X-Ray *K*-Absorption Spectral Investigations of Some Copper(II) Complexes involving Metal–Metal Interaction

By **Jagdish Prasad, Vijai Krishna,** and **Hira Lal Nigam,***,† Department of Chemistry, University of Allahabad, Allahabad-2, India

The *X*-ray *K*-absorption edge position and the extended fine structure of copper in some copper(II) complexes involving metal–metal exchange interaction have been investigated using a 40-cm bent-crystal spectrograph. The present observations do not support the hypothesis of increasing edge shift as a consequence of metal–metal interaction. Edge widths have been correlated with the co-ordination stoicheiometries, and it has also been found that the edge position shifts towards higher energy as the metal–metal distance decreases. Estimates of average metal–ligand bond distances have also been made.

X-RAY absorption-edge (*X*-a.e.) spectrometry has, in recent years, been exploited to yield useful information about the nature of metal–ligand bonds and the ligand-field symmetry in co-ordination compounds.[1-4] Relatively very little *X*-ray absorption spectroscopic work has been done on compounds involving metal–metal exchange interactions, the study of which has been a dominant theme of inorganic chemistry over the last two decades because of (*a*) the puzzling nature of metal–metal bonds [5,6] and (*b*) the potential uses of these compounds in industry [7] either in catalysis or in preparing materials [8] of specific electric and magnetic properties. The present investigations, therefore, are motivated by the idea of studying the vexed and still unresolved problem of binding in such compounds using the *X*-a.e. technique.

EXPERIMENTAL

The complexes used in the present investigations, *viz.* tetra-acetatodicopper(II), $[Cu_2(O_2CMe)_4]$, di-μ-methoxo-bis-[(pentane-2,4-dionato)copper(II)], $[Cu_2(OMe)_2(pd)_2]$, potassium trihalogenocuprates(II), $K[CuX_3]$, and tetrahalogenobis(pyridine *N*-oxide)dicopper(II), $[Cu_2X_4(pyo)_2]$ (X = Cl or Br), were prepared following the methods described elsewhere.[9-13]

TABLE 1

Shifts in the *K*-absorption edge, the relative energies of principal absorption maxima, and the edge widths of copper in some copper(II) complexes (in eV)

Complex	$\lambda_K \pm 0.05$ *X*-ray units	$(\nu/R)_K$	$\Delta E \pm 0.6$	$\lambda_A \pm 0.05$ *X*-ray units	$(\nu/R)_A$	$E_A \pm 0.6$	Edge width ± 0.6
Cu metal	1 377.7	661.44					
$[Cu_2(O_2CMe)_4]$	1 376.14	662.19	10.2	1 374.38	663.04	21.7	11.5
$[Cu_2(OMe)_2(pd)_2]$	1 376.04	662.24	10.9	1 374.24	663.11	22.7	11.8
$K[CuCl_3]$	1 376.97	661.79	4.7	1 375.21	662.64	16.3	11.6
$K[CuBr_3]$	1 376.80	661.88	6.0	1 374.83	662.82	18.7	12.7
$[Cu_2Cl_4(pyo)_2]$	1 376.88	661.84	5.4	1 375.02	662.73	17.5	12.1
$[Cu_2Br_4(pyo)_2]$	1 377.04	661.76	4.3	1 374.96	662.76	17.9	13.6

A 40-cm bent-crystal transmission spectrograph with a mica crystal oriented to reflect from (100) planes was used for recording spectra to first order. The dispersion of the spectrographic set-up was found to be 12.5 *X*-ray units per millimetre. A Machlett sealed *X*-ray tube having a tungsten target was used to supply continuous radiation at 20 kV and 10 mA. The reference lines used were $L\alpha_1$, $L\alpha_2$, $L\beta_1$, and $L\beta_4$ of tungsten and their wavelengths were adopted from the standard tables of Bearden.[14] The absorbing screens were prepared by evenly spreading the substance in fine powder form on Scotch tape. After several trials, screens of suitable thickness were obtained which gave maximum contrast in the aborption spectra. All the spectrograms were photographed on Kodak *X*-ray films. The screens were placed between the *X*-ray tube window and the analysing crystal. The exposure time varied from 15 to 20 h. Several spectrograms were analysed by a Kipp and Zonen Moll microphotometer (type A) using a magnification of eight times.

