

Determination of bond length from EXAFS spectra of some copper(II) mixed ligand complexes

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Abstract: X-ray absorption spectra at the K-edge of copper have been studied in two copper mixed ligand complexes having P-methoxybenzaldehyde as one of the ligands. Copper(II) complexes of two previously prepared ligands L₁=(P-methyl anilino)- P-methoxy phenyl acetonitrile and L₂ =(P-methoxy anilino)-P- methoxy phenyl acetonitrile were synthesized. The two ligands were prepared which included the reaction of P-methoxybenzaldehyde with P-toluidine and P-anisidine respectively. The complexes are : [Cu(L₁)₂](NO₃)₂ and [Cu₂(L₂)₂(H₂O)₈](NO₃)₂ in which P-methoxybenzaldehyde has been used as primary ligand and P-toluidine and P-anisidine have been used as secondary ligands. The X-ray absorption spectra have been recorded at BL-8 Dispersive Extended X-ray Absorption Fine Structure (EXAFS) beamline at the 2.5-GeV INDUS-2 Synchrotron Source, RRCAT, Indore, India. The normalized EXAFS spectra have been Fourier transformed. EXAFS maxima and minima positions have been obtained. The bond length have been determined using four different methods, i.e., Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation methods. Both LSS and Fourier transformation methods give phase uncorrected bond lengths and hence results obtained from them have been compared with each other. The data obtained has been processed using EXAFS data analysis program Athena.

Keywords: Copper complexes, EXAFS, Athena, RRCAT, LSS

Introduction

The chemistry of nitrile and α -aminonitrile compounds and their derivatives has received special attention because of their application as potential ligands for a large number of metal ions (1). Nitriles and α -aminonitrile derivatives had a biological activities (2) as herbicides(3), pharmacological agents (4) and biological synthesis of chemical compounds by its microbial metabolism in some organisms (5) [1,2,3].

The Extended X-ray Absorption Fine Structure (EXAFS) yields information regarding the nearest neighbors of the central metal ions, i.e. bond length. The Fourier transform of an EXAFS spectrum provides information on the distribution of atomic shells as a function of distance from the target absorber. These distances are called phase uncorrected bond lengths. The bond lengths can also be determined by three other methods, namely, Levy's, Lytle's, and Lytle, Sayers and Stern's (LSS) methods. The LSS method also gives phase uncorrected bond length of the first shell [4,5]. Hence, it is worth comparing the bond lengths obtained from LSS method with those obtained from Fourier transformation method. A search through literature reveals that there is no work has been done on the EXAFS of copper(II) complexes of the L₁ and L₂. Keeping this in view, we have studied X-ray K absorption spectra of copper in the mixed ligand copper complexes having L₁ and L₂ as primary ligands. The results of the study have been reported in this paper.

Table 1. Copper (II) mixed ligand complexes and molecular formulae

Complex	Molecular formula
[bis{(p-methyl anilino)-p-methoxyphenyl acetonitrile} copper(II)] nitrate	[Cu(L ₁) ₂](NO ₃) ₂
[Octaaqua-di- μ -{(p-methoxy anilino)-p-methoxy phenyl acetonitrile } dicopper(II)] nitrate	[Cu ₂ (L ₂) ₂ (H ₂ O) ₈](NO ₃) ₂

Experimental Details

The two complexes studied in the present investigations are [Cu(L₁)₂](NO₃)₂ and [Cu₂(L₂)₂(H₂O)₈](NO₃)₂ in which P-methoxybenzaldehyde has been used as primary ligand and P-toluidine and P-anisidine have been used as secondary ligands. The ligand L₁=(P-methyl anilino)- P-methoxy phenyl acetonitrile and L₂=(P-methoxy anilino)-P- methoxy phenyl acetonitrile were synthesized. The two ligands were prepared by Strecker's procedure [6,7] which included the reaction of P-methoxybenzaldehyde with P-toluidine and P-anisidine respectively. The two mixed ligand copper complexes are listed in Table 1 along with their molecular formulae. The X-ray absorption spectra at the K-edge of copper of these complexes have been recorded at BL-8 Dispersive EXAFS beamline at the 2.5-

GeV INDUS-2 Synchrotron Source, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. On this beamline, the X-ray intensities I_0 and I_t are obtained as the CCD outputs without and with the sample, respectively. Using the relation, $I_t = I_0 e^{-\mu x}$, where μ is the absorption coefficient and x is the thickness of the absorber, the absorption $\mu(E)$ corresponding to the photon

energy (E) are obtained. The experimental data have been analyzed using the available computer software packages Origin 6.0 professional and Athena. Firstly, the normalized $\mu(E)$ versus E spectra are obtained, then $\chi(k)$ versus k spectra are obtained, and finally, the Fourier transforms of the latter are obtained.

Table 2. Energy E (eV) and wave vector k (\AA^{-1}) for EXAFS maxima and minima at the K absorption edge of copper in the complexes and their corresponding values of n and energy level Q

Structure	n	Q	[Cu(L ₁) ₂](NO ₃) ₂		[Cu ₂ (L ₂) ₂ (H ₂ O) ₈](NO ₃) ₂	
			E	k	E	k
A	0	2.04	17.57	2.15	19.24	2.25
α	1	-	42.67	3.35	43.95	3.4
B	2	6.04	67.07	4.2	70.30	4.3
β	3	-	100.84	5.15	100.84	5.15
C	4	12.00	150.91	6.3	127.90	5.8
γ	5	-	168.14	6.65	170.68	6.7
D	6	20.00	-	-	-	-

Results and Discussion

The normalized X-ray absorption spectra of copper complexes are shown in Fig.1. Following the principal absorption maximum, there are distinct EXAFS features extending up to 350 eV on the high-energy side of the K absorption edge. The EXAFS spectra converted into k space have been given in Fig. 2. The slope of channel No n

verses wave vector k curves, shown in Fig.3, have been used to evaluate the bond length by LSS method. The slope of energy level Q verses energy E curves, shown in Fig 4, have been used to evaluate the bond length by Lytle method. The values of energy E and wave vector k corresponding to these maxima and minima have been shown in Table 2. The magnitudes of Fourier transform of Fig. 2 are shown in Fig. 5.

