

# Notes

## Clarification of the Crystal Structure of $[(\text{HC}(\text{Ph}_2\text{PO})_3)_2\text{Cu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

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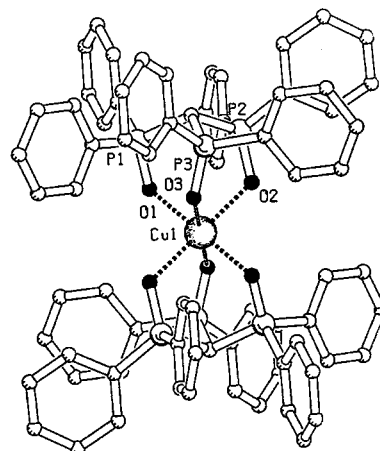
### Introduction

In the past decade, several extended X-ray absorption fine structure (EXAFS) studies on copper(II) complexes have contradicted conclusions drawn from X-ray diffraction (XRD) and/or EPR data. These complexes include  $[\text{Cu}(\text{en})_3]\text{SO}_4$ ,<sup>1</sup>  $\text{K}_2\text{-PbCu}(\text{NO}_2)_6$ ,<sup>1</sup>  $(3\text{-chloroanilinium})_8[\text{CuCl}_6]\text{Cl}_4$ ,<sup>2</sup>  $(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$ ,<sup>3</sup> and  $[\{(\text{C}_5\text{H}_4\text{N})_3\text{CH}\}_2\text{Cu}][\text{NO}_3]_2$ .<sup>4</sup> For the first four cases, the XRD data at room temperature were interpreted as showing the copper center either in a tetragonally compressed or in a perfectly octahedral environment, geometries which are very unusual for a six-coordinate Cu(II) complex and thus suspect. Analysis of the EXAFS spectra of the above compounds indicated that the complexes are in fact tetragonally elongated at the local level, and that the previously deduced geometry was due to effective disorder in the crystals of two different conformers with long and short bonds interchanged. For  $[\{(\text{C}_5\text{H}_4\text{N})_3\text{CH}\}_2\text{Cu}][\text{NO}_3]_2$ , the copper ion lies on a special position so that all six Cu–N bonds are crystallographically equivalent.<sup>4</sup> However, EXAFS measurements were also able to show in this case that the local copper octahedra are tetragonally elongated.

The above ambiguities occur because the XRD and EPR show averaged geometries. In the latter case this is due to the rapid exchange of the two conformers on the time scale of the EPR experiments. EXAFS, however, is a much faster technique and reveals a superposition of the conformer geometries rather than their average. X-ray crystallography gives a space-averaged picture of the structure, and the examples mentioned above show that this is sometimes misleading and demonstrates the power of EXAFS to clarify structural anomalies.

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**Figure 1.** The room temperature structure of the cation in  $[(\text{HC}(\text{Ph}_2\text{PO})_3)_2\text{Cu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (plotted using PLATON<sup>15</sup>).

$[(\text{HC}(\text{Ph}_2\text{PO})_3)_2\text{Cu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  contains Cu bonded to the six oxygen atoms of the tripod ligands as shown in Figure 1, the water molecules being uncoordinated to the metal. The complex crystallizes in a triclinic space group with the Cu(II) on an inversion center.<sup>5</sup> The structure observed at room temperature by XRD yielded the bond lengths (2.128 ( $\times 2$ ), 1.977 ( $\times 2$ ), 2.152 ( $\times 2$ ) Å) from which it was inferred that the complex has the unusual tetragonally compressed coordination geometry.<sup>5</sup> A compressed copper(II) geometry is rare, but not unknown.  $\text{KCuAlF}_6$  is at present the only confirmed example involving six identical ligands.<sup>6,7</sup>

A redetermination of the X-ray structure<sup>8</sup> of  $[(\text{HC}(\text{Ph}_2\text{PO})_3)_2\text{Cu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  confirmed the basic results of Shieh et al.<sup>6</sup> To determine whether the tetragonally compressed geometry inferred for this compound is real, or the result of an average of dynamic distortions, we have determined the local Cu(II) geometry using EXAFS. This shows that, in common with previous studies on other systems,<sup>1–4</sup> the true local coordination geometry about the Cu(II) is tetragonally elongated, so that the observed XRD structure is a result of the averaging of two structural conformers.

### Experimental Section

**Synthesis.** CAUTION: Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities. Single crystals of  $[(\text{HC}(\text{Ph}_2\text{PO})_3)_2\text{Cu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  were prepared using the method given in the literature.<sup>5</sup> In addition to the previously reported triclinic form, crystals of a monoclinic anhydrous modification were also obtained.<sup>9</sup> These were readily identified by their different morphology and were removed by hand.