RESULTS AND DISCUSSION

(i) *Absorption-edge Shifts.*—In Table 1 are given the shifts in the *K*-absorption edge and the relative energies of the principal absorption maxima of the copper(II) complexes. The edge-shift values for $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$ were significantly larger than those of the remaining complexes. Agarwal and Verma [15] measured the edge shift for copper(II) acetate and found

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† *Present address*: Chemistry Department, Indore University, Indore, India.

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an unusually large value. These workers argued that the large value may be a consequence of metal–metal interaction *via* δ-bond formation between the $3d_{x^2-y^2}$ orbitals of the two copper atoms in the dimer. They formulated a rule which stated that a large edge shift, by implication, may be diagnostic of a metal–metal bond. In the case of copper(II) carboxylates the quenching of paramagnetism is explained by superexchange.[16] Also, earlier studies of this complex reveal beyond doubt that the so called δ-bond interaction is either very weak or non-existent.[17-21] If superexchange is envisaged as leading to such an increase in shift, a marked increase in the edge-shift values would also be expected in $K[CuX_3]$ and $[Cu_2X_4(pyo)_2]$ (X = Cl or Br) where superexchange is well established.[22] On the basis of our measurements on these complexes involving metal–metal exchange interaction, it may, therefore, be concluded that the boosting in edge shift cannot be made a criterion for the existence of a metal–metal interaction. Recently, the shifts in the *K*-absorption edge of copper in the pentane-2,4-dionate and its chloro-, bromo-, and nitro-substituted derivatives have been reported [23] to be abnormally high (*ca.* 11 eV).* The possibility of the existence of metal–metal interaction in these complexes has been ruled out on the basis of magnetic and spectral measurements.[24,25] The suppression in edge-shift values due to covalency has been observed by many workers.[26-28] No such trend in edge shifts, however, was found for $K[CuX_3]$ (X = Cl or Br).

TABLE 2

Correlation between edge widths and co-ordination stoicheiometry

Complex	Co-ordination stoicheiometry Cu : O : X *	$\Sigma(X_M - X_L)$	Edge width E_W/eV	$[E_W\Sigma(X_M - X_L)]^{\frac{1}{2}}$
$[Cu_2(O_2CMe)_4]$	1 : 4	6.4	11.5	8.6
$[Cu_2(OMe)_2(pd)_2]$	1 : 4	6.4	11.8	8.7
$K[CuCl_3]$	1 : 6	6.6	11.6	8.7
$K[CuBr_3]$	1 : 6	5.4	12.7	8.3
$[Cu_2Cl_4(pyo)_2]$	1 : 2 : 2	5.4	12.1	8.0
$[Cu_2Br_4(pyo)_2]$	1 : 2 : 2	5.0	13.6	8.2

* X = Cl or Br.

(ii) *Absorption-peak Shifts.*—On comparing the peak-shift values (Table 1) for the isomorphous complexes $K[CuCl_3]$ and $K[CuBr_3]$, one finds that the shift is larger for the latter. The complex $K[CuBr_3]$ may be comparatively more covalent than $K[CuCl_3]$. An increase in E_A values has been observed [2] with increasing covalent character of the metal–ligand bond. Similar conclusions can be drawn by comparing the peak shifts of the complexes $[Cu_2X_4(pyo)_2]$ (X = Cl or Br). One must bear in mind that there are a number of factors, *viz.* effective nuclear charge ($Z_{eff.}$), electronegativity, crystal structure, interatomic distances, *etc.*, which influence the edge and peak shifts.[2,29,30] No integrated approach embracing the variety of parameters involved in edge and peak shifts has yet been developed. Several observations may be found in the literature where the trends of a regular decrease in edge shift or an increase in peak shift with increasing covalency seem to be upset, *e.g.* in the pair [31] [32] $K[CuF_3]$ and $K[CuCl_3]$, in the series [26] YCl_3, $Y[NO_3]_3$, and $Y_2[SO_4]_3$, and also in the series [27] SrF_2, SrO, and SrS. Similarly, measurements on $[Cu_2(O_2CMe)_4]$ do not yield a simple interpretation (see Table 1). Further, on comparing the edge positions for $K[CuCl_3]$, $[Cu_2Cl_4(pyo)_2]$, and $[Cu_2(O_2CMe)_4]$, it may be seen that as the metal–metal distance decreases (Table 4), the edge positions (ΔE and E_A) shift to higher energy. However, in some diamagnetic copper(II) complexes known to involve direct metal–metal interaction, it has been found [33] that neither edge shifts nor peak shifts show any abnormal increases.

