K-NEXAFS investigations on some copper (II) complexes

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Near edge X-ray absorption fine structure (NEXAFS) covering energy range up to about 50 eV have been studied. The present studies include some copper (II) complexes of biological interest with 3-arylazo-7-hydroxy-4-methylcoumarin as ligand. Studies have been carried out on Seifert X-ray generator and Cauchois type bent crystal X-ray spectrograph of O.4-m radius. The observed X-ray parameters e.g. chemical shift, shift of principal absorption maximum, edge-width, fractional oxidation number and percentage covalency have been used to explain the structure of the complexes and these parameters have also been correlated with earlier chemical studies.

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A NEXAFS spectrum contains information on bound-state electronic transitions and multiple-scattering resonances associated with a given absorption edge. It is sensitive to the details of the atomic geometry of the first few neighbour atom shells, i.e., the multiple-scattering resonances in the X-ray absorption near edge structure region often serve as a fingerprint of a particular structural arrangement of atoms in the vicinity of the absorber. K-edge spectra show the largest net absorption, and also the largest emission of fluorescent photons per photon absorbed. Hence K-edge spectroscopy is generally the most sensitive.

The X-ray absorption fine structure near the edge covering energy range up to nearly 50 eV is called X-ray absorption near edge structure (XANES). X-ray absorption spectra are sensitive to chemical condition of the absorbing atom under investigation. Therefore, much attention has been paid by different workers in measuring the change in the position of the main edge, and the chemical shift (ΔE) calculated. These workers have shown that the chemical shift is not only governed by valence, but also depends upon several factors such as fractional oxidation number, coordination number, covalency etc. We elucidate the structure of six complexes. Herein, we report X-ray absorption spectroscopic findings of six copper (II) complexes of biological interest with 3-arylazo-7-hydroxy-4-methyl Coumarin as ligand, viz;

- 3-(4'-chloro) phenyl azo-7-hydroxy-4-methylcoumarin, 34CPA7H4MC, C16H11N2O3Cl, 3-(2'-chloro) phenyl azo-7-hydroxy-4-methylcoumarin, 32CPA7H4MC, C16H11N2O3Cl, 3-(3'-chloro) phenyl azo-7-hydroxy-4-methylcoumarin, 33CPA7H4MC, C16H11N2O3Cl, 3-(3'-nitro) phenyl azo-7-hydroxy-4-methylcoumarin, 33NPA7H4MC, C16H11N2O3S, 3-(2'-nitro) phenyl azo-7-hydroxy-4-methylcoumarin, 32NPA7H4MC, C16H11N2O3S, 3-(3'-nitro) phenyl azo-7-hydroxy-4-methylcoumarin, 33NPA7H4MC, C16H11N2O3S

Molecular graph of the ligand (3-arylazo-7-hydroxy-4-methylcoumarin)

Structure 1

where R is: 4-Cl, 2-Cl, 3-Cl, 4-NO2, 2-NO2, and 3-NO2

Experimental

All the six complexes were synthesized using the standard method. These complexes were further purified and confirmed before X-ray studies by XRF (X-ray fluorescence).

In the present investigation, a Seifert sealed X-ray tube with tungsten target operating at 16 kV, 55 mA was used as the source of continuous radiation. A 0.4 m Cauchois type curved crystal transmission spectrograph in its improved form was used to record the spectra. Mica crystal, optically pure and free from deformities has been used as diffracting medium. The performance of spectrograph can easily be observed by recording the MoKβ doublet taken on the spectrograph with 201 planes of a mica crystal reflecting in second order. The doublet is seen clearly resolved. The resolution may be defined quantitatively as Δλ/λ,
which is the reciprocal of resolving power. The resolution of the spectrometer was better than 1000 and the dispersion was about 0.63 eV/mm on the photographic film in the second order.

Absorption screens were prepared by uniformly spreading the fine powder sample on 1 cm² area of cellophane tape. Another piece of cellophane tape was put over it, sealing the substance in between. The screen that gave the best spectra was found to generally have the thickness of the order of 8 to 10 mg/cm². The exposure times is varied from 3-4 hrs.

