

K-Absorption Edges of Some Cu(II) Complexes Involving Metal-Metal Exchange Interaction

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K-Absorption edges and the extended fine structures of some copper(II) complexes involving metal-metal exchange interaction formed with dithiols and dithiones as ligands have been recorded employing a 40-cm curved crystal spectrograph of transmission type. Edge-widths of thiol complexes have been found to agree with their coordination stoichiometries, but in the case of dithione complexes, computation of their coordination stoichiometries appears to suggest the possibility of molecular association. Average metal-ligand bond distances for these complexes have also been calculated from the maxima-minima separations in the observed fine structures.

THE use of X-ray absorption edge spectroscopy (XAES) as a conventional tool for investigating many vital problems in the field of coordination chemistry has been emphasized¹⁻⁶. However, very little X-ray spectroscopic work is known⁷ to have appeared on compounds involving metal-metal exchange interaction. The present paper, therefore, is an attempt to apply this technique in the case of some especially chosen set of Cu(II) complexes showing metal-metal exchange interaction, the nature of which continues to evade an adequate explanation^{8,9}. The studies comprise of measurements of edge-width, observations on edge structure and extended fine structure.

Materials and Methods

Copper(II) complexes with the following ligands with 1-phenyl-tetrazoline-5-thione ($C_7H_6N_4S$), 1-*p*-bromo-phenyl tetrazoline-5-thione ($C_7H_5N_4SBr$), 2-mercaptopyrimidine-4-ol ($C_4H_4N_2OS$), and 3,4,5-pyridazine trithiol ($C_4H_4N_2S_3$) were chosen. The methods of preparation and characterization of these complexes, viz. $Cu(C_7H_6N_4S)_2$, $Cu(C_7H_4N_4SBr)_2$, $Cu(C_4H_2N_2OS) \cdot 2H_2O$ and $Cu_5(T)_2(TH)_2 \cdot 10H_2O$; T = $C_4HN_2S_3$, have been described earlier¹⁰⁻¹².

X-ray absorption studies were carried out on a Machlett sealed X-ray tube having a tungsten target which was operated at 20 kV and 10 mA. A 40-cm radius Cauchois type curved crystal spectrograph using (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 ~ 12 XU/mm. Tungsten $L_{\alpha 1}$, $L_{\alpha 2}$, $L_{\beta 1}$ and $L_{\beta 4}$ emission lines were used as reference standards and their wavelengths were taken from standard tables of Bearden¹³. The absorbing screens were prepared by evenly spreading the substance in the fine powder form on Scotch tape. After several trials, screens of suitable thickness were obtained and were 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 with magnification 8X for each sample.

Results and Discussion

The measured edge-widths, i.e. the energy difference between the principal absorption maximum, A and the main edge, K are presented in Table 1. A correlation between edge width and coordination stoichiometry as also the overall metal-nearest neighbour electronegativity difference $\Sigma|X_M - X_L|$ determined from the latter are given in Table 2. The edge-width of $Cu_5(T)_2(TH)_2 \cdot 10H_2O$ and $Cu(C_4H_2N_2OS) \cdot 2H_2O$ reasonably satisfy the empirical relationship (1) proposed by Nigam *et al.*^{14,15}.

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

provided $X_M = X_L$, where X_M and X_L are Pauling electronegativities of the metal and its nearest neighbours respectively. The complex $Cu_5(T)_2(TH)_2 \cdot 10H_2O$ has earlier¹² been shown to contain five copper atoms having three different types of coordination stoichiometries (Table 2). The measured edge-width, 14.1 eV for this complex satisfies the coordination stoichiometries (a) and (b) (Table 2). However, the edge-widths for the complexes, $Cu(C_7H_6N_4S)_2$ and $Cu(C_7H_4N_4SBr)_2$ show deviation from this relationship. These complexes have earlier been shown¹⁰ to be square planar consisting of CuN_2S_2 chromophore. Accordingly, the value obtained for $\Sigma|X_M - X_L|$ would be 3.4. However, the value computed from the $X-EW$ relationship using the measured edge-widths is found to be ~ 4.9 . It can be seen that this value very nearly corresponds to the coordination stoichiometry, Cu:N:S::1:3:3; $\Sigma|X_M - X_L| = 5.1$. That the metal atom might have one nitrogen and one sulphur atom as its nearest neighbours in addition to the CuN_2S_2 chromophore, appears to be conceivable in view of the following facts. On the basis of diamagnetic and semiconducting properties of the

