

K absorption spectral studies of mixed ligand copper complexes with imidazole as one of the ligands

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The copper K absorption spectra of nine copper(II) mixed ligand complexes with imidazole (ImH) as primary ligand have been recorded in the X-ray absorption near edge structure (XANES) region using 400 mm Cauchois spectrograph. The various parameters determined were position of inflection point of the absorption edge, principal absorption maximum and edge-width. The data for chemical shift of the absorption edge have been interpreted to yield the effective nuclear charge and the oxidation state of the metal ion in the complexes. The edge-widths have been correlated with the coordination geometry of the complexes. The main absorption edge has been found to split into two components and this has also been explained. The present results have been compared with those reported earlier from chemical studies. The effects of variation of the secondary ligands on the various parameters have also been discussed.

Keywords: Cu imidazole complexes, Cu K-absorption spectra, Chemical shifts

1 Introduction

The imidazole ring as a histidine moiety, functions as ligand toward transition metal ions in a variety of biologically important molecules including iron-heme systems, vitamin B₁₂ and its derivatives and several metallo-proteins. The effectiveness of the imidazole group to act as a metal binding site has been attributed to its great flexibility, its availability at physiological pH (pka ca. 7.0) and its capacity to form both σ - and π -bonds with metal ions. Hence, in the present work, X-ray absorption spectroscopic studies have been done on nine copper(II) mixed ligand complexes having imidazole (ImH) as primary ligand, viz., Cu(ImH)₂Cl₂, [Cu(ImH)₂](Im⁻)Cl, [Cu(ImH)₆(NO₃)₂], [Cu₂(dien)₂(Im⁻)](ClO₄)₃, Cu(ImH)₄(ClO₄)₂ and [Cu(ImH)₄X₂], where X = NO₃, Cl, Br, 1/2SO₄ and inorganic anionic ligand (X) as secondary ligand. The arrangement of the imidazole rings around copper gives rise to Cu(C₃H₄N₂)₄²⁺ ions which are linked together by X²⁻ ions forming symmetry related chains directed along the a-c diagonal. The donor environment around the metal ion and the geometry of the complex is listed in Table 1. The structures of these complexes are given in Figs 1(A to D).

X-ray absorption spectroscopy is a unique tool for studying at the atomic and molecular scale and the local structure around the absorbing element in a

material. It is well known that the X-ray absorption near edge structure (XANES) is influenced by the immediate surroundings of the absorbing atom. The edge position and shape are sensitive to formal valence state, ligand type and coordination environment. Hence, the edge features (position and shape) reflect oxidation states and coordination environments in the vicinity of the absorber. Studies of the absorption edge help in understanding the environment of a metal ion in its compounds and complexes. The chemical information obtainable from the XANES region is notably the formal valence (very difficult to experimentally determine in a nondestructive way) and coordination environment. An important and common application of XANES is to use the shift of the edge position to determine the valence state. Chemical shifts as obtained by X-ray absorption spectroscopic studies have yielded useful information in various kinds of samples having biological relevance and utility in pharmacology¹⁻⁷. The XANES technique is now routinely applied to discern coordination and oxidation states of metals in compounds and complexes⁸. In the present work, Cu K-absorption spectra have been recorded in the XANES region with a view to investigate the oxidation state, effective nuclear charge and coordination environment of copper in the nine complexes under consideration.

Table 1 — Formulae, donor environment around the metal ion and geometry of the complexes

Complex no.	Formula of the complex	Oxidation state of the metal	Donor environment around the metal Ion	Geometry of the complex
1	$\text{Cu}(\text{ImH})_4(\text{ClO}_4)_2$	+II	4N	square planar
2	$\text{Cu}(\text{ImH})_4(\text{NO}_3)_2$	+II	4N, 2O	elongated octahedral
3	$\text{Cu}(\text{ImH})_4\text{Cl}_2$	+II	4N, 2Cl	elongated octahedral
4	$\text{Cu}(\text{ImH})_4\text{Br}_2$	+II	4N, 2Br	elongated octahedral
5	$\text{Cu}(\text{ImH})_2\text{Cl}_2$	+II	2N, 2Cl, Cl (apical)	distorted tetragonal pyramidal
6	$\text{Cu}(\text{ImH})_4\text{SO}_4$	+II	4N, 2O, (SO_4)	distorted octahedral
7	$[\text{Cu}(\text{ImH})_6](\text{NO}_3)_2$	+II	6N	octahedral
8	$[\text{Cu}(\text{ImH})_2](\text{Im}^-)\text{Cl}$	+II	3N, Cl	square planar
9	$[\text{Cu}_2(\text{dien})_2(\text{Im}^-)](\text{ClO}_4)_3$	+II	4N	square planar

