

## Single-crystal neutron-diffraction study of 3.4% Zn-doped $(\text{ND}_4)_2\text{-}[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$ at 20 K

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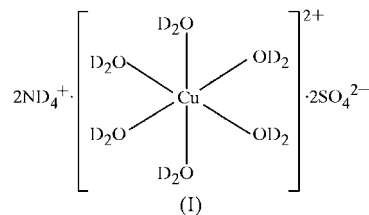
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Doping the perdeuterated ammonium copper Tutton salt  $(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$  [perdeuterated diammonium hexa-aquacopper(II) bis(sulfate)] with Zn leads to a change in the structure from dimorph *A* (low density) to dimorph *B* (high density). This change, which accompanies a switch in the direction of the Jahn–Teller distortion, had previously been observed to occur with substitution of  $\text{Zn}^{2+}$  at the  $\text{Cu}^{2+}$  site of between 1.3 (*A*) and 3.4% (*B*). In this study, the single-crystal neutron-diffraction analysis of  $(\text{ND}_4)_2[(\text{Cu}/\text{Zn})(\text{D}_2\text{O})_6](\text{SO}_4)_2$  at 20 K, with 3.4% Zn doping and a deuterium substitution of 85% on the H-atom sites, reveals that the structure is entirely of type *B*, with the Cu/Zn site at an inversion centre and with no evidence of disorder or unusual atomic displacement parameters that might occur near a phase transition boundary.

### Comment

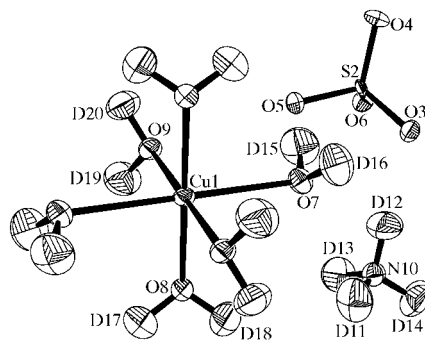
The crystal structure of the ammonium copper Tutton salt is very sensitive to small perturbations, which lead to one of two possible packing motifs or dimorphs (Hathaway & Hewat, 1984; Simmons *et al.*, 1993; Schultz *et al.*, 1997, 2003; Hitchman *et al.*, 1999). At room temperature and pressure,  $(\text{NH}_4)_2\text{-}[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$  adopts structure *B* (high density), whereas the perdeuterated salt  $(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$  is isostructural with the alkali metal salts  $\text{A}_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$  (*A* = K, Rb and Cs), which adopt structure *A* (low density). The difference between the two structural forms is due primarily to the direction of the Jahn–Teller distortion, in which Cu–O8 is elongated in form *A* and Cu–O7 is elongated in form *B* (see Fig. 1 for atom labels). There are accompanying changes in the hydrogen-bonding network in the crystal structure, which also result in slight contractions of the *a* and *b* axes and an increase of the *c* axis of crystal lattice *A* relative to *B*.



The application of mild hydrostatic pressure ( $\sim 200$  bar at 298 K) reversibly transforms fully deuterated  $(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$  from the *A* to the *B* form (Simmons *et al.*, 1993; Schultz *et al.*, 1997, 2003). From EPR (electron paramagnetic resonance) analyses, the structure was found to change abruptly from that of the pure hydrogenous salt (*B*) to that of the fully deuterated salt (*A*) at  $\sim 50\%$  deuteration with no evidence of an intermediate phase (Henning *et al.*, 2000). This result was confirmed with single-crystal neutron diffraction data obtained at 20 K from a crystal with 42% deuteration, which exhibited the fully hydrogenated structure *B* (Henning *et al.*, 2000) without any evidence of disorder.

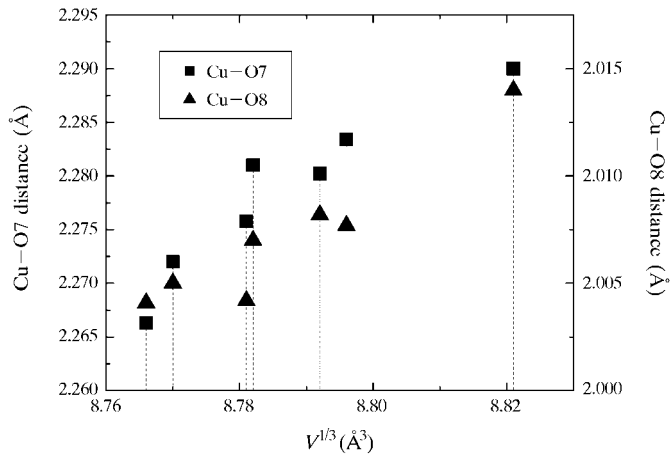
The hydrogenated chromium Tutton salt switches from form *A* to *B* with a few percent Zn substitution on the chromium site (Araya *et al.*, 1993), as does the deuterated copper salt (Simmons *et al.*, 2000). From the X-ray data analyses at room temperature, it was shown that the switch from form *A* to *B* occurs somewhere between 1.3 and 3.4% Zn substitution on the Cu site.

