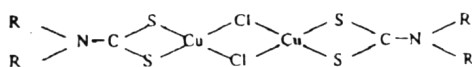


X-ray absorption near edge studies of some binuclear copper(II) complexes

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X-ray K-absorption near edge studies have been carried out on the binuclear copper (II) dithiocarbamate (dtc) complexes having the following general structure :



where R = me (methyl); et (ethyl); npr (normal propyl); chx (cyclohexane)

It has been found that the chemical shift values are higher in the chlorine adducts as compared to the values of chemical shift reported by us in an earlier work for the parent complexes, showing that the chlorine adducts are more ionic. The observed splitting of the principal absorption maximum (1s→4p) in the chlorine adducts has been explained in terms of the splitting of the metal 4p orbital degeneracy.

Keywords : XANES, binuclear copper(II) dithiocarbamate; chemical shift; principal absorption maximum.

1. Introduction

Binuclear copper centers occur in a number of naturally occurring enzymes (Malkin & Malmstrom, 1970); (Malkin, 1973); (Malmstrom, Andreasson & Reihamar, 1975); (Mason, 1976); (Fee, 1975). Nature of the biological binuclear copper sites and their functional role in the activity of the proteins has drawn much attention in recent past. The best understood examples of binuclear copper centers are those which occur as a portion of the active site in the blue multi copper oxidases. The binuclear copper(II) complexes can be found in a number of geometries. They are the best systems for establishing magneto structural correlations and for testifying the existing models for describing the nature and intensity of the exchange interactions between paramagnetic centres. Understanding of these interactions in binuclear species forms the necessary background to design the synthesis of more complex systems with unusual magnetic properties.

In the present work, X-ray spectroscopic studies have been carried out on the following binuclear copper(II) complexes :

- i) $(\text{me}_2\text{dtc})_2\text{Cu.CuCl}_2$
Bis(N-N'-dimethyldithiocarbamate) di-m-chloro copper(II)
 - ii) $(\text{npr}_2\text{dtc})_2\text{Cu.CuCl}_2$
Bis(N-N'-di-n-propyldithiocarbamate) di-m-chlorocopper(II)
 - iii) $(\text{et}_2\text{dtc})_2\text{Cu.CuCl}_2$
Bis(N-N'-diethylthiocarbamate) di-m-chloro copper(II)
 - iv) $(\text{chx}_2\text{dtc})_2\text{Cu.CuCl}_2$
Bis(N-N'-dicyclohexyldithiocarbamate) di-m-chloro copper (II)
- These binuclear copper (II) complexes have the general structure shown in the abstract.

2. Experimental

e X-ray absorption spectra were recorded on a laboratory XAFS spectrometer consisting of a 40-cm bent crystal spectrograph having (-201) reflecting planes of muscovit mica as analyser, a sealed Rich-Seifert tungsten target X-ray tube operated of 17kV and 60 mA. The spectra was recorded photographically and the intensity records were taken on a Carl Zeiss microphotometer coupled with a recorder. At least nine independent measurements were taken for a sample and the results presented here are an average of such measurements. The resolution of the spectrometer ($\lambda/d\lambda$) was better than 1000 and the dispersion was about 0.6 pm/mm on the photographic film in the second order. $\text{WL}_{\alpha 2}$ and $\text{WL}_{\beta 4}$ emission lines were used as reference lines to establish the wavelength scale. The error in the measurements were of the order of ± 0.3 eV. Other details are given in an earlier communication (Shrivastava *et al.*, 1988).

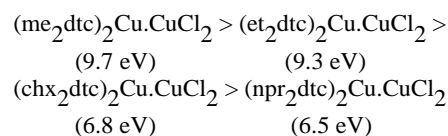
3. Results and Discussion

3.1 Chemical Shift

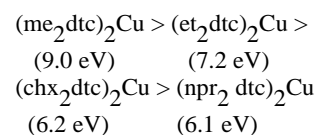
Earlier also X-ray chemical shifts (Wakita *et al.*, 1993) and XAS studies (Furenid *et al.*, 1995; Kau *et al.*, 1987) have been utilised to obtain important chemical information regarding the coordination in the complexes belonging to the transition metals.

The edge shift ΔE known as chemical shift and is defined as follows $\Delta E = E_K(\text{compound}) - E_K(\text{metal})$.

In the present case, a perusal of Table 1 shows that the trend of variation of the chemical shifts is



In earlier studies (Sharma, 1996) the trend of variation of the chemical shifts for the parent dithiocarbamate complexes was :



We find that the trend of variation of chemical shifts follows the same order in both the series of complexes.