where ImH = Imidazole, Im⁻ = Imidzolate anion and dien = diethylenetriamine

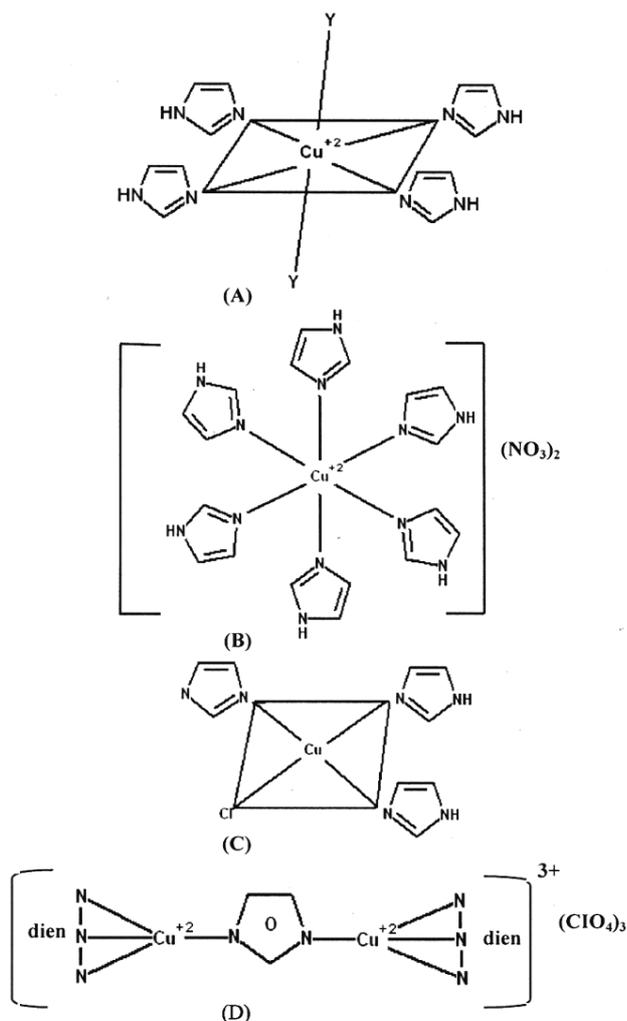


Fig. 1 — Structure of (A) $\text{Cu}(\text{ImH})_4 \text{X}_2$, where $\text{X} = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br}, 1/2\text{SO}_4$, (B) $[\text{Cu}(\text{ImH})_6](\text{NO}_3)_2$, (C) $[\text{Cu}(\text{ImH})_2](\text{Im}^-)\text{Cl}$ and (D) $[\text{Cu}_2(\text{dien})_2(\text{Im}^-)](\text{ClO}_4)_3$

