X-ray diffraction and extended X-ray absorption fine structure study using synchrotron radiation of cobalt (II) complexes

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Abstract. XRD and EXAFS investigation of cobalt (II) macro cyclic complexes were carried out. These complexes were synthesised by chemical route method. On the analysis of the complexes with X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS), XRD analysis shows that complexes are crystalline in nature and having particle size and lattice parameter in the range of few micro meter and EXAFS technique extract the local structure of complexes. The nearest neighbouring atom distance commonly known as ‘bond length’ were calculated using Fourier transform method. The bond lengths determined from these methods were also compared with the bond length obtained from several other known techniques.

1. Introduction:
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. The most common technique for characterizing abundant soil minerals is X-ray diffraction (XRD), which relies on long range ordering of atomic planes to probe crystalline structure at a length scale of approximately 50 Å or more [1]. EXAFS have been used extensively in the investigation of local atomic structures such as the number and type of neighboring 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, have 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.

1. Co (II) (2-[2[1-(2-hydroxyphenyl)ethyl] amino phenyl] ethanimidoyl]chloride (Co₂M₂₁H₂HEAPEtCl) - complex 1.
2. Co (II) (2-[2[1-(3-hydroxyphenyl)ethyl] amino phenyl] ethanimidoyl] chloride. (Co₂M₂₁H₂HEAPEtCl)-complex 2.

2. Experimental Technique:
2.1. Preparation of Schiff base
The ligand of 2-[2[1-(hydroxyphenyl)ethyl] amino phenyl] ethanimidoyl] phenol was synthesized by mixing an ethanolic solution of 0.01 mole of O-Phenylenediamine (1.08g) with same solvent of 0.01 mole of 2-hydroxyacetophonone (1.36g). The reaction mixture was refluxed for two hours, then the formed precipitate was filtered, washed several time with ethanol and dried in a desiccators over...
calcium hydroxide. The yield of the reaction was 73%. The following structure represents the formation of the Schiff base.

2.1. Preparation of complex
Co (II), with 2-[(2-[1-(2-hydroxyphenyl)ethyl] amino phenyl) ethanimidoyl] phenol were synthesized by mixing-ethanolic solution. (50ml) of the 0.01mol of CoCl$_2$.6H$_2$O respectively and few drops of ammonia solution were added to adjust the pH until the complexes isolated. The reaction mixture was refluxed for three hours. And left cool and filtered by suction. The precipitates were washed several times with ethanol, then ether. The complexes were dried in desiccators over anhydrous calcium chloride. The yields were 75% and 78% respectively [5-6]

$$MX_2 + 2L \rightarrow M(L)_2 + 2X$$

In this equation, M is metal Co (II) and X is Cl and L Ligand: 2-[(2-[1-(2-hydroxyphenyl) ethyl]aminophenyl)ethanimidoyl]phenol.

(XRD) measurements were carried out with Cu Kα radiation using a BRUKER D8 Advanced with a rotating anode scanning (0.01 step in 2q) over the angular range 10° - 80° at room temperature generating X-ray by 40 kV and 100 mA power settings. Monochromatic X-rays of $\lambda = 1.5406$ Å Kα$_1$ line from a Co target were made to fall on the prepared samples. 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:
The pattern has been indexed using JCPDF software and lattice parameters have been using the Braggs law. The Braggs condition is:

$$2dsin\theta=n\lambda$$

Here d is lattice spacing and given by

$$a^2 = \lambda^2 (h^2+k^2+l^2) /4sin^2\theta$$

In cubic structure a=b=c , $\alpha=\beta=\gamma=90$. The particle size of the determined by Debye sherrar formula

$$t=0.9\lambda/Bcos\theta$$

where, $\lambda=1.54$ Å, B=Width. Calculated Lattice parameter and particle size are shown in table 1
Table 1. Lattice parameter and particle size

| Complex  | Particle size (nm) | Lattice parameter(Å) |
|----------|--------------------|----------------------|
| Complex 1 | 13.99              | 5.6                  |
| Complex 2 | 10.07              | 16.79                |

(i) Levy’s method
In Levy’s method, the bond lengths are given by $R_1 = \left[\frac{151}{\Delta E}\right]^{1/2}$ 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 [2].

(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 $R_e$ of equivalent polyhedron through the relation [3]
$$R_e = \left[\frac{37.60}{M}\right]^{1/2}$$

(iii) Lytle, Sayers and Stern’s (LSS) method
In the LSS method for determination of the nearest neighbor distances, n versus k graph is plotted. The slope of n versus k plot, gives the value of $2(R_1 - a_1)/\pi$ where $R_1$ is the bond length [3-4].

(iv) Fourier transform 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.

Energies of the maxima and minima position are tabulated in table 2. The bond lengths are calculated using Levy’s, LSS and Lytle methods. The values of bond length R is tabulated in table 2. The bond lengths obtained in Co(II) Complexes by LSS, Levy’s, and Lytle method with F.T. method are comparable each other.

Table 2: Average values of the bond length in (Å) for the Co (II) Complexes.

| Complexes | $R_{\text{LSS}}$ | $R_{\text{Levy}}$ | $R_{\text{Lytle}}$ | $R_{\text{F.T.}}$ |
|-----------|------------------|-------------------|--------------------|-------------------|
| Complex 1 | 1.41             | 2.72              | 1.97               | 1.52              |
| Complex 2 | 1.45             | 3.06              | 1.92               | 2.0               |
4. Conclusion
The XRD studies done on the two macro cyclic complexes of cobalt showed that they are crystalline in nature and lattice parameter in the range of angstrom.
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.2 that the phase uncorrected bond lengths obtained from these two methods agree with each other within the limits experimental error.

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