Correlation of X-Ray Absorption Parameters with Schultz index

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Abstract. A novel application of topological Index in estimating some X-ray parameters is described. X-Ray Absorption parameters (Chemical Shift and Effective Charge) are correlated with Schultz index. Some Cobalt (II) complexes were used to establish this type of correlation. The result have indicated that the chemical shift and effective charge are sensitive to the topological structure of coordinating ligand moieties. The topological understanding of molecular properties can lead to the development of new areas of present and future interest. i.e. designing of new drugs, tracking the effects of pollutants in environment and the prediction of carcinogenicity of a molecule.

1 Introduction

Earlier, we have established a between topological Index (Winer and Randic) and X-ray parameters¹,². In continuation of our earlier work, we now establish a correlation between Schultz index and some X-ray absorption parameters:

2 Generation of Schultz index

The Schultz index³ is also known as molecular topological index (MTI) and is defined as

\[ \text{MTI} = \sum_{i=1}^{n} e_i \]

Where, \( e_i \) (i, 2, ...., ...., n) represent the elements of the following row matrix of order n.

\[ V(G) [A(G) + D(G)] = [e_1, e_2, e_3, ...., ...., e_n] \]

Where V(G) is the valency row matrix, A(G) and D(G) are the adjacency and distance matrices, respectively.
The vertex-adjacency matrix \( A = A(G) \) of a labeled graph \( G \) of a molecule with \( n \) vertices is defined as
\[
A_{ij} = \begin{cases} 
1 & \text{if vertices are adjacent} \\
0 & \text{otherwise}
\end{cases}
\]
And distance matrix is defined as
\[
D(G) = \sum_{i < j} d(i,j)
\]
Here, \( d_{ij} \) is the element of distance matrix \( D \).

3. Results and Discussion

Table 1 contains molecular formulae. Molecular graphs along with their Schultz indices while chemical shifts with respect to cobalt and effective charge of the complexes used for correlation are reported in Table 2.

Table 1. Molecular formulae. Molecular graphs and Schultz indices of substituted Hydroxypyridine ligands used in the present work.

| No. | Name                                | Molecular formulae | Molecular graphs | Schultz indices |
|-----|-------------------------------------|--------------------|------------------|----------------|
| 1.  | 2,3-dihydroxypyridine (DHP)         | C₅H₅NO₂            | ![DHP](image)    | 820            |
| 2.  | 2-amino 3-hydroxypyridine (AHP)     | C₅H₆N₂O           | ![AHP](image)    | 911            |
| 3.  | 3-hydroxypyridine 2-carboxylic acid (HPC) | C₆H₅NO₃ | ![HPC](image)   | 1451           |
| 4.  | 3-hydroxy 2-piconilamide (HPC)      | C₃H₆N₂O₂          | ![HPC](image)    | 1578           |

Table 2. Chemical shift \( (\Delta E) \) and effective charge for the complexes used for correlation.

| No. | Complex | Chemical shift \((\Delta E \pm 0.3eV)\) | Effective nuclear charge \( Z_{eff} \) |
|-----|---------|--------------------------------------|-------------------------------------|
| 1   | Co-DHP  | 13.68                                | 1.52                                |
| 2   | Co-AHP  | 12.56                                | 1.40                                |
| 3   | Co-HPC  | 10.50                                | 1.24                                |
| 4   | Co-HPA  | 9.82                                 | 1.20                                |
The X-ray K-absorption edge structure of the cobalt (II) complexes show several features of interest. The shift of the X-ray absorption edge $\Delta E_i$ ($i=K,L,M,\ldots$) of an element in a compound with respect to that of pure element is given by

$$\Delta E_i = E_i (\text{compound}) - E_i (\text{element})$$

The position of X-ray absorption edge depends on the valence of the absorbing ion, the effective charge on the central atom, and also upon the geometry of the complex. According to Agarwal and Verma, the chemical shift is towards the higher energy side of the metal edge. It increases progressively with increase of the valence of the cations, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of a metal-metal bonding. In the present work, the K-absorption edge of all the four complexes is found to be on the higher energy side. The order of chemical shift as indicated by their values has been found to be as follows.

Co-DHP > Co-AHP > Co-HPC > Co-HPA

The larger values of chemical shifts in all the complexes show that the complexes are more ionic in character. As the shift is taken to be proportional to the ionic character, the role of various bonds attached to the central cobalt ion is prominent in determining the overall chemical shift in a metal complex. Further, not only ligation of a particular type, e.g., Co-O or Co-N is responsible in imparting ionic character to the complex but their position in the planar ring/axial position also contributes to the ionic character. As it is not possible to assess individually the contribution of these factors to the chemical shift values, it is only the relative ionic character that can be assessed from the observed values of chemical shift.

It has already been reported by a number of workers that chemical shift depends on the effective charge and different approaches are available for the estimation of effective charge. We have estimated the effective charge by using Gianturco and Coulson’s method which can be applied to the complex system. The details of the method have already been reported in our earlier work.

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### Fig 1

Co rrelation of Schultz Index with chemical shift for Co (II) hydroxypyridine complexes

### Fig 2

Co rrelation of Schultz Index with Effective Charge for Co (II) hydroxypyridine complexes
Fig 1 & 2 shows correlation between Schultz indices of substituted hydroxypyridine ligands and corresponding X-ray absorption parameters. The correlation assumes the general form

$$\Delta E = -m(TI) + C$$

Where TI stands for a particular topological index.

It is evident from the plot (Fig 1 & 2) that $\Delta E$ and $Z_{\text{eff}}$ correlate according to the family of the complex to which they belong. The Fig. 1 represents the correlation for Schultz indices and chemical shift while Fig.2 demonstrates the correlation for Schultz indices and effective charge. Both the plots yield excellent straight lines.

The correlation factors are 0.989 and 0.977 respectively. It is gratifying that the correlations with the Schultz index are better than that with the Wiener index. The results obtained in this study show that the correlation of $\Delta E$ and $Z_{\text{eff}}$ with Schultz indices is very effective. We can say that the chemical shift thus estimated indicates that topological indices of the organic molecules acting as ligands can be used for estimating chemical shift theoretically. However, this is possible only for a particular metal complex of closely related ligands (coordinating species)

4 Conclusion

Topological indices contain valuable structural information as evidenced by the success of their widespread applications. Topological indices are not, however, a panacea; users of topological indices must be aware of their limitations and the pitfalls which can accompany their use. The correlation between Schultz indices and X-ray parameters of molecules can lead to the development of a new area of present and future interest. It would be of great help to chemists as well as physicists.

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