(iii) *Edge Widths.*—The edge widths are shown in Table 1 and are related to the electronegativity differences between the central metal ion and its surrounding neighbours in the co-ordination sphere according to a semi-empirical correlation proposed by Nigam and Srivastava [34] [equation (1)]. Table 1 shows that the

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

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* 1 eV ≈ 1.60×10^{-19} J.

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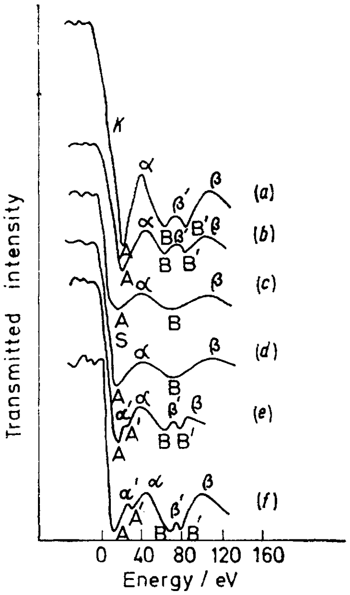
measured edge widths for the complexes $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$ are similar. These binuclear complexes have been shown [9,10] to involve square-planar co-ordination by four oxygen atoms. Further, it may be seen (Table 2) that as the co-ordination stoicheiometry varies as a result of gradual replacement of metal–oxygen by metal–halogen bonds in $[Cu_2Cl_4(pyo)_2]$ and $[Cu_2Br_4(pyo)_2]$ the edge width shows a marked increase. Similar conclusions can be drawn by comparing the edge widths for $K[CuCl_3]$ and $K[CuBr_3]$. In fact, edge width has been observed [34] to increase with increasing covalent character of the metal–ligand bond. Using equation (1), the measured edge width (11.6 eV) for the complex $K[CuCl_3]$ suggests the co-ordination stoicheiometry to be Cu : Cl 1 : 6. An *X*-ray crystal-structure investigation of this complex has also shown [35] the presence of four short and two long Cu–Cl bonds from each copper atom. Similarly, the experimental edge width (12.8 eV) for the isomorphous complex $K[CuBr_3]$ also satisfies the co-ordination stoicheiometry Cu : Br 1 : 6.



K-Absorption spectra of some copper(II) complexes: (*a*) $[Cu_2(O_2CMe)_4]$; (*b*) $[Cu_2(OMe)_2(pd)_2]$; (*c*) $[Cu_2Br_4(pyo)_2]$; (*d*) $[Cu_2Cl_4(pyo)_2]$; (*e*) $K[CuBr_3]$; (*f*) $K[CuCl_3]$

(iv) *Edge Structure.*—Plots of the transmitted intensity against energy for the *K*-absorption spectra of the complexes are shown in the Figure. The energy scale is based, as usual, on the first inflection point of the copper-metal *K*-edge as zero. The shoulder (S) appearing more or less on all the curves, except those of $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$, at *ca.* 10 eV to lower energy with respect to the main peak may be assigned, as suggested by Glen and Dodd,[2] 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 configurations $3d^94s$ and $3d^94p$ are *ca.* 10 eV apart.[36] In Cu^{2+}, the $1s \rightarrow 4s^*$ absorption may become allowed due either to mixing of states (*s–d* or *s–p*) or to symmetry changes produced by vibrational excitation.[2,3]

The main peaks due to $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$ were narrow and sharp (Figure) which may be due to the presence of a high density of normally unoccupied states with *p* symmetry in the neighbourhood of the absorbing atom or due to formation of exciton levels.[37,38] A general broadening observed for the other complexes may be related to splitting of triply degenerate $4p^*$ antibonding levels of lower order due to symmetry distortions and/or spectroscopic ligand-field effects.[2]

TABLE 3

Relative energies (eV) of absorption maxima and minima in the *K*-edge fine structure of some copper(II) complexes

