

Structural studies of amino acid complexes-I EXAFS study of glutamic acid complex of copper

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Abstract. The ambiguity in the assignment of stereochemistry and co-ordination to Cu(II) complexes can be resolved by using x-ray absorption spectroscopic technique. The difficulty in the structural assignment of the Cu-glutamate complex is studied in detail. The Cu-acetylacetonate complex has also been studied as an example of square planar geometry. The Cu-glutamate complex is a distorted octahedral molecule.

Keywords. X-ray absorption spectra; EXAFS; distorted octahedral coordination; amino acid.

1. Introduction

In order to understand the exact role of metal ions in biological systems a study of the structure, physico-chemical aspects and reactivity of ligands occurring in living systems with biologically significant metals, is essential. Copper ion and amino acids constitute one such system.

Glutamic acid is a dibasic, tridentate ligand. A molecular disease 'sickle cell anemia' is due to the occurrence of valine in place of glutamic acid in haemoglobin (Horne 1978). A number of copper(II)-protein complexes containing this amino acid are isolated in plants. Copper uptake by roots of wheat plants may partly be through the glutamate complex (Touchton *et al* 1980). In lower animals like crabs and snails the oxygen carrier system is based on copper (Lippard 1979). Hence, the Cu-amino acid systems must be studied in details.

Solution chemistry of binary and ternary complexes of amino acids is well established, while the solid state and structural aspects are less explored. The physico-chemical properties of the compounds such as the charge on the metal ion, its relation to molecular symmetry, edge structure study and chemical bonding have not been studied extensively. In recent years, x-ray absorption spectral studies are assuming importance since the study of various aspects like the shape of the absorption discontinuity, edge shift, edge width and the profile of the absorption edge can be correlated to the stereochemistry of the molecule (Srivastava and Nigam 1973). The absorption characteristics, when studied upto a few hundred electron volts on the high energy side of the main absorption edge, constitute the x-ray absorption fine structure. The fine structure upto a few tens of electron volts in the vicinity of the absorption edge is known as the Kossel structure and beyond it is the Kronig fine structure. Several theories, grouped as long range order (LRO) and short range order (SRO) theories, are

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proposed to explain the fine structure (Agarwal 1979). The phase shifts of the spherical wave functions due to scattering in the presence of absorbing atoms is the basis of the Lytle, Sayers and Stern (LSS) theory (Sayers 1970). The present communication reports the EXAFS data in the light of the LSS theory for six-coordinated copper glutamate and four coordinated copper acetyl acetate complex.

2. Experimental

2.1 Preparation of complexes

Copper glutamate, $\text{CuG} \cdot 2\text{H}_2\text{O}$ (Shugan 1951) and copper acetyl-acetate, $\text{Cu}(\text{acac})_2$ were prepared by reported methods (Sharma 1956).

2.2 X-ray absorption study

The Cauchois type bent mica crystal spectrograph of 400 mm diameter was used for recording absorption spectra. The instrument could resolve the $\text{MoK}\alpha_{1-2}$ doublet. A Carl Zeiss photodensitometer was used for measuring the intensities of absorption bands from the photographic film.

3. Results and discussion

The d^9 configuration of $\text{Cu}(\text{II})$, as a result of the Jahn-Teller effect, shows tetragonally distorted octahedral coordination, and therefore, square-coordination cannot be sharply and easily differentiated from it (Cotton and Wilkinson 1970). Common techniques like electronic absorption and magnetic character cannot clarify this point. The molecular frame is known from x-ray diffraction data and disposition of atoms, bond distances and bond angles are known. However, the decision upon the relation between the central metal atom and the atoms occupying axial positions is difficult to arrive at.

It is observed that if interatomic distances between Cu and the axial atom ($\text{Cu}-L_{ax}$ distances) are more than 3 Å, the distances between Cu and the atoms in the planar positions ($\text{Cu}-L_{pl}$ distances) hardly change with further change in $\text{Cu}-L_{ax}$. The $\text{Cu}-L_{pl}$ distance in such limiting instances is 1.9 Å. With further change in $\text{Cu}-L_{ax}$ there is hardly any change in $\text{Cu}-L_{pl}$. This clue may be useful in deciding upon the coordination (Gazo *et al* 1976). Roughly this may be taken as a guide for clear choice of 4 to 6 coordination polyhedra. As a result of shortening of $\text{Cu}-L_{ax}$ distance, $\text{Cu}-L_{pl}$ distance increases and when $\text{Cu}-L_{ax} = \text{Cu}-L_{pl}$ an undistorted octahedral structure is obtained. However, it can be said that if $\text{Cu}-L_{ax}$ exceeds 2.75 Å there is no harm in regarding it as square planar geometry. What has been said above can be summarised by taking illustrative examples (table 1).