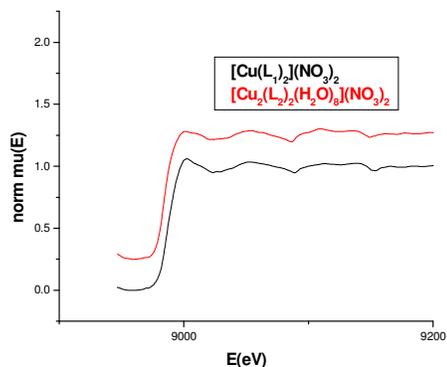


Figure 1. The normalized XAFS spectrum of copper complexes

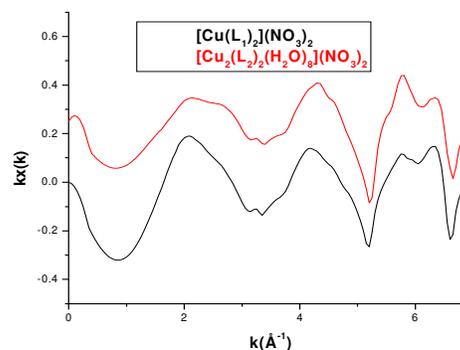


Figure 2. $\chi(k)$ versus k curves for the copper complexes

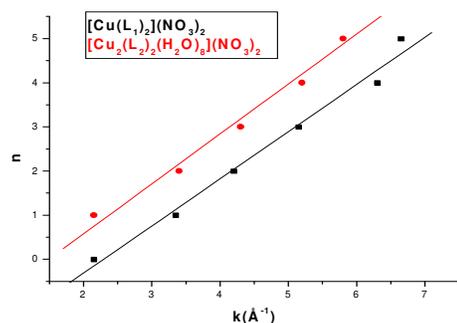


Figure 3. n versus k curves for the copper complexes

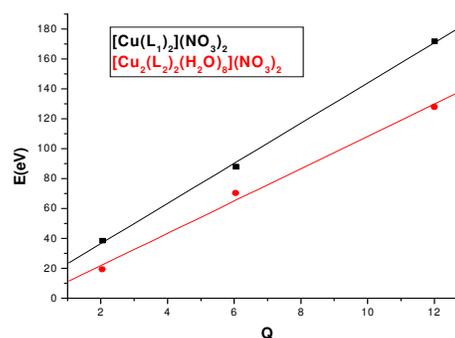


Figure 4. Q versus E curves for the copper complexes

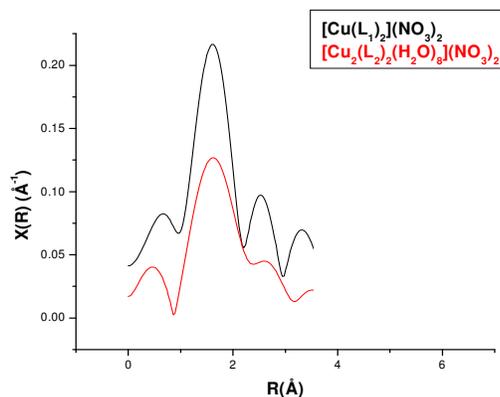


Figure 5. Magnitude of Fourier transform of $\chi(k)$ versus k curves for the copper complexes

Table 3. Values of first shell bond lengths (in Å) calculated from Levy's, Lytle's, LSS and Fourier transform methods for the complexes.					
S. No.	Complex	Phase corrected		Phase uncorrected	
		Levy's method R_L	Lytle's method R_S	LSS method $R_{1-\alpha_1}$	FT method R
1.	[Cu(L ₁) ₂](NO ₃) ₂	2.14	1.67	1.62	1.66
2.	[Cu ₂ (L ₂) ₂ (H ₂ O) ₈](NO ₃) ₂	2.2	1.86	1.69	1.62

The Fourier transformation technique can be used for the determination of the bond lengths. However, only the phase-uncorrected bond length has been determined by this method. The bond length can also be determined from EXAFS data by three graphical methods. In fact, before the Fourier transformation technique was formulated, the bond length used to be extracted from the EXAFS data by the three graphical methods. Thus, the bond lengths have been determined for the copper complexes with the help of three methods, i.e. Levy's[8] Lytles[9] and Lytle, Sayers and Stern's (LSS)[10,11] methods and the results are given in Table 3.

Conclusions

X-ray absorption spectra of mixed ligand copper complexes at the K-edge of copper have been recorded at the recently developed EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. From the positions of the EXAFS maxima and minima, the bond length in the complexes has been determined by three different methods viz. Levy's, Lytle's and LSS methods. From the Fourier transforms of the EXAFS spectra, the bond length (uncorrected for phase shift) has been determined. It has been observed that the values of the phase-uncorrected bond length, i.e. $R_{1-\alpha_1}$, as determined from LSS method and that determined from the Fourier transformation method, are in good agreement with each other.

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