Probing the Structure of Axial Water Bound to Copper: An ESEEM Analysis of ^{17}O-Water in Tutton Salt

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Electron Spin-Echo Envelope Modulation (ESEEM) signals attributed to axial water bound to Cu^{+2} have been detected and analyzed in ^{17}O-water enriched potassium zinc sulfate hexahydrate (ZKS) tutton salt crystals. The magnetic field orientation dependence of low frequency modulations were measured to fit hyperfine and quadrupole coupling tensors of a ^{17}O (I=5/2) nucleus. The hyperfine tensor exhibits axial symmetry with the largest value directed normal to the metal equatorial plane in the host structure. Comparisons with quantum chemical calculations position this nucleus about 2.3 Å from the copper. The nuclear quadrupole tensor directions were found to correlate with the O8 water geometry. When Cu(II) dopes into tutton salt, a Jahn-Teller distortion swaps the relative longer and intermediate metal O7 and O8 bond lengths of the zinc host (Fig. 1). Therefore only those unit cells containing the copper impurity conform to the pure copper tutton structure. This study provides further support for this model. Moreover, coupling interactions from distant $H_2{}^{17}O$ such as in the present case have important implications in studies of copper enzymes and proteins where substrates have been proposed to displace weakly bound water in the active site.

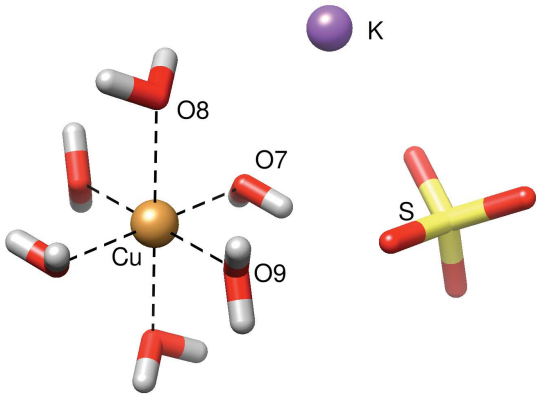

Fig. 1. Copper hexahydrate in Tutton salt. The relative lengths of metal-O7 and metal-O8 are interchanged when Copper substitutes for Zinc in ZKS. The Jahn-Teller effect causes the Cu-O8 bond to lengthen compared to Cu-O9 and Cu-O7.