# Theoretical Analysis of EXAFS Spectra of Copper (II) amino Acid Using IFEFFIT Method

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*Authors' contributions*

*This work was carried out in collaboration between all authors. Author AM designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author SN managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.*

**Original Research Article**

## ABSTRACT

A Theoretical approach for studying the structure of copper (II) amino acid complexes have been carried out using extended X-ray absorption fine structure (EXAFS). The fine structure of the complexes was done for six copper (II) amino complexes. The theoretical bond lengths of the complexes were calculated by using interactive fitting of EXAFS using fast Fourier inverse transformation (IFEFFIT) method. This method is also called as Fourier transform method. The Lytle, Sayers and Stern method and Levy's method have been used for determination of bond lengths experimentally of the studied complexes. The results of both methods have been compared with theoretical IFEFFIT method. On comparing the results, the theoretical approach is also described in the present publication.

## 1. INTRODUCTION

Amino acids are molecules containing an amine group, a carboxylic acid group and a side chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen. They are particularly important in biochemistry, where the term usually refers to alpha-amino acids. Amino acids are critical to life, and have

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many functions in metabolism. One particularly important function is to serve as the building blocks of proteins, which are linear chains of amino acids. Amino acids can be linked together in varying sequences to form a vast variety of proteins. Twenty-two amino acids are naturally incorporated into polypeptides and are called proteinogenic or standard amino acids. Of these, twenty are encoded by the universal genetic code. Eight standard amino acids are called "essential" for humans because they cannot be created from other compounds by the human body, and so must be taken in as food. Due to their central role in biochemistry, amino acids are important in nutrition and are commonly used in food technology and industry. In industry, applications include the production of biodegradable plastics, drugs, and chiral catalysts [1].

It is found that the amino acid has significant influence in the spectra and the results obtained are in agreement with the well-known structure of transition metal complexes. Amino acids are of great chemical, biological, industrial and medicinal importance.

The complexes studied are as follow:-

(1) Copper (II) alanine, (2) Copper (II) glycine, (3) Copper (II) valine, (4) Copper (II) serine, (5) Copper (II) threonine, (6) Copper (II) histidine.

In the present communication, the X-ray K-absorption edge structural studies of copper (II) complexes with amino acids have been reported. A comparison of theoretical analysis X-ray absorption fine structure and experimental measurements of copper complexes is incorporated in the paper. X-ray absorption fine structure is divided into two parts. Following the edge, there appears a structure on its higher energy side. The fine structure near edge covering energy range up to nearly 50 eV is called X-ray absorption near edge structure (XANES). The structure extending over several hundred electron volts above 50 eV, beyond XANES region is called extended X-ray absorption fine structure (EXAFS). X-ray absorption technique has been developed as a powerful tool for investigation of structural information of compound and complexes in solid form. These studies have been used for calculations of inter-atomic distances of complex systems. This involves different techniques for calculating the bond lengths using different methods mentioned and used in this publication. One of the theoretical method is FT method (Fourier transform method).With the help of this method, it has been reported that it is a worth to compare with experimental methods. The FT method is applicable for complex systems. Using EXAFS function χ (k) one can get the redial distance and transform into k space. This relation gives the Fourier transform (FT) for any compound or complex attached to metal.

In the present investigation, .04 m Cauchios type curved crystal transmission spectrograph in it's improved from has been used to record the spectra. Mica crystal, optically pure and free from deformities has been used as a diffracting medium. The performance of the spectrograph can easily be observed by recording the MoKβ $_{1,\,3}$ doublets taken on the spectrograph with 201 planes of the mica crystal reflecting in the second order. The sealed molybdenum target X-ray tube was operated at 26kV and 5mA. The exposure time was only one minute. The doublet is seen clearly resolved. The resolution may be defined quantitatively as Δλ/λ, which is the reciprocal of resolving power [2] Good resolution then means as a small numerical value of Δλ/λ. Absorption screens were prepared by uniformly spreading the fine powder sample on 1 cm$^2$ area of cellophane tape. Another piece of cellophane tape was put over it, sealing of the substances in between. The screen which gave the substance best spectra was found to have generally had a thickness of 15-30 mg/cm$^2$ .The exposure time is varied from 2 to 3 hours. The absorption screen of aqueous

