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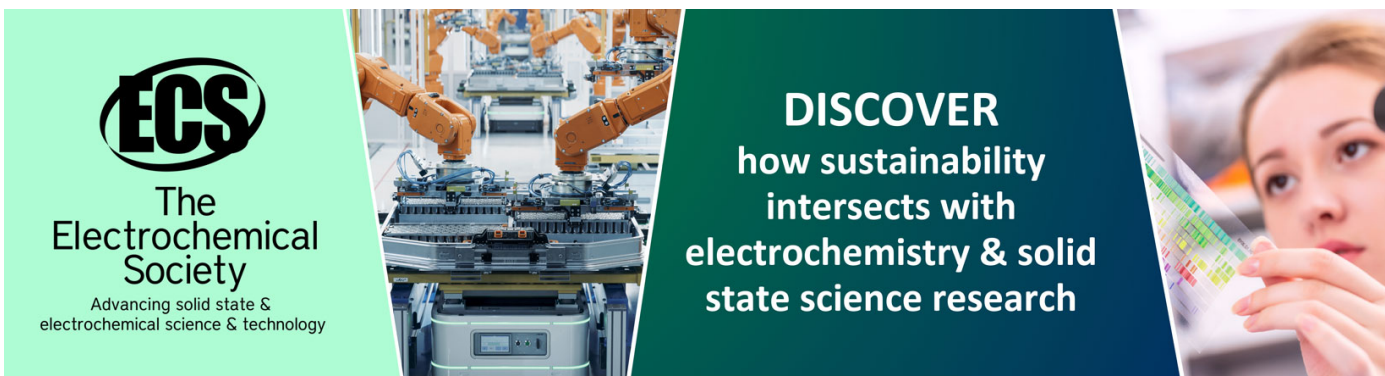
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XAFS studies on copper(I) complexes containing scorpionate ligands

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Abstract. X-ray Absorption Spectroscopy (XAS) has been used to probe the local structure of copper(I) complexes containing scorpionate ligands. The EXAFS analysis, performed by using the GNXAS package, has permitted the identification of the local environment of the copper site. Copper is found to be 4-fold coordinated with two sets of Cu-N and Cu-P interactions describing a quasi planar figure, in the case of $\{\text{Cu}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2][\text{H}_2\text{B}(\text{tz}^{\text{NO}_2})_2]\}$. An additional coordination is revealed for the copper complex of bis(1,2,4-triazol-1-yl)acetate due to the interaction of the copper with the acetate of the scorpionate ligand. XANES spectra behaviour confirms the occurrence of copper in the +1 oxidation state.

1. Introduction

The well known biochemistry of copper underlines the crucial role played by this metal in different enzymes that catalyze oxidation/reduction phenomena correlated with the antioxidant systems of living organisms. It has been established that the properties of copper-coordinated compounds are largely determined by the nature of ligands and donor atoms bound to the metal ion [1]. Phosphane complexes of group 11 metals, especially those including the gold(I) and copper(I) ions, have been proposed as alternative anticancer drugs to the cisplatin reference drug [2]. For instance, $[\text{Cu}(\text{thp})_4][\text{PF}_6]$ complex has been shown to be about 1 order of magnitude more cytotoxic than cisplatin and some less hydrophobic mixed scorpionates-phosphane copper(I) complexes, $\{\text{Cu}[(\text{PR}_3)_2][\text{H}_2\text{B}(\text{tz}^{\text{NO}_2})_2]\}$, were proved to retain high cytotoxic activity against a panel of human tumor cell lines [1].

Because these materials are frequently polycrystalline and no crystal structure are likely to be obtained using XRD, the XAFS probe [3] is a good alternative for the structural studies, as demonstrated several times in the structural characterization of liquids [4], solutions [5], amorphous and inorganic materials [6]. The present note shows the identification of the metal sites occupied by copper in the studied compounds. Our group already studied by XAS a Fe complex of a scorpionate ligand [7].

2. Methods

2.1. Synthesis.

All reagents were purchased from Aldrich and used without further purification. The complexes $\{\text{Cu}(\text{PPh}_3)[\text{Tpms}]\}$ (**1**) where Tpms = tris(pyrazolyl)methanesulfonate, [8], $\{\text{Cu}[\text{PPh}_2(4\text{-C}_6\text{H}_4\text{COOH})][\text{HB}(\text{btz})_3]\}$ (**2**) where $[\text{HB}(\text{btz})_3]^-$ = hydrotris(1,2,3-benzotriazolyl)borate [9], $\{\text{Cu}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2][\text{H}_2\text{B}(\text{tz}^{\text{NO}_2})_2]\}$ (**3**) where $[\text{H}_2\text{B}(\text{tz}^{\text{NO}_2})_2]^-$ = dihydrobis(3-nitro-1,2,4-triazol-1-yl)borate [10] and $\{\text{Cu}[\text{P}(\text{CH}_2\text{OH})_3]_2[\text{HC}(\text{CO}_2)(\text{tz})_2]\}$ (**4**) where $[\text{HC}(\text{CO}_2)(\text{tz})_2]^-$ = bis(1,2,4-triazol-1-yl)acetate ligand [11] were synthesized in accordance with the literature.