Complex	*K*	A	α′	A′	α	B	β′	B′	β
$[Cu_2(O_2CMe)_4]$	10.2	21.7			43.2	65.8	76.0	86.0	108.0
$[Cu_2(OMe)_2(pd)_2]$	10.9	22.7			43.7	63.5	75.0	84.0	103.8
$K[CuCl_3]$	4.7	16.3	27.0	31.5	48.0	71.5	76.0	81.9	100.0
$K[CuBr_3]$	6.0	18.7	23.0	27.5	39.7	62.0	71.5	77.4	86.4
$[Cu_2Cl_4(pyo)_2]$	5.4	17.5			43.4	74.0			108.2
$[Cu_2Br_4(pyo)_2]$	4.3	17.9			41.0	70.8			102.8

(v) *Extended Fine Structure.*—The energy separations of the fine structures of the *X*-ray *K*-absorption spectra of these complexes are presented in Table 3. In the fine-structure spectra, the absorption minima are designated as α, β, γ, *etc.* and the successive maxima as B, C, D, *etc.* Structures in the regions A and B are labelled α′,A′ and β′,B′ respectively. The fine structures of *K* absorption in $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$ nearly coincide (Figure and Table 3). These complexes have similar configurations around each copper atom. It may be noted that structure β′B′ is present in all the cases except $[Cu_2X_4(pyo)_2]$. The binuclear complexes, $[Cu_2X_4(pyo)_2]$ (X = Cl or Br) possess a distorted square-planar configuration [13,39] consisting of two oxygen and two chlorine or bromine atoms, but the spectra due to these complexes are quite different from those of $[Cu_2(O_2CMe)_4]$ and $[Cu_2(OMe)_2(pd)_2]$, involving all four oxygen donors (Table 2). The spectra due to these complexes are generally broadened throughout (Figure). A well resolved structure, α′A′, was observed for $K[CuX_3]$ (X = Cl or Br). It may be attributed to the unequal bond strength (bond distance) of the two halogen atoms above and below the $[Cu_2X_6]^{2-}$ ions. It may, therefore,

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be concluded that the fine structure is determined not only by the immediate neighbours of the atom in question as remarked by Coster and Kiestra [40] but also by their nature. Further, on comparing the spectra of K[$CuCl_3$] and [$Cu_2Cl_4(pyo)_2$] with their corresponding bromo-analogues, it is found that the fine-structure energy values of the maxima and minima show a shift towards higher energy in the chloro-complexes. It is pertinent that the energy values of the maxima and minima observed here are of the same order as reported by Obashi and Nakamura [31] for K[$CuCl_3$].

TABLE 4

Average metal–ligand bond distances for copper(II) complexes

Complex	ΔE (β − B)/eV	Measured average $r \pm 0.1$ Å	r(X-ray diffraction)/Å	Refs.
[$Cu_2(O_2CMe)_4$]	42.2	1.88	Cu–O 1.97 Cu–O(H_2O) 2.20 Cu–Cu 2.64	42
[$Cu_2(OMe)_2(pd)_2$]	40.3	1.93		
K[$CuCl_3$]	28.5	2.30	Cu–Cl 2.25, 2.27 Cu–Cl 2.32, 2.31 Cu–Cu 3.44	35
K[$CuBr_3$]	24.4	2.48		
[$Cu_2Cl_4(pyo)_2$]	34.2	2.10	Cu–Cl 2.20, 2.22 Cu–O 1.98, 2.03 Cu–Cu 3.25	39
[$Cu_2Br_4(pyo)_2$]	32.0	2.17		

The difference in energy, ΔE, from maximum B to the next minimum β may be used [41] to compute the radius of the first co-ordination sphere around the central metal ion through the Bragg relation (2). Values of r_1 for the

$$r_1 = (151/\Delta E)^{\frac{1}{2}} \qquad (2)$$

complexes are presented in Table 4. As is evident from this Table, the results are in good agreement with those of X-ray diffraction, for complexes where the structures are already known.[35,39,42] For other complexes, the estimated bond distances appear to lie within the expected range of reported metal–ligand bond lengths.

Conclusions.—Abnormal increases in edge shifts as observed by some workers for complexes involving metal–metal interaction cannot be used as a criterion for either direct metal–metal bonding or superexchange interaction. The edge position, in general, appears to shift towards higher energy as the metal–metal distance decreases.

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