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Structural and EPR Study of the Dependence on Deuteration of the Jahn−Teller Distortion in Ammonium Hexaaquacopper(II) Sulfate, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$

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The variation of the EPR spectra with degree of deuteration of the partially deuterated Tutton salt ammonium hexaaquacopper(II) sulfate, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, has been measured at 293 K. The measurements indicate that the structure changes quite abruptly from that of the pure hydrogenous salt to that of the fully deuterated salt at ∼50% deuteration. The structure of a crystal in which ∼42% of the hydrogen atoms were replaced by deuterium was elucidated at 15 K by single-crystal time-of-flight neutron diffraction. The hexaaquacopper(II) complex exhibits an orthorhombically distorted, tetragonally elongated octahedral coordination geometry (Cu−O bond distances of 2.281(1), 2.007(1), and 1.975(1) Å). The structure is very similar to that reported for the undeuterated salt at 9.6 K, and markedly different from that of the fully deuterated compound at 15 K, which has similar Cu−O bond lengths but with the directions of the long and intermediate bonds interchanged. There is no evidence for disorder or partial switching of the Cu−O bond directions. This is consistent with the temperature dependence of the EPR spectrum of the ∼42% deuterated compound, which indicates a thermal equilibrium between the two structural forms close to room temperature similar to that reported for the undeuterated compound, but complete reversion to the low-temperature phase on cooling to 5 K. The possible influence of deuteration upon the hydrogen-bonding distances and the bearing of this upon the structural modifications of the compound are discussed.

Introduction

The Jahn−Teller effect has been used to explain a variety of structural distortions and spectroscopic anomalies in many transition-metal compounds.[1] This is especially true for six-coordinate complexes of copper(II), high-spin chromium(II), and low-spin cobalt(II). An area of particular current interest is the Tutton salts which have the general formula $A_2[M(H_2O)_6](SO_4)_2$ where A = K, Rb, Cs, or NH_4 and M is a divalent metal ion.[2−5] In the unit cell of these salts, the $Cu(H_2O)_6^{2+}$ complex lies on an inversion center and can be described as an orthorhombically distorted tetragonally elongated octahedron with four Cu−O bond lengths of ∼2.0 Å and two Cu−O bond lengths of ∼2.3 Å. The ammonium compound has essentially the same structure as the alkali metal salts (structure type **A**), except that the direction of the Jahn−Teller distortion of the $Cu(H_2O)_6^{2+}$ complex is switched by 90° in the crystal lattice (structure type **B**) as depicted schematically in Figure 1. The fully deuterated ammonium complex, however, adopts structure type **A**, the compound being unique in exhibiting such a Jahn−Teller "isotope switch" upon deuteration.[6] Application of ∼240 bar of hydrostatic helium gas pressure at room temperature transforms the deuterated material to structure type **B**, thus exhibiting a "pressure switch" with a hysteresis of ∼100 bar.[7,8] These switches are accompanied by slight changes in the dispositions and hydrogen-bonding interactions of the ammonium and sulfate counterions. The corresponding potassium salt exhibits no such "pressure-switch", suggesting that hydrogen bonding interactions involving the ammonium groups may influence this behavior.[9] The temperature dependence of the observed bond distances and EPR data indicate that at room temperature both the hydrogenous and fully deuterated ammonium Cu(II) Tutton salts are undergoing a dynamic equilibrium between the two structure types, which are separated in energy by only a small amount.[7−9] The cooperative nature of the temperature-dependent dynamic

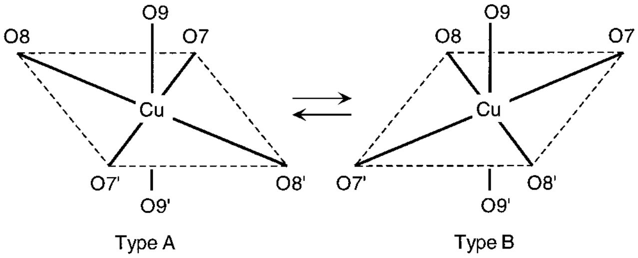

Figure 1. Schematic showing the direction of the Jahn−Teller distortion in structure types **A** and **B**.

