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Correlation of Wiener indices with X-ray K-absorption parameters of some copper (II) mononuclear and binuclear complexes

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Abstract : An application of Wiener indices in estimating X – ray K – absorption parameters is given. X- ray K-absorption parameters are correlated with Wiener indices of some copper II mononuclear/ copper II – copper II / copper II - nickel II, complexes of salicylglycine as one of the ligand. The chemical shift is positive, i.e., it is towards the high energy side of the metal edge. The results obtained in these studies with analysis of the data show that Wiener indices (W) can be successfully used for estimating parameters like chemical shift (ΔE), effective nuclear charge (Z_{eff}).

Introduction - XANES can be used to study the structural parameters of metal complexes and compounds[1]. The first topological index characterising the branching (tree) in aliphatic hydrocarbon was introduced by Wiener[2] in 1947. A linear correlation with various properties when plotted against Wiener indices can be used for the prediction of structure of molecules even before their synthesis.

Wiener indices (W) has been used for estimating chemical shift (ΔE_K) and effective nuclear charge (Z_{eff}) for a series of mixed ligand copper complexes as follows.

1. [(salgly)Cu(H_2O)]
2. [(salgly)Cu(ImH)]
3. [(salgly)Cu-Im-Cu(salgly)]Na
4. [(salgly)Cu-Im-Ni(slagly)]Na

Where salgly = salicylideneglycinate and ImH = imidazole.

Generation of Wiener indices –The procedure to calculate the Wiener indices for above series is described briefly below:

Chemical Graph - The K – absorption will depend on the structure of molecular graph described by topological indices of the ligand. The topological indices are usually obtained from the molecular graph of the ligands where in the atoms (vertices) are represented by a dot "**.**" and the bond (edges) by small lines " _ "[3,4,5].

The Wiener index (W) is the sum of all distances in graph G, where G is a connected graph whose vertices are labelled 1,2,3,4…, n. The distance d_{ij} between the vertices i and j is the length of the shortest path which connects i and j .

$$W = W(G) = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} d_{ij} \text{ ....1}$$

The Wiener index (W) as defined above is half the sum of the off – diagonal elements of the distance matrix (D). The Wiener index (W) has been studied extensively[6,7].

Experimental – Copper(II) complexes of mixed ligands were prepared by copper perchlorate hexahydrate (Aldrich), nickel perchlorate hexahydrate (Aldrich) and imidazole (S.D.Fine chemicals) along with methanol / acetonitrile solutions of $Cu(ClO_4)_2.6H_2O$ and salgyl[8,9].

A Chirana sealed X– Ray tube with tungsten target having two beryllium windows operating at 20KV and 10mA was used as the source of continuous radiation. Tungsten WL_α, $K_{\beta 1,3}$ emission lines were used as reference lines. A bent crystal spectrograph of diameter 0.4 m was used in this work to record the spectra using (100) reflection planes of mica on Agfa/Konica X-ray films. The data acquisition system adopted in the present work[10] consists of interfacing a microdensitometer with personal computer (P.C.) using a stepper motor controller unit. A proper software programme involving the data port and status port of the LPT (printer port) have been used in the present work.

Results and Discussion - Table 1 contains the molecular formula and molecular graph of ligands used. The Wiener index (W) for these ligands are also given in this table, while the X-ray K- absorption parameters are reported in table 2

Table 1: Molecular Formulae, Molecular Graph & Wiener Index of Ligands used in the present work

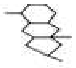
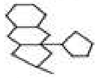
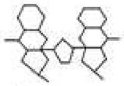
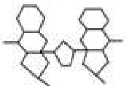
Ligand	Molecular formula	Molecular Graph	Wiener Index(W)
I.	[(salgly)Cu(H_2O)]		376
II.	[(salgly)Cu(ImH)]		612
III.	[(salgly)Cu-Im-Cu(salgly)]Na		3335
IV.	[(salgly)Cu-Im-Ni(salgly)]Na		3335

Table 2 (see in next page)

It has been shown in table 2 that the K- edge of complexes is found to be shifted towards high energy side of copper K-Edge. The chemical shift ΔE_k is positive.

The edge width and the shift of the principal absorption maxima of copper complexes are also included in table 2. The shift of the X-ray absorption edge ΔE_k of an element in a compound / complex with respect to that of the pure element is written as:

$\Delta E_k = E_K$ (compound) – E_k(metal)

Extensive studies have been reported[11-13] on chemical shift of X-ray absorption edges. Two main factors contribute to the observed high energy shifts of X-ray absorption edges i.e.

