Determination of first shell radial distance in cobalt as central absorbing atom in Mixed Ligand Complexes with Schiff base and 3-hydroxy picolinamide Ligands

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ABSTRACT

X-ray absorption spectra at the K-edge of cobalt have been studied in cobalt mixed ligand complexes having Schiff base and 3-hydroxypicolinamide ligands. The X-ray absorption spectra have been recorded at BL-8 Dispersive Extended X-ray Absorption Fine Structure (EXAFS) beamline at the 2.5-GeV INDUS-2 Synchrotron Source, RRCAT, Indore, India. The normalized EXAFS spectra have been Fourier transformed. The position of the first peak in the Fourier transform gives the value of first shell bond length, which is shorter than the actual bond length as a result of energy dependence of the phase factors in the sine function of the EXAFS equation. This distance is thus the phase-uncorrected bond length and has also been determined by Lytle, Sayers and Stern’s (LSS) graphical method. The results obtained from LSS and the Fourier transformation methods are comparable with each other. The first shell bond length has also been estimated by Lytle’s and Levy’s methods from the EXAFS data.

Keywords: XAFS, Athena, Absorption, Fourier transform
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1. Introduction

X-ray absorption spectroscopy (XAS) refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. The absorption of X-rays on the high energy side of absorption edges does not vary monotonically in condensed matter but has a complicated behavior which extends past the edge up to about ~1 keV. This non-monotonic variation has received the name of X-ray absorption fine structure (XAFS). The X-ray absorption fine structure is typically divided into two regimes: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). This review describes the basic phenomenon of XAFS, theory of EXAFS and the method of extracting structural parameters by EXAFS which relate to the local environment surrounding the absorbing atom. Also, it has been pointed out that XANES can be used to extract information about the oxidation state, three dimensional geometry, and coordination environment of elements under investigation.

X-ray absorption spectroscopy has been extensively used to obtain information about the molecular structure viz. the oxidation state and the effective nuclear charge of the absorbing atom in compounds and complexes. The Extended X-ray Absorption Fine Structure (EXAFS) yields information regarding the nearest neighbors of the central metal ions, i.e. bond length. Hence, we have studied X-ray absorption spectra at the K-edge of cobalt in mixed ligand cobalt complexes, having Schiff base and 3-hydroxy picolinamide ligands.

The five studied complexes are given in table 1.

2. Experimental

In the present work EXAFS spectra of the five mixed ligand cobalt complexes have been recorded using Indus-2 synchrotron dispersive EXAFS beam line at RRCAT, Indore. In the dispersive mode, a bent crystal polychromator is used, to select a band of energy from the white synchrotron beam, which is horizontally dispersed and focused on the sample. The transmitted beam intensity from the sample is recorded on a position sensitive CCD detector, thus enabling recording of the whole EXAFS spectrum around an absorption edge in a single shot.

The energy calibration of the beamline for a particular setting of the polychromator can be done using the method outlined by Gaur et al.2. For the measurement of absorption spectra of cobalt (II) mixed ligand complexes the CCD channels are calibrated at the cobalt K-edge of 7708.9 eV. The absorption spectra and
corresponding derivative spectra of cobalt foil and Dy$_2$O$_3$ pellet were recorded. The absorption edges of cobalt foil and Dy$_2$O$_3$ pellet are found to appear at CCD channel numbers of 788 and 1154, respectively. From the known values of cobalt and Dy$_2$O$_3$ K-edges at 7708.9 eV and 7790.1 eV, respectively$^{2,3}$, the CCD channels are calibrated with respect to energy. A dispersion of 0.2218 eV per channel is obtained in the present setting.

3. Methodology

The EXAFS appearing on high energy side of the K-absorption edge have been recorded in all the cobalt complexes, using the synchrotron DEXAFS beamline set-up. Following the principal absorption maxima, there are distinct EXAFS features, extending up to 350 eV on the high energy side of the K-absorption edge.