If a compound of category A or D is chosen, there is hardly any controversial situation. Categories B and C must be carefully examined. X-ray diffraction data and x-ray absorption data together solve the problem to a fair degree of satisfaction. In the present study, x-ray diffraction and x-ray absorption data already reported in the literature regarding one member of the B category, CuO , have been chosen, which are in favour of square planar geometry. Another example, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, belongs to the C

Table 1. Relation between axial and equatorial bond distances and stereochemistries of copper compounds.

Compound	Category	$R-L_{\mu}$	$R-L_{ax}$	Remarks	Reference
Copper(tropolone) ₂	A	1.91Å	3.30Å	Unambiguous examples of	McIntyre <i>et al</i> 1965
Cu(C ₆ H ₄ OHCOO) ₂ ·4H ₂ O		1.88Å	3.00Å	square planar geometry	Hanic and Michalay 1960
Na ₂ Cu(CO ₃) ₂	B	1.93Å	2.77Å	May be regarded as square planar.	Healy and White 1972
CuO		1.95Å	2.78Å	Extreme elongation of the tetragonal geometry	Asbrink and Norrby 1970
CuSO ₄ ·5H ₂ O	C	1.97Å	2.41Å	Not much elongated; tetragonal geometry;	Bacon and Curry 1962
Cu(phthalate) ₂ ·H ₂ O		1.94Å	2.58Å	can be said to be distorted octahedron.	Prout <i>et al</i> 1971
Cu(CH ₃ OCH ₂ COO) ₂ ·2H ₂ O	D	2.03Å	2.13Å	Fairly good examples of octahedral case,	Prout <i>et al</i> 1968
CuCrO ₄		2.05Å	2.15Å	but distortion is still present.	Brandt 1948
K ₂ PbCu(NO ₂) ₆	E	2.11Å	2.11Å	Perfect octahedral at room temperature,	Isaacs and Kennard 1969
				between 276 K and 193 K it is orthorhombic	Joesten <i>et al</i> 1977
Ca(Cu, Zn) ₄ (OH) ₆ (SO ₄) ₂ ·3H ₂ O		2.11Å	2.11Å	No distortion	Sabelli and Zanazzi 1968
Cu(H ₂ O) ₆ SiF ₆		2.07Å	2.07Å		B J Temple (unpublished results)

category, in favour of octahedral geometry, but of course, distorted. This consideration is further applied to $\text{Cu}(\text{acac})_2$. In the present study x-ray absorption spectral data for this compound are reported for the first time.

X-ray diffraction data for both $\text{Cu}(\text{acac})_2$ and $\text{CuG}2\text{H}_2\text{O}$ have been taken from literature (Koyama *et al* 1953; Gramaccioli and Marsh 1966).

The reflectance spectra and magnetic data are in agreement with monomeric structures and are not given here.

Figure 1 shows the essential frameworks of the molecules. Table 2 contains XAS and various energy parameters calculated from the absorption data. Table 3 contains EXAFS data. Table 4 shows parameters related to the proposed stereochemistry. Figure 2 shows the absorption curves for the two compounds.

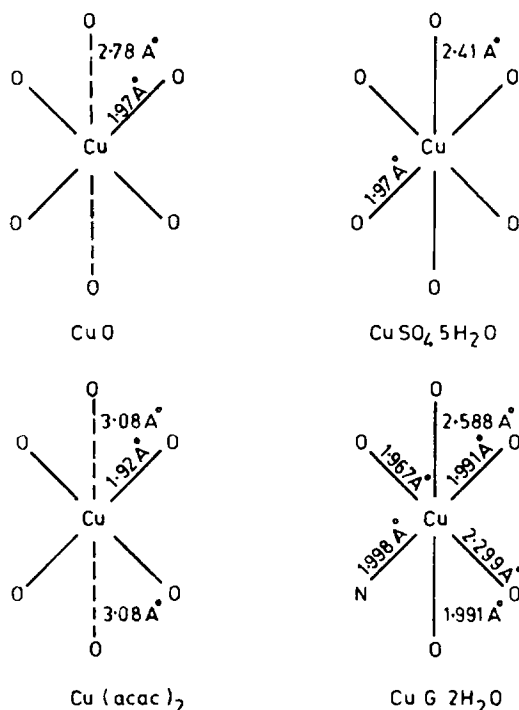


Figure 1. Essential framework of the copper compounds.