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TABLE 1 — EDGE-WIDTHS OF THE ABSORPTION EDGES

Compound	λ_A (XU) (± 0.05)	$(\nu/R)_A$	λ_K (XU) (± 0.05)	$(\nu/R)_K$	$\Delta(\nu/R)$	$W(\nu/R)$ eV (± 0.6)
$\text{Cu}(\text{C}_7\text{H}_5\text{N}_4\text{S})_2$	1375.20	662.64	1377.53	661.53	1.11	15.1
$\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{SBr})_2$	1375.26	662.62	1377.48	661.55	1.07	14.5
$\text{Cu}(\text{C}_4\text{H}_2\text{N}_2\text{OS}) \cdot 2\text{H}_2\text{O}$	1375.03	662.73	1376.81	661.87	0.86	11.7
$\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$	1374.55	662.96	1376.70	661.92	1.04	14.1

TABLE 2 — CORRELATION BETWEEN EDGE-WIDTHS AND COORDINATION STOICHIOMETRY

Compound	Coordination stoichiometry				$\Sigma X_M - X_L $	Edge-width $[EW \Sigma X_M - X_L]^\ddagger$ (eV)	
	Cu	O	S	N			
$\text{Cu}(\text{C}_7\text{H}_5\text{N}_4\text{S})_2$	1	—	2	2	3.4	15.1	7.2
	1	—	3	3*	4.8	—	8.5
$\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{SBr})_2$	1	—	2	2	3.4	14.5	7.0
	1	—	3	3*	5.0	—	8.5
$\text{Cu}(\text{C}_4\text{H}_2\text{N}_2\text{OS}) \cdot 2\text{H}_2\text{O}$	1	2	1	2	6.0	11.7	8.4
$\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$	(a)	1	4	1	5.1	14.1	8.4
	(b)	1	2	3	—	—	8.4
	(c)	1	3	1	1	6.5	—

*Computed from edge-width.

complexes, $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4\text{S})_2$ and $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{SBr})_2$, it has been suggested¹⁰ earlier that the molecule should adopt a polymeric configuration in which diamagnetism arises from the direct intramolecular exchange between the two copper atoms, supported virtually in contact with one another by four bridging tetrazoline-5-thione groups and the semi-conductivity of these complexes has been explained by through conjugation, the metal atoms using their valence shell 'd' orbitals to form $d\pi-p\pi$ bonds to the adjacent ligands. Raising of coordination stoichiometry on the basis of computation from edge-width value has been proposed¹⁵ recently in the Co(II) complex with 1-phenyltetrazoline-5-thione.

K-absorption spectra of the complexes studied here are shown in Fig. 1. The energy scale is based on the first inflection point of the metallic copper edge as zero in the usual manner. The shoulder appearing on all the curves (marked as S for illustration in Fig. 1) at ~ 10 eV lower energy with respect to the main peak, may be assigned, as suggested by Glen and Dodd², to a normally disallowed transition $1s \rightarrow 4s^*$ antibonding. It may be noted that in Zn^{2+} which provides a close approximation to the K-excited Cu^{2+} ion, the configuration $3d^9 4s$ and $3d^9 4p$ are about 10 eV apart¹⁶. In Cu^{2+} , therefore, the $1s \rightarrow 4s^*$ transition may well be expected to occur at ~ 10 eV below $1s \rightarrow 4p^*$ as observed. This transition may, become allowed due either to mixing of states ($s-d$ or $s-p$) or to symmetry changes produced by vibrational excitations¹⁷. Further, comparing the edges of $\text{Cu}(\text{C}_7\text{H}_5\text{N}_4\text{S})_2$ and $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{SBr})_2$, one observes that this transition is more prominent in the latter case. Though either of the complexes involve square planar configuration, the substituent bromine in the aryl radical may probably be responsible for additional perturbation and consequently more distortion due to steric hindrance in the complex, $\text{Cu}(\text{C}_7\text{H}_4\text{N}_4\text{SBr})_2$ which has been reflected in the observed spectra. Broad