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[‡] University of Tasmania.
(1) Falvello, L. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4463−4475.
(2) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 659−662.
(3) Brown, G. M.; Chidambaram, R. *Acta Crystallogr. B* **1969**, *25*, 676−687.
(4) Hathaway, B. J. *Struct. Bonding* **1984**, *57*, 55−118.
(5) Alcock, N. W.; Duggan, M.; Murray, A.; Tyagi, S.; Hathaway, B. J.; Hewat, A. *J. Chem. Soc., Dalton Trans.* **1984**, *1984*, 7−14.
(6) Hathaway, B. J.; Hewat, A. W. *J. Solid State Chem.* **1984**, *51*, 364−375.
(7) Simmons, C. J.; Hitchman, M. A.; Stratemeier, H.; Schultz, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 11304−11311.
(8) Schultz, A. J.; Hitchman, M. A.; Jorgensen, J. D.; Lukin, S.; Radaelli, P. G.; Simmons, C. J.; Stratemeier, H. *Inorg. Chem.* **1997**, *36*, 3382−3385.
(9) Rauw, W.; Ahsbahs, H.; Hitchman, M. A.; Lukin, S.; Reinen, D.; Schultz, A. J.; Simmons, C. J.; Stratemeier, H. *Inorg. Chem.* **1996**, *35*, 1902−1911.

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switching has recently been modeled in terms of fluctuating domains of the two structures which may result from the hydrogen-bonding interactions linking the Cu complexes in the lattice.[10]

Thus, the Jahn–Teller distortion in the ammonium copper Tutton salt is both isotope and pressure switchable. The influence of isotopic substitution raises an interesting question with regard to the thermal equilibrium. If the degree of substitution is varied, does the position of the equilibrium progressively shift from favoring one structure to favoring the other, or does a sharp structural switch occur at a particular H/D ratio? To answer this question we have prepared the ammonium Cu(II) Tutton salt with a range of deuterium concentrations and monitored the structures at room temperature using EPR spectroscopy. In addition, in order to more closely examine the affects of deuteration on the hydrogen-bonding interactions and the Jahn–Teller distortion of the copper(II) complex, we have carried out a single-crystal neutron diffraction study at 15 K and ambient pressure of the structure of a crystal in which slightly less than half of the hydrogen atoms have been replaced by deuterium. We present here the results of these investigations.

Experimental Section

Synthesis. The mixed hydrogen/deuterium Tutton salts were prepared by dissolving equimolar proportions of $(NH_4)_2SO_4$ and $CuSO_4{\cdot}5H_2O$ in 10 mixtures of H_2O and 99.5% D_2O with the two solvents in various proportions, and allowing the solution to evaporate in an evacuated desiccator over silica gel. Each sample was recrystallized once from the mixed solvent with the same D_2O/H_2O ratio from which it was prepared. The deuterium content of each sample was estimated using a Kratos Concept ISQ mass spectrometer operating at 70 eV. This was done by placing a small amount of the sample on the mass spectrometer probe, heating, and measuring the relative intensities of the peaks corresponding to masses 18, 19, and 20 due to the evaporated water. Here the peak at 18 was due to a combination of H_2O and OD^-, and the proportion was estimated by measuring the ratio of OD^- to D_2O, and OH^- to H_2O, for 99.9% D_2O and H_2O, respectively (this ratio was 0.2 in each case). A small correction was also made for residual background H_2O, obtained by running a spectrum under identical conditions but with no sample present. For the two samples with close to 50% deuterium content, the concentration was checked by repeating the measurements at different heating rates, and the mass peaks were measured as a function of time, and the results were found to be reproducible to better than ~±3%, neglecting systematic errors. A sample in which the deuteration was almost complete was prepared by dissolving equimolar amounts of $(NH_4)_2SO_4$ and anhydrous $CuSO_4$ in the minimum of boiling 99.9% D_2O and allowing the resulting solution to evaporate almost to dryness in an evacuated desiccator over silica gel. This sample was recrystallized four times from 99.9% D_2O, and mass spectroscopic analysis suggested that it had a final deuterium content of ~95%.

The crystals for the neutron diffraction study were prepared by dissolving $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ in an approximately 50/50 solution of H_2O and D_2O. Gentle heat was applied to enhance the dissolving process. The open beaker containing the solution was placed into a desiccator containing standard Drierite desiccant. After approximately 2 days several large crystals formed on the bottom of the beaker. A crystal, which appeared to be single according to visual observations, was cleaved to $1 \times 2 \times 2.5$ mm^3 and mounted onto an aluminum pin with an organic solvent based adhesive. The neutron diffraction analysis suggested an average deuterium content of ~42% (see following section).