Table 2. Shifts* in K absorption edge (E_k), relative energy of principal absorption maxima edge width and energy parameter of $\text{Cu}(\text{II})$ compounds.

Compound	E_k	E_k	E_A	E_A	Edge width		
					10-6	Slope M	$R_{1-\alpha}$ (Å)
Copper sulphate pentahydrate	8986.69	6.4	8994.19	13.9	7.6	1.41	1.11
Copper oxide	8983.83	3.54	8999.58	19.29	9.98	2	1.57
Copper glutamate	8985.28	4.98	8992.76	12.465	7.48	2.28	2.2
Copper acetylacetonate	8987.99	7.65	8997.91	17.62	9.98	3	2.36

* With respect to copper metal K_1 edge $E_M = 8980.29$ eV

Table 4. Correlation between edge widths and coordination stoichiometry.

Complex	Coordination stoichiometry	$\Sigma(X_m - X_l)$	Edge width	Constant = $[\Sigma(X_m - X_l)EW]^{1/2}$
CuSO ₄ · 5H ₂ O	M:O:N	9·6	7·6	8·5
CuO	1:4	6·4	15·75	8·5
Cu-glutamate	1:5:1	9·1	7·48	8·25
Cu-(acac) ₂	1:4	6·4	9·98	7·99

The EXAFS data on treatment with the Lytle theory (Lytle *et al* 1975) show the slope (M) of the plots of n vs k which can be used to find out the EXAFS parameter ($R_1-\alpha$). This ($R_1-\alpha$) EXAFS parameter can be used for explaining the nature of chemical bonding as follows:

In CuSO₄ · 5H₂O, the copper atom is surrounded by an approximate square of four oxygen atoms and the fifth and sixth apices of the distorted octahedron of Cu⁺² atom are occupied by two other oxygen atoms, at a non-bonding distance. In CuO the fifth and the sixth apices of the octahedron are occupied by two other Cu⁺² ions at a non-bonding distance. This may also be true in the case of Cu(acac)₂, which may be due to the symmetrical position of 'acac' groups around Cu⁺², while the bonding is square planar.

However, drastic changes in EXAFS energy values and consequently in ($R_1-\alpha$) parameters suggest that degree of covalency increases in the order CuSO₄ · 5H₂O, CuO, Cu · G · 2H₂O and Cu(acac)₂. This is as per expectation, because CuSO₄ · 5H₂O and CuO are ionic solids. ($R_1-\alpha$) value for Cu · G · 2H₂O lies in between those for CuO and Cu(acac)₂ and this suggests distorted symmetry. This is because Cu(acac)₂ is the most symmetrical among the four compounds. By losing the charge on the central metal atom Cu · G · 2H₂O may lose its symmetry and the octahedron is distorted and this picture is reflected in the EXAFS study.

That the Cu(acac)₂ complex is four-coordinated and Cu · G · 2H₂O six-coordinated is further confirmed by the fact that the edge width for lower coordination is higher, while it is less for higher coordination. Table 2 shows that the edge width for Cu(acac)₂ is 9·98 and the reported value for CuO, which is four-coordinated, is 9·98. The edge width for Cu · G · 2H₂O is 7·48 and the reported value for CuSO₄ · 5H₂O which is six-coordinated, is 7·6 (Tunnel *et al* 1935). The octahedral Cu²⁺ complex has a d^9 configuration and the copper atom uses dsp^2 hybrid orbitals. In such a structure the M–O bond distance is necessarily more than that in tetrahedral sp^3 hybridization. Levine (1973) suggests that the bond distance d is inversely proportional to the fractional covalency and that a parallel trend is observed with respect to α also, that is, $d \propto V_{FC}$ and $d \propto 1/\alpha$ therefore $V_{FC} \propto \alpha$. It is obvious, therefore, that Cu–O bonds in Cu · G · 2H₂O must be having predominantly covalent character. Moreover, copper complexes with distorted tetrahedral structure are orange in colour whereas CuSO₄ · 5H₂O, Cu(acac)₂ and Cu · G · 2H₂O are blue in colour and therefore, octahedral or square planar (Cotton and Wilkinson 1972).

