XRD, IR and XAFS studies of cobalt complexes having amino pyrazole dicarboxylate (APD) as ligand

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Abstract. X-ray absorption fine structure spectroscopic (XAFS) studies have been done on two cobalt complexes using APD (diethyl 4-amino-1-phenyl-1H-pyrazole-3,5 dicarboxylate) as ligand. The X-ray absorption spectra of the complexes have been recorded on beam line of synchrotron at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore (India). The X-ray diffraction of the samples has also been carried out. FTIR studies of two samples were also reported in the present communication.

1. Introduction
X-ray Absorption Fine Structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. XAFS can be applied not only to crystals, but also to materials. XAFS is often divided into X-ray absorption near edge structure (XANES), which lies within the first 40 eV of the edge position and extended X-ray absorption fine structure (EXAFS), which lies beyond 40 eV above the absorption edge. We have studied the X-ray absorption spectra at the K-edge of cobalt of a series of three cobalt complexes have been investigated.

X-ray diffraction (XRD) is a tool to identify the crystalline nature of the samples. Infrared spectroscopy is one of the most important analytical techniques. FT-IR provides information about identify unknown materials, determine the quality or consistency of a sample and determine the amount of components in a mixture.

The present study deals with analysis and structural information of samples using X-ray diffraction, FTIR and X-ray K-absorption spectra of two cobalt (II) complexes i.e.

1. Bis-(diethyl 4-amino-1-(P-nitrophenyl) -1H-pyrazole-3,5 dicarboxylate) cobalt (II) chloride (Co(D4A1(P-n)1HP35D).
2. Bis-(diethyl 4-amino-1-(4-bromophenyl) -1H-pyrazole-3,5 dicarboxylate) cobalt (II) chloride (Co(D4A1(4-br)1HP35D).

2. Experimental
All the studied complexes have been prepared by chemical root method. The X-ray K-absorption spectra of the cobalt complexes have been recorded using synchrotron radiation. The X-ray spectroscopy setup is available at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore and is called beamline. This beamline BL-8 has been recently commissioned at the 2.5 GeV INDUS-2 Synchrotron radiation source.
The infrared absorption spectra of the complexes were measured at room temperature, in the wave number range 4000 to 400 cm\(^{-1}\) on Jasco FTIR-300 spectrometer using the KBr pellet technique. The X-ray diffraction pattern of cobalt complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode with tube voltage of 40 kV and current of 100 mA. Copper target was used as the source of X-rays at wavelength \(\lambda=1.54\text{Å}\).

3. Result and discussion

3.1 X-ray Diffraction

X-ray diffraction patterns for two cobalt complexes (Co(D4A1(P-n)1HP35D) and Co(D4A1(4-br)1HP35D) were recorded and calculated parameters are given in table 1. All the complexes had a monoclinic crystal lattice.

3.2 Fourier Transform Infrared spectroscopy (FTIR):
The IR spectra of samples were taken in the range between 4000–400 cm\(^{-1}\). IR spectrums of the synthesized samples are depicted in Figure 2.

3.3 X-ray absorption near edge structure:
The X-ray absorption near edge structure (XANES) parameters i.e., chemical shift, shift of principal absorption maxima and edge-width have been determined.

3.3.1 Chemical Shift

The shifts of the k-absorption edge of cobalt in the complexes with respect to that of cobalt metal have been determined according to the equation:

\[ \Delta E = E_k (\text{Complex}) - E_k (\text{Metal}) \]

where the cobalt metal K-edge \(E_k = 7710.2\text{eV}\).

The K-absorption edge of cobalt has been found to be shifted towards the high energy side in all the complexes studied as compared to the k-absorption edge in the metal. The values of chemical shifts of the cobalt complexes is 8.19 eV for Co(D4A1(P-n)1HP35D) and 8.22 eV for Co(D4A1(4-br)1HP35D). These values of the chemical shifts suggest that cobalt is in oxidation state +2 in all of the complexes.

3.3.2 Principal absorption maximum

The distance (in eV) of the principal absorption maximum \(A\) with respect to the respective K-absorption edge of cobalt complexes are 15.43 eV for Co(D4A1(P-n)1HP35D) and 15.26 eV for Co(D4A1(4-br)1HP35D). The order of shift of principal absorption maximum for cobalt complexes is in reverse order of the chemical shift. The reverse order represents that the shift of the principal absorption maximum is inversely proportional to ionic character for the complexes.

3.3.3 Edge width

The edge-width of cobalt complexes is 7.24 eV and 7.04 eV for Co(D4A1(P-n)1HP35D) and Co(D4A1(4-br)1HP35D). The order of the edge-width is in the reverse order of chemical shift. This represents that the edge width is inversely proportional to ionic character for this series.

![Figure 1.X-ray diffractometer records of complexes](image-url)
Figure 2. IR spectra of complexes.

Table 3. Results of X-ray diffraction and FTIR studies of complexes

| Complex                  | Lattice parameter a (nm) | b (nm) | c (nm) | Unit cell volume (10^8 cm^3) | IR ν max (cm^−1) |
|-------------------------|--------------------------|--------|--------|-------------------------------|------------------|
| (Co(D4A1(P-n)1HP35D)    | 14.1                     | 6.48   | 10.29  | 936.12                        | 1739.54 (C=O stretching), 1522.79 (NO2 stretching), 1258.81 (C-O stretching) |
| (Co(D4A1(4-br)1HP35D)   | 12.58                    | 6.88   | 13.68  | 1137.22                       | 3218.52 (N-H stretching), 1687.26 (C=O stretching), 1266.53 (C-O stretching), 509.63 (C-Br stretching) |

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