solution was prepared by using a perspex sheet as done by an earlier worker [3] with dimensions 5 cm x 5 cm x .2 cm and having a circular hole of 1.5 cm diameter as its centre for filling the solution. One side was covered with another piece of cellophane tape and the solution was filled inside hole. The other side was closed with another piece of the cellophane tape. Care was taken so that no air bubble is left inside the solution. The aqueous solution was prepared dissolving 20-30 mg powder in doubly distilled water. Sometimes the solution was heated up to 600C for dissolving the powder into water. The concentration of aqueous solution was 100 mg/cm3. The exposure time is varied from 4 to 12 h. After this process, the scanning of the X-rays films were completed on Carl-Ziess Microdensitometer coupled with a Pc to convert the data into IFEFFIT analysis.

This work has been used to determine the bond length using the conventional methods like Levy's and Lytle, Sayers and Stern (L.S.S.) [4-5]. The details of the calculation of bond length with these methods are described by Johar [6]. For this 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. This determination is confined to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radiuses from the element. Modeling EXAFS spectra to determine the average, local-molecular coordination environment of an absorber atom is a multistep process that is best learned through hands-on experience. Therefore, we describe here the process of building a structural model has been described by giving examples for certain steps with specific reference to the EXAFS data analysis programs Athena for background removal and Artemis for optimizing the theoretical model to the measured spectrum by Ravel and Newville [7]. These programs are user-friendly GUI interfaces to IFEFFIT Ravel [8]. IFEFFIT is interactive engines that contains the algorithms for fitting the theoretical FEFF calculations also Zabinsky et al. [9] have explain to the measured spectrum, hence the name IFEFFIT.

## 2. METHODOLOGY

The steps of XAFS data processing is governed by (a) pre-edge subtraction, (b) edge-step normalization, (c) post-edge background subtraction, (d) converting the XAFS oscillations to k-space (k: photoelectron wave-vector) and (e) Fourier transforming the oscillations to radial coordinate (r) space. The present version, FEFF8, of the program allows e.g. calculations of phase shifts, effective scattering amplitudes (f-eff from which FEFF gets its name) for possible single and multiple scattering pathways using curved wave scattering theory, for XAFS and XANES spectra [10-12]. The present version, FEFF8, of the program allows e.g. calculations of phase shifts, effective scattering amplitudes (f-eff from which FEFF gets its name) for possible single and multiple scattering pathways using curved wave scattering theory, for XAFS and XANES spectra". XANES is an element-specific electron spectroscopic technique which is highly sensitive to bond angles, bond lengths and the presence of adsorbents. It is widely used in surface science and has also been used to study polymers and magnetic materials. XANES is distinguished from the closely related EXAFS method in that XANES concentrates on fine structure within about 30 eV of the absorption edge while EXAFS considers the extended spectrum out to much higher electron kinetic energies. The atomic background absorption, which is normally assumed to be a smooth monotonically decreasing function with increasing energy, was recently shown to have structure in the NEXAFS region. For accurate evaluation of XANES and XAFS spectra such variations can be of importance, and improved background calculations have been introduced in the later FEFF program codes.
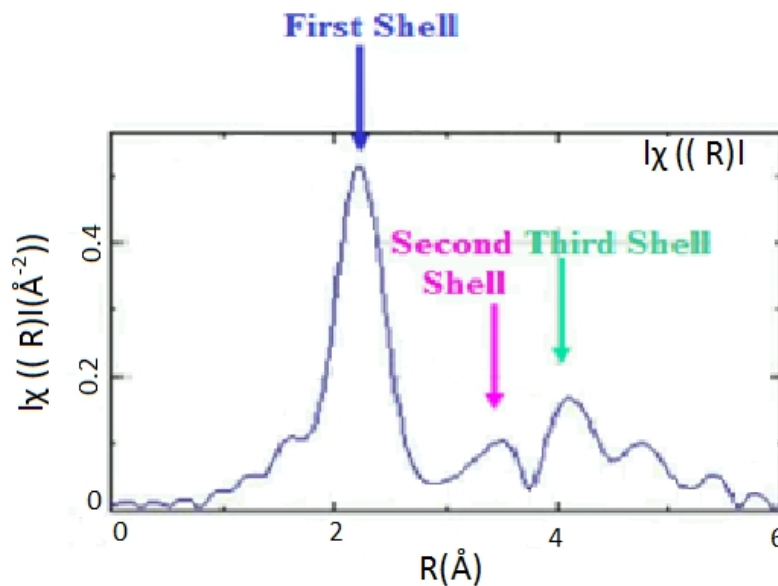
## 2.1 Fourier Transform