Neutron Data Collection. The sample was mounted on the single-crystal diffractometer (SCD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and cooled to 15 K with a Displex closed-cycle helium refrigerator.[11] One histogram of data was collected to check for crystal quality and to determine the initial orientation matrix using an autoindexing routine.[12] Thirty-one time-of-flight histograms were collected with different χ and ϕ settings and covered approximately two octants of data ($\pm h$, k, l). Bragg reflections in each histogram were integrated and corrected for the Lorentz factor, the incident spectrum, and the detector efficiency. A wavelength-dependent spherical absorption correction was applied, but symmetry-related reflections were not averaged because of the wavelength dependence of extinction.[13]

Table 1: Neutron Data Collection Parameters for $(N(H/D)_4)_2[Cu((H/D)_2O)_6](SO_4)_2$

temp, K	15
cryst size, mm^3	$1 \times 2 \times 2.5$
space group	$P2_1/a$ (No. 14)
a, Å	9.095(4)
b, Å	12.228(5)
c, Å	6.345(3)
β, deg	106.34(4)
V, Å^3	677.2(5)
Z	2
radiation	neutrons, $\lambda = 0.7-4.2$ Å
data collection technique	TOF Laue with position-sensitive area detector
$\mu(\lambda)$, cm^{-1}	$1.164 + 0.664\lambda$
extinction param g (rad^{-1})	$1.14(5) \times 10^{-5}$
no. of reflns in final ls with $F_o^2 > 3\sigma(F_o^2)$	4966
no. of unique reflns	3471
variables	169
function minimized	$\sum w(F_o - F_c)^2$
$R_w(F^2)$	0.114
$R(F^2)$	0.108
$R_w(F)$	0.056
$R(F)$	0.065
GOF	3.20

Refinement. The atomic positions of the hydrogenated structure were used as a starting point in the refinement because the lattice parameters are comparable.[7] The atomic positions and thermal parameters for the non-hydrogen atoms refined in a routine manner. The hydrogen/deuterium positions were modeled by putting both a hydrogen and a deuterium atom on the same site with each initially at 50% occupancy. The occupancies were constrained to sum to unity on each site and allowed to refine. As noted by Reynolds and co-workers,[14] the zero-point motion of hydrogen should be a factor of $\sqrt{2}$ greater than that for deuterium, which is consistent with previous studies on the ammonium copper Tutton salt.[7] Therefore, the isotropic thermal parameters of the hydrogen atoms were allowed to vary, while those of deuterium were constrained to be $1/\sqrt{2}$ of the hydrogen thermal parameters. The occupancy on the H/D positions refined to ~58% H on all sites. Since hydrogen and deuterium have scattering lengths of $-0.37406(11) \times 10^{-12}$ and $0.6671(4) \times 10^{12}$ cm, respectively, the total amount of scattering at each position is close to zero $(0.58(-0.3739) + 0.42(0.6671) = 0.0633)$.[15] Because the weak scattering from these sites makes it difficult to model these positions with high precision, they were refined with isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. Although it is possible to have both forms of the hexaaquacopper complex disordered over the same site, refinements attempting to model the alternative cluster did not indicate that any disorder was present. Several Fourier maps of the region confirmed this. The refinements were performed with the GSAS program.[16] Data collection and refinement parameters are summarized in Table 1, and the positional parameters, bond distances and angles,

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(10) Hitchman, M. A.; Maaskant, W.; van der Plas, J.; Simmons, C. J.; Stratemeier, H. *J. Am. Chem. Soc.* **1999**, *121*, 1488–1501.

(11) Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999–1003.

(12) Jacobson, R. A. *J. Appl. Crystallogr.* **1986**, *19*, 283–286.

(13) Howard, J. A. K.; Johnson, O.; Schultz, A. J.; Stringer, A. M. *J. Appl. Crystallogr.* **1987**, *20*, 120–122.

(14) Figgis, B. N.; Sobolev, A. N.; Young, D. M.; Schultz, A. J.; Reynolds, P. A. *J. Am. Chem. Soc.* **1998**, *120*, 8715–8723.

(15) Sears, V. F. *Neutron News* **1992**, *3*, 26–37.