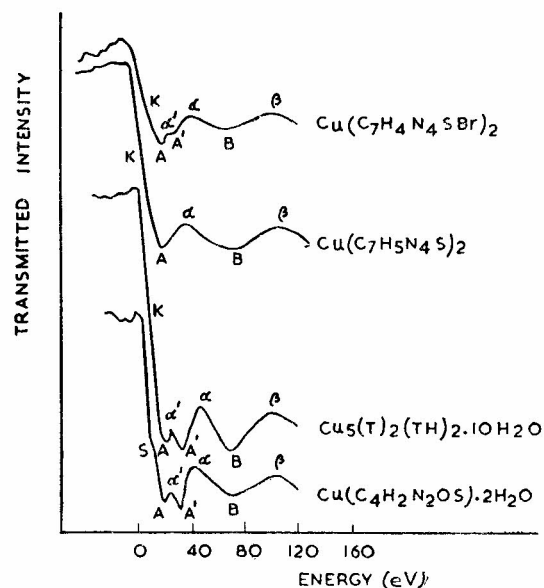


Fig. 1 — X-ray absorption spectra of some Cu(II) complexes [A and B refer to absorption maxima and α and β to absorption minima. Structures in the region $A\alpha$ and $B\beta$ are labelled as $\alpha'A'$ and $\beta'B'$ respectively]. S refers to shoulder

bands at 900 nm and 550 nm have been observed^{11,12} in the visible spectra of the distorted octahedral complexes $\text{Cu}(\text{C}_4\text{H}_2\text{N}_2\text{OS}) \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$. It is interesting to note that broad nature of the band has been shown to be indicative of John-Teller distortion¹⁸. A comparatively intense $1s \rightarrow 4s^*$ absorption in the complex, $\text{Cu}(\text{C}_4\text{H}_2\text{N}_2\text{OS}) \cdot 2\text{H}_2\text{O}$ may probably be due to unsymmetrical nature of the band appearing at 900 nm which seems to be resolved into two bands.

The positions of various maxima and minima in the extended fine structure spectra of these complexes are given in Table 3. The spectra of

TABLE 3 — POSITIONS IN MAXIMA AND MINIMA IN THE EXTENDED FINE STRUCTURE SPECTRA OF SOME COPPER(II) COMPLEXES*

Compound	A	α'	A'	α	B	β
Cu(C ₇ H ₅ N ₄ S) ₂	16.3	—	—	37.0	73.5	108.9
Cu(C ₇ H ₄ N ₄ SBr) ₂	16.0	21.2	25.0	39.0	72.0	105.8
Cu(C ₄ H ₂ N ₂ OS)·2H ₂ O	17.5	23.6	29.0	37.8	68.4	102.5
Cu ₅ (T) ₂ (TH) ₂ ·10H ₂ O	10.6	24.0	31.0	46.0	71.0	103.0

*Capitals A, B, etc. refer to absorption maxima and Greek letters α , β , etc. to absorption minima. Structures in the region A α and B β are labelled as α' , A' and β' , B' respectively.

TABLE 4 — METAL-LIGAND AVERAGE BOND LENGTHS

Compound	$\Delta E(\beta-B)$ (eV)	Calculated (Å)
Cu(C ₇ H ₅ N ₄ S) ₂	35.4	2.06
Cu(C ₇ H ₄ N ₄ SBr) ₂	33.8	2.11
Cu(C ₄ H ₂ N ₂ OS)·2H ₂ O	34.1	2.10
Cu ₅ (T) ₂ (TH) ₂ ·10H ₂ O	32.0	2.17

Cu(C₇H₅N₄S)₂ and Cu(C₇H₅N₄SBr)₂ are more or less the same (Fig. 1), both from energy position and transmitted intensity considerations. It may be recalled that both the complexes involve similar surroundings. However, a small kink $\alpha'A'$ appearing in the case of Cu(C₇H₅N₄SBr)₂, may probably be due to the effect of the substituent bromine as discussed in preceding pages. In the fine structure spectra of the complexes Cu(C₄H₂N₂OS)·2H₂O and Cu₅(T)₂(TH)₂·10H₂O, the fluctuations at A and α' are very small and a sharp peak, A' of higher intensity than the principal absorption maximum, A has appeared on its higher energy side.

The difference in energy, ΔE from the second maximum, B to the next minimum, β gives a measure of the radius of the first coordination sphere¹⁹ around the central metal atom through the Bragg

relation (2)

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

The estimated bond distances in these complexes are given in Table 4 and are found to lie within the expected range of reported metal-ligand bond lengths.

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