Aqua Copper(II) in Frozen Glasses: A Third Unexpected Journey Away From Axial Symmetry

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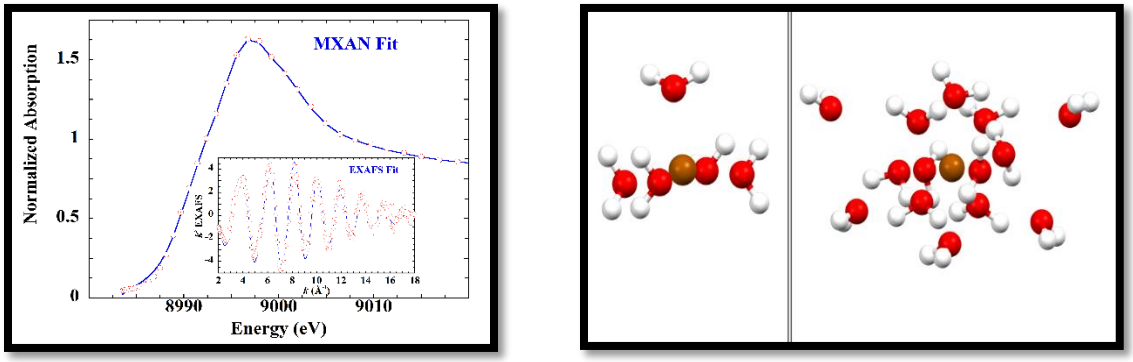
$[Cu(aq)]^{2+}$ evidences a distinct disinclination to conform to theoretical expectations of coordination number or geometry.[1, 2] MXAN analysis of the K-edge X-ray absorption spectra (XAS) of Cu(II) in liquid water solution (1 M $HClO_4$) indicated structural equilibration between an axially elongated (2.23 Å) square pyramid and a pseudo-octahedron with axial waters at greatly disparate distances (2.06 Å and non-bonding 2.99 Å).[3] We have now studied the K-edge XAS of $[Cu(aq)]^{2+}$ in 40% 1,3-propanediol or 1,5-pentanediol frozen aqueous glasses (Figure).



Left panel: The MXAN and EXAFS fits to the Cu K-edge XAS of 0.1 M $Cu(ClO_4)_2$ in a frozen (10 K) aqueous 1 M $HClO_4$ 40% diol glass. Right panel: flash freezing (pentane slush) trapped $[Cu(aq)]^{2+}$ in an axially asymmetric pseudo-octahedron with an organized second shell of water molecules (right) or in a square pyramid (axial 2.24 Å) with no detectable second solvation shell (left). Eight (2×4) equatorial Cu(II)-OH_2 distances of 1.94-1.95 Å are identical to those in the liquid state.

MXAN analysis revealed that Cu^{2+} in frozen aqueous glass occupied either an axially elongated $[Cu(H_2O)_5]^{2+}$ square pyramid or within an axially dissymmetric $[Cu(H_2O)_6]^{2+}$ pseudo-octahedron that was compressed relative to the liquid-state ion. The more convergent axial Cu(II)-OH_2 distances of 2.14 Å and 2.28 Å are closer to the bond lengths of the classical JT-elongated octahedron. As with Cu(II) in 1 M $HClO_4$, a second solvation shell was detectable only near the latter ion.

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2. Rotzinger, F. P., *J. Phys. Chem. B* **2005,** *109*, 1510-1527
3. Frank, P.; Benfatto, M.; Qayyam, M.; Hedman, B.; Hodgson, K. O., *J. Chem. Phys.* **2015,** *142*, 084310 10.1063/1.4908266.