Table 1

Data for the K-absorption edge of copper in chlorobridge binuclear copper(II) complexes.

Complex	$\lambda_{K \text{ edge}}$ ($\pm 0.05 \text{ m\AA}$)	$E_{K \text{ edge}}$ ($\pm 0.3 \text{ eV}$)	E_A ($\pm 0.3 \text{ eV}$)	Chemical Shift ΔE_K (eV)	Edge Width ($E_A - E_K$) (eV)	Shift of Principal absorp. maxima (eV)
Copper Metal	1380.63	8980.3	9001.2	-	20.9	-
(me ₂ dtc) ₂ CuCuCl ₂	1379.14	8990.0	9003.5	9.7	13.5	23.2
(npr ₂ dtc) ₂ Cu.CuCl ₂	1379.63	8986.8	9002.0	6.5	15.2	21.7
(et ₂ dtc) ₂ Cu.CuCl ₂	1379.20	8989.6	9003.2	9.3	13.6	22.9
(chx ₂ dtc) ₂ Cu.CuCl ₂	1379.58	8987.1	9001.9	6.8	14.8	21.6

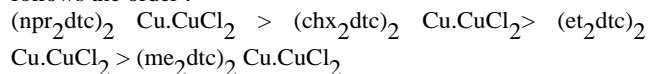
A perusal of Table 2 shows that reaction of CuCl₂ on copper (II) dithiocarbamates, thereby forming (R₂dtc)₂Cu.CuCl₂ type of complexes increases the chemical shift values in every case. Such an increase in the value of the chemical shifts can be explained as follows: Each copper centre is surrounded by two sulphur, two chloride in the chlorine adducts instead of the four sulphur atoms in parent (R₂dtc)₂Cu complexes. The entry of two chlorine significantly increases the ionic bonding, consequently increasing the chemical shift value. On the Pauling's electronegativity scale, the values of electronegativity for sulphur and chlorine are respectively 2.5 and 3.0 thus Cu-Cl bond is more ionic than Cu-S bond. Thus, the change in the overall contribution of the ionicity has been well reflected in our chemical shift studies.

Earlier workers (Joshi, Shrivastava, Kumawat & Pandeya, 1993); (Shah, Shrivastava, Pandeya, Srivastava & Prasad, 1983); (Nigam, Rajput & Shrivastava, 1986); (Koul & Padalia, 1983) have reported the chemical shift values of various copper (II) complexes between 6.8 - 12.9 eV. Our values of chemical shift reported in earlier investigation range between 6.1 - 9.0 eV for the parent (R₂dtc)₂Cu complexes (Sharma, 1996) and between 6.5 - 9.7 eV for (R₂dtc)₂Cu.CuCl₂ complexes presently studied. On the basis of this results all our complexes under present investigations possess oxidation state +2.

3.2 Edge-width

Edge-width can be defined as the difference of the energy between the inflection point of the absorption edge K and the principal absorption peak A.

The Table 1 includes the values of edge width for all the Cu (II) binuclear dithiocarbamate complexes. The edge width follows the order:



Earlier workers (Srivastava & Nigam, 1973); (Nigam & Srivastava, 1971); (Keeling, 1963); (Krishna, Prasad & Nigam, 1976); (Srivastava & Nigam, 1970); (Obashi, 1977) have suggested that the edge-width of the K-absorption edge increases with the increase of covalent character of the metal-ligand bonds, provided other factors like symmetry etc. remains the same. These binuclear chlorine adduct dithiocarbamate complexes are more ionic as compared to their parent dithiocarbamate complexes for which the data has been reported earlier (Sharma 1996). A look on Table 1 shows that edge-widths are not so large as compared to the values reported for the parent (R₂dtc)₂ Cu complexes. (Sharma, 1996). In the present case the complexes are not highly covalent but still they have some covalent character. From the present studies it may

be inferred that these complexes are ionic in nature as compared to parent (R₂dtc)₂ Cu complexes.