The Fourier Transform (FT) equivalently describes a signal as a sum of terms of the form exp (±ikr), with complex coefficients. EXAFS data basically consist of sums of damped sine waves, and the rapidly oscillating contributions correspond to longer path lengths. An FT of the data therefore gives something analogous to a map of the distribution of distances (or half-path lengths when multiple scattering is considered). It is equally valid to represent the data in either k-space or r-space; one should use the best representation for the task at hand. Fourier methods can be tricky, and it's not hard to make mistakes in transformation and filtering.

The Fourier transformation of χ(k) is defined by

$$FT(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} k^n \, \chi(k) \, e^{i2kR} \, dk$$

For EXAFS, the canonical variables are k (in Å$^{-1}$) and R (in Å), and the Fourier transform (FT) of an EXAFS spectrum gives a pseudo-radial distribution function.



**Fig. 1. Fourier transform of χ (k) shows bond length with first, second and third shell.**

The Fourier transform of χ(k) can be seen in the Fig.1. The larger peak located at approximately 2 Å is a group of atoms that exist on the corresponding radius (commonly called coordination shell) around the absorbing atom and produce the collective constructive interference.  In many cases, multiple shells of scatterers do not give rise to multiple peaks in the FT. Similarly, interference between two different peaks in the FT may give rise to a spurious third peak. The latter results from the fact that the FT of an EXAFS spectrum is actually a complex number, with both real and imaginary components. Typically, however,

only the modulus of the FT is plotted with first second and third shell. This is useful for visualizing the major contributions to the EXAFS spectrum, but should never be used for quantitative data analysis.

## 3. RESULTS AND DISCUSSION

The normalized absorption spectra of copper (II) amino acid complexes are shown in Fig. (2). The value of bond length calculated by LSS and Levy's are two methods reported in Table 1. The values of $R_{IFEFFIT}$ is also shown in the Table 1. The EXAFS spectra of copper (II) amino acid complexes converted into k space have been given in Figs. 3(a,b,c,d,e.f).The magnitudes of Fourier transform of copper (II) amino acid complexes are shown in Figs. 4(a,b,c,d,e,f) and the first shell bond lengths hence calculated have been shown in Table 1. The maxima and minima of the spectra for different values of k have been labeled with the conventional Latin and Greek alphabets respectively.

The bond lengths have been determined using the following four methods, i.e;

a) Levy's method, b) Lytle, Sayers and Stern's (LSS) method,

**a) Levy's method:** According to Levy's method the bond lengths of compounds or complexes are given by the relation $R_1 = [151/\Delta E]^{1/2}$ Å, where $\Delta E$ is the difference in eV of the energies of the EXAFS maximum B and minimum $\beta$ and $R_1$ is the radius of the first coordination sphere [4]. The bond lengths of the reported complexes were raging from 1.67 Å to 2.44 Å. The variation in the bond lengths are due to change in ligation of metal with different ligands attached to the complexes.

**b) Lytle, Sayers and Stern's (LSS) method:** The LSS method used for determination of the nearest neighbouring distances between metal and ligands. In this method, theory of the extended X-ray absorption fine structure (EXAFS) was considered for short range order in materials. According to this, fine structure on high energy side of an absorption discontinuity arises due to the interference between the out going photoelectron and the backscattered waveform the near by atoms [5]. The EXAFS function using scattering theory was used for giving the equation for calculating the bond lengths. This equation gives the value of $(1/2+n)$ $\pi = 2k (R_1) + 2\beta_1$, where $R_1$ is the bond length.