2 Experimental Details

The complexes have been prepared according to the standard methods reported in literature⁹⁻¹¹ and their purity was checked. A sealed Machlett tube with a tungsten target was employed as X-ray radiation source and operated at 17 kV and 15 mA. The X-ray absorption spectra at the K-edge of copper have been recorded on a bent crystal 400 mm Cauchois type transmission spectrograph employing a mica crystal, oriented to reflect from (100) planes for dispersion. The dispersion of the spectrograph was about $0.8 \text{ eV}/10^{-2} \text{ mm}$ of the X-ray film. The resolution of the spectrograph was tested by recording the Mo $\text{K}\beta_{1,3}$ doublet as two separate lines, which was adequate for this study. All the samples have been studied in solid state (powder form). The absorption screens have been prepared by spreading about 30 mg of substance on 1 cm^2 area of cellophane tape and covering it by another piece of cellophane tape. The exposure time was 2-3 h on Kodak X-ray films. For calibrating the spectra, the tungsten emission lines $\text{WL}\alpha_2$, $\text{WL}\beta_4$ and $\text{WL}\beta_6$ were used as reference lines and their energies have been taken from the Tables of Desletts *et al.*¹². The measurements at the K absorption edge have been made on digital records obtained using a Carl-Zeiss G II microphotometer. For recording the K absorption edge and the associated fine structures, it was found that accurate results have been obtained when the photographic film was advanced through 10^{-2} mm and recorded the photo-detector readings. The digital spectra records have been fed into the computer. Computer programs Origin and Athena¹³ have been used for data analysis. Derivative spectra have been used for obtaining the K-edge position. For

each sample, several microphotometer records have been taken and each film was scanned at three heights. Thus, the values of the K-edge features reported herein are the average of at least 9 measurements. The accuracy in the measurement of K-edge was ± 0.05 eV.

3 Results and Discussion

The shapes of the copper K absorption discontinuity and the associated near edge structure (XANES) for all the nine complexes studied are shown in Fig. 2. The successive curves have been displaced vertically for the better representation. The curves in Fig. 2 represent the normalized K absorption spectra obtained with the help of computer program Athena¹³. The K absorption edge is found to split into two components, namely, K_1 edge and K_2 edge in these complexes. The energies of the E_{K1} edge and E_{K2} edge and the principal absorption maximum (E_A) along with the values of the edge-width ($E_A - E_{K1}$) and

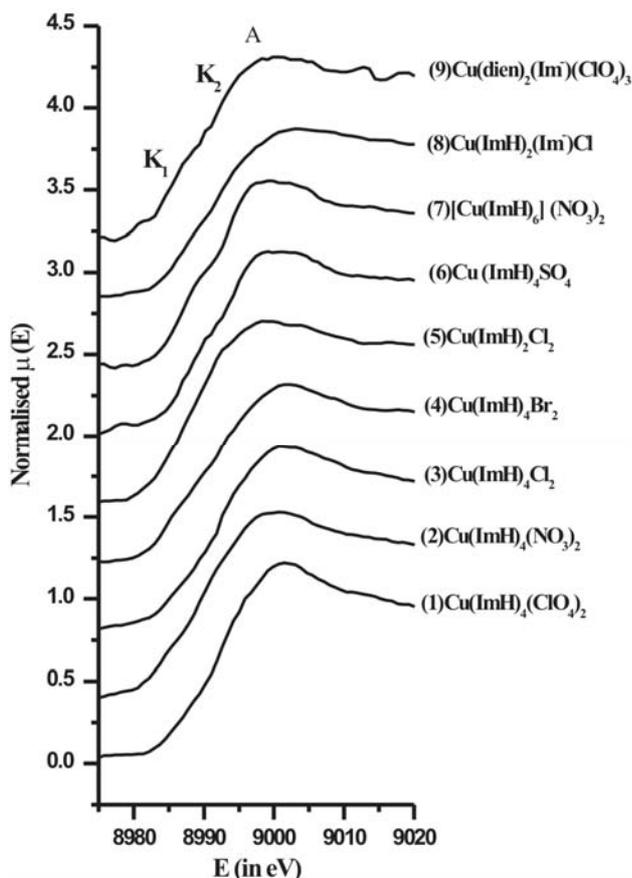


Fig. 2 — Copper K-edge XANES spectra for the mixed ligand copper complexes. The different spectra have been shifted vertically for better presentation

the chemical shift ΔE_{K1} are given in Table 2. These values have been obtained with the help of the derivative spectra. It can be readily seen from Table 2 that the K absorption edge of copper is shifted towards the high energy side in all the complexes studied as compared to the K absorption edge in the metal.

