No.	Complexes	Abbreviations
1	Co [3-N-(3nitro)-thiourea-pentanone-2]	Co [3N3NTU2P]
2	Co [3-N-(4nitro)-thiourea-pentanone-2]	Co [3N4NTU2P]
3	Co [3-N-(2-chloro)-thiourea-pentanone-2]	Co [3N2CTU2P]
4	Co [3-N-(3-chloro)-thiourea-pentanone-2]	Co [3N3CTU2P]
5	Co [3-N-(4-chloro)-thiourea-pentanone-2]	Co [3N4CTU2P]

2. Methodology

The phenomenon of extended X-ray absorption fine structure (EXAFS) refers to the oscillation of the X-ray absorption coefficient as a function of X-ray energy above threshold. It has been attributed to an interference of the ejected photoelectrons at the site of the absorbing atom. For K-Shell excitation the



modulating part of the absorption coefficient called the extended X-ray absorption fine structure (EXAFS) is described by

$$\chi(k) = \frac{m}{4\pi\hbar^2k} \sum_j \frac{N_j}{R_j^2} t_j(2k) \exp[-2R_j/\lambda] \times \sin 2[kR_j + \delta_j(k)] \exp[-2k^2\sigma_j^2] \quad (1)$$

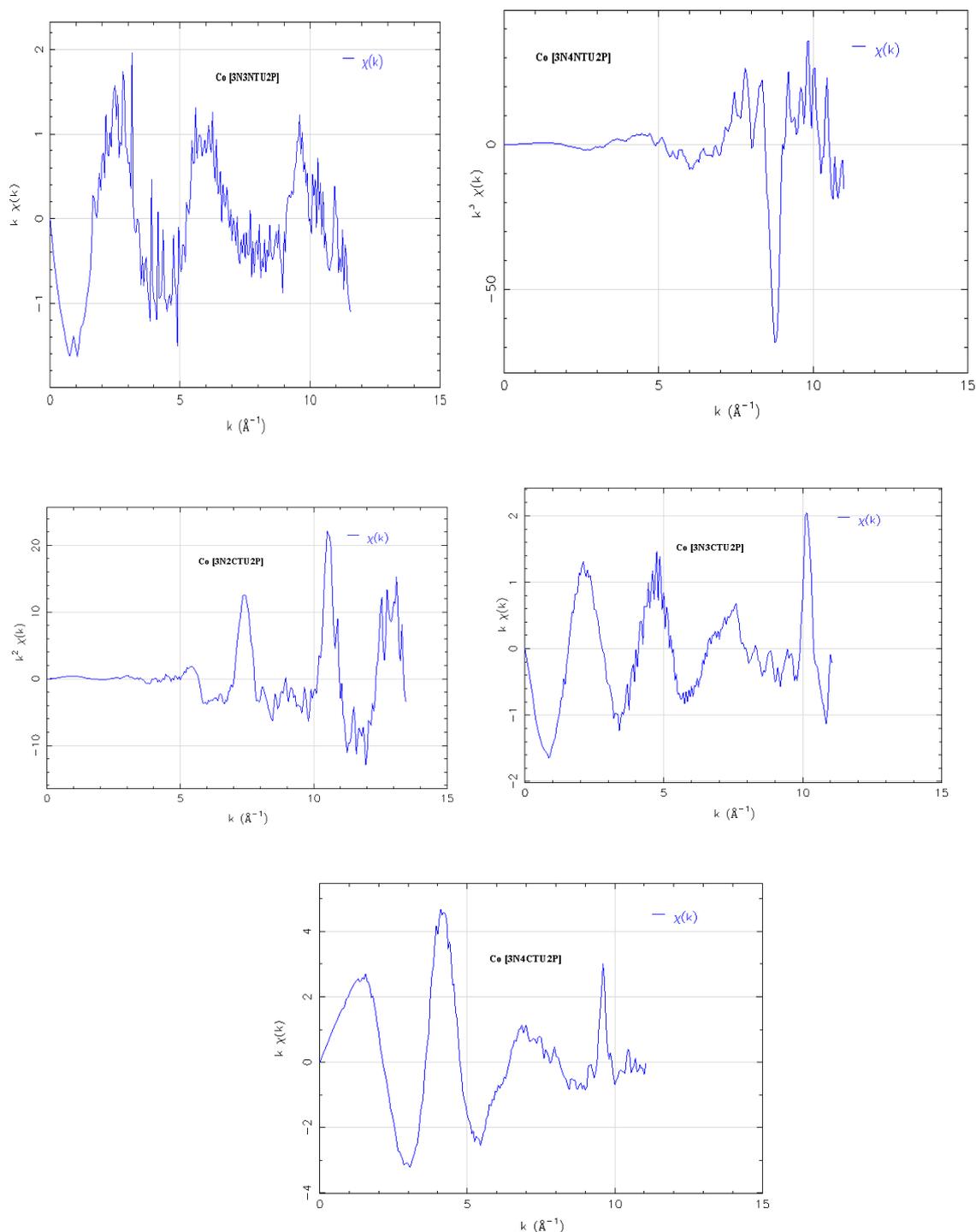


Figure 1. $\chi(k)$ versus k curves for cobalt complexes.

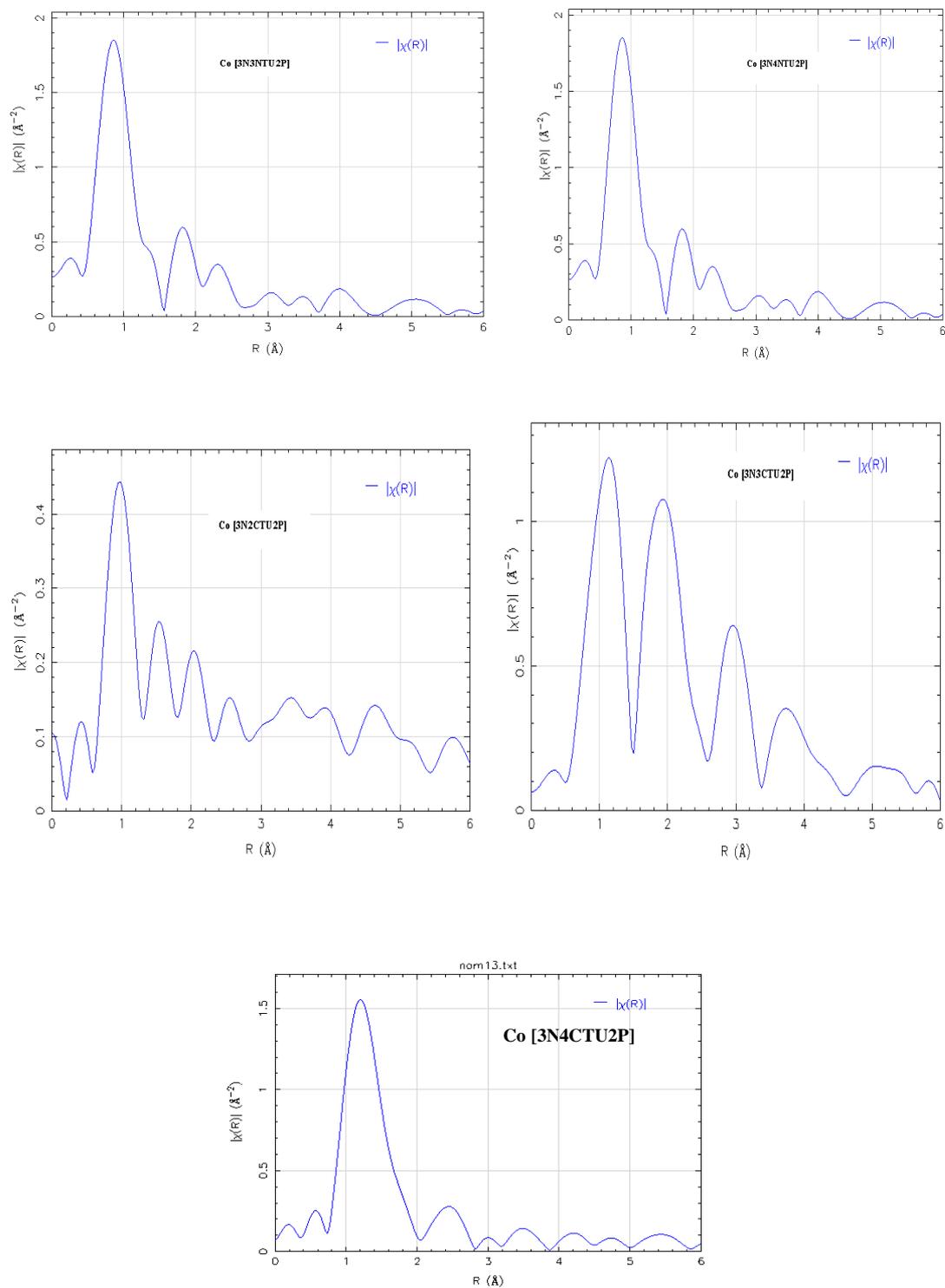


Figure 2. Magnitude of F.T of $\chi(k)$ for cobalt complexes.