**EXAFS Measurements.** X-ray absorption measurements were made at the Australian National Beamline Facility (ANBF) on bending-

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magnet beamline 20B at the KEK Photon Factory, Tsukuba, Japan. The sample was finely ground and diluted with boron nitride to give a 70% edge drop. Kapton tape was used as windows to a 5 mm circular aperture in a 1 mm thick aluminum sample holder.

At room temperature, four scans of the X-ray absorption were collected and averaged over four stages: 8730–8930 eV (10 eV steps), 8930–9030 (0.5) eV, 9030–9430 (2) eV, and 9430–10430 (4) eV. Energies were calibrated using a Cu foil internal standard with the first inflection point being assigned as 8980.3 eV. The 2.5 GeV storage ring delivered a current of between 368 and 265 mA. The monochromator was a Si(III) channel cut double crystal detuned to 50% of the maximum intensity in order to eliminate most of the interference due to higher harmonics. The data were collected in transmission mode using standard N<sub>2</sub>-filled ionization chambers.

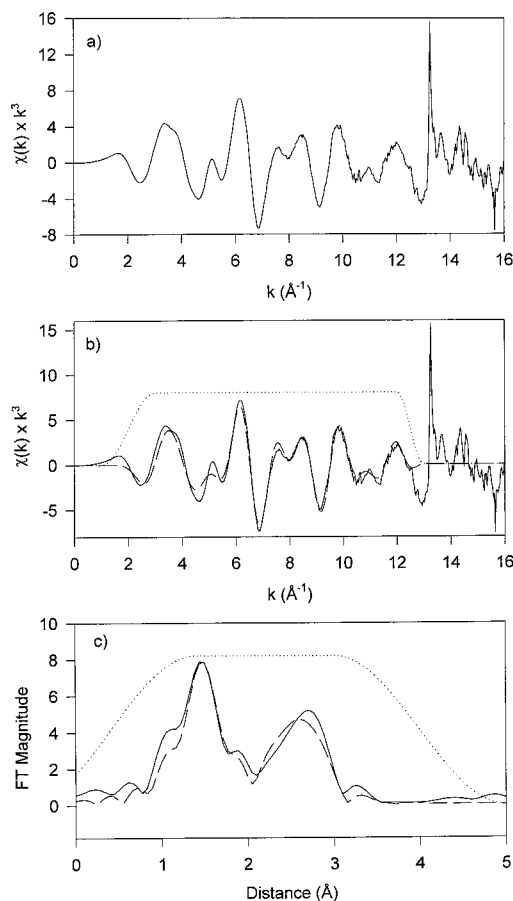
The raw data were generally noise free until  $k \approx 12$ . The large sharp spike at about  $k \approx 13$  is a monochromator glitch. The scans were averaged on the basis of signal-to-noise ratios. A background correction was applied by fitting a polynomial and a five-region spline to the pre-edge and EXAFS regions, respectively. Data were normalized to an edge jump of 1, and  $k = 0$  was calculated from  $E_0 = 9000$  eV. The calculated EXAFS was fitted to the observed  $k^3$  weighted data over the range 3(1)–12(0.5) Å<sup>-1</sup>, with the  $R$  range from 1.4(1) to 3(1) Å. The EXAFS analysis was performed with the program suite XFIT<sup>10</sup> with FEFF 4.0<sup>11</sup> and FEFF 6.01<sup>12</sup> for single and multiple scattering, respectively. The convergence of the fitting process was monitored as described previously.<sup>3</sup>

## Results and Discussion

**EXAFS Experiments.** The averaged raw  $k^3$  weighted EXAFS of [HC(Ph<sub>2</sub>PO)<sub>3</sub>]<sub>2</sub>Cu](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O is shown in Figure 2a. The EXAFS (Figure 2b) and its Fourier transform amplitude (Figure 2c) are shown together with the fitted calculated spectrum. The initial modeling of the EXAFS using FEFF4 gave best fits from models with the copper center in either a tetragonally elongated [1.98(2), 1.98(2), 2.26(2) Å] or rhombic geometry [1.92(2), 2.02(2), 2.25(2) Å]. The model was then extended to include all atoms within 4 Å, and multiple scattering was used in the analysis. The capping carbons, lying 3.34 Å from the Cu<sup>2+</sup> ion, were important because they restrict the movement of the phosphorus atoms and thus retain the integrity of the ring systems. When the positions of the phosphorus and carbon atoms were refined, the angles and bond lengths were restrained to within 5° for the angles and within 0.01 Å for the bond lengths. Details of the position, Debye–Waller factors, and restraints of the fitted atoms are contained in the Supporting Information. The calculation included up to 29 unique paths with an effective length <4 Å and up to four legs. The final best-fit Cu–O bond lengths are given in Table 1. The best fit O–Cu–O angles were not significantly different from the published values.