3.1 Pre-edge feature

Kau *et al*¹⁴, have carried out systematic studies on a large number of Cu(I) and Cu(II) model complexes and correlated the XANES spectra with oxidation state and geometry. According to them, the peak like feature at about 8983–8984 eV is present in the K absorption edge of Cu(I) complexes but not in those of Cu(II) complexes. The absence of such a feature in the spectra of presently studied complexes (Fig. 2), suggests that copper has oxidation state +2 in the complexes.

3.2 Position of the edge

Richtmyer *et al*¹⁵, have shown that the X-ray absorption edge is an arctangent curve and the inflection point on this curve gives the position of the absorption edge. The energy of this point corresponds to the binding energy of K shell in case of K absorption edge. In case of the presently studied copper complexes, the absorption edge is found to split in two components K_1 and K_2 (Fig. 2). Hence, in such cases, the inflection point of the first rise in the absorption edge corresponds to the binding energy corresponding to that edge, i.e., the inflection point on the K_1 edge corresponds to the binding energy E_0 or E_K of the K level.

In the present work to determine the exact position of the inflection point, the first derivative of the $\mu(E)$ versus E curve has been computed. The first maximum on the first derivative curve (figure not shown here) gives the position of the inflection point and hence, the position of the K_1 absorption edge. If there is any difficulty in measuring the position of the edge from the first derivative spectra, then the second derivative of the $\mu(E)$ versus E curve is used for this purpose. The first zero crossing point on this second derivative curve (figure not shown here) also gives the position of the K_1 absorption edge correctly.

For the K absorption edge, the position of the edge is written as E_K in eV. The values of E_K (i.e., E_{K1}) for the K absorption edge of copper in its complexes studied are given in Table 2.

Table 2 — XANES data for the mixed ligand copper complexes

Complex no.	Complex	E_{K1}	E_{K2}	E_A	Chemical shift $E_{K1}-8980.5$ (eV)	Shift of the principal absorption maximum (eV)	Edge-width $E_w=E_A-E_{K1}$ (eV)	E N C	$\Sigma(X_L \sim X_M)$	$[E_w \Sigma(X_M \sim X_L)]^{1/2}$
		(eV) ± 0.5	(eV) ± 0.5	(eV) ± 0.5						
	Copper metal	8980.5	8991.8	8995.0	-	0.0	14.5	-	-	-
1	Cu(ImH) ₄ (ClO ₄) ₂	8986.3	8993.5	9001.0	5.8	6.0	14.7	0.71	4.4	8.0
2	Cu(ImH) ₄ (NO ₃) ₂	8986.8	8994.3	9001.3	6.3	6.3	14.5	0.77	7.6	10.5
3	Cu(ImH) ₄ Cl ₂	8986.2	8993.7	9001.3	5.7	6.3	15.1	0.70	6.6	10.0
4	Cu(ImH) ₄ Br ₂	8985.9	8994.2	9002.1	5.4	7.1	16.2	0.67	6.2	10.0
5	Cu(ImH) ₂ Cl ₂	8986.7	8992.6	9000.0	6.2	5.0	13.3	0.75	5.5	8.5
6	Cu(ImH) ₄ SO ₄	8987.5	8994.7	9000.9	7.0	5.9	13.4	0.84	7.6	10.0
7	Cu(ImH) ₆ (NO ₃) ₂	8987.0	8992.8	9001.7	6.5	6.7	14.7	0.79	6.6	9.8
8	Cu(ImH) ₂ (Im ⁻)Cl	8987.1	8995.0	9001.6	6.6	6.6	14.5	0.80	4.4	8.0
9	Cu(dien) ₂ (Im ⁻)(ClO ₄) ₃	8987.0	8992.7	9002.1	6.5	7.1	15.1	0.79	4.4	8.1

Note: $X_{Cu} = 1.9$, $X_O = 3.5$, $X_N = 3.0$, $X_{Cl} = 3.0$, $X_{Br} = 2.8$ (George *et al.* 1967)

