Determination of bond lengths from extended X-ray absorption fine structure in cobalt(III)-oxo cubane-like clusters

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Abstract. The extended X-ray absorption fine structure (EXAFS) at the K-edge of cobalt has been studied in two cobalt complexes having Co(III)-oxo cubane-like clusters of the type Co\(_4\)O\(_4\)(O\(_2\)CR)\(_4\)L\(_4\) where R is CH\(_3\) and L is pyridine (py) in one of the complex and ammonia (NH\(_3\)) in the other complex. The spectra have been recorded at BL-9 scanning EXAFS beamline at the 2.5-GeV INDUS-2 Synchrotron, RRCAT, Indore, India. The positions of EXAFS maxima and minima have been reported. Using this data, the bond length has been determined by simple bond determination methods, viz., Levy’s, Lytle’s and Lytle, Sayers and Stern’s (LSS) methods. The normalized EXAFS spectra have been Fourier transformed and the value of the bond length has also been determined from the position of the first peak in the Fourier transform. This distance is the phase-uncorrected bond length. LSS method also gives such bond length. The results obtained from Fourier transform and LSS methods have been found to be comparable to each other. For the pyridine complex, the value obtained from Levy’s method has been found to be in agreement with the available crystallographic value.

1. Introduction
X-ray absorption spectra at the K-edge of cobalt have been studied in two cobalt complexes having Co(III)-oxo cubane-like clusters of the type Co\(_4\)O\(_4\)(O\(_2\)CR)\(_4\)L\(_4\) where R is CH\(_3\) and L is pyridine (py) in one complex and ammonia (NH\(_3\)) in other complex. Das and Chakrabarty [1], have discussed the synthesis and physicochemical characteristics of these complexes and also the role of these complexes in catalytic oxidation under homogeneous conditions. The present paper deals with the determination of bond lengths from extended X-ray absorption fine structure (EXAFS) data of these complexes using four different simple bond determination methods, without doing rigorous theoretical calculations.

2. Experimental
The complexes Co\(_4\)O\(_4\)(CH\(_3\)COO)\(_4\)(Py)\(_4\) and Co\(_4\)O\(_4\)(CH\(_3\)COO)\(_4\)(NH\(_3\))\(_4\) were prepared according to the standard methods reported in literature [1] and their purity was checked by standard methods. X-ray absorption spectra at the K-edge of cobalt have been recorded at the BL-9 scanning type EXAFS beamline at the 2.5-GeV INDUS-2 synchrotron, RRCAT, Indore, India. The key component of the beamline is double crystal monochromator (DCM) which is used for energy selection from the white synchrotron beam. The optics of this beamline consists of two Rh and Pt coated meridional cylindrical
Table 1. EXAFS data for Co complexes

| EXAFS Structure | n (for LSS method) | Q (for Lytle’s method) | Co$_4$O$_4$(CH$_3$COO)$_4$(Py)$_4$ | Co$_4$O$_4$(CH$_3$COO)$_4$(NH$_3$)$_4$ |
|-----------------|-------------------|------------------------|---------------------------------|---------------------------------|
|                 |                   |                        | k (Å$^{-1}$) | E (eV) | k (Å$^{-1}$) | E (eV) |
| A               | 0                 | 2.04                   | 2.35        | 21.00  | 1.85        | 13.01  |
| α               | 1                 | 3.20                   | 3.20        | 38.94  | 3.10        | 36.54  |
| B               | 2                 | 6.04                   | 4.40        | 73.61  | 4.10        | 63.92  |
| β               | 3                 | 5.63                   | 5.63        | 120.31 | 5.23        | 103.80 |
| C               | 4                 | 12                     | 6.95        | 183.66 | 6.70        | 170.68 |
| γ               | 5                 |                         | 7.80        | 231.33 | 7.30        | 202.62 |

For explanation of n and Q, see text.

mirrors and two Si(111) crystals. First one is plane crystal and second one is mechanically bendable (Sagittal) crystal which helps to focus beam horizontally at the fixed sample position.

3. Data Analysis
The X-ray absorption spectra, recorded at the beamline, have been processed and analyzed using the available computer software package, *Athena* [2]. The spectrum was first normalized by regressing a linear function to the pre-edge region (-200 to -30 eV before the edge energy) and by regressing a linear or quadratic function to the post-edge region (50–1000 eV above the edge energy). Normalized $\mu(E)$ spectrum was produced by subtracting the pre-edge line from the entire spectrum data and then dividing the spectrum by the step height [3]. Normalized $\mu(E)$ data were converted to the EXAFS signal $\chi(k)$ data, which were then Fourier transformed. The $\chi(k)$ spectra obtained from normalized $\mu(E)$ spectra and the Fourier transforms are given in figure 1 and figure 4 respectively. The inflection point on the K-edge was taken as the reference point for the measurements of the extended fine structure. The maxima in the EXAFS have been designated by capital Latin letters A, B, C, etc., whereas the minima by small Greek letters $\alpha, \beta, \gamma$, etc. The positions of these maxima and minima are given in table 1 in energy E (eV) as well as in wave vector $k$ (Å$^{-1}$).