Table 2

Difference in chemical shifts in the parent complexes and chlorine adducts

Complex	Chemical shift (eV)	Difference in (eV)
(me ₂ dtc) ₂ Cu.CuCl ₂	9.7	0.7
(me ₂ dtc) ₂ Cu	9.0	
(et ₂ dtc) ₂ Cu.CuCl ₂	9.3	2.1
(et ₂ dtc) ₂ Cu	7.2	
(chx ₂ dtc) ₂ Cu.CuCl ₂	6.8	0.6
(chx ₂ dtc) ₂ Cu	6.2	
(npr ₂ dtc) ₂ Cu.CuCl ₂	6.5	0.4
(npr ₂ dtc) ₂	6.1	

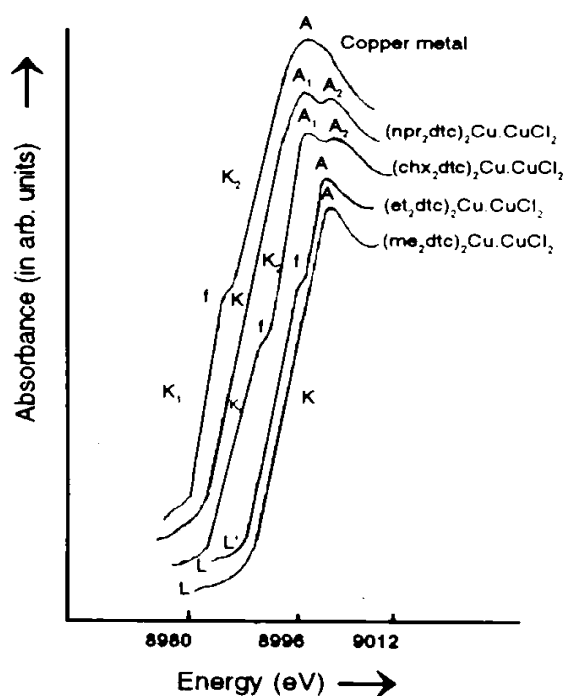


Figure 1

K-XANES spectra for copper (II) binuclear dithiocarbamate complexes

3.3 Shift of the principal absorption maximum

On the higher energy side of the K-edge there appears a pronounced absorption peak and this is referred to as the principal absorption maximum.

The values of shift in principal absorption maxima are given in Table 1 and are estimated relative to K-energy of copper metal. The principal absorption maximum in transition metal complexes is known to arise due to transition of electron from 1s level to a vacant orbital of appropriate symmetry.

A change in the valency of the metal ion has been observed to result in a corresponding shift of the principal absorption maximum to shorter wavelength side as the valency increases. Table 1 shows that the values of the shift of the principal absorption maximum for these complexes are lying in a very narrow range i.e. 21.6 to 23.2 eV, i.e., (me₂dtc)₂ Cu.CuCl₂ (23.2); (et₂dtc)₂ Cu.CuCl₂ (22.9); (npr₂dtc)₂ Cu.CuCl₂ (21.7) and (chx₂dtc)₂ Cu.CuCl₂ (21.6). The uncertainties in the measurement of the principal absorption maximum are ± 0.3 eV.

Hence in our case, the valency of all the complexes has been the same, i.e., copper (II). We have observed the splitting of the principal absorption maxima ($1s \rightarrow 4p$) transition marked on the spectra as A_1 and A_2 (Fig.1) in the two complexes viz., $(npr_2dtc)_2Cu.CuCl_2$ and $(chx_2dtc)_2Cu.CuCl_2$ under investigation. This type of splitting (Srivastava & Nigam, 1973); (Cotton & Ballhausen, 1956); (Cotton & Hanson, 1957) has been explained in terms of the splitting of the metal 4p orbital degeneracy under the influence of the crystal field symmetry due to surrounding ligands. The principal absorption maximum ($1s \rightarrow 4p$) for these complexes is expected to split into two components that may be assigned as $1s \rightarrow A^*(4p_z)$ and $1s \rightarrow B^*(4p_x, 4p_y)$. The observed energy separation between the components A_1 and A_2 follows the sequence which is the same as that for chemical shifts values.

3.4 Near edge structure

Apart from A_1 and A_2 features, other near edge structure features have been observed in the K-absorption region of these samples. The positions of the point where the K-absorption commences (L), the small pre-edge structure (L') on the low energy side of the main K-edge and the kink 'f' separating the K_1 and K_2 edges are shown in Fig. 1

Near edge structure features have been observed only in two complexes viz., $(et_2dtc)_2Cu.CuCl_2$ and $(Chx_2.dtc)_2Cu.CuCl_2$. The width of the discontinuity between K_1 (at which the 3d level ends) and K_2 (where the 4s level starts), should, in principle, provide the energy of the band gap (3d -4s) of the sample (Deshpande & Mande, 1986). The band gap values obtained for the two complexes are 3.0 and 6.7 eV respectively for $(et_2.dtc)_2Cu.CuCl_2$ and $(chx_2.dtc)_2Cu.CuCl_2$.

Here we find that as the chemical shift increases, the band gap energy decreases. Similar observation has been reported for $Cu(dmg)_2$ and $Cu(sal)_2$ by earlier workers (Kumawat *et al.*, 1993)

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