Co (II) Complexes with Schiff Base Ligands: Synthesis and EXAFS Study

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Abstract. The synthesis of transition metal Schiff base complexes of Co(II) are prepared by chemical root method. Obtained by the condensation of O-phenylenediamine, salicylaldehyde and isatin/2-hydroxy-1Naphthaldehyde is presented. The complexes were characterized by Co-K-edge EXAFS measurements using the dispersive beam line at 2.5GeV energy of Indus-2 synchrotron radiation source RRCAT Indore. The recorded EXAFS data were analyzed using the computer software Athena for determine the nearest neighboring distances (bond lengths) of these complexes with conventional methods and were compared with Fourier transform (FT) analysis.

1. Introduction:
Schiff base have been playing an important part in the development of Co-ordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of application in numerous scientific areas. They play in important role in both synthetic and structural research, because of their preparative accessibility and structural diversity. Schiff base of o-phenylediamine and its complexes have a variety of application including biological, clinical and analytical [1-2].

The nature of a complex sample is best revealed by the application of several different experimental techniques, with each individual measurement providing both unique and complementary information. EXAFS have been used extensively in the investigation of local atomic structures such as the number and type of neighbouring atoms, inter-atomic distances and disorder. Since the application of EXAFS does not require the materials to have long-range order. It is well suited for determining the local structures of both non-crystalline materials. The well-marked EXAFS feature on the high energy side of the K-absorption edge up to several hundred eV has been observed in the cobalt complexes. From the knowledge of EXAFS, we have calculated the bond length for the following cobalt complexes with the help of Levy’s, LSS, Lytle and Fourier transform methods.

2. Experimental Technique:
2.1. Preparation of Schiff base L₁/L₂:
A solution of o-phenylenediamine (0.005 mol) in alcohol was added to a mixture of isatin/2-hydroxy 1naphthaldehyde (0.005 mol) and salicylaldehyde (0.005 mol) in 20 ml alcohol. The mixture was refluxed for about 30 minutes. The mixture was cooled in ice. The resulting precipitate was then filtered, washed with ethanol and dried.
2.1. Preparation of complex: To an ethanolic solution of the Schiff base Ligand L₁/L₂ an ethanolic solution of the metal (cobalt chloride) was added in molar ratio (1:1). The mixture was refluxed for about 30 minutes. The mixture was cooled in ice. The resulting precipitate was then filtered, washed with ethanol and dried.

EXAFS Analysis
The X-ray absorption spectra have been recorded using synchrotron radiation. The X-ray spectroscopy setup is available at Raja Ramanna Centre for Advanced Technology (RRCAT) and is called beam line. This beam line BL-8 has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation sources.

3. Result and discussion:
EXAFS Bond determination using Different methods
(i) Levy’s method
In Levy’s method, the bond lengths are given by \( R_1 = \left[ \frac{151}{\Delta E} \right]^{1/2} \) \( \text{Å} \), Where, \( \Delta E \) is the difference in eV of the energies of the EXAFS maximum B and minimum and \( R_1 \) is the radius of the first coordination sphere [1].

(ii) Lytle’s method
The energy values (E) of the EXAFS maxima, according to Lytle for p symmetry, i.e., Q = 2.04, 6.0, 12.0, and 20.0. To evaluate the radius \( R_s \) of equivalent polyhedron through the relation \( R_s = \left[ \frac{37.60}{M} \right]^{1/2} \).

(iii) Lytle, Sayers and Stern’s (LSS) method
In the LSS method for determination of the nearest neighbour distances, gives the value of \( 2(R_1 - \alpha_1) / \pi \) where \( R_1 \) is the bond length [3-4].

(iv) Fourier transforms method
Bond length has also been determined by the Fourier transformation method for the cobalt complexes studied however, determined only the phase uncorrected bond lengths by this method. No attempt has been made to employ the fitting procedures by which phase corrected bond length can be determined, because the required crystallographic data is not available for any of the complexes studied.

The bond lengths are calculated using Levy’s, LSS and Lytle methods. The values of bond length R is tabulated in table 1. The bond lengths obtained in Co(II) Complexes by LSS, Levy’s, and Lytle method with F.T. method are comparable each other.

4. Conclusion
As pointed out above, the LSS method, Levy’s, Lytle and the Fourier transformation method give the value of bond length R, are comparable to each other. This distance is called the phase uncorrected bond length. It can be seen from table 1 that the phase uncorrected bond lengths obtained from these two methods agree with each other within the limits experimental error.

Table 1: Average values of the bond length in (Å) for the Co (II) Complexes.

| Complexes | RLSS | RLevy | RLytle | RF.T. |
|-----------|------|-------|--------|-------|
| Co foil   | 1.45 | 1.55  | 1.35   | 1.38  |
| Co1       | 1.38 | 1.48  | 1.37   | 1.37  |
| Co2       | 1.39 | 1.44  | 1.32   | 1.35  |
Figure 1 Energy spectra of Co foil, Co complex 1 and Co complex 2.

Figure 2 $k$ vs $\chi(k)$ spectra of Co foil, Co complex 1 and Co complex 2.

Figure 3 Bond length by Fourier Transformation magnitude of Co foil, Co complex 1 and Co complex 2.

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