Evidence of distorted fivefold coordination of the Cu^{2+} aqua ion from an x-ray-absorption spectroscopy quantitative analysis

M. Benfatto*
Laboratori Nazionali di Frascati–INFN, P.O. Box 13, 00044 Frascati, Italy

P. D'Angelo
*Dipartimento di Chimica, Università di Roma "La Sapienza," Piazzale Aldo Moro 5, 00185 Roma, Italy
and INFM, UdR Camerino, Italy*

S. Della Longa
*Dipartimento di Medicina Sperimentale, Università L'Aquila, 67100 L'Aquila, Italy
and Laboratori Nazionali di Frascati–INFN, P.O. Box 13, 00044 Frascati, Italy*

N. V. Pavel
Dipartimento di Chimica, Università di Roma "La Sapienza," Piazzale Aldo Moro 5, 00185 Roma, Italy

A combined x-ray-absorption near-edge structure and extended x-ray-absorption fine-structure quantitative analysis, based on fitting procedures of both low- and high-energy ranges, has been carried out at the Cu K edge. This allowed an accurate determination of the structural parameters associated with the first hydration shell of the Cu^{2+} aqua complex. The existence of an average fivefold coordination has been evidenced, ruling out the recently proposed regular pyramidal configuration with five equal Cu-O distances. Our structural results are compared with recent neutron-diffraction data performed by the second-difference isotopic substitution method.

I. INTRODUCTION

Nowadays it is well established that a thorough understanding of many chemical properties of ionic solutions should be based on a precise knowledge of their coordination geometry. An important and sometimes demanding task in this context is to determine the structure of aqua complexes of several metal ions. A large number of studies has been carried out, and the structural properties of the first hydration shell for many metal ions are now understood reasonably well.[1] In contrast, the coordination geometry of the Cu^{2+} ion in water solution is still a puzzle, although copper is one of the most important transition elements in biological systems. So far, the $[Cu(H_2O)_6]^{2+}$ complex is generally assumed to be a Jahn-Teller (JT) distorted octahedron, as the coupling between the ϵ_g electronic state and the normal vibrational modes of the same symmetry removes the electronic degeneracy of these states. However, the results obtained from a large variety of experimental techniques, such as x-ray diffraction, neutron diffraction, extended x-ray-absorption fine structure (EXAFS), and x-ray-absorption near-edge structure (XANES) give rise to different geometrical arrangements of the oxygen atoms around the Cu^{2+} ion. In particular, a reliable determination of the axial Cu-O bond lengths is still far from being achieved and the experimental data give a spread of distances ranging from 2.1 to 2.6 Å.[1,2] Conversely, the equatorial Cu-O bond lengths are well characterized, and several experimental techniques provide a distance value in the range between 1.94 and 2.0 Å.[1,2] Recently, the existence of a regular fivefold coordination around the Cu^{2+} ion in

water solution with a Cu-O distance of about 1.96 Å has been proposed on the basis of a combined neutron diffraction and first-principle molecular-dynamics simulation investigation.[3]

During the past several years it has been shown that x-ray-absorption spectroscopy (XAS) is particularly well suited for the investigation of the local solvent structure of ions dissolved in water, due to its atomic selectivity and its sensitivity to dilute solutions.[4,5] The theoretical understanding of the XAS techniques allows an interpretation of the absorption spectrum accounting for all the scattering events of the photoelectron on its way out of the atomic cluster. Due to recent advances it is now possible to apply the fitting procedures generally employed to interpret the EXAFS data,[6] to the XANES region,[7,8] as well, so that the whole energy range of the absorption spectrum can be used for a quantitative determination of the structural parameters. The importance of this approach stems from the high sensitivity of the XANES region to the fine details of the geometrical arrangement of the scattering atoms around the absorber. In this paper we present a combined EXAFS and XANES analysis of Cu^{2+} aqueous solutions to provide a definitive answer to the ion coordination geometry.