3.3 Chemical shift

The shift of the X-ray absorption edge i ($i = K, L, M, \dots$) of an element in a compound/complex with respect to that of the pure element is written as:

$$\Delta E_i = E_i(\text{complex}) - E_i(\text{metal})$$

In the present case i is K, i.e., K absorption edge is under consideration. It is well known that the position of the K-edge and thus the chemical shift depends on the valence state of the absorbing ion. But the valence state is not the only factor that governs the magnitude of the chemical shift. At least two other factors that must be considered to explain the values of chemical shifts are stereochemistry and covalent bonding. For the present complexes, the chemical shift values lie in the range 5.4–7.0 eV. Ballal and Mande^{16,17}, Saxena and Anikhindi¹⁸ and Nigam and Gupta¹⁹ have shown that compounds having copper in oxidation state in +1 show chemical shifts less than 5 eV while those having copper in oxidation state in +2 show chemical shifts more than 5 eV. Recently, Vyas *et al.*²⁰, and Katare *et al.*²¹, have reported the chemical shift values of various copper(II) complexes between 5.7–12.9 eV. Hence, on the basis of values of the chemical shifts, all our complexes are found to have copper in oxidation state +2.

A comparison of the change in chemical shift on introduction of Br, Cl and NO₃ as secondary ligands is of interest. The chemical shifts for the three complexes, Cu(ImH)₄Br₂, Cu(ImH)₄Cl₂ and Cu(ImH)₄(NO₃)₂ are 5.4, 5.7 and 6.3 eV, respectively (Table 2). The chemical shift in these three complexes follows the order Br⁻ < Cl⁻ < NO₃⁻. This order can be explained on the basis of the order of these ligands in

the spectrochemical series, which is also the same, i.e., Br⁻ < Cl⁻ < NO₃⁻. Thus, the variation of the chemical shift follows the sequence in the spectrochemical series for the three ligands Br⁻, Cl⁻ and NO₃⁻.

A slightly smaller value for bromo complex in comparison to chloro complex has been observed earlier also. While Kumar *et al.*²², have reported the chemical shifts of Co(bipy)Cl₂ and Co(bipy)Br₂ as 11.5 and 10.2 eV, respectively, Shrivastava *et al.*²³, have reported the chemical shifts for Co(mchsc)₂Cl₂ and Co(mchsc)₂Br₂ as 6.5 and 5.4 eV, respectively. In these reports, such decrease in chemical shift from chloro to bromo derivatives have been attributed to the large polarizability of the bromide ion.

For the complexes under study, the order in which the secondary ligands contribute to the chemical shift is: Br < Cl < ClO₄ < NO₃ < SO₄ when the primary ligand is (ImH)₄. As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it. Hence, the above order may also be taken as representative of the relative ionic character of the bonding in these complexes.

3.4 Effective nuclear charge (ENC)

Various methods have been proposed for the estimation of effective nuclear charge. Suchet's method and other methods based on the work of Ovsyannikova *et al.*²⁴, and Gianturco and Coulson²⁵ have been applied by a large number of researchers to estimate Z_{eff} (electrons/atom) on the metal atom. In the present work, Z_{eff} has been obtained from the measured chemical shift by using the semi-experimental method²⁵ by employing the procedure

suggested by Nigam and Gupta¹⁹. According to this method, the shift in the 1s electron binding energy under different oxidation state of copper atom is determined from Hartree Fock (HRF) calculations of 1s atomic function given in the Tables of Clementi and Roetti²⁶ using Koopman's theorem¹⁹. A graph has been plotted between the theoretical shift in the binding energy and the oxidation number for copper (figure not shown here). The effective nuclear charge Z_{eff} on the copper atom in the complexes studied has then been determined from this plot corresponding to the measured value of the edge shifts and the data is given in Table 2. It has been found that the value of Z_{eff} varies between 0.67-0.84 electrons/atom in the copper complexes studied.

3.5 Principal absorption maximum

In Table 2, the data for the principal absorption maximum E_A for the complexes, have also been included. It has been observed that with respect to copper metal, the value of E_A is shifted towards the higher energy side. The shift of principal absorption maximum depends on the type of overlap between metal and ligand orbitals. The greater the overlap of the metal and the ligand orbitals, more stable are the bonding molecular orbitals and hence the corresponding anti-bonding molecular orbitals are more unstable.