**Table 1. Average values of bond length (in $A^0$) for Copper (II) complexes of amino acids**

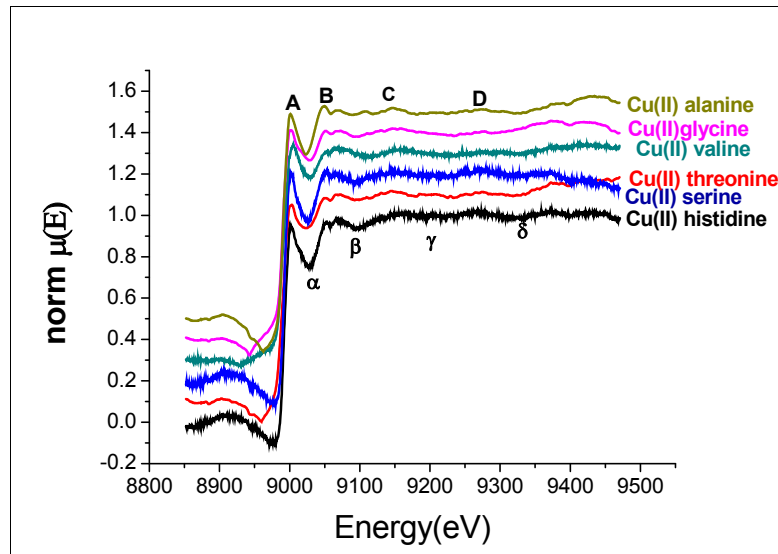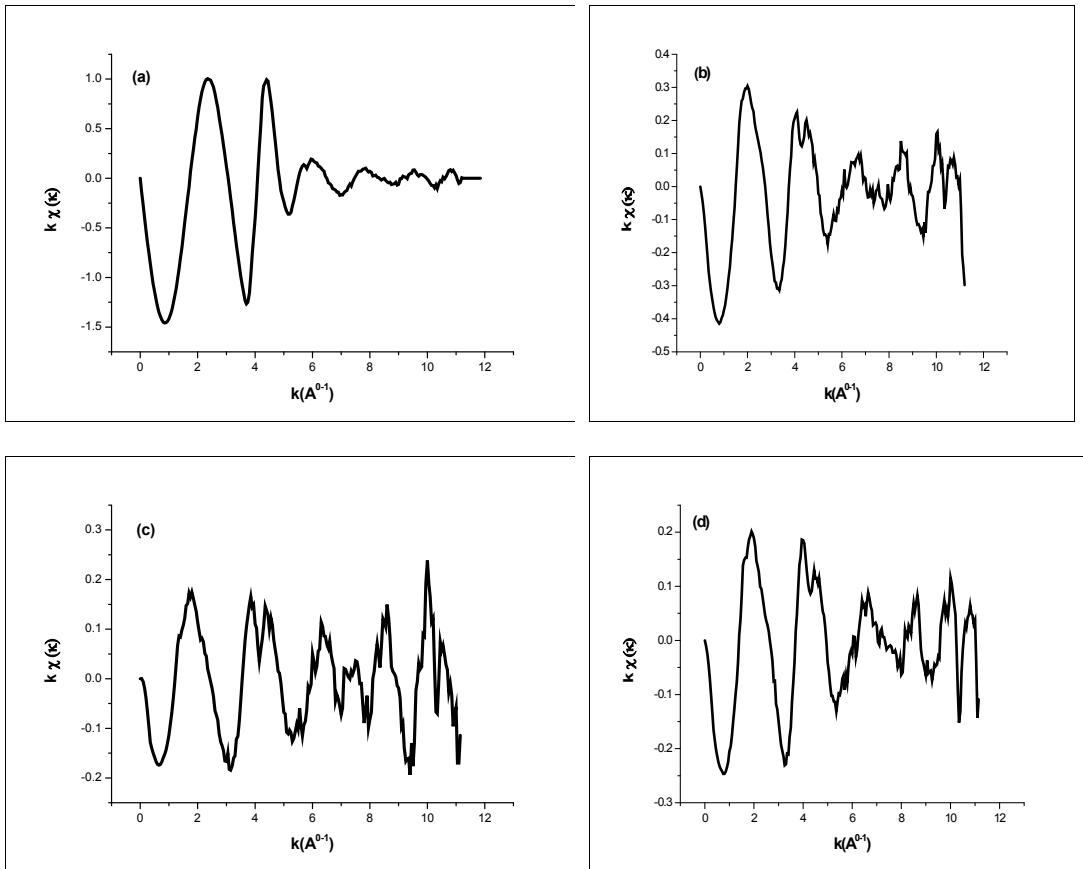| Complexes | $R_{LSS}$ (Experimental) | $R_{LEVY'S}$ (Experimental) | $R_{IFEFFIT}$ (Theoretical) |
|---|---|---|---|
| Cu-alanine | 1.82 | 1.56 | 1.58 |
| Cu-glycine | 2.96 | 2.94 | 2.27 |
| Cu-serine | 1.91 | 1.88 | 1.96 |
| Cu-valine | 2.09 | 1.83 | 1.82 |
| Cu-histidine | 2.78 | 2.51 | 2.23 |
| Cu-theronine | 1.84 | 1.98 | 1.97 |