(i) The tighter binding of the core level because of the change of the effective charge (or screening) of the nucleus caused by the participation of the valence electrons in the chemical bonds formation.

(ii) Appearance of the energy gap Eg when we go from a metal to a compound or complex.

In general, the chemical shift is towards the high energy side of the metal edge[14] increasing progressively with increase of valence of the cation. Of course the shift may also be suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding. In the present work the K- absorption edges of all the copper complexes are found to be on the high energy side.

The shifts of the principal absorption maxima depend upon the type of overlap between metal atoms and ligand orbitals.

Earlier workers[15-17] have reported the chemical shifts values of various copper(II) complexes between 6.8 – 12.9eV. For the present studies complexes, the shift value lies in the range 8.1 to 9.3eV and hence on the basis of this comparison all our complexes under present investigation possess oxidation state 2^+. The observed changes in the chemical shifts values will depend on the relative ionic character of the complexes. The shifts of the principal absorption maxima depend upon the type of overlap between metal atoms and ligand orbitals. The results reported in this paper shows that the shifts of the principal absorption maxima are indicative of distorted tetrahedral geometry for these complexes. Further the higher values of chemical shifts as obtained for other complexes also support the hydroxylation of the copper centres. This implies that due to hydroxylation the effective charge on the central metal copper ion has increased resulting in the high energy values of chemical shifts.

Central metal copper ion is surrounded by the two oxygen and two nitrogen in complex II whereas three oxygen and one nitrogen in case of complex I, which results in increase of effective charge and hence the chemical shifts values for the binary complexes III and IV are less than those for mononuclear complexes which has also been confirmed with the experimental data given in table 2.

We have used Gianturco and Coulson[18] method for calculating effective nuclear charge.

The correlation assumed the general form

$\Delta E = AX + B$

Where A is the slope, while B is the intercept and X is the particular topological index. Based on this the following model is obtained for modelling ΔE and Z_{eff} for the complexes.

$\Delta E = -0.0003W + 9.2090$

It is evident from the plot Figure 1 and 2 that the observed (Y_{obs}) and calculated value with Wiener index (Y_{cal}) of chemical shift yield excellent straight lines for both chemical shift and effective nuclear charge. The results obtained in this study demonstrate that the correlating of ΔE and Z_{eff} with Wiener indices is very effective. We can say that the edge shift thus estimated indicates that topological indices of the organic molecules acting as ligands can be used for estimating edge shift theoretically.

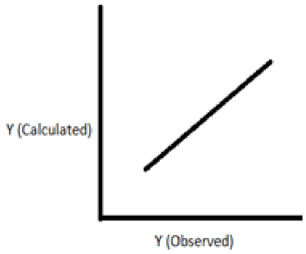


Figure 1
For Chemical shift ΔE_k

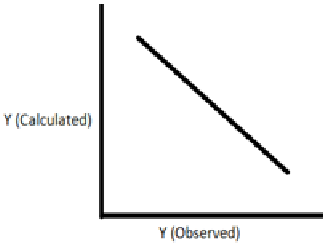


Figure 2
For Effective Nuclear Charge Z_{eff}

Conclusion: Topological indices (Wiener) contains valuable informations about molecular structure and molecular properties. The prediction of the properties of the molecules before their synthesis should be made by topological indices. The topological understanding of molecular properties can lead to the development of new areas of present and future interest i.e. designing of new drug tracking the effect of pollutants in the environment and the prediction of carcinogenicity of a molecule.

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Table 2: Chemical Shift and other X-ray Absorption Parameters for complexes used for correlation in present work

Ligands	Chemical shift ΔE_k meV			Effective nuclear charge (Zeff)			Principal absorption maxima (±0.3 eV)	Edge width (± 0.3_{eV})
	Y_{ob}	Y_{cal}	E_{mV}	Y_{ob}	Y_{cal}	Error		
I.	9.3	9.1	-.2	0.97	0.97	0.00	25.5	16.2
II.	8.8	9.0	+.2	0.94	0.98	-0.04	25.3	16.5
III.	8.3	8.2	-.1	0.90	1.03	-0.13	25.2	16.9
IV.	8.1	8.2	+.1	0.89	1.03	-0.14	24.3	16.2

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