

## On K-Edge Fine Structure Spectra of Some Cu(I) Complexes

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X-ray K-absorption spectra of some copper(I) complexes, viz.  $\text{Cu}(\text{C}_2\text{HN}_2\text{S}_3)$ ,  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$ ,  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  and  $\text{Cu}_4[(\text{tu})_9](\text{NO}_3)_4$  have been recorded using a 40-cm curved crystal spectrograph of transmission type. Measurements on a well-characterized copper(II) complex,  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  have also been recorded for the sake of comparison. The energies of various maxima and minima appearing in the extended fine structure spectra register a shift towards higher energy side in the case of  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  as compared to those of Cu(I) complexes. The edge structures of Cu(I) complexes are generally in agreement with their stereochemistries. Metal-ligand average bond distances have also been calculated from the maxima-minima separation in the observed fine structure.

VALENCY effects on X-ray absorption edges and principal absorption maxima are now well established<sup>1-4</sup> in a variety of chemical entities but very little work has appeared<sup>5</sup> on their extended fine structure spectra. Also, the structures of the absorption edges have been correlated<sup>6-8</sup> with the coordination symmetry of the compounds. The present paper reports the effect of valency on the K-absorption spectra in some Cu(I) complexes, majority of which are known to be in tetrahedral coordination. Their fine structure spectra has been also studied.

### Materials and Methods

X-ray absorption studies were carried out using a Machlett sealed X-ray tube having a tungsten target which was operated at 20 kV and 10 mA. A Cauchois type curved (40 cm radius) crystal spectrograph having (100) reflection planes of mica as analyser, was employed to record the spectra on Kodak X-ray films. The dispersion of the spectrographic set up was found to be  $\sim 12$  XU/mm. Tungsten  $L_{\alpha_1}$ ,  $L_{\alpha_2}$ ,  $L_{\beta_1}$  and  $L_{\beta_2}$  emission lines were used as reference standards and their wavelengths were adopted from standard tables<sup>9</sup>. The absorbing screens were prepared by evenly spreading the substance in finely powdered form on Scotch tapes.

Screens of suitable thickness were chosen after several trials and placed between the X-ray tube window and the analysing crystal. The exposure time varied from 15 to 20 hr. Several spectrograms were taken on a Kipp and Zonen Moll microphotometer (type A) with a magnification of 8x.

The compounds chosen for the study were:  $\text{Cu}(\text{C}_2\text{HN}_2\text{S}_3)$  (I),  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$  (II),  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  (III),  $\text{Cu}_4[(\text{tu})_9](\text{NO}_3)_4$  (IV) and  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  (V), where  $\text{C}_2\text{HN}_2\text{S}_3$ ,  $\text{PPh}_3$ , tu and  $\text{C}_6\text{H}_7\text{N}$  represent 1,3,4-thiadiazole-2,5-dithiol, triphenylphosphine, thio-urea and  $\alpha$ -picoline respectively. Methods of preparation are reported in literature<sup>10-13</sup>.

### Results and Discussion

Table 1 shows the shifts in the main K-edge and also the relative energies of the principal absorption maxima observed in the various complexes. As expected, the shift of the edge position to the higher energy side is larger for  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  as compared with those of Cu(I) complexes. Further, the complex,  $\text{Cu}(\text{C}_2\text{HN}_2\text{S}_3)$  (I) gives the smallest  $E_A$  value amongst all the Cu(I) complexes under study. This complex has been shown<sup>10</sup> to involve Cu(I) in a linear polymeric chain structure of the type  $[-R-S-Cu(I)-S-R-]_n$  with *sp*-hybridization as against *sp*<sup>3</sup> hybridization in the other Cu(I) complexes

TABLE 1 — SHIFTS IN THE K-ABSORPTION EDGE AND THE RELATIVE ENERGIES OF THE PRINCIPAL ABSORPTION MAXIMUM OF COPPER IN SOME COMPLEXES

No.	Complexes	$\lambda_K$ (XU)†	$(\nu/R)_K$	$\Delta E$ (eV)‡	$\lambda_A$ (XU)†	$(\nu/R)_A$	$E_A$ (eV)‡
	Cu metal	1377.7	661.44	—	—	—	—
(I)	$\text{Cu}(\text{C}_2\text{HN}_2\text{S}_3)$	1377.54	661.52	1.1	1376.47	662.03	8.0
(II)	$\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$	1377.51	661.54	1.4	1375.76	662.38	12.8
(III)	$\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$	1377.37	661.60	2.2	1375.84	662.34	12.2
(IV)	$\text{Cu}_4(\text{tu})_9(\text{NO}_3)_4$	1377.26	661.66	3.0	1375.62	662.45	13.7
(V)	$\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$	1376.70	661.92	6.5	1375.08	662.70	17.1

†  $\pm 0.5$  unit. ‡  $\pm 0.6$  unit.

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with a distorted tetrahedral structure. The absorption maximum in the complex (I) represents the transition  $1s \rightarrow 4p$  whereas in the other Cu(I) complexes, the absorption maxima would correspond to the transition  $1s \rightarrow 4p^*$  (antibonding). The latter transition would involve a larger energy and consequently a higher shift in the absorption peaks in the complexes (II-IV). A comparison of the edge-shifts and energies of the main peak for the complexes,  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$  (II) and  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  (III) reveals that edge shift for III is higher than that of the complex (II) whereas the relative energies of the main peak show a reverse trend. Copper ion in II is coordinated<sup>11</sup> with one oxygen and three phosphorus atoms but in III coordination takes place through two oxygen and two phosphorus atoms. A comparatively higher degree of covalency expected in the former may be considered<sup>3,14,15</sup> to rationalize this observation.