II. METHODS

A. Experimental details

Stock solutions of $Cu(ClO_4)_2$ were prepared by dissolving CuO in a slight excess of perchloric acid; details of their preparation and analysis are described in Ref. 9. Two solu-

tions 0.1 and 0.005 M were prepared, and XAS spectra at the Cu K edge were recorded in transmission and fluorescence mode, respectively, at the EMBL spectrometer at HASYLAB.[10] Measurements were performed at room temperature with a Si(220) double-crystal monochromator and 50% harmonic rejection achieved by slightly detuning the two crystals from a parallel alignment. For each sample several spectra were recorded and averaged after performing an absolute energy calibration. Additional measurements for the deconvolution study have been performed at the ESRF-BM29 spectrometer in transmission geometry.[11]

B. Theoretical details

An EXAFS data analysis has been performed using the GNXAS set of programs. For a detailed description of this method, see Ref. 6. Phase shifts have been calculated using the muffin-tin (MT) approximation with MT radii of 0.2 and 0.9 Å, for hydrogen and oxygen, respectively, and 1.2 Å for copper. The hydrogen MT radius chosen corresponds to about 0.06 electrons for the integral of the charge density.

A XANES data analysis has been performed by the MXAN method, which was described in detail in Ref. 7. The x-ray-absorption cross section is calculated in the framework of the full multiple-scattering scheme within the muffin-tin approximation for the shape of the potential that was calculated using the same MT radii of the EXAFS analysis. The real part of the exchange term has been calculated using the Hedin-Lunqvist energy-dependent potential. The inelastic losses are taken into account by a convolution with a Lorentzian broadening function having an energy-dependent width. It contains a constant parameter Γ_c, which accounts for both the core-hole lifetime and the experimental resolution, and an energy-dependent part $\Gamma(E)$ accounting for any damping associated with the inelastic losses of the photoelectron in the final state.[7,8,12] Both parameters are refined during the fitting procedure. Hydrogen atoms have been included in the calculations, and water molecules have been placed in the so-called "dipole" configuration, according to which the ion, oxygen and two hydrogen atoms lie in one plane.[5]

Least-square fits of the XANES and EXAFS experimental data have been performed by minimizing the R_{sq} function defined as

$$R_{sq}(\{\lambda\}) = \sum_{i=1}^{N} [\alpha_{exp}(E_i) - \alpha_{mod}(E_i; \lambda_1, \lambda_2, \ldots, \lambda_p)]^2 \times W(E_i),$$

where N is the number of experimental points E_i, $\{\lambda\} = (\lambda_1, \lambda_2, \ldots, \lambda_p)$ are the p parameters to be refined, and $W(E_i)$ is a weight function. The exact expressions of $W(E_i)$ can be found in Refs. 6 and 7 for the EXAFS and XANES analyses, respectively.

III. RESULTS

Two different starting coordination models have been used to perform both the EXAFS and XANES analyses of this system. In particular the XAS data have been fitted, as-
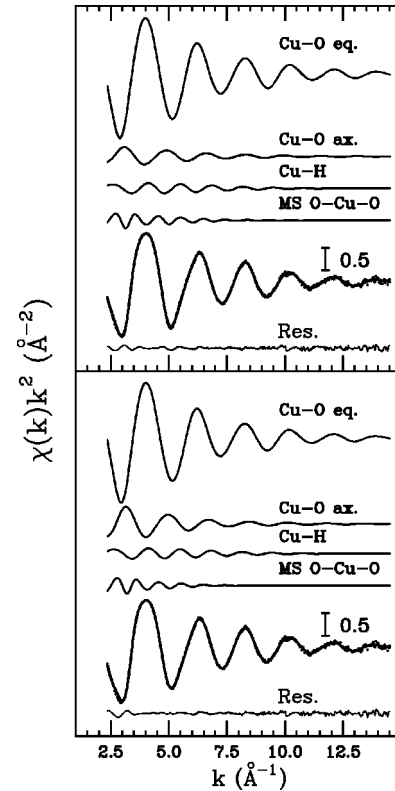

FIG. 1. EXAFS fit of the 0.1-M Cu^{2+} water solutions assuming fivefold and sixfold coordination models (upper and lower panels, respectively). From the top to the bottom of each panel, the following curves are reported: the equatorial Cu-O signal, the axial Cu-O signal, the Cu-H first shell signal, the equatorial MS O-Cu-O linear signal, the total theoretical signal compared with the experimental spectrum, and the residual curve.

suming the presence of four oxygens in the equatorial plane and one or two axial oxygens, representing a square pyramidal and a JT distorted octahedral configuration, respectively.