Where k is the electron wave vector, N_j is the number of atoms in the j^{th} coordination shell, R_j is the average radial distance to the j^{th} atom, $t_j(2k)$ is the back-scattering matrix element encountered by the electrons, λ is the mean free path of the electron, the 2^{nd} exponential containing σ_j^2 is a Debye-Waller-type term where σ_j is the rms fluctuations of the atom about R_j , and $\delta_j(k)$ is a phase shift. The form of this equation is a sine like scattering from each shell of atoms at R_j with the EXAFS signal proportional to the number of atoms surrounding the absorbing atom and inversely proportional to R_j^2 . Each coordination shell contributes a sine like term of period $2kR_j$. The total result is a summation over all the coordination shells within range of the effect. Several attempts have been made to extract structural information from EXAFS. The most general methods used are fitting procedures [3] and Fourier Transform methods. The Fourier transform method can be applied to structures that are more complicated. From $\chi(k)$ a radial structure function $|\phi_n(r)|$ can be derived given by

$$\phi_n(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} k^n \chi(k) e^{2ikr} dk \quad (2)$$

where n is usually either 1 or 3, and k_{\min} and k_{\max} are the minimum and maximum values of k , respectively. The $n = 3$ transform weights less the low-energy portion of $\chi(k)$, where the undesirable uncertainties occur, while it weights most the high-energy portion of $\chi(k)$. For this reason, we will employ $\phi_3(r)$ as our standard transform in the case. Shells of scattering atoms surrounding the absorbing atom generate the maxima of this function. The positions of the peaks in $|\phi(r)|$ are shifted compared to true distances due to contribution of the scattering phases that depend on k .

The analysis of Fourier transformation of $k^n \chi(k)$ into r -space was carried out using the IFEFFIT. This will ensure that the FT gives the correct contribution due to all constituent frequencies in $\chi(k)$. This is important for accurate determination of local structure. The k range for Fourier transform was $2 < k < 9 \text{ (\AA)}^{-1}$.

3. Results and discussion

The XAFS and magnitude of the Fourier transform of XAFS are shown in figure 1 and figure 2 respectively for five cobalt complexes. The first strong peak at 2.1 \AA for [3N3NTU2P] complex in the magnitude of the Fourier transform is due to the sulfur nearest neighbors around the cobalt ions the peaks are shifted towards smaller distances because of the phase shifts. The different Co-S bond distances are described in Table 1. Comparison of bond length to LSS, Lytle, Levy's to the bond length calculated by MathCAD programming and IFEFFIT have been done. The inverse Fourier transform of this peak in k -space gives the contribution to EXAFS from the sulfur nearest neighbors. The method employed for theoretical analysis of EXAFS and verification of various structural parameters using MathCAD programming is simpler than commonly used IFEFFIT technique. [4] In contrast to conventional EXAFS fitting analysis, other kinds of EXAFS analysis computation originated from the Tikhonov regularization method [3-4] is the iterative solution projection method using numerical algorithm [5] of manipulating matrix inversion computation under the ill-posed mathematical problem. The EXAFS spectra obtained using equation (1) in MathCAD programming for cobalt (II) complexes of thiourea are shown in figure 3. The bond length is measured from magnitude of Fourier Transform shown in figure 4 for cobalt (II) complexes of thiourea series.