Table 2: Atomic Positions, Occupancy, and Isotropic or Equivalent Thermal Parameters

atom	*x*	*y*	*z*	^{1}H occ[a]	U_{iso} or U_{eq} (Å^2)[b,c]
Cu(1)	0.0	0.0	0.0		0.0034
S(2)	0.4202(2)	0.1346(1)	0.7426(2)		0.0036
O(3)	0.43003(9)	0.22756(7)	0.5960(1)		0.0061
O(4)	0.55801(9)	0.06712(8)	0.7826(1)		0.0070
O(5)	0.28445(9)	0.06785(8)	0.6320(1)		0.0059
O(6)	0.40175(9)	0.17897(8)	0.9511(1)		0.0063
O(7)	0.18743(9)	0.11870(8)	0.1778(1)		0.0073
O(8)	−0.15765(9)	0.10952(7)	0.0287(1)		0.0064
O(9)	−0.00634(9)	−0.06446(8)	0.2827(1)		0.0063
N(10)	0.14179(6)	0.34157(5)	0.35759(8)		0.0072
H(11)	0.0784(9)	0.3262(7)	0.202(1)	0.576(3)	0.045(3)
H(12)	0.2397(6)	0.2949(5)	0.4006(8)	0.537(3)	0.036(2)
H(13)	0.0725(7)	0.3208(5)	0.4539(9)	0.558(2)	0.030(3)
H(14)	0.1686(8)	0.4232(7)	0.374(1)	0.585(2)	0.036(3)
H(15)	0.2294(9)	0.0948(7)	0.327(1)	0.585(2)	0.039(4)
H(16)	0.2696(9)	0.1284(7)	0.111(1)	0.590(2)	0.032(3)
H(17)	−0.2611(9)	0.0950(7)	−0.062(1)	0.594(2)	0.029(4)
H(18)	−0.1357(8)	0.1841(7)	−0.001(1)	0.590(2)	0.022(4)
H(19)	−0.1056(9)	−0.0555(8)	0.317(1)	0.600(2)	0.026(4)
H(20)	0.0218(8)	−0.1423(6)	0.311(1)	0.583(2)	0.030(3)

[a] Occupancy of site by hydrogen. Deuterium occupancy = 1 − hydrogen occupancy. [b] Only non-hydrogen atoms were refined anisotropically, where $U_{eq} = {}^1/_3\sum_{ij}\mathbf{U}_{ij}a_j^*a_j^*a_i\cdot a_j$. [c] Isotropic thermal parameters for deuterium were constrained to be $1/\sqrt{2}$.

Table 3: Atomic Distances (Å) and Angles (deg) in $(N(H/D)_4)_2[Cu((H/D)_2O)_6](SO_4)_2$

atoms	dist, Å	atoms	dist. Å
Cu(1)−O(7)	2.281(1)	N(10)−H(13)	1.024(5)
Cu(1)−O(8)	2.007(1)	N(10)−H(14)	1.023(9)
Cu(1)−O(9)	1.975(1)	O(7)−H(15)	0.962(8)
S(2)−O(3)	1.486(2)	O(7)−H(16)	0.961(7)
S(2)−O(4)	1.463(2)	O(8)−H(17)	0.967(8)
S(2)−O(5)	1.482(2)	O(8)−H(18)	0.963(8)
S(2)−O(6)	1.482(2)	O(9)−H(19)	0.991(8)
N(10)−H(11)	1.011(7)	O(9)−H(20)	0.989(8)
N(10)−H(12)	1.027(5)		

atoms	angle, deg	atoms	angle, deg
O(7)−Cu(1)−O(8)	89.08(5)	H(12)−N(10)−H(13)	109.6(4)
O(7)−Cu(1)−O(9)	89.22(5)	H(12)−N(10)−H(14)	110.4(5)
O(8)−Cu(1)−O(9)	88.84(4)	H(13)−N(10)−H(14)	110.5(5)
O(3)−S(2)−O(4)	109.9(1)	Cu(1)−O(7)−H(15)	109.3(5)
O(3)−S(2)−O(5)	108.3(1)	Cu(1)−O(7)−H(16)	115.1(5)
O(3)−S(2)−O(6)	108.7(1)	H15(1)−O(7)−H(16)	109.0(6)
O(4)−S(2)−O(5)	109.3(1)	Cu(1)−O(8)−H(17)	115.0(5)
O(4)−S(2)−O(6)	111.0(1)	Cu(1)−O(8)−H(18)	114.8(4)
O(5)−S(2)−O(6)	109.6(1)	H(17)−O(8)−H(18)	106.0(7)
H(11)−N(10)−H(12)	111.8(5)	Cu(1)−O(9)−H(19)	114.7(5)
H(11)−N(10)−H(13)	105.0(5)	Cu(1)−O(9)−H(20)	118.5(4)
H(11)−N(10)−H(14)	109.4(6)	H(19)−O(9)−H(20)	105.3(7)

and hydrogen bond distances are given in Tables 2, 3, and 4, respectively. The atomic numbering adopted in this study is the same as in ref 7.