2.2. XAS data collection and analysis

Samples for the XAS experiments were mixed with boron nitride and then pressed as pellets (3 tons). X-ray absorption experiments (Cu K-edge) were performed at Daresbury Laboratory, Warrington, England using the beam line 7.1. The storage ring operates at 1.6 GeV and a typical current of 240 mA. Data were acquired in transmission mode using ionisation chamber. Harmonics were rejected by detuning (80%). Spectra were collected from 200 eV before the edge up to $k = 13$ every 0.03 k with a three second integration time. A Cu foil internal energy calibration was measured simultaneously with each spectrum. The pre-edge background was removed by subtraction of a linear function extrapolated from the pre-edge region, and the XANES spectra were normalized at the unity (9000 eV) by extrapolation of the atomic background as it comes out from the EXAFS analysis.

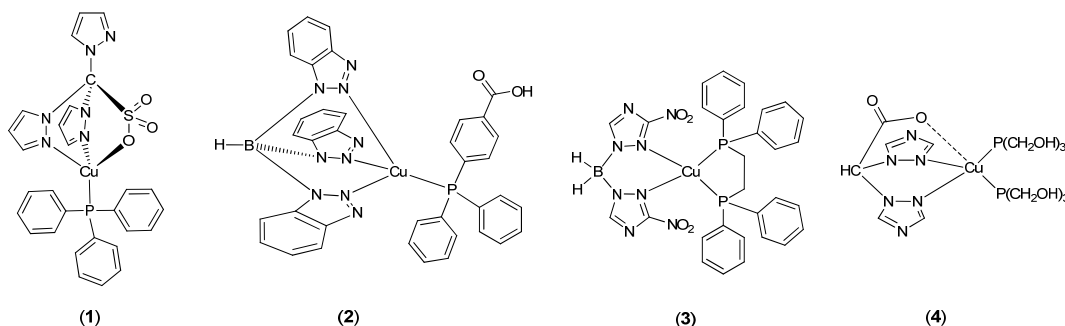


Figure 1. Structures of the Cu(I) complexes **1-4**.

The EXAFS analysis was performed using the GNXAS package [12] which is based on Multiple Scattering (MS) theory. The phase shifts for the photoabsorber and backscatterer atoms were calculated *ab-initio* starting from the structural model reported in [8], according to the muffin-tin approximation and allowing for 10% overlap between the muffin-tin spheres. The Hedin-Lundqvist complex potential [13] was used for the exchange-correlation potential of the excited state. The core hole lifetime, Γ_c , was fixed to the tabulated value and included in the phase shift calculation.

3. Results and Discussion

The copper metal K-edge is a very well studied case in the XAFS community, most likely due to the large demand of the biologists for the determination of its site in proteins.

XANES spectra of Cu complexes display a rising edge shoulder feature which is assigned to the $1s \rightarrow 4p$ electronic transition [14,15]. For Cu(I) the rising edge shoulder occurs at about 8982-8984 eV, while for Cu(II) it shifts to higher energies, at about 8987 eV. In the case of Cu(I) the transition shows the highest intensity and resolution for linear two-coordinated complexes and becomes less intense and broadened as the coordination number increases and/or the symmetry is lowered [14,15].

Figure 2 displays the Cu K-edge XANES spectra of the investigated complexes. The general shape of the curves evidences differences in the rising edge and edge region, demonstrating the sensitivity of the local geometry of the photo-absorber atom (Cu) to the XANES profile of the complexes. As expected for a Cu(I) complex, a rising edge shoulder at about 8983 eV appears in each spectrum, with differences in the normalized intensities. From a comparison of an extensive data set [14] it can be

concluded that the intensities of the 8983 eV peak are not indicative of digonal or trigonal geometry, but they all resemble those of 4-coordinated Cu(I) complexes. The lowest intensity is found for complex **4** which is a *distorted* 5-fold coordinated core on the basis of EXAFS data analysis.

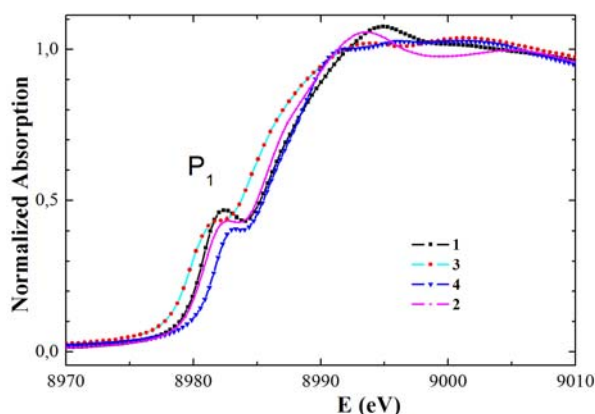


Figure 2. Normalized XANES spectra at the Cu K-edge of the copper complexes. The rising edge shoulder (P1) is assigned to the $1s \rightarrow 4p$ transitions. In Cu(I) complexes the transition becomes less intense and broadened as the coordination number increases and/or the symmetry is lowered.