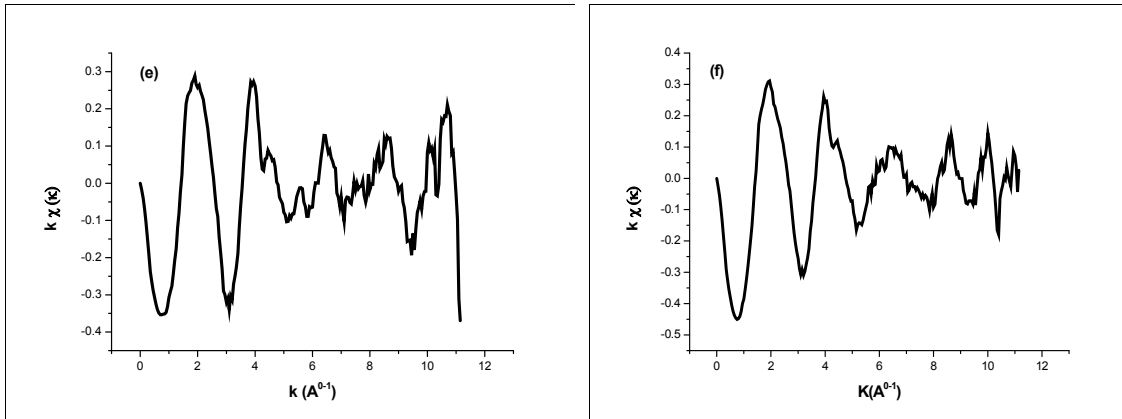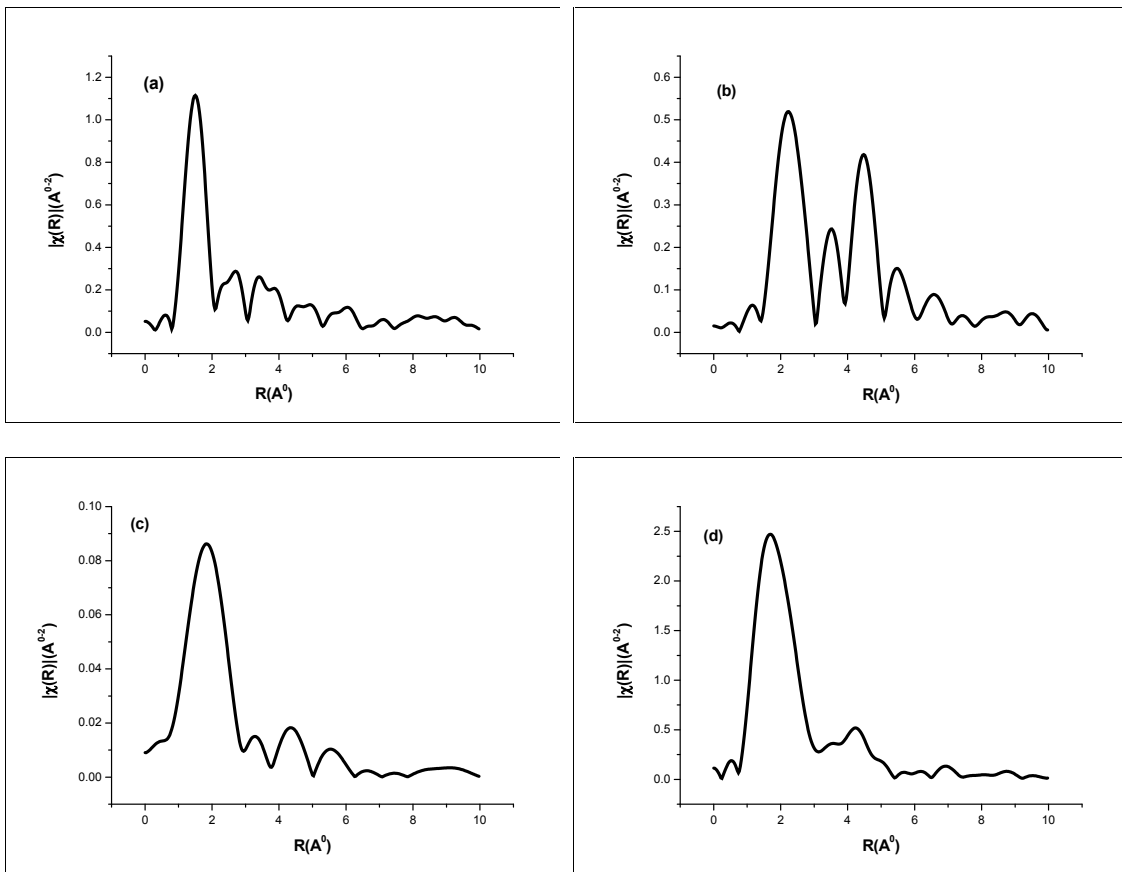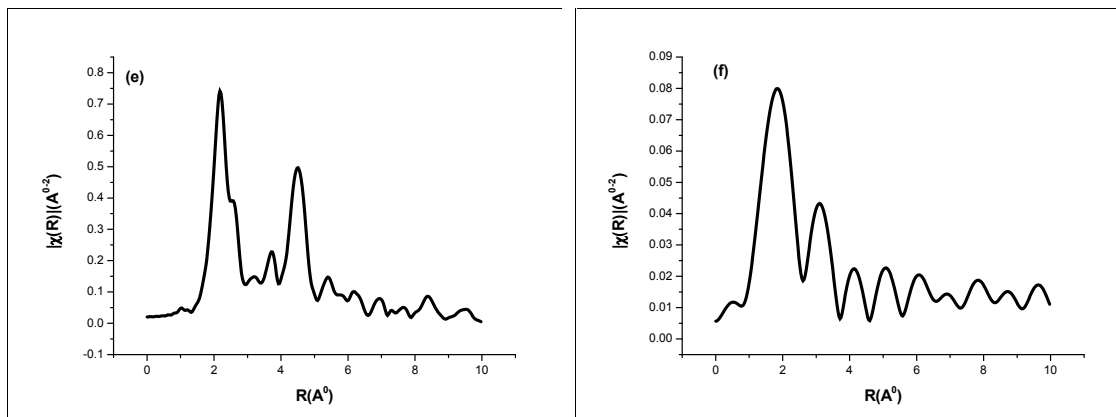**Fig. 2. The normalized absorption spectrum for copper (II) amino acid six complexes**

**Fig. 3(a,b,c,d,e,f). χ(k) versus k curve for copper (II) amino acid six complexes.**

**Fig. 4. (a,b,c,d,e,f) Magnitude of Fourier transform of the χ(k) versus k curve copper (II) amino acid six complexes.**

## 4. CONCLUSION

The set of six copper complexes have been studied by using the laboratory X-ray spectroscopic set-up with fixed target. The present work also describes the theoretical study using for Fourier transform technique on these samples. One can compare the theoretical and experimental results of the bond length distance using the methods reported in this communication. It has been found that the IFEFFIT method using Fourier transform for theoretical results is ranging from 1.58 Å to 2.27 Å shorter than the actual distance due to energy dependence of the phase factors in sine function of the EXAFS equation. The experimental values reported are in consistent with the theoretical values. The Fourier transform method is widely used to extracted EXAFS data signal and it convert into R space. The reported graphs also give information about the radial distance by using IFEFFIT method.

## ACKNOWLEDGEMENTS

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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