The Fourier transformation technique can be used for determination of the bond lengths. However, only the phase uncorrected bond length has been determined 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 length can also be determined from EXAFS data by three graphical methods. In fact before the Fourier transformation technique was formulated, the bond length used to be extracted from the EXAFS data by the three graphical methods. Thus, the bond lengths have been determined for the cobalt complexes with the help of three methods, i.e., Levy’s, Lytle’s and Lytle, Sayers and Stern’s (L.S.S.) methods$^4$ and the results are given in table 2. However, the distance found from Fourier transform is about 0.2 Å - 0.5 Å shorter than the actual distance due to energy dependence of the phase factors in the sines function of the EXAFS equation. The peaks in the Fourier transform are shifted towards the origin by an amount $\alpha_1$ and hence the peaks are at distances $R_1-\alpha_1$. For the first peak $j=1$ and hence the position of the first peak determines the distance $R_1-\alpha_1$.

It is important to note here that the distance $R_1-\alpha_1$ should be equal to the distance found from the L.S.S. graphical method. Hence, both the L.S.S. method and the Fourier transformation method give the value $R_1-\alpha_1$, i.e., both the methods give the value of bond lengths which have not been corrected for the phase shifts. We have called this distance as the phase uncorrected bond length.

The normalized spectra shown in fig. 1, are $\mu(E)$ versus E curves obtained using the synchrotron DEXAFS beamline set-up. From these curves, $\chi(k)$ versus k curves are obtained which are given in figs.2. The Fourier transformed spectra obtained from $\chi(k)$ versus k curves are given in figs. 3. The position of the first peak in the Fourier transform gives the value of $R_1-\alpha_1$ and the values are collected in table 2 for all the complexes.

It is seen from this table that the value of $R_1-\alpha_1$ as determined from L.S.S. method and that determined from the Fourier transformation method are in good agreement with each other, i.e., both the L.S.S. method and Fourier transformation method give nearly the same value of the phase uncorrected bond length, i.e., $R_1-\alpha_1$.

3. Results and discussion

The intensities $I_0$ and $I_a$ are obtained as the CCD outputs without and with the sample respectively. Using the relation, $I_1 = I_0e^{-\mu x}$, where $\mu$ is the absorption coefficient and x is the thickness of the absorber, the absorption $\mu(E)$ corresponding to the photon energy (E) are obtained. When the absorption is plotted as a function of E, the experimental spectra show three features: (1) a decrease in X-ray absorption with increasing energy in the pre-edge region, (2) a sharp rise at certain energy called edge and (3) a series of wiggles or oscillatory structure that modulate the absorption in the post-edge region. The experimental data has been analyzed using the available computer software package Athena. Firstly, the normalized $\mu(E)$ versus E spectra are obtained, then $\chi(k)$ versus k spectra are obtained and finally the Fourier transforms of the latter are obtained.

The normalized absorption spectra with the pre-edge along zero, an edge step of one and the post-edge region oscillating around one are shown in fig.1. Following the principal absorption maximum A, there are distinct EXAFS features extending up to 350 eV on the high energy side of the K-absorption edge.

Conversion to k-space should be done before background subtraction so that the background fit does not preferentially follow the data at high energy (which oscillate slowly in energy space). Usually the experimental data are not collected on an even grid in k-space (although this is desirable), and therefore interpolation is performed when the change of variable is made. A uniform grid in k-space is desirable so that standard discrete Fourier transform algorithms can be used.
To convert to k-space, the value of $E_0$, the threshold energy must be specified. Fortunately the precise value is immaterial as long as it is within a rydberg or so of the edge, and that it is consistent for standard and unknown. Typically the half-maximum point on the edge is taken, or the bottom of the edge, or the top. Physically somewhere near the bottom of the edge, close to the fermi level, is probably preferred. Only relative shifts in $E_0$ between standard and unknown are very important: if both are shifted the same amount the answer will be the same to a good approximation. Relative $E_0$ shifts primarily affect the data at low values of $k$ which are distinguishable from changes in other structural parameters. Thus, ambiguities in absolute $E_0$ position, and small (~ 3 eV) differences in relative $E_0$ position, do not introduce corresponding ambiguities in structure determination by EXAFS. The choice of $E_0$ does pose significant uncertainties for k-space analysis in the XANES region, however.

The EXAFS spectra converted into k space have been given in fig.2. The bond lengths have been calculated using L.S.S., Levy's and Lytle's methods as shown in table 2. The Fourier transform separates a signal into its Fourier components and is a complex function containing both real and imaginary parts. The magnitude of the Fourier transform is an envelope of the real and imaginary parts of the Fourier transform. It is like a radial distribution function of the atoms about the absorber atom because there is usually a peak corresponding to the first shell of atoms and the R value of the peak is related to the bond length of the first shell. The magnitudes of Fourier transform of cobalt foil and its complexes are shown in figs. 3 and the first shell bond lengths hence calculated have been shown in table 2. This bond length is, however, phase uncorrected bond length, i.e., $R_1 - \alpha_1$.