EPR Measurements. Powder electron paramagnetic resonance (EPR) spectra were measured over a temperature range using a Bruker ESP300e spectrometer at X-band frequency (∼9 GHz) with the temperature measured and controlled using an Oxford Instruments ESR-910 flow cryostat with an ITC4 temperature controller. Single-crystal spectra were obtained using a JEOL JES-FE spectrometer operating at a Q-band frequency of ∼34 GHz. The crystals were mounted on a standard JEOL rotation accessory. For the fully hydrogenous and deuterated samples, the principal *g*-values and the orientation of the **g**-tensor of the $Cu(H_2O)_6^{2+}$ group were determined at 293 K as described previously,[17] by rotation of a crystal in the (001), (010), and *bc** crystal planes. For these compounds, results similar to those already reported[9,18] were obtained, with the principal *g*-values lying close to the Cu−O bond directions (though, as noted previously,[9] the directions of the intermediate and highest *g*-value are interchanged in the two compounds; see following discussion). The *g*-values along the three Cu−O bond directions may be measured most accurately by rotation in the *bc** crystal plane. For the samples with intermediate deuterium content, crystals were therefore mounted to rotate in this plane, and the *g*-values with the magnetic field close to the three Cu−O bond directions were estimated. This was done by specifying the directions of the *g*-values,[17] with one defined to lie exactly along the Cu−O(9) bond, a second at 90° to this and in the plane defined by the Cu−O(9) and Cu−O(8) bonds, and the third orthogonal to these and close to the Cu−O(7) direction. Two sets of measurements were made for the hydrogenous and fully deuterated compounds, and these suggest a reliability of better than ∼0.01 for the *g*-values.

Table 4: Hydrogen-Bonding Distances in $(N(H/D)_4)_2[Cu((H/D)_2O)_6](SO_4)_2$

A−H···B	A···B	H···B	angle
O(7)−H(15)···O(5)	2.836(2)	1.887(8)	168.7(7)
O(7)−H(16)···O(6)	2.826(2)	1.885(8)	165.6(8)
O(8)−H(17)···O(4)	2.669(2)	1.702(8)	178.8(8)
O(8)−H(18)···O(6)	2.715(2)	1.753(8)	178.0(6)
O(9)−H(19)···O(5)	2.732(2)	1.753(8)	168.9(9)
O(9)−H(20)···O(3)	2.692(2)	1.711(8)	170.5(6)
N(10)−H(11)···O(6)	2.883(2)	1.918(8)	158.6(6)
N(10)−H(12)···O(3)	2.890(1)	2.001(5)	158.0(4)
N(10)−H(13)···O(3)	2.979(2)	1.872(6)	172.2(5)
N(10)−H(14)···O(5)	2.844(2)	1.826(9)	173.1(6)

Results and Discussion

The *g*-values at 293 K associated with the Cu−O(7), Cu−O(8), and Cu−O(9) bond directions are plotted for the range of deuterium concentrations in Figure 2a. For low deuterium concentrations the highest and intermediate *g*-values occur along the Cu−O(7) and Cu−O(8) bond directions, respectively, but for high deuterium concentrations these are reversed in direction. The trend follows that already reported for the hydrogenous and fully deuterated salts.[10,18] The "switch" occurs quite sharply at a concentration of ∼50%. The lowest *g*-value, that along the Cu−O(9) bond, changes little as a function of deuterium substitution. The *g*-values thus suggest that phase **B** persists up

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(16) Larson, A. C.; Von Dreele, R. B. GSAS−General Structure Analysis System; Los Alamos National Laboratory: Los Alamos, 1994.

(17) Dawson, K.; Hitchman, M. A.; Prout, K.; Rossotti, F. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1509.

(18) Waite, T. D.; Hitchman, M. A. *Inorg. Chem.* **1976**, *15*, 2155.