The best-fit analyses of the 0.1 M Cu^{2+} water solution EXAFS spectrum are shown in Fig. 1. The results obtained for the five- fold and sixfold-coordinated complexes are shown in the upper and lower panels, respectively. During the fitting procedure the coordination numbers have been kept fixed. The $\chi(k)$ signals are shown multiplied by k^2 for a better visualization. The first four curves from the top of each panel are the Cu-O equatorial, Cu-O axial, and Cu-H first shell signals, and the multiple-scattering (MS) contribution associated with the two linear O-Cu-O configurations of the equatorial plane. The reminder of the figure shows the total theoretical contributions compared with the experimental spectrum and the resulting residuals. Note that MS signals associated with the rectangular configurations and the O-Cu-O axial path are negligible in this energy range. The structural parameters obtained from the two fitting procedures are reported in Table I. The outstanding result of this analysis is that the EXAFS experimental data can be reproduced with the same accuracy, using both a square pyramidal or a JT distorted octahedral coordination. In particular the σ^2 factors and the coordination numbers associated with the axial oxygens are highly correlated, and this hampers a

TABLE I. First shell structural parameters for the Cu^{2+} 0.1-M water solution obtained from the EXAFS data analysis assuming fivefold and sixfold coordination models. N is the coordination number, R is the metal-ligand average distance, σ^2 is the mean-square variation, and β is the skewness of the ion-ligand distribution function (Ref. 6).

	N	R (Å)	σ^2 (Å^2)	β
Fivefold coordination				
Cu-O$_{eq.}$	4	1.956(4)	0.0053(5)	0.0(1)
Cu-O$_{ax.}$	1	2.36(2)	0.010(3)	0.8(2)
Cu-H	8	2.71(3)	0.013(4)	0.9(4)
Sixfold coordination				
Cu-O$_{eq.}$	4	1.961(4)	0.0058(5)	0.0(1)
Cu-O$_{ax.}$	2	2.36(2)	0.020(3)	0.5(2)
Cu-H	8	2.71(3)	0.013(4)	0.7(4)

unique determination of these parameters.

To discriminate between these two models we have performed a similar analysis for the XANES energy region of the spectrum with the MXAN set of programs,[7] starting from both fivefold and sixfold coordination geometries. The results of the minimizations are depicted in Fig. 2 for the 0.1-M Cu^{2+} aqueous solution. The best-fit analysis for the fivefold coordination model is shown in the upper panel, and the structural parameters obtained from the minimization correspond to a square pyramid with four equatorial oxygens at 1.97(1) Å and one axial oxygen at 2.39(6) Å. The best fit obtained for a JT distorted octahedron with four equatorial oxygens at 1.99(1) Å and two axial oxygens at 2.56(4) Å is shown in the lower panel. A Γ_c value of 2.3 eV has been obtained in both cases. EXAFS and XANES fitting procedures have also been applied to the 0.005-M solution, and the structural parameters determined were equal, within 0.01 Å, to the ones obtained for the 0.1-M solution.

The XANES theoretical spectrum associated with the fitted fivefold model is in much better agreement with the experimental data, as compared to the sixfold one. In particular in the latter case the theoretical curve is not able to completely reproduce the sharp feature associated with the white line, and clear discrepancies are evident in the energy range above 100 eV. This finding is confirmed by the increase of the error function value R_{sq} going from the square pyramidal model to the octahedral model. In the insets of Fig. 2 we show the comparison between the experimental data, in which a deconvolution of the core-hole width [1.5-eV full width at half maximum (FWHM)] has been performed using a suitable algorithm,[13] and the theoretical fitted curves which do not include the damping associated with the core-hole lifetime and the experimental resolution. In the case of the square pyramidal model the theoretical signal accurately reproduces the experimental rising edge up to about 20 eV, and in particular the small hump appearing at about 4 eV. Conversely, the theoretical fitted curve associated with the octahedral model shows a sharp peak at the edge which is not present in the deconvoluted experimental data.

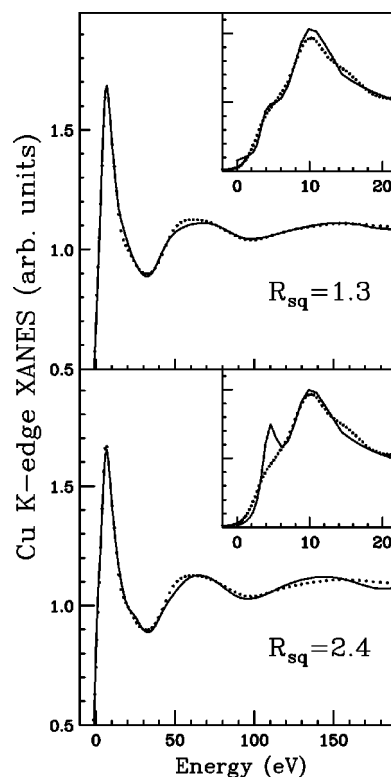When looking at the structural results obtained from the