In order to measure the wavelength of the edge, the method of reference lines has been used. The $L_{\beta_1}, L_{\eta_1}$ and $L_{\alpha_2}$ emission lines of tungsten ($74^W$) were used as reference lines. The wavelengths of $L_{\beta_1}, L_{\eta_1}$ and $L_{\alpha_2}$ were taken from Cauchois and Senemau's table.

For each sample several micro-photometer records were taken on Carl-Zeiss G II micro-photometer, coupled with a Carl-Zeiss G1 BI recorder with magnification of 10X. Such recordings were made at least on three films and each film was scanned at three heights. Thus the value of the K-absorption edge reported herein is the average of at least nine measurements. The accuracy in the measurements was within ± 0.2 eV. The other details for the experimental procedure were described elsewhere.

**Result and discussion**

The profiles of the K-absorption discontinuity of six copper (II) complexes obtained from a number of micro-photometer traces are shown in Fig. 1a and 1b.

![Fig. 1—Profiles of the K-absorption discontinuity of copper (II) complexes](image)

<table>
<thead>
<tr>
<th>Name of the complex</th>
<th>Edge position $E_x$ (eV)</th>
<th>$E_1$ (eV)</th>
<th>Chemical shift $\Delta E_x$ (eV)</th>
<th>Shift in principal absorption maximum (eV)</th>
<th>Edge width (eV)</th>
<th>FON electron/atom</th>
<th>% Covalency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (II) 34CPA7H4MC</td>
<td>8985.04</td>
<td>8994.71</td>
<td>7.6</td>
<td>14.3</td>
<td>6.7</td>
<td>0.93</td>
<td>57.14</td>
</tr>
<tr>
<td>Copper (II) 32CPA7H4M</td>
<td>8987.49</td>
<td>8993.05</td>
<td>7.1</td>
<td>12.7</td>
<td>5.5</td>
<td>0.88</td>
<td>58.33</td>
</tr>
<tr>
<td>Copper (II) 33CPA7H4M</td>
<td>8989.23</td>
<td>8995.68</td>
<td>8.8</td>
<td>15.3</td>
<td>5.6</td>
<td>1.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Copper (II) 33NPA7H4M</td>
<td>8990.75</td>
<td>8998.27</td>
<td>10.4</td>
<td>18.0</td>
<td>7.4</td>
<td>1.09</td>
<td>44.04</td>
</tr>
<tr>
<td>Copper (II) 32NPA7H4M</td>
<td>8990.41</td>
<td>8998.97</td>
<td>10.0</td>
<td>18.3</td>
<td>8.6</td>
<td>1.05</td>
<td>45.80</td>
</tr>
<tr>
<td>Copper (II) 34NPA7H4M</td>
<td>8990.62</td>
<td>8997.31</td>
<td>10.2</td>
<td>16.9</td>
<td>6.7</td>
<td>1.10</td>
<td>38.09</td>
</tr>
</tbody>
</table>

Energy of copper absorption edge ($E_x$) present study = 8980.40 eV².

The findings of the X-ray absorption studies have been reported in Table 1.

**Chemical shift**

Considerable work has been reported on chemical shift of X-ray absorption edge. The shift of X-ray absorption edge $i$ (i=$K,L,M$) of an element in a...
compound with respect to that of pure element has been written as, $\Delta E = E_{\text{compound}} - E_{\text{element}}$.

The position of X-ray absorption edge depends on the valence of the absorbing ion, fractional oxidation number of the central atom, and also upon the geometry of the complex. According to Agrawal and Verma, the chemical shift is towards the higher energy side of the metal edge and it increases progressively with increase in the valance of the cations, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding. In the present work the K-absorption edge of all the 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:

Copper (II) 32CPA7H4M <copper (II) 34CPA7H4MC <copper (II) 33CPA7H4M <copper (II) 32NPA7H4M <copper (II) 34NPA7H4M <copper (II) 33NPA7H4M

Larger values of chemical shift in all the six complexes show that the complexes are more ionic in character. The shift is taken to be proportional to ionic character. The role of various bonds attached to the central metal copper ion is prominent in determining the overall chemical shift in a metal complex. Further, not only legation of a particular type, e.g. Cu-O or Cu-N is responsible in imparting ionic character to the complex but their position in planer 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 value, it is only the relative ionic character that can be assessed from the observed values of chemical shifts.