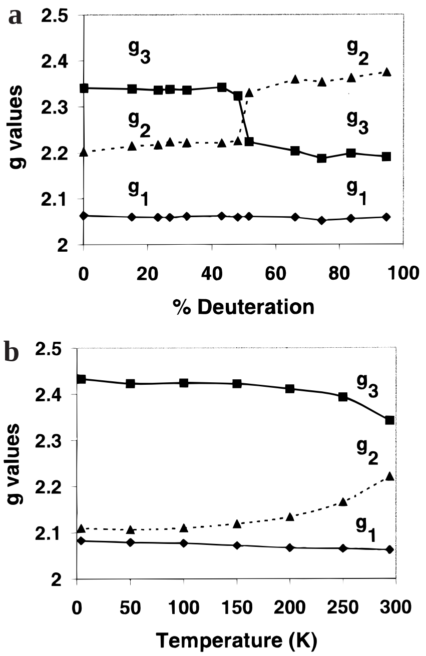

Figure 2. (a) Variation of the molecular *g*-values of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ at 293 K as a function of % deuteration. g_1, g_2, and g_3 are approximately parallel to the Cu−O(9), Cu−O(8), and Cu−O(7) bond directions, respectively. (b) Temperature dependence of the *g*-values of a sample of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ in which ~42% of the hydrogen atoms were replaced by deuterium.

to ~50% deuterium content and then alters quite sharply to type **A**. There is no evidence for any intermediate phase.

It is well established[5,6,9,10] that at higher temperatures both the hydrogenous and the fully deuterated compound exhibit a thermal equilibrium with the other form. At room temperature, about 25% of the $Cu(H_2O)_6^{2+}$ complexes in both salts have the Cu−O(7) and Cu−O(8) bond lengths interchanged compared with the structure at low temperature. The constancy of the *g*-values over the ranges 0−50% and 50−95% deuterium concentration suggests that at 293 K the position of the equilibrium is not significantly affected by the H/D ratio except for the sharp switch in phase at ~50%. The influence of temperature on the equilibrium was studied for the sample with ~42% deuterium substitution used in the neutron diffraction experiment. The variation of the *g*-values on going from 293 to ~5 K is shown in Figure 2b. The two higher *g*-values diverge on cooling, reaching a constant value below ~120 K. The low temperature *g*-values (2.08, 2.11, 2.43) are quite similar to those reported[19] for the pure hydrogenous compound at 160 K (2.076, 2.131, 2.433), suggesting that for the partially deuterated sample the equilibrium shifts completely to the lower energy form on cooling. The steep temperature dependence of the *g*-values between 250 and 293 K is very similar to that described for the *g*-values and Cu−O bond lengths of the fully deuterated compound.[6,10] This was interpreted in terms of cooperative interactions between the $Cu(H_2O)_6^{2+}$ complexes,[10] suggesting that similar behavior occurs for the partially deuterated compound.

$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ with ~42% of the hydrogen atoms replaced by deuterium has a unit cell (Figure 3) basically similar to those of the other Tutton salts (space group $P2_1/a$, No. 14). The lattice parameters are very close to those of the hydrogenous salt studied by X-ray diffraction at 5 K (a = 9.0964(9) Å, b = 12.2225(11) Å, c = 6.3447(7) Å, β = 106.295(7)°)[20] and similar to those reported for hydrogenous and fully deuterated salts under ~1.5 kbar pressure (structure type **B**).[7] The main structural

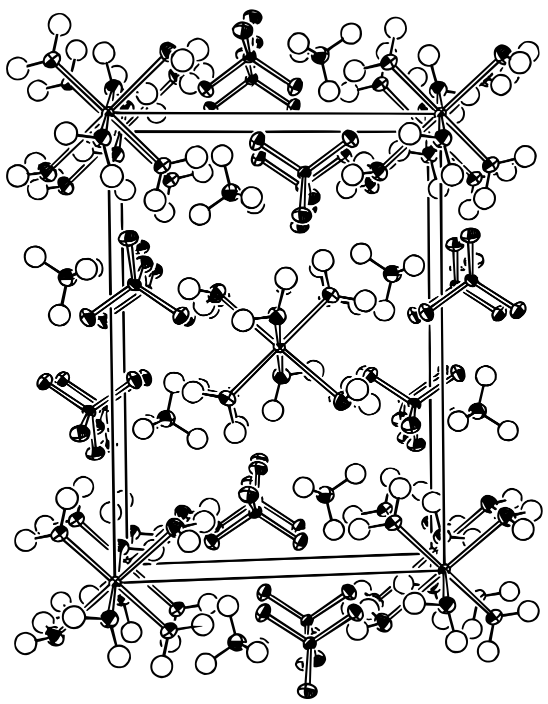

Figure 3. Unit cell packing of the 42% deuterated $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ salt. The *a*-axis is horizontal, and the *b*-axis is vertical.