Further, it has been shown that there is an empirical correlation between edge width and coordination stoichiometry expressed in terms of the overall metal nearest neighbour electronegativity difference as

$$[\Sigma(X_m - X_l) \text{ edge width}]^{1/2} = \text{constant}$$

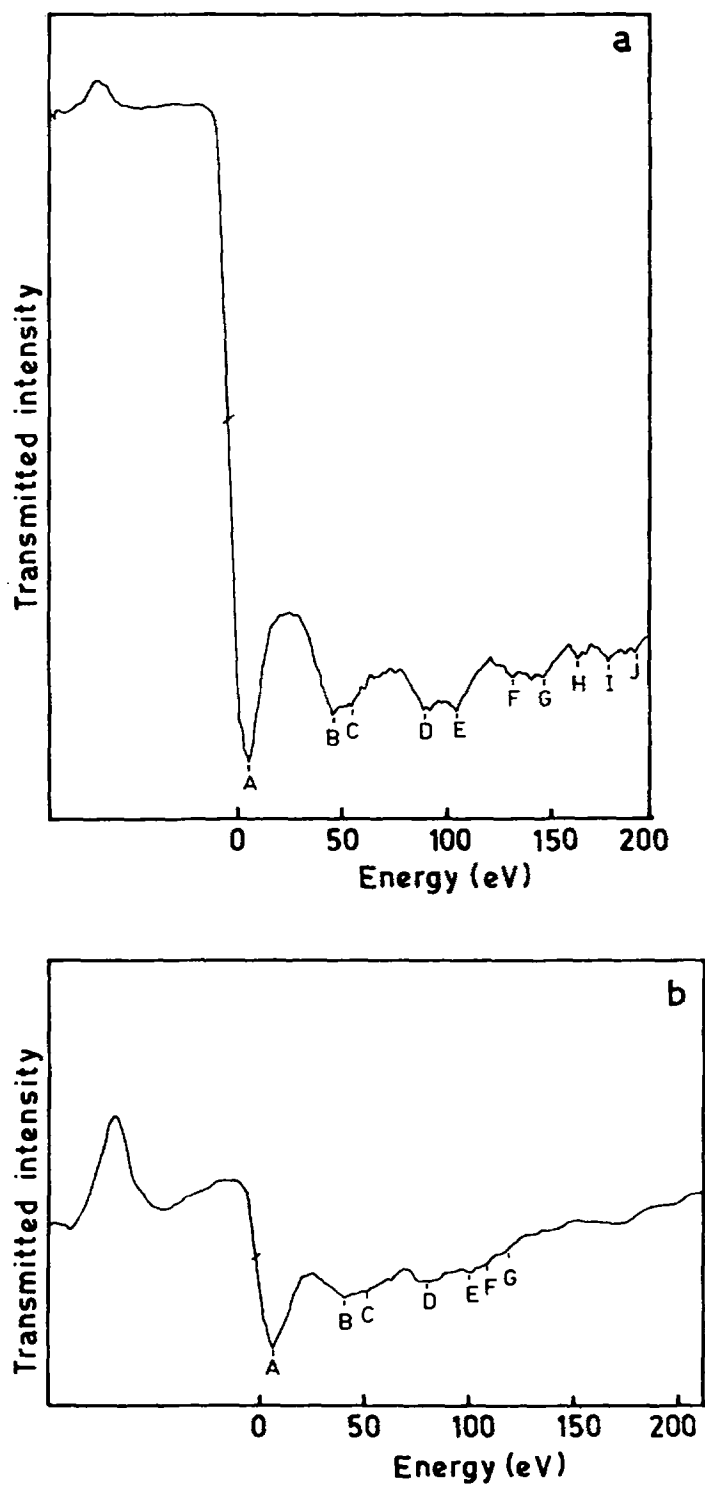


Figure 2. K absorption edge and EXAFS of a. copper glutamate, b. copper acetylacetonate.

This relation is valid for O_h geometry for $CuSO_4 \cdot 5H_2O$ and $Cu \cdot G \cdot 2H_2O$ and square planar geometry for CuO and $Cu(acac)_2$ (Srivastava and Nigam 1973).

4. Conclusion

When the value of the EXAFS parameter ($R_1 - \alpha$) increases, the degree of covalency shows an increase in trend. In the two compounds studied in the present work the high values (around 2.3) for this parameter show a high degree of covalency in these complexes.

From substitution in the empirical formula $[\Sigma(X_m - X_l)EW]^{1/2}$ for $Cu(acac)_2$ as Cu_1O_4 and $Cu \cdot G \cdot 2H_2O$ as $Cu_1O_5N_1$, fairly constant values in the range 8 to 8.5 are obtained in conformity with a square planar structure for the former and an octahedral structure for the latter.

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