Attempts to fit the EXAFS spectrum using a model based on the room temperature crystal structure were unsuccessful, refinement leading to a structure involving four short and two long copper–oxygen bonds. When the model was constrained to have the tetragonally compressed structure, the best fit that was obtained had an  $R$  value of 0.31, almost twice that of the best-fit elongated structure.

The standard deviations were estimated using two methods. The first method used XFIT<sup>10</sup> to fit a series curves with random noise added to the smoothed EXAFS curve at the level found in the original spectrum. The noise in the observed EXAFS was estimated using Fourier filtering. The second method was to



**Figure 2.** (a) Unprocessed EXAFS of the triclinic form of [HC(Ph<sub>2</sub>PO)<sub>3</sub>]<sub>2</sub>Cu](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O at 298 K. The EXAFS (b) and the Fourier transform amplitude (c) for [HC(Ph<sub>2</sub>PO)<sub>3</sub>]<sub>2</sub>Cu](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O at 298 K: observed (—), calculated from refined model (---), window used in the Fourier Filter (···).

**Table 1.** EXAFS Analysis<sup>a</sup> of [(HC(Ph<sub>2</sub>PO)<sub>3</sub>]<sub>2</sub>Cu](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O at 298 K

$E_0$ (eV)	$S_0^2$	$R$ value	
8986(2) eV	1.0(1)	0.189	
shell	distance (Å)	$\sigma^2$ (Å <sup>2</sup> )	
O(1)	Cu–O	1.96(2)	0.0034(20)
O(2)	Cu–O	1.96(2)	0.0041(30)
O(3)	Cu–O	2.22(5)	0.0261(60)
P(1)	O–P	1.50(1)	0.0035(25)
	P–C	1.84(1)	
P(2)	O–P	1.51(1)	0.0017(5)
	P–C	1.85(1)	
P(3)	O–P	1.50(1)	0.0016(5)
	P–C	1.86(1)	

<sup>a</sup> Standard deviations are given in parentheses.

estimate standard deviations by extracting several EXAFS spectra using slightly different spline curves. These EXAFS spectra were then modeled using the same method as for the initial spectrum. Both methods gave similar results, and the standard deviations were taken as the higher values obtained. The final  $R$  value for the best-fit structure was 0.189.

**Structure of the Complex.** The room temperature EXAFS of [HC(Ph<sub>2</sub>PO)<sub>3</sub>]<sub>2</sub>Cu](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O was successfully interpreted using a model with four short and two long Cu–O bonds (1.96(2), 1.96(2), 2.22(2) Å). The model refined the two shortest bonds to be equal within the estimated standard deviation. We note that the Debye–Waller factor is larger for the longest Cu–

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O3 bond. This was also observed for the longer bonds in the EXAFS of both  $\text{KCuAlF}_6$ <sup>7</sup> and  $(\text{ND}_4)_2\text{Cu}(\text{D}_2\text{O})_6(\text{SO}_4)_2$ .<sup>3</sup>

Attempts to duplicate the EXAFS with a model involving two short and four long bonds were unsuccessful, giving rise to a substantially larger *R* value. The apparent tetragonal compression observed by X-ray diffraction [2.130(2), 1.979(2), 2.137(2) Å]<sup>5</sup> therefore probably results from a disorder between structural isomers in which the long and intermediate Cu–O bonds to O(1) and O(3) are interchanged. The disorder results from the fact that the Jahn–Teller Mexican hat potential energy surface of the Cu(II) has three minima at different energies. The variations in the bond lengths observed in the XRD crystal structure analysis are therefore not real changes, but are due rather to a change in the population of the two lower energy minima. Such behavior has been observed in several other systems.<sup>13</sup> For  $[\text{HC}(\text{Ph}_2\text{PO})_3]_2\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ , the third minimum is too high in energy to be populated at room temperature. The close similarity of the two longer Cu–O bond lengths

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determined by XRD at room temperature implies that there is near equal occupancy of the two lowest minima. Assuming that the structural isomers are in dynamic equilibrium, it may be possible to determine the relative energies of the minima by determining the crystal structure over a temperature range, and we hope to undertake such a study.

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**Supporting Information Available:** Listings of the final coordinates of all fitted atoms, together with Debye–Waller factors and the constraints/restraints used in the fitting process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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