4. Results and Discussion
The aim of the present work is to determine bond lengths in the complexes from the EXAFS data by four different methods and to compare the results with the available crystallographic data in case of the pyridine complex as well as to compare and discuss the results obtained from the different methods for both the complexes. The methods of determining bond length from the different methods are given below.

4.1 Levy’s method:
Levy [4] has given a method for obtaining the bond lengths from the analysis of EXAFS. According to Levy, the distance $\Delta E$, from the maximum at B to the minimum at $\beta$ should be a measure of the radius $R_1$ of the first coordination sphere through Bragg relation $R_1 = (151 /\Delta E)^{1/2}$ Å. The values of $R_1$ determined by this method are given in table 2. $R_1$ calculated in this way represents the average bond length. The value of bond length for the pyridine complex is available from crystallographic measurements and hence we have compared the crystallographic value [1], given in table 1, with that determined from Levy’s method. It is clear from table 2 that the two values are in agreement with each other in the pyridine complex.
4.2 Lytle’s method:
Lytle [5] has proposed a theory in which a nearly spherical polyhedron is constructed in the lattice and approximated by a sphere of equivalent volume with radius R_s. In this method photoelectron ejected as a result of absorption of X-rays are thought of as if they are in a particle in a box. Lytle has found that an absorption maximum will occur whenever E satisfies the equation: \( E = \left( \frac{\hbar^2}{2mR_s^2} \right)Q \), where h is Planck’s constant, m is the electron mass, and Q represents the zero roots of the half-order Bessel function, given in table 1. The plots of E vs. Q for the complexes studied are found to be linear and are shown in Fig 2. If M is the slope of this straight line, R_s can be determined from the plot using the relation: \( R_s = \left( \frac{37.60}{M} \right)^{1/2} \text{Å} \). The values of R_s are given in table 2. It may be remarked here that the interatomic distance obtained by this method has to be multiplied by a factor greater than unity and appropriate to the geometry of the system to obtain the correct bond length.
4.3 Lytle, Sayers and Stern’s (L.S.S.) method:
According to this method [6], plot of n vs k for the different maxima (n= 0, 2, 4, …) and minima (n= 1, 3, 5, …) should result in a straight line. n vs k graphs for the complexes studied are found to be linear and are given in figure 3. The slope (M’) of this line is given by $M' = \frac{2(R_1 - \alpha_1)}{\pi}$. The value of $(R_1 - \alpha_1)$ can be obtained from the slope of the plot. Once $\alpha_1$ is evaluated for a standard, $R_1$ for unknown materials can be determined. It is found that for chemically similar systems, the value of $\alpha_1$ remains more or less the same. The values of $R_1$ thus obtained by this method are given in table 2. The distance $R_1$ obtained from this method is phase uncorrected bond length.

4.4 Fourier transform method:
The position of the first peak in the Fourier transform (figure 4) corresponds to the distance between the absorbing atom and its nearest neighboring atoms, i.e., the radius of first coordination sphere. However, the bond length thus obtained is less than the actual bond length, because it is phase uncorrected. The values for the phase uncorrected bond lengths, as determined from the Fourier transforms, for the two complexes are given in table 2. The phase corrected bond length can be determined by fitting appropriate theoretical model to the experimental Fourier transform curve. This has not been done in the present work.

5. Conclusions
The values of the bond length as determined from Lytle’s method are found to be slightly lesser than the corresponding bond lengths obtained by Levy’s method. This may be ascribed to the fact that Levy’s method gives the radius of coordination sphere directly whereas Lytle’s method does not. In the later method, the inter-atomic spacing is obtained by multiplying the obtained bond length by an appropriate factor. The value of bond length for the pyridine complex is available from crystallographic measurements and hence we have compared the crystallographic value for this complex, with that determined from Levy’s method. It has been found that the two values are in agreement with each other in the pyridine complex, showing that the Levy’s method is suitable method for determining bond length, when it is not possible to determine phase corrected bond length.
from the Fourier transform by fitting an appropriate theoretical model to the experimental Fourier transform curve. Regarding the values of the phase-uncorrected bond length obtained from LSS method, it has been found that they are comparable with the values of phase-uncorrected bond length obtained from Fourier transformation method.

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