Shift of the principal absorption maximum and edge width

The shift of the principal absorption maxima depends upon the type of overlap between metal and the ligand orbitals. The greater the overlap between metal and ligand orbitals, the more stable are bonding molecular orbitals and hence more unstable the antibonding orbitals. The principal absorption maximum for octahedral complexes of 3d transition metal are assigned to $1s \rightarrow T_{1g}^*$, the principal absorption maxima shift to the higher energy side. Thus the shifts in the absorption maxima are found to be quite large in all the complexes as seen from Table 1. The order of the shift of principal absorption maxima in six copper (II) complexes (ranges from 12.7 eV to 18.3 eV) is as follows:

Copper (II) 32CPA7H4M <copper (II) 34CPA7H4MC <copper (II) 33CPA7H4M <copper (II) 34NPA7H4M <copper (II) 33NPA7H4M <copper (II) 32NPA7H4M

Nigam and co-workers have suggested that the edge width of K-absorption edge increases with increase in covalent character of the metal-ligand bond, provided other factors like molecular symmetry etc. remain the same. The experimental data (Table 1) of edge width of copper (II) complexes show that the edge width varies from 5.5 eV to 8.6 eV. The order of edge width does not match with the order of chemical shift. This is because the edge width does not solely depend on those factors that are responsible for chemical shift. It is now well established that the octahedral complexes show less edge width values compared to tetrahedral ones. Our values support octahedral structure.

Chemical shift and percentage covalency

The chemical shift is also treated as a measure of covalency. According to Agarwal and Verma, the covalent character of the bond governs chemical shift. Chemical shift increases with decrease in covalency. Using Clementi's result for 1s orbital energy in different oxidation states of copper atom, shift in 1s orbital energies in different oxidation states have been calculated and a theoretical graph is plotted between shift in binding energy of 1s electron and percentage covalency. The percentage covalency of metal-ligand in six complexes has been calculated using this theoretical plot. The results reported in Table 1 reveal that for each complex, increase in covalent nature of bonding causes corresponding shift towards the lower energy side.

Chemical shift and fractional oxidation number

It has already been reported by a number of workers that chemical shift depends upon the fractional oxidation number. The fractional oxidation number on the absorbing ion can also be estimated from the measured chemical shift. Different approaches are available for the estimation of fractional oxidation number. We have used Gianturco and Coulson method for the calculation of fractional oxidation number, which can be applied to the complex system. In this method shift in 1s electron energy under different oxidation states of copper atom is determined from Hartree-Fock-Rotham (HRF) calculations of atomic function.
A graph is plotted between shift in binding energy (calculated theoretically) and oxidation number of copper. This plot is used to estimate the value of fractional oxidation number corresponding to the measured value of edge shift. The data reported in Table 1 indicate that fractional oxidation number of the six copper complexes vary from (0.88 to 1.10) electron/atom. In our present work we observed a parabolic relationship between $\Delta E$ and fractional oxidation number as shown in Fig. 2.

Sarode et al. also observed similar type of relation but in establishing this relation they used Suchet's method\textsuperscript{27}.

Fractional oxidation number and % covalency

Observations in Table 1 shows that the covalency in metal-ligand bond increases with decrease in fractional oxidation number. Figure 3 shows correlation between fractional oxidation number and percentage covalency.

Splitting of the main edge

Van Nordstrand\textsuperscript{28} has investigated the structure of the K-absorption edge of transition metals in variety of solids and has suggested a criterion of coordination symmetry based on the edge structure. Cotton and Hanson\textsuperscript{29} have reported that low energy absorption curves predominate in complexes having tetrahedral or lower symmetry and no such absorption is noticed in octahedral complexes. None of the six complexes under investigation shows any splitting of the K-absorption edge, thereby indicating octahedral structure.

To conclude, in all six copper (II) complexes, the chemical shift is found to be on the higher energy side. The shift of principal absorption maximum and edge-width values obtained for the six complexes is indicative of octahedral structure. Due to the presence of Cu-O and Cu-N bonds in these complexes, the shift of principal absorption maximum is found to be much higher. The values of chemical shift of these complexes have been correlated with percentage covalency and fractional oxidation number. The values of fractional oxidation number match with the chemical shift values confirming that the percentage covalency in metal-ligand bond increases with the decrease in fractional oxidation number. There is no splitting of the K-absorption edge in the three complexes, which confirms the octahedral geometry.

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References

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