5. Conclusions

X-ray absorption spectra of mixed ligand cobalt complexes at the K-edge of cobalt have been recorded at the recently developed EXAFS beamline set-up at the Indus-2 synchrotron source at RRCAT, Indore.

From the positions of the EXAFS maxima and minima, the bond lengths in the complexes have been determined by three different methods viz. Levy's, Lytle's and Lytle, Sayers and Stern's methods.

The normalized spectra, i.e., $\mu(E)$ versus $E$ curves have been obtained. From these curves, $\chi(k)$ versus $k$ curves have been obtained, which have then been Fourier transformed using the software Athena. From the Fourier transforms of the EXAFS spectra the bond lengths (uncorrected for phase shift) have been determined.

It has been observed that the value of the phase uncorrected bond length, i.e., $R_1 - \alpha_1$ as determined from L.S.S. method and that determined from the Fourier transformation method are in good agreement with each other, i.e., both the L.S.S. method and Fourier transformation method give nearly the same value of the phase uncorrected bond length.

6. References

Table 1 Cobalt (II) mixed ligand complexes with Schiff base and 3-hydroxy picolinamide ligands

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of complex</th>
<th>Abbreviation</th>
<th>Colour of complex</th>
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<tbody>
<tr>
<td>01</td>
<td>Co(II) 3-hydroxypicolinamide -4-(phenyl(phenylimino) methyl) benzene-1,3-diol</td>
<td>[Co(HPA)(PPIMBD)]</td>
<td>Dark green</td>
</tr>
<tr>
<td>02</td>
<td>Co(II) 3-hydroxypicolinamide -4-(phenyl(tolylimino) methyl) benzene-1,3-diol</td>
<td>[Co(HPA)(PTIMBAD)]</td>
<td>Tobacco brown</td>
</tr>
<tr>
<td>03</td>
<td>Co(II) 3-hydroxypicolinamide -4-((4-chlorophenylimino) (phenyl) methyl) benzene-1,3-diol</td>
<td>[Co(HPA)(CPIPMBD)]</td>
<td>Brown</td>
</tr>
<tr>
<td>04</td>
<td>Co(II) 3-hydroxypicolinamide -4-((4-nitrophenylimino) (phenyl) methyl) benzene-1,3-diol</td>
<td>[Co(HPA)(NPIPMBD)]</td>
<td>Tobacco brown</td>
</tr>
<tr>
<td>05</td>
<td>Co(II) 3-hydroxypicolinamide -4-((4-methoxyphenylimino) (phenyl) methyl) benzene-1,3-diol</td>
<td>[Co(HPA)(MPIPMBD)]</td>
<td>Dark brown</td>
</tr>
</tbody>
</table>

Table 2 First shell bond length (Å) calculated from Levy’s, Lytle’s, L.S.S. and Fourier transform (F.T.) methods for Cobalt (II) mixed ligand complexes of Schiff base and 3-hydroxy picolinamide ligands

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Mixed Ligand Co(II) Complex</th>
<th>Phase corrected</th>
<th>Phase uncorrected</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Levy’s Method R1 (Å)</td>
<td>Lytle’s Method R2 (Å)</td>
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<tr>
<td>01</td>
<td>Co Metal</td>
<td>2.08</td>
<td>1.62</td>
</tr>
<tr>
<td>02</td>
<td>[Co(HPA)(PPIMBD)]</td>
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<td>1.64</td>
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<tr>
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<tr>
<td>06</td>
<td>[Co(HPA)(MPIPMBD)]</td>
<td>2.00</td>
<td>1.76</td>
</tr>
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</table>

Fig. 1 XAFS spectra of cobalt (II) Schiff base and 3-hydroxy Picolinamide mixed ligand complexes
Fig. 2 $\chi(k)$ versus $k$ spectra of cobalt (II) Schiff base and 3-hydroxy Picolinamide mixed ligand complexes

Fig. 3 Magnitude of Fourier transform of $\chi(k)$ versus $k$ spectra of cobalt (II) Schiff base and 3-hydroxy Picolinamide mixed ligand complexes