The plots of transmitted intensity versus energy of the  $K$ -absorption spectra of these complexes are shown in Fig. 1. The energy scale is based on the first inflection point of the metallic copper  $K$ -edge as zero in the usual manner. The edges of  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  (III) and  $\text{Cu}_4(\text{tu})_9(\text{NO}_3)_4$  (IV) are clearly split up into two successive components  $K_1$  and  $K_2$  thus resembling type-IV spectra of Van Nordstrand's classification<sup>5</sup> and is diagnostic of tetrahedral structure. The crystal structure analyses of these complexes have shown<sup>11,12</sup> that each copper involves tetrahedral coordination. However, no splitting in the absorption edge has been observed in the tetrahedral complex,  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$  (II) and the reason for the same is not clear.

An initial absorption appearing as a wide hump in the low energy region of the main edge in the case of square-planar complex,  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  (V) (probable symmetry,  $C_{2v}$ ) may be assigned to  $1s \rightarrow 3d$  quadrupole transition ( $\Delta l = \pm 2$ ). The presence of one unpaired electron has been shown<sup>13</sup> earlier in the  $3d$  orbitals ( $\mu_{\text{eff}} = 2.20$  B.M.). The broad nature of this band may probably be due to the extensive splitting of the  $d$ -orbital set ( $A_2 + B_1 + B_2$ ).

The shoulder ( $s$  in Fig. 1) in  $\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$  (V) appearing at  $\sim 10$  eV on the low energy side of the main peak may be assigned<sup>16,17</sup> to a normally disallowed transition  $1s \rightarrow 4s^*$  (antibonding). This transition may become allowed due either to mixing of states ( $s-d$  or  $s-p$ ) or to symmetry changes produced by vibrational excitation. It can be seen that the principal absorption maximum is unsplit in all Cu(I) complexes, as expected from theoretical

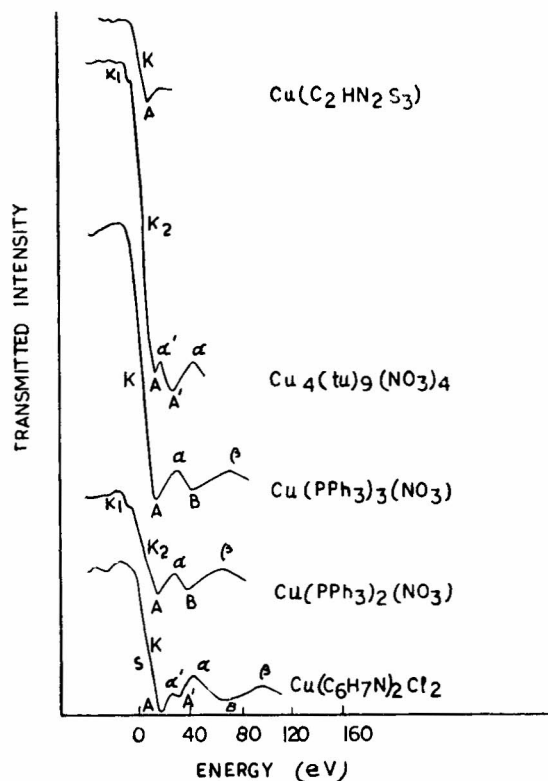


Fig. 1 — X-ray absorption spectra of some copper complexes

predictions<sup>18</sup> since  $4p^*$  (antibonding) levels will not split in the linear or tetrahedral fields.

It has been observed that the extended fine structure are largely similar for  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  and  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$  (Table 2 and Fig. 1). Further, the energy values of the various maxima and minima in the fine structure spectrum of V are significantly larger than those for Cu(I) complexes. The appearance of the structure  $\alpha'$ ,  $A'$  to the right of the main peak in the complexes (V) and (IV) may be due to unequal bond strength, similar to that observed by Seka and Hanson<sup>19</sup> in  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . An X-ray crystal structure determination on a similar compound,  $\text{Cu}(\text{pyridine})_2\text{Cl}_2$  has also shown<sup>20</sup> the presence of four short and two long bonds around each copper atom. However, in  $\text{Cu}_4(\text{tu})_9(\text{NO}_3)_4$ , the lack of symmetry due to effective five coordination<sup>12</sup> may be supposed to be responsible for the observed feature.

TABLE 2 — THE RELATIVE ENERGIES OF MAXIMA AND MINIMA IN THE FINE STRUCTURE SPECTRA (in eV) AND THE METAL-LIGAND AVERAGE BOND DISTANCE OF SOME COPPER COMPLEXES

Complex	A	$\alpha'$	$A'$	$\alpha$	B	$\beta$	$\Delta E(\beta - B)$	Measured bond distance $r \pm 0.1$ (Å)
$\text{Cu}(\text{NO}_3)(\text{PPh}_3)_3$	12.8	—	—	26.5	35.0	65.0	30.0	2.23
$\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2^*$	12.2	—	—	25.0	34.5	62.7	28.2	2.31
$\text{Cu}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$	17.1	26.0	32.0	40.6	64.8	98.3	33.5	2.12

\*Cu-P and Cu-O bond distances are found to be 2.256 and 2.223 Å respectively from X-ray diffraction.

The energy separation,  $\Delta E$ , between the maximum,  $B$  to the next minimum,  $\beta$  may be used to calculate<sup>21</sup> the average radius of the first coordination sphere around the central ion using the Bragg relation (1).

$$r_1 = (151/\Delta E)^{1/2} \text{ \AA} \quad \dots(1)$$

The results of such calculations are given in Table 2. It is worth mentioning that the measured bond distance in the case of  $\text{Cu}(\text{NO}_3)(\text{PPh}_3)_2$  is in good agreement with the X-ray crystal structure data<sup>22</sup>.

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