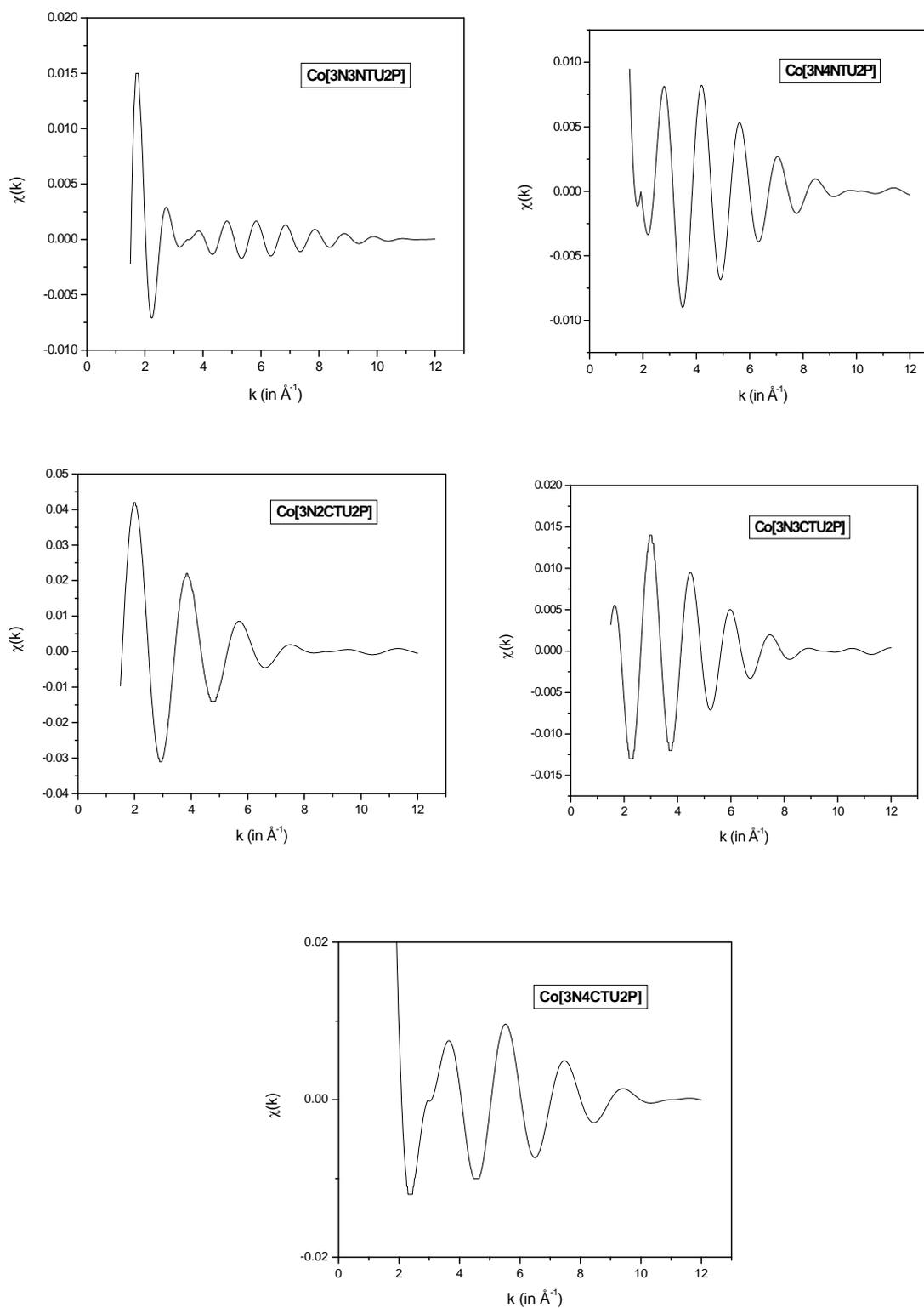


Figure 3. Calculated $\chi(k)$ versus k curves for cobalt complexes.