FIG. 2. Comparison between the best fit theoretical XANES spectra (solid line) of the fivefold and sixfold coordination models (upper and lower panels, respectively) and the raw experimental data (dotted line). In these fitting procedures only two structural parameters, the Cu-O$_{eq}$ and the Cu-O$_{ax}$ distances, are minimized, while the coordination angles are kept fixed to 90° and 180°. The final structures are an elongated square pyramid and a JT distorted octahedron, respectively. In the insets, the edge regions of the same theoretical spectra not including any damping factor are compared with the experimental data where a deconvolution of the core-hole width (the full width at half maximum is 1.5 eV) is performed.

EXAFS and XANES analyses, it is evident that there is a good agreement both in the equatorial and the axial Cu-O distances for the square pyramidal model. Conversely a quite different value of the axial Cu-O distance is obtained in the case of the JT distorted octahedral coordination. A similar analysis has been applied to a series of $3d$ transition-metal ions in a water solution, and the existence of octahedral hydrated Ni^{2+}, Co^{2+} and Zn^{2+} complexes has been found. The ion-O bond length distances obtained from both the EXAFS and XANES fitting procedures are equal within the statistical errors of the MXAN procedure.[7,12]

On the basis of these results the hydrated Cu^{2+} complex is bound to five water molecules which are placed in a square pyramidal configuration. In particular, four water molecules are tightly bound to the Cu^{2+} ion in the equatorial plane while the axial water molecules are only weakly bound to the metal ion. This finding is supported by the larger distance and Debye-Waller factor associated with the axial oxygen. This geometry suggests a dynamical picture in which the axial oxygens undergo a fast exchange, with the second shell water molecules giving rise to a mean axial coordination number equal to 1. The simultaneous presence of fourfold
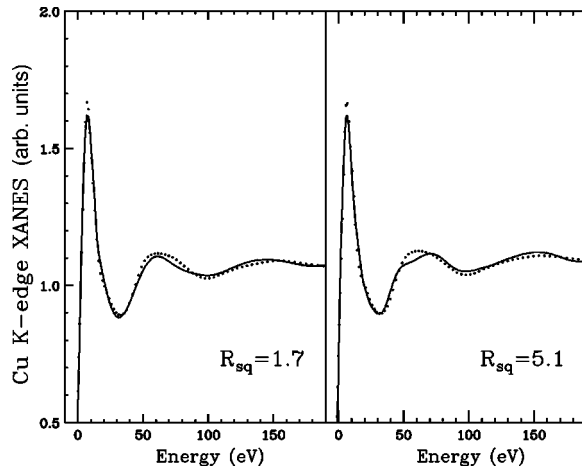
FIG. 3. The left panel shows the comparison between the best-fit XANES spectrum (solid line) of a fivefold coordination model corresponding to an elongated trigonal bypyramid and the experimental data (dotted line). In this fit two independent sets of distances, three in-plane and two axial Cu-O bond lengths and one O-Cu-O in-plane angle have been minimized. The right panel shows the comparison between the theoretical XANES spectrum (solid line) corresponding to the JT distorted octahedron obtained by the EXAFS analysis and the experimental data (dotted line).

and sixfold coordination geometries can be discarded as both configurations give rise to characteristic fingerprints in the XANES region[14,15] which are not present in the experimental data. This is particularly evident in the experimental spectra shown in the inset of Fig. 2 where the core-hole broadening has been eliminated. Moreover, from a more general theoretical consideration, each geometry gives rise to peculiar multiple-scattering signals which cannot be mimicked by a linear combination of MS signals associated with different geometries.

The compatibility of the XANES spectrum with the existence of a trigonal bipyramid has been assessed by carrying out an analysis in which two sets of Cu-O distances, associated with three in-plane and two axial oxygens were minimized. The results of the fitting procedure are shown in the left panel of Fig. 3 and they correspond to two axial Cu-O distances of 2.03 Å and three in-plane Cu-O distances of 1.91 Å with an O-Cu-O angle of 118°. In this case the agreement between the experiment and the calculation is not very good, and this is also evident from the high R_sq value. Moreover, the Γ_c value obtained from the minimization was unreasonably large (2.8 eV). This behavior is most probably due to the presence of anomalous features in the theoretical curve which need to be suppressed. We also attempted to fit the EXAFS experimental data with this model, but a very bad agreement between the experimental and theoretical data was obtained.

