EXAFS and XRD studies of copper and cobalt complexes of amino acid

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Abstract. The present paper deals with the synthesis of transition metal schiff base complexes of Para amino benzoic acid (PABA) by chemical root method. The synthesized metal complexes were characterized by XRD analysis, Extended X-ray absorption fine structure (EXAFS) is a technique that has been used for determining the metal ligand bond length using conventional X-ray source and also by EXAFS analysis using IFEFFIT programming. Bond lengths determined from these data analysis methods are compared with the bond lengths obtained from LSS, Levy’s and Lytle’s methods. All the complexes show the crystalline simple cubic structure. Bond lengths of the complexes are in good agreement obtained by theoretical and experimental methods.

1. Introduction
The transition metal Schiff base complexes of amino acid have been playing an important role in the development of coordination chemistry. Schiff base metal complexes have been widely studied, because of their antifungal and biological applications. X-ray diffraction studies provide information about the shape of the unit cell and the size of the particles [1]. The structure extending from 40 to 1000eV from the edge is called extended X-ray absorption fine structure (EXAFS) [2, 3] and gives information about the local structure of the complexes. The aim of the present investigation is to measure the X-ray K-absorption spectra and X-ray diffraction studies of copper and cobalt complex of Para amino benzoic acid (PABA), and to compare first shell inter atomic distance using the programmed called IFEFFIT.

2. Preparation of Schiff base ligand
In order to prepare these complexes, we have taken an an ethanolic solution of the prepared benzoin (0.01 mol) and amino acids (0.01mol) in a 500cm³ round bottom flask, 3.0gm of anhydrous sodium acetate was added. The mixture was refluxed for an hour on steam bath. To precipitate the product, the content was poured into an ice-cold water which was separated and recrystallized from rectified spirit, suction filtered, washed with water, and dried in a vacuum dessicator.

2.1 Synthesis of Complexes
Ethanolic solutions of CuCl₂ (0.025mol) and Schiff base (0.05mol) were mixed and the resulting mixture followed by drop wise addition of ammonia until the chelate separated, which were then suction filtered,
washed with ethanol and ether before dried in vacuum dessicator. The crystals were recrystallized from rectified spirit and dried. Then the complex was in powered form and was ready for our spectroscopic studies.

3. Experimental Technique

In the present study, X-ray diffraction studies were carried out using Bruker D8 Advace `X-ray diffractometer. The X-ray were produced using a sealed tube and the wavelength of X-ray was 0.154nm (Cu K-alpha). The X-ray were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector).

X-ray absorption fine structure studies were carried out using a conventional Siefert sealed X-ray tube with Tungsten target operating 20 kV and 40 mA. After this process, the scanning of the X-ray films was completed on Carl-Ziess microdensitometer coupled with computer to convert the data into IFEFFIT analysis.

4. Results and discussion

4.1. XRD analysis

The crystal structure and lattice parameter were analyzed by Bragg’s law, 2dsinθ=λ and particle size is calculated by Debye Scherer’s formula, t=0.9λ/B cosθ. The XRD pattern of the complexes is reported in figure 1. The particle size and lattice parameter are shown in table 1. The X-ray analysis shows the complexes are crystalline in nature [4].

Table 1 Particle size and lattice parameter by XRD.

| Complex     | Particle size (nm) | Lattice parameter (Å) |
|-------------|--------------------|-----------------------|
| Cu(PABA)    | 9.44               | 5.67                  |
| Co(PABA)    | 20.04              | 6.55                  |

![Figure 1: XRD pattern of copper and cobalt complexes](image_url)
4.2. EXAFS analysis

The bond lengths of copper and cobalt complexes were calculated using IFEFFIT method and compared with LSS, Levy’s, lytle’s methods [5,6,7].

According to LSS method, we have determined the bond length using the slope of n vs k plot. The phase parameter \( \alpha \) and \( \beta \), the metal ligand bond length \( R_1 \) have been estimated with expression \((1/2+n)\pi=2k (R_1-\alpha)+2\beta-\pi\). The EXAFS curves are shown in figure 4.

Using the Levy’s method, the bond length has been obtained from the expression \( r=(151/\Delta E)^{1/2} \) where, \( \Delta E \) is the energy difference between first maxima and first minima [8].

Lytle method is modification of LSS method and the bond length is given by the expression \( R=(37.60/M)^{1/2} \) where \( M \) is slope between E vs Q plots.

In FEFFIT programming the EXAFS data were analyzed by the standard procedure. The pre-edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interest above the edge was removed from the spectrum using spline fit. The data converted to energy space and then to k space (figure 3). A Fourier transform is applied to these data to convert into the \( r \)-space is shown in figure 2. The bond lengths of copper and cobalt complexes calculated by IFEFFIT programming is compared with LSS, Lytle and Levy’s methods as depicted in table 2.

| Name of complex | \( R_{\text{LSS}} \) | \( R_{\text{Lytle}} \) | \( R_{\text{Levy's}} \) | \( -\beta \) | IFEFFIT |
|-----------------|-----------------|-----------------|-----------------|-----------------|---------|
| Cu(PABA)        | 2.46            | 1.78            | 1.97            | 2.16            | 1.2     |
| Co(PABA)        | 2.10            | 1.61            | 1.85            | 2.06            | 2.06    |

**Figure2:** Magnitude of Fourier transform of \( k2\pi(k) \) for copper and cobalt complexes obtained from FEFFIT program
Figure 3: EXAFS function for copper and cobalt complexes obtained from FEFFIT program.

Figure 4 X-ray absorption discontinuity for copper and cobalt complex

5. Conclusion
As is evident from the analysis of X-ray diffraction pattern, one can conclude that the samples exhibit crystalline nature and shape of unit cell is simple cubic. Results indicate that the bond lengths determined by Fourier transforming the FEFFIT programming are comparable with the bond length obtained by LSS, Levy’s and Lytle methods. The theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of the EXAFS spectra of copper and cobalt complexes described here is in good agreement with physical reality.

6. References
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