

Freshly synthesized copper(I) chloride was dissolved with the requisite amounts of sodium chloride, sodium thiosulfate, ammonium chloride and sodium hydroxide in water to achieve the solution compositions listed in the supplementary data Tables S1–S4. { All chemicals were of analytical-grade or better and were used as received. Refinement of EXAFS data provides information on the number and nature of nearest neighbors and the distances between them, and can be used to test the speciation model derived from the XANES data and provide additional characterization of the complexes and their changes with temperature and salinity. For four coordinate Cu(I) compounds the pre-edge is broad, the average normalized absorption amplitude is 0.72, and the crest is shifted by 1.5 eV towards higher energy compared to linear and trigonal compounds.<sup>33</sup> XANES spectra for a given stoichiometry and geometry of Cu(I) thiosulfato and ammine complexes were calculated ab initio using the FDMNES package developed by Joly,<sup>34</sup> following the procedure outlined in Brugger et al.<sup>5</sup> and Testemale et al.<sup>35</sup>. For the distribution of species calculations, activity coefficients were estimated with the "b-dot" equation,<sup>26</sup> using the b-dot parameters listed for NaCl solutions from Helgeson and Kirkham