In the last step of our investigation we used the JT distorted octahedral model, as determined from the EXAFS data analysis, to calculate the corresponding XANES theoretical signal. A comparison between this theoretical curve and the experimental data is shown in the right panel of Fig. 3. Relevant discrepancies are present in the whole energy range, and a very large R_{sq} value is obtained.
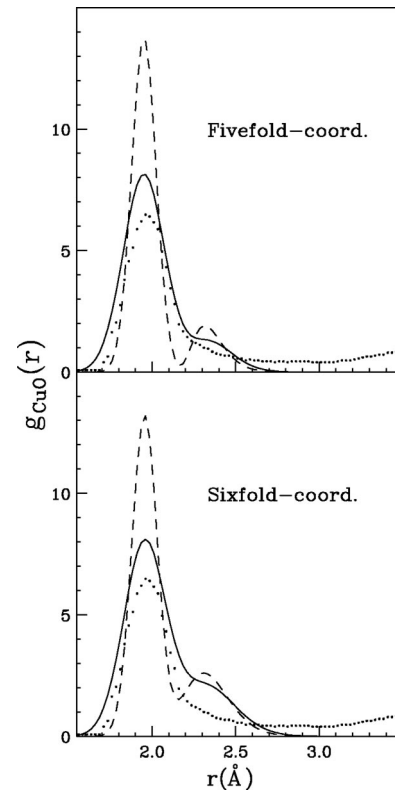

FIG. 4. Cu-O pair correlation functions $g_{CuO}(r)$ as derived from the EXAFS analysis (dashed line) for the fivefold and sixfold coordination models (upper and lower panels, respectively), compared with the partial pair correlation function obtained by neutron diffraction method (dotted line) (Ref. 3). The solid lines represent the EXAFS $g_{CuO}(r)$'s convoluted with a Gaussian function with a full width at half maximum at 0.1 Å.

A combined EXAFS and XANES analysis has also been performed starting from the regular trigonal bipyramid recently proposed.[3] In this case a very bad fit to the experiment has been obtained with both techniques. For the sake of brevity these last results have not been shown here.

To examine the compatibility of our results with the partial pair correlation function $g_{CuO}(r)$ obtained by the second-difference isotopic method in neutron diffraction (ND),[3] we calculated the $g_{CuO}(r)$'s associated with the two Cu^{2+} coordination models as derived from the EXAFS data analysis. The EXAFS $g_{CuO}(r)$'s have been convoluted with a Gaussian function (the FWHM is 0.1 Å) in order to reproduce the spatial resolution of neutron-diffraction measurements (Fig. 4) and a density of 1 has been assumed. The EXAFS pair distribution function associated with the fivefold coordination complex shows a better agreement with the ND data for all the principal features. As far as the sixfold model is concerned, the EXAFS $g_{CuO}(r)$ shows larger differences in the region of the axial Cu-O distance at about 2.4 Å. Note that a coordination number of 5 is obtained from the ND data only if the integration range is extended up to 2.8 Å, thus including the axial distance region. A coordination number equal to 6 is not obtained even by increasing the density of the solution of 20%.

Several examples of elongated square pyramidal Cu^{2+}

sites have reported in the literature in the solid-state physics and inorganic and biological chemistry fields.[16–18] A recent XAS investigation of the solvation of Cu^{2+} ions in liquid ammonia has shown the existence of a pentacoordinated complex in a square pyramidal geometry.[19] Moreover, infrared spectroscopic investigations on the hydrogen bonds formed between the Cu^{2+} first and second hydration shells, have shown the presence of inequivalent Cu-O bond distances.[20]

IV. CONCLUSIONS

This work presents a combined EXAFS and XANES investigation based on fitting procedures, which allowed an accurate determination of the coordination geometry of the Cu^{2+} ion in aqueous solution. It has been shown that, at variance with the generally accepted JT octahedral model, the Cu^{2+} hydration complex is fivefold coordinated. On the basis of our results, the XANES spectrum resulting from a combination of square planar and JT octahedral complexes is not able to reproduce the features present in the experimental data. Moreover, the square pyramid and trigonal bipyramid configuration with five equal Cu-O distance recently proposed [3] can be discarded. These experimental results can stimulate deeper theoretical and experimental investigations of the hydration environment and dynamics of the Cu^{2+} ion in water solution.

*Email address: benfatto@lnf.infn.it

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