X-ray K-absorption studies of some schiff base copper complexes

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The chemical shifts and widths of copper K-edges are reported for some schiff base copper complexes by means of X-ray absorption spectroscopy in which a Cauchris type bend spectrograph has been utilized. The metal-ligand distances have been computed using Levy's method. The results are examined to understand the nature of metal-ligand bonding. The observed linear relationships between chemical shifts (E, eV) and bond distance (Å) and edge width and metal-ligand electronegative differences have been interpreted in terms of changes in the degree of covalency of the metal-ligand bonding in the synthesised copper complexes.

Schiff bases are popular ligands used in the preparation of metal ion complexes. However, the X-ray spectral studies of such complexes are less explored. The structural properties of the compounds such as charge on the metal ion, its relation to molecular symmetry, nature of bonding now-a-days can be conveniently studied using X-ray absorption technique[1]. The absorption characteristics, when studied upto a few hundred electron volts on the high energy side of the main absorption edge constitute the X-ray absorption fine structure[2,3]. The bonding and symmetry studies from the chemical shift and edge width of the K-absorption edge for some copper complexes with schiff based is presented in this note.

Experimental

The schiff bases were prepared by following the method reported in literature[4,5]. 4-Aryl-2 aminothiazole (1 mol) and 3-chlorosalicylaldehyde/3:5-dichlorosalicylaldehyde/3-methyl salicylaldehyde/5-bromosalicylaldehyde (1 mol) were dissolved in ethanol and the mixture refluxed for 1h. The schiff base thus formed was filtered, recrystallised from ethanol and dried *in vacuo*. The purity of the prepared schiff bases was checked by elemental analyses and their molecular weights. Thin layer chromatographic analysis was also made to confirm their purity. The

copper complexes were prepared by dissolving copper acetate (1 mol) and schiff base (2 mols) in ethanol and the mixture refluxed for 45 min. The crystals separated were washed with ethanol and dried *in vacuo*. The data are presented in Table 1.

The X-ray absorption studies were made on a Cauchris type bend mica crystal spectrograph of 400 mm diameter. The instrument could resolve the $M_0K_{\alpha1,2}$ doublet. A Carl Zeiss photodensitometer was used for measuring the intensities of absorption bands from the photographic film.

Results and discussion

The transmitted intensity versus energy (eV) for the copper complexes was plotted. The chemical shifts (E_{eV}) in each case were measured with reference to $WL\alpha_1$ emission line and $WL\beta_4$ emission line on both sides of the absorption edge following Levy's method[6]. The values of chemical shifts (E) and edge width for the complexes under investigation are given in Table 1.

The metal-ligand bond distances (r) were computed using the relation,

$$r = (151/\Delta E)^{1/2} \qquad \ldots (1)$$

where ΔE is the energy difference between second maxima and minima respectively of the post-edge structure of K-edge. The values of bond distances are listed in Table 1. For the present series of copper complexes, the metal-ligand electronegativity differences $\Sigma(E_M - E_L)$ have also been calculated (Table 1). It is known that $[\Sigma(E_M - E_L) \text{ edge width}]^{1,2}$ = constant = K. Using the electronegative values and edge width obtained, we found that the values for the constant turns out to be ~8.5. It is observed that for complexes 1, 3, 4 and 5, the K values are similar and indicate covalent bonding characteristics. It appears that substitution by bromine in place of chlorine does not affect the bonding characteristics appreciably. However, substitution by more chlorine atoms in a ligand results in high K value (compound 2) while substitution of two chlorine and two bromine atoms show lowest K value (compound 6) for the corresponding complexes. Thus the complex involving more substituents in the ligand (chlorine and its inductive effect) shows the highest degree of covalency. All the complexes thus show ionic-covalent character of the M L bonds which also gets affected by the substituents in the ligand. The

Table 1—The K-absorption data of some schiff base copper complexes

Metal/complexes	Energy in eV	Chemical shift (E) eV	Edge width	$E_M - E_I$	Constant K	Bond distance (Å)
Cu metal	8980.37	—	—	—	—	—
$Cu[C_{32}H_{20}N_4O_2S_2Cl_2]$	8987.68	7.315	7.30	9.89	8.5	2.60
$Cu[C_{12}H_{16}N_4S_2O_2Cl_6]$	8987.61	7.248	8.64	9.21	8.9	3.28
$Cu[C_{34}H_{22}N_4O_2S_2Cl_6]$	8986.35	5.985	7.85	9.20	8.5	2.91
$Cu[C_{32}H_{20}N_4O_2S_2Br_2]$	8985.55	5.187	7.84	9.05	8.4	2.84
$Cu[C_{34}H_{24}N_4O_2S_2Br_2]$	8985.09	4.728	7.98	8.76	8.4	1.95
$Cu[C_{32}H_{18}N_4O_2S_2Br_2Cl_2]$	8986.35	5.985	8.24	7.87	8.0	2.86

values of K indicate the Oh (octahedral) geometry for the complexes.

The evaluation of chemical shift (E) data indicates that introduction of increase in chlorine molecules results in decrease of chemical shift and increase in edge width (compound 1 and 2). The replacement of chlorine by bromine (compound 1 and 4) lowers the chemical shift but does not affect the edge width appreciably. The modification of thiazole part by CH_3 group and salicylaldehyde in place of chlorine by bromine (compound 1 and 5) also lowers down the chemical shift but do not influence the edge width.

Thus chemical shift behaviour is dependent upon the substituents in the ligand.

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