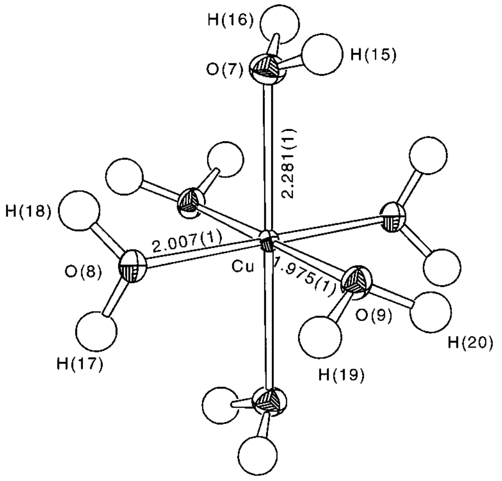

Figure 4. Neutron structure of the 42% deuterated hexaaquacopper cation at 15 K. Thermal ellipsoids are drawn at the 95% probability level.

feature is the hexaaquacopper(II) complex, which is pseudooctahedral with a tetragonal expansion along the Cu−O(7) axis (Figure 4). The copper atom sits on an inversion center. The Cu−O(7) bond is 2.281(1) Å while the other two bond lengths within the complex, Cu−O(8) and Cu−O(9), are 2.007(1) and 1.975(1) Å, respectively. The corresponding distances determined by X-ray diffraction for the hydrogenous salt at 9.5 K, 2.2758(9), 2.0042(8), and 1.9737(9) Å,[20] are very similar, implying that partial deuteration has very little effect on the copper−oxygen bond lengths within the same structure type.

Refinement of the structure suggested that overall ~42% of the hydrogen atoms were replaced by deuterium. This is consistent with the initial solution composition of ~50/50 D_2O/H_2O. The high rate constants for the exchange of water on

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(19) Mabbs, F. E.; Porter, J. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3219.

(20) Figgis, B. N.; Sobolev, A. N.; Simmons, C. J.; Hitchman, M. A.; Stratemeier, H.; Tregenna-Piggott, P. L. W.; Riley, M. J. Unpublished results.

copper and of the hydrogen atoms on the ammonium group should allow complete equilibrium to occur during the dissolution and crystallization process. A close look at the refinement suggests that slightly more deuterium goes to the ammonium cation (H11−H14) as compared to the water molecules (∼3%). An equilibrium isotope effect is expected such that the light nuclei prefer sites with lower vibrational frequencies. Infrared stretching modes measured previously for the ammonium copper Tutton salt doped with ∼5% deuterium showed that the lowest vibrational frequency occurs with the hydrogen atoms bonded to the nitrogen atom,[21] which would predict a trend opposite to that implied by the refinement of the neutron scattering. However, the differences are not very large and there is some overlap between O−H and N−H stretching peaks.[21] The poor scattering at the hydrogen/deuterium positions makes it difficult to accurately determine the hydrogen/deuterium compositions, and we think that the difference between the water and ammonium cations is probably not significant. It should be noted that the hydrogen atoms on the ammonium cation have slightly larger thermal ellipsoids compared to previous work.[7] This could be related to the rotation of the ammonium cation by ∼30° between the fully hydrogenated (type **B**) and fully deuterated structures (type **A**). Therefore the larger thermal ellipsoids suggest that some disorder is present in the structure which may contribute to the higher than expected goodness-of-fit parameter, although attempts to model the disorder were not successful.

A point of major interest is the cause of the structural difference between the hydrogenous and fully deuterated ammonium Cu(II) sulfate salts. It had been postulated that the increase in mass of the water ligands upon deuteration should cause the Jahn−Teller distortion of the $Cu(H_2O)_6^{2+}$ ion to expand slightly, and that this might underlie the phase difference.[9] However, recently it was shown that this supposition is incorrect.[20] In an experiment in which the salt was prepared using $H_2{}^{18}O$, which has the same ligand mass as D_2O, it was found to retain structure type **B** rather than switching to structure type **A**.[20] Further evidence for deuteration having no direct effect on the copper chromophore is obtained by comparing the Jahn−Teller radius ρ for different salts, defined as