The figure 2 as well as data of table 1 reveal an almost 2 eV chemical shift toward lower energy of the $1s \rightarrow 4p$ peak for compound **3** respect to **4**. This may be due to the local coordination geometry as well as to the combined inductive and steric effects of the ligands in complex **3**, which make the charge of the coordination metal less positive.

Table 1. Selected EXAFS best-fitting results of complexes **1-4**. The estimated parameter errors are indicated in parentheses. The last column indicate the XANES $1s-4p$ amplitude and energy position.

	Cu-N / Å $\sigma^2 / \text{\AA}^2$	Cu-P / Å $\sigma^2 / \text{\AA}^2$	Cu-O / Å $\sigma^2 / \text{\AA}^2$	Cu-N / Å $\sigma^2 / \text{\AA}^2$	E_0 S_0^2	$1s-4p$ E (eV), norm. Int.
1	2.000 FIX ^a 0.008(4)	2.147 FIX ^a 0.004(1)	2.341 FIX ^a 0.035(5)	2.032 FIX ^a 0.014(2)	8981(1) 0.89(5)	8982.3, 0.47
2	2.070(5) ^c 0.014(3)	2.245(4) ^a 0.004(1)	/	/	8983(1) 0.90(5)	8982.5, 0.43
3	2.03(2) ^b 0.028(6)	2.22(2) ^b 0.007(3)	/	/	8980(1) 0.90(5)	8981.6, 0.43
4	1.98(1) ^b 0.006(3)	2.27(2) ^b 0.004(2)	2.29(2) ^a 0.004(2)	/	8983(1) 0.90(5)	8983.3, 0.40

^apath degeneracy = 1; ^bpath degeneracy = 2; ^cpath degeneracy = 3.

The strategy for the EXAFS fitting analysis was to refine the non structural parameters for the complex **1** whose structure is available (and used as a model compound for the computation of the various singular EXAFS signals) and keeping fix the structural parameters at the crystallographic values [8]. Hereafter, we have analyzed complexes **2-4**. As an example, figure 3 reports the details of the EXAFS data analysis for complex **2**.

The inter-atomic distances and the corresponding EXAFS Debye-Waller factor (best-fit) of the samples investigated are shown in table 1. The statistical errors associated with the parameters obtained with the EXAFS analysis are also indicated. They were determined by correlation maps (contour plots) for each pair of parameters. From the table we can observe that the Cu site is different in the various complexes investigated, as we can observe from the value of the Cu-N and Cu-P first shell distances. The Cu-P distance is not only dependent on the number of phosphane ligands directly coordinated to Cu, but also on the steric hindrance. For example compound **4** is a rare example of 5-fold coordinated copper(I) complex, displaying an additional Cu-O interaction of about 2.29 Å, due to the carboxylic tail of the scorpionate ligand and the longest Cu-P distance among the investigated

complexes. This experimental evidence comes out to joint effects namely number of P donor groups, presence of the phosphane with minor steric hindrance, tripodal nature of the ligand. Table 1 also reveals a large Debye-Waller values for the first shell of complexes **2** and **3**. This is due to the structural disorder of the first shell distances.

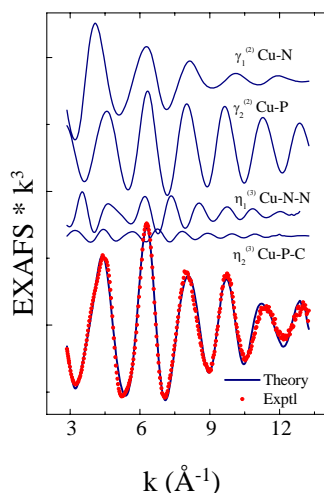


Figure 3. Details of the EXAFS analysis of the Cu K-edge of complexes **2** using GNXAS. The method is based on the decomposition of the EXAFS signals into a sum of several contributions, the n-body terms. It allows the direct comparison of the raw experimental data with a model theoretical signal. The procedure avoids any filtering of the data and allows a statistical analysis of the results. The figure shows the individual EXAFS contributions, in terms of two-body (γ) and three-body (η) signals, to the total theoretical signal. The comparison of the total theoretical signal (—) with the experimental one (...) is also reported at the bottom. Besides the fact that the Cu-P and Cu-N first shell largely contribute to the total one, all signals are rather important in the determination of the total theoretical one.

4. Conclusions

The coordination of copper(I) complexes containing scorpionate ligands has been identified by EXAFS spectroscopy, due to the intrinsic difficulty of growing appropriate crystals of these complexes. The XANES curves couple well with the EXAFS and confirm the Cu(I) oxidation state.

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