Since, the principal absorption maximum occurs due to the transitions from 1s orbital to the unoccupied anti-bonding molecular orbitals ($1s-5t_{1u^*}$ in octahedral), the principal absorption maximum, therefore, shifts to the higher energy side²⁷. The energy range of chemical shift in these complexes is between 5.4-7.0 eV while the range for shift of principal absorption maximum is between 5.0-7.1 eV. Hence, on the basis of the shift of the principal absorption maximum also it can be inferred that copper is in +2 oxidation state in these complexes.

3.6 Edge-width

Table 2 presents the values of the edge-width ($E_A - E_{K1}$). The edge-width of the K absorption edge has been found to lie in the range 13.3-16.2 eV. In general, edge-width of the K absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc., remain the same²². The values of the edge-width are 16.2, 15.1 and 14.5 eV for bromo, chloro and nitro complexes, respectively. This order is just opposite to that of the chemical shift values in

these complexes. The reverse trend for these two complexes is justified on the basis of the above-mentioned criterion. The edge-width may be taken roughly to define band width which is expected to increase in the degree of covalency of the bond.

The edge-widths E_W are related to the electronegativity difference between metal atom (X_M) and its neighbouring atom (X_L) in the coordination sphere in a manner proposed by Nigam and Srivastava²⁸. Their relationship may be expressed in the form:

$$\text{Constant} = [E_W \sum (X_M \sim X_L)]^{1/2}$$

where X_M and X_L are the Pauling's electronegativities of the central metal atom and the nearest neighbours, respectively and the summation on the right hand side extends over all the atoms in the coordination sphere.

The values of the constant $[E_W \sum (X_M \sim X_L)]^{1/2}$ for all the complexes are given in Table 2. The complexes having lower geometry, i.e., square planar, the values of the constant are also lower, i.e., from 8.0 to 8.1. For higher geometry, i.e., tetrahedral, the values of the constant is slightly higher, i.e., 8.5. For still higher geometry, i.e., octahedral, the values of the constant is still higher, i.e., from 9.8-10.5. It may be noted that edge-width and $\sum (X_M \sim X_L)$ may be taken roughly to define band width and the ionic/covalent character of the metal-ligand bond, respectively. The band width may be expected to increase in the degree of covalency of the bond, which, in turn, is known to follow a decrease in the value of ($X_M \sim X_L$).

4 Conclusions

X-ray absorption spectra at the K-edge of copper have been studied in the mixed ligand complexes $\text{Cu}(\text{ImH})_4(\text{ClO}_4)_2$ (1), $\text{Cu}(\text{ImH})_4(\text{NO}_3)_2$ (2), $\text{Cu}(\text{ImH})_4\text{Cl}_2$ (3), $\text{Cu}(\text{ImH})_4\text{Br}_2$ (4), $\text{Cu}(\text{ImH})_2\text{Cl}_2$ (5), $\text{Cu}(\text{ImH})_4\text{SO}_4$ (6), $[\text{Cu}(\text{ImH})_6](\text{NO}_3)_2$ (7), $[\text{Cu}(\text{ImH})_2](\text{Im}^-)\text{Cl}$ (8), $[\text{Cu}_2(\text{dien})_2(\text{Im}^-)](\text{ClO}_4)_3$ (9), where ImH = Imidazole, Im^- = Imidzolate anion and dien = diethylenetriamine. The Cu K-edge has been found to split into two components, i.e., K_1 and K_2 in all of these complexes. The energies of K_1 edge (E_{K1}), K_2 edge (E_{K2}), principal absorption maxima (E_A) have been reported. From these, the shift of the K_1 -edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of

the complexes. The chemical shift in the three complexes **2**, **3** and **4** follows the order $\text{Br}^- < \text{Cl}^- < \text{NO}_3^-$. This order can be explained on the basis of the order of these ligands in the spectrochemical series, which is also the same, i.e, $\text{Br}^- < \text{Cl}^- < \text{NO}_3^-$.

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