X-Ray K-Absorption Studies of Some Cu(II) Complexes

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K-Absorption edges of copper(II) in complexes of 5,5'-thiodisalicylic acid [C_6H_3(OH)(COOH).
S.(COOH).(OH).C_6H_3] and α-mercaptopropionic acid [CH_3.CH(SH).COOH] have been investigated.
Edge-shifts and edge-widths have been measured and their correlation respectively with nature
of metal-ligand bond and coordination stoichiometry have been discussed. The edge-structures
have been found to agree with the coordination symmetry suggested for the complexes.

THE importance of X-ray spectroscopy for the chemical analysis (XSCA) as a tool for providing a direct probe into the region of metal-ligand overlap has been recognized[1-4]. The shift in the absorption edge, the edge-width and the edge-structure show dependence on the valency of the metal ion[5], the coordination stoichiometry[6] and stereochemistry of a complex[7,8]. The present paper seeks to correlate the various spectral features with the nature of metal-ligand bond involved in some copper(II) chelates formed by using 5,5'-thiodisalicyclic acid (TDSA) and α-mercaptopropionic acid (α-MPA) as ligands.

Materials and Methods

The complexes employed were H_2[Cu(TDSA)$_2$·(H$_2$O)$_2$]·7H$_2$O, (NH$_4$)$_2$[Cu(TDSA)$_2$(NH$_3$)$_2$]·5H$_2$O and H$_3$[Cu$_3$(α-MPA)$_3$·3H$_2$O·1·5O], which have earlier been prepared and characterized by Nigam *et al.*[9,10]. Copper sulphate pentahydrate has also been included in the list for the sake of comparison.

X-ray absorption studies were carried out on a Machlett sealed X-ray tube having a tungsten target, which was operated at 15-20 kV and 8-10 mA. A bent crystal transmission spectrograph using a mica sheet oriented to reflect from (100) planes and curved cylindrically to a radius of 40 cm was used for recording the spectra on Kodak X-ray films. The reference lines used were Lα$_1$, Lα$_2$, Lβ$_1$ and Lβ$_4$ of tungsten and their wavelengths were adopted from standard tables of Bearden[11]. Absorbing screens were prepared by uniformly spreading the finely powdered substance between two thin cellotapes and were placed between the X-ray tube window and the analysing crystal. Several spectrograms were taken for each sample. The exposure time varied from 15-20 hr. The spectrograms were analysed from a Kipp and Zonen Moll microphotometer (type A) with magnification 8X and 25X, the former has been used for measurements.

Results and Discussion

A representative microphotometric trace of K-absorption edge of H$_2$[Cu(TDSA)$_2$(H$_2$O)$_2$]7H$_2$O at

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8X magnification has been shown in Fig. 1. Table 1 contains the edge-shifts of copper in copper sulphate and in the Cu(II) complexes mentioned above. A perusal of Table 1 shows that the edge-shift for complex (I) is much smaller than that for complex (II). Earlier investigations[9] have shown that νCu—O in these two complexes appear at 515 and 400 cm^{-1} leading to force constants values of 2·52 and 1·21 respectively, thus implying a substantially enhanced covalent bond strength of the metal-ligand bond in complex (I). It may be noted that lowering in edge-shift values with increase in the covalent character of the bond has been observed by many workers[12-14]. The edge-shift values for CuSO$_4$·5H$_2$O and the complex (I) also appear to support the above hypothesis. Each copper atom in either complex involves octahedral coordination by oxygen atoms. The complex (I) may be expected to be more covalent in which two bidentate ligands hold the central metal ion in the rings through carbonyl groups whereas in CuSO$_4$·5H$_2$O, only one bidentate sulphate ion forms the chelate.

The edge-widths of these complexes (Table 2) and their respective coordination stoichiometries (Table 3) reasonably satisfy the semi-empirical correlation (1) proposed by Nigam *et al.*[6,15].

$$[\text{Edge-width}\cdot\Sigma|X_M-X_L|]^{\frac{1}{2}} = \text{constant for a given metal in a given region} \quad \ldots(1)$$

provided $X_M \neq X_L$, where X_M and X_L are the Pauling electronegativities of the metal and the donors respectively. Table 2 shows that the measured edge-widths for CuSO$_4$·5H$_2$O and complex (I) are similar, as expected, the metal ion being surrounded by six oxygen atoms in both the cases. Further, it may be seen (Table 3) that as the coordination stoichiometry varies as a result of gradual replacement of metal-sulphur bonds in the complex (I) by metal-nitrogen bonds in the complex (II), the edge-width shows a marked increase in the latter.

The transmitted intensity vs energy curves of the absorption edges of these complexes are shown in Fig. 2 in which the energy is based on the first inflection point of the K-edge in metal as zero. It is clear from Fig. 2 that the absorption edges for CuSO$_4$·5H$_2$O and complex (I) register monotonous