$$\rho \approx (2\delta_x{}^2 + 2\delta_y{}^2 + 2\delta_z{}^2)^{1/2}$$

where δ_x, δ_y, and δ_z are the bond displacements from the mean value of the entire cluster. The current structure has a ρ of 0.336 Å, which is very similar to that for the hydrogenous ammonium salt at 1 bar and 9.5 K (0.333 Å)[20] and at ∼1.5 kbar and 15 K (0.324 Å),[7] demonstrating that deuteration has little influence on the Jahn−Teller radius when the same structure type is maintained. In the fully deuterated ammonium Cu(II) Tutton salt, and other salts adopting phase **A**, somewhat larger ρ values (0.369−0.390 Å) are observed.[9] The difference in Jahn−Teller radii for the two phases may possibly contribute to the behavior of the fully deuterated ammonium Cu salt under pressure: the reduction in Jahn−Teller radius as the pressure increases presumably tends to favor the phase associated with the smaller value of ρ.

Therefore, the cause of the structural difference between the hydrogenous and fully deuterated salts at 1 bar presumably lies in the intermolecular hydrogen-bonding interactions. These mediate the lattice perturbation experienced by the $Cu(H_2O)_6^{2+}$ ion, and it has been suggested that deuteration must change them to produce a Jahn−Teller potential surface with the tetragonal distortion to the O(7) atoms, rather than O(8) as in the hydrogenous salt.[7] On the basis of the so-called Ubbelohde effect,[22] one would expect slightly longer O···O hydrogen bond distances upon deuteration, and this might underlie the phase difference. Such an explanation would be consistent with the fact that the structure of the fully deuterated salt alters to that of the hydrogenous compound under pressure. However, previous tabulations indicate that this effect is only significant for hydrogen bonds of 2.65 Å or less,[23] whereas the hydrogen bonds in the Tutton salts are all greater than 2.65 Å, as seen in Table 4. Thus, it is not surprising that the hydrogen bonds from the X-ray study at ambient pressure and low temperature[20] are nearly identical to those in the present study of the partially deuterated salt under the same conditions. The present data therefore provide no clear structural trend to explain why deuteration induces a phase change for the ammonium Cu(II) Tutton salt.

The balance between the two structural motifs is clearly very delicate. The fact that a pressure of only 200 bar at 295 K can induce the phase change of the fully deuterated salt implies an energy difference of less than 0.1 kJ per formula unit.[9] The driving force for the phase change may involve a number of factors, and any consideration of these is quite speculative. As already mentioned, one contributing factor may be the smaller Jahn−Teller distortion associated with phase **B**. It is also interesting to note that in phase **B**, that is the hydrogenous and partly deuterated compound, and fully deuterated salt under pressure, where Cu−O(8) is ∼2.0 Å, the shortest hydrogen bond is O(8)−H(17)···O(4). In the structure type **A** adopted by the fully deuterated salt at 1 bar, where Cu−O(8) increases to ∼2.3 Å, the O(8)−H(17)···O(4) also increases by ∼0.1 Å. This is consistent with a previous proposal that the more strongly bonded equatorial water molecules are then more strongly polarized, which leads to stronger hydrogen bonds than those with the axial water molecules.[24] If this is correct, then a very small decrease in the hydrogen bond contact to the axial water molecule with the elongated Cu−O bond readily produces an unfavorably short hydrogen bond, which is relieved by switching if that pathway is available. Investigations of the related chromium Tutton salt may provide additional information on this aspect, since a similar Jahn−Teller distortion is observed in this system, and in this case the hydrogenous and fully deuterated compounds both adopt phase **A**.[25]

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Supporting Information Available: Listing of anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Chen, Z.; Fei, S.; Strauss, H. L. *J. Am. Chem. Soc.* **1998**, *120*, 8789−8796.

(22) Robertson, J. M.; Ubbelohde, A. R. *Proc. R. Soc. London, Ser. A* **1939**, *170*, 222.

(23) Jeffery, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997; pp 123−128.

(24) Beagley, B.; Eriksson, A.; Lindgren, J.; Persson, I.; Pettersson, L. G. M.; Sandstrom, M.; Wahlgren, U.; White, E. W. *J. Phys.: Condens. Matter* **1989**, *1*, 2395−2408.

(25) Figgis, B. N.; Kucharski, E. S.; Reynolds, P. A. *Acta Crystallogr. C* **1991**, *47*, 419.