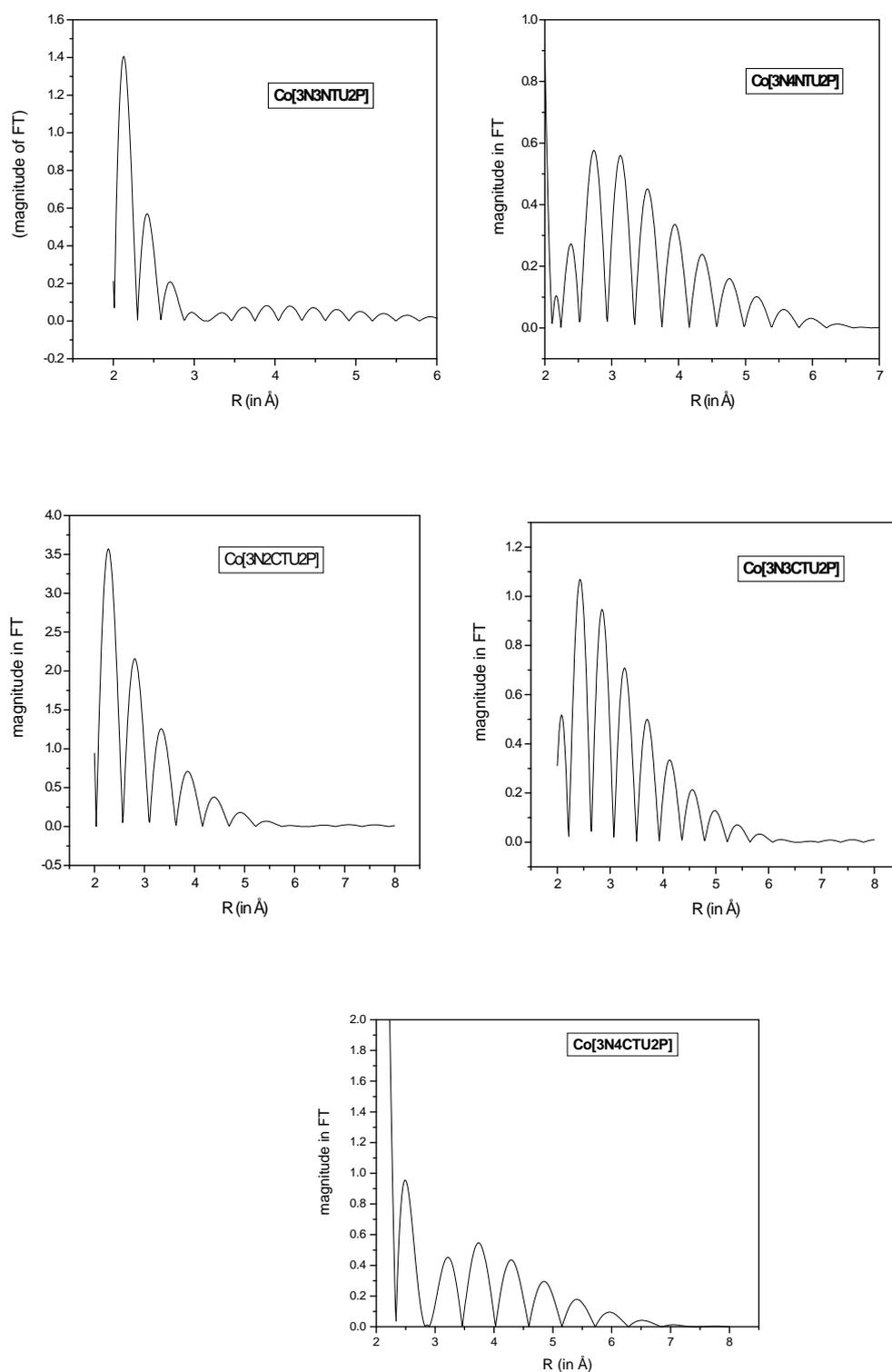


Figure 4. Magnitude of Fourier transform of calculated $\chi(k)$ for cobalt complexes.

4. Conclusions

Fourier transform technique provides results with great accuracy. This method is simple and straight forward, thereby providing a physical picture of the X-ray absorption process. This method appears to have a great potential in studying systems such as crystalline and amorphous materials. The atomic distance of central atom with the first nearest neighbour is not affected very much by changing the various substituents in the ligand. The reason is that the substituents are not directly linked to the central atom. Results indicate that bond lengths determined by Fourier transforming the calculated data resembles with the bond lengths obtained by LSS method, Levy method and Lytle method. As the imaginary part of Fourier Transform coincides with the amplitude of Fourier Transform, this verifies that experimentally obtained phase shift parameter is consistent with theoretically calculated data. Thus, the theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of the EXAFS spectra describes in good agreement with physical reality. The calculated EXAFS curves for cobalt complexes of thiourea series are in good agreement with experimental EXAFS curves for all complexes studied within experimental error. A perusal of bond length values are obtained by magnitude of Fourier Transform of calculated EXAFS data indicates that the calculated values are in good agreement with the values obtained by LSS method, Levy method and Lytle method.

Table 1. The average values of metal-ligand bond length in (\AA)⁻¹ for cobalt complexes.

<i>S.N</i>	<i>COMPLEXES</i>	R_{LSS}^a	R_{Lytle}^a	R_{Levy}^a	R_{FT} (MATHCAD)	R_{FT} (ATHENA)
1	Co [3N3NTU2P]	1.01	3.4	3.4	2.1	1.07
2	Co [3N4NTU2P]	1.04	2.5	2.5	2.7	0.88
3	Co [3N2CTU2P]	0.89	2.0	2.0	2.2	0.98
4	Co [3N3CTU2P]	0.90	1.9	2.4	2.4	1.13
5	Co [3N3CTU2P]	1.02	1.8	1.9	2.5	1.19

5. References

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- [5] Vaarkamp M, Dring I, Oldman R J, Stern E A and Koningsberger D C 1994 *Phys Rev B* **50** 7872.