TABLE 1 — SHIFTS IN THE K-ABSORPTION EDGE OF COPPER IN COPPER SULPHATE AND THE COMPLEXES

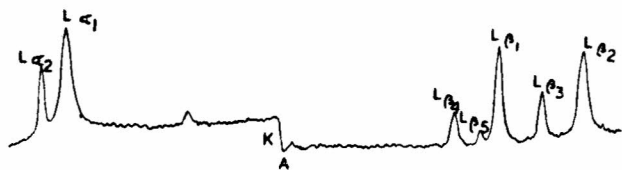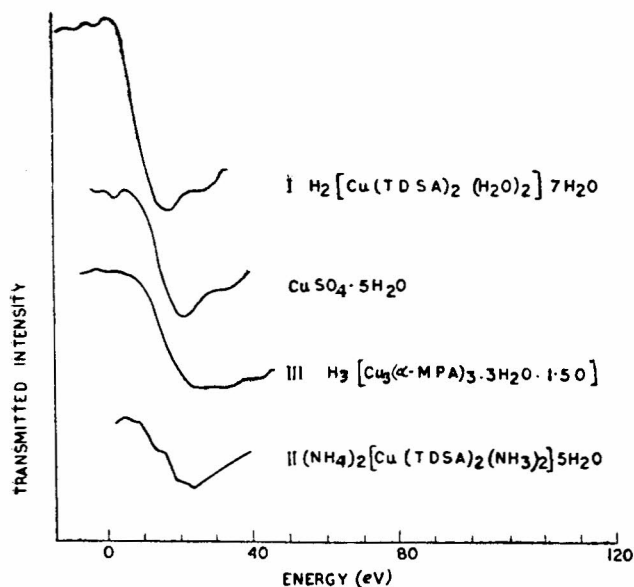| Compound	λ_K (XU) (± 0.05)	$(\nu/R)_K$	$\Delta(\nu/R)$	Δ eV ± 0.6
Cu (metal)	1377·7	661·44	—	—
CuSO$_4$.5H$_2$O	1375·64	662·43	0·99	13·4
(I) H$_2$[Cu(TDSA)$_2$.(H$_2$O)$_2$].7H$_2$O	1376·47	662·03	0·59	8·0
(II) (NH$_4$)$_2$[Cu(TDSA)$_2$(NH$_3$)$_2$].5H$_2$O	1375·54	662·49	1·05	14·2
(III) H$_3$[Cu$_3$(α-MPA)$_3$(H$_2$O)$_3$.1·50]	1375·32	662·59	1·15	15·6

Fig. 1 — Microphotometric trace of K-absorption edge of H$_2$[Cu(TDSA)$_2$H$_2$O].7H$_2$O [magnification 8 ×]

Fig. 2 — X-ray absorption spectra of some copper complexes

TABLE 2 — WIDTHS OF THE ABSORPTION EDGES

Compound	λ_A(XU) (± 0.05)	$(\nu/R)_A$	$(\nu/R)_K$	$\Delta(\nu/R)$	Edge-width eV(± 0.6)
CuSO$_4$.5H$_2$O	1374·48	662·99	662·43	0·56	7·6
I	1375·27	662·61	662·03	0·58	7·8
II	1374·22	663·12	662·49	0·63	8·6
III	1373·26	663·58	662·59	0·99	13·4

TABLE 3 — CORRELATION BETWEEN EDGE-WIDTHS AND COORDINATION STOICHIOMETRY

Compound	Coordination stoichiometry (M : O : S : N)	$\Sigma \lvert X_M - X_L \rvert$	Edge-width	$[(EW) \Delta Z]^{1/2}$
CuSO$_4$.5H$_2$O	1 : 6	9·6	7·6	8·5
I	1 : 6	9·6	7·8	8·6
II	1 : 4 : 2	8·6	8·6	8·6
III	1 : 3 : 1	5·4	13·4	8·5

curves resembling type-I spectra of Van Nordst-rand's classification[16], characteristic for octahedral configurations. The observed splitting of the main edge in the case of octahedral complex (II), however, presents a deviation from the above mentioned classification which may probably be attributed to distortion due to a change in the symmetry from near O_h to D_{4h}. Further, comparing the absorption edges of complexes (I) and (II), a band appearing in the low energy region of the main edge may be seen in the latter case only. It is well known[17] that the metal $3d$ unpaired electron in these complexes occupies the dx^2-y^2 orbital. The E_g set in O_h symmetry is doubly degenerate while it splits into $A_{1g}(dz^2)$ and $B_{1g}(dx^2-y^2)$ in D_{4h} symmetry. Thus, the partially filled B_{1g} orbital would be singled out in complex (II) and the initial absorption may be assigned as $1s \rightarrow B_{1g}$ (quadrupole transition $\Delta 1 = \pm 2$). A faint low

energy absorption has also been observed in case of complex (III) (Fig. 2). This compound has been shown[10] to be trinuclear involving metal-metal inter-action ($\mu_{\text{eff}} = 1·0$ BM) with the copper atoms situated at the apices of an equilateral triangle and consequently two of the three unpaired electrons are paired up, thus leaving an odd electron ($\uparrow\downarrow \uparrow$). The expected overall vacancy in the $3d$ region appears to be responsible for the observed feature. One has to observe caution in interpreting such features as the copper impurity line may appear very close to this. However, the absense of such structures in other compounds would lead to above assignments.

The principal absorption maximum of the complex (II) has been split up into two components, thus agreeing with the coordination symmetry (D_{4h}) obtaining in it, as suggested by Cotton and Ballhausen[18]. The axially coordinated ammonia groups through nitrogen atoms are expected to move away from the metal ion more loosely than the planar oxygens of thiodisalicylic acid ligands on considerations of electronegativity. Consequently, the p orbitals which transform as A_{2u} may be relatively lowered in energy. The two components of the main peak may therefore, be designated as $1s \rightarrow A^*_{2u}$ and $1s \rightarrow E^*_u$ in the increasing order of energy. A higher order splitting of the main peak for this complex may probably be due to the presence of ammonia groups which have been observed[19,20] to cause splitting irrespective of symmetry considerations. The unsplit nature of the main peak for CuSO$_4$.5H$_2$O and the complex (I) is

similarly in agreement with its near O_h symmetry. A general broadening of the main peak observed in complex (III) may be due to sulphur atoms acting as donors. Sulphur ligands have usually been found to cause a broadening of the principal absorption maximum[21,22].

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