In this study, we analyzed the single crystal neutron diffraction structure, at 20 K, of (I) with 3.4% Zn doping. From refinement of the neutron scattering length, the overall deuteration was 85.8 (4)%. As depicted in Fig. 1 and tabulated in Table 1, the structure has switched from the *A* form to the *B* form such that the Jahn–Teller distortion involves Cu1–O7 as the longest bond [2.2663 (17) Å] and Cu1–O8 as the intermediate bond [2.0041 (17) Å]. At room temperature, the structure of (I) exhibits long, intermediate and short Cu–O bond lengths [2.177 (3), 2.098 (3) and 1.965 (2) Å, respectively], apparently as a result of thermal equilibrium between forms *A* and *B*. Examination of the atomic displacement parameters of (I) at 20 K provides no evidence for disorder, similar to the observation of the 42% deuterated ammonium



**Figure 1**

The neutron structure of (I) at 20 K, showing displacement ellipsoids drawn at the 90% probability level.



**Figure 2**  
Plot of Cu—O7 and Cu—O8 distances versus the cube root of the unit-cell volume for ammonium copper Tutton salts with structure *B*. The vertical lines correspond to structures (I)–(VII) from left to right.

copper structure [(V) in Table 2]. This situation is in contrast to the neutron structure of  $(\text{NH}_4)_2[\text{Cr}_{0.22}\text{Zn}_{0.78}(\text{H}_2\text{O})_6](\text{SO}_4)_2$  at 15 K, which clearly indicated the presence of disorder in the aqua ligands affected by the chromium Jahn–Teller distortion (Cotton *et al.*, 1994).

Hydrogen-bond distances and angles are listed in Table 2. This network of hydrogen bonds is entirely consistent with those observed for other structural determinations of ammonium copper Tutton salts with structure type *B* (Simmons *et al.*, 1993; Figgis *et al.*, 2000; Henning *et al.*, 2000; Dobe *et al.*, 2003).

Table 3 lists Cu—O bond distances for seven low-temperature structures of ammonium copper Tutton salt with form *B*. Examination of Table 3 indicates that there is no systematic variation with pressure or H/D substitution. However, as shown in Fig. 2, the bond distances for all of the structures appear to scale with the lattice constants.

### Experimental

Crystals of (I) were prepared by mixing a molar ratio of 2%  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with 98%  $\text{CuSO}_4$  in the manner described by Simmons *et al.* (2000). The resulting sample was recrystallized three times from 99.8%  $\text{D}_2\text{O}$ . The actual Zn/Cu ratio (3.4% Zn) was determined by analysis using a Varian SpectraAA-800 atomic absorption spectrometer.

**Table 3**  
Comparison of Cu—O bond lengths and other parameters of form *B* at low temperature.

Structure	Radiation	<i>T</i> (K)	<i>P</i> (MPa)	<i>D</i> (%)	Cu—O7 ( $\text{\AA}$ )	Cu—O8 ( $\text{\AA}$ )	Cu—O9 ( $\text{\AA}$ )	<i>V</i> ( $\text{\AA}^3$ )	$\rho^g$ ( $\text{\AA}$ )
(I) <sup>a</sup> , 3.4% Zn	N	20	0	85.8 (4)	2.2663 (17)	2.0041 (17)	1.9774 (17)	673.6 (2)	0.319
(II) <sup>b</sup>	N	14	140	0	2.272 (2)	2.005 (2)	1.979 (2)	674.5 (2)	0.324
(III) <sup>c</sup>	X	9.5	0.1	0	2.2758 (9)	2.0042 (8)	1.9737 (9)	677.07 (12)	0.333
(IV) <sup>d</sup> , metastable	N	15	0.1	100 <sup>f</sup>	2.2802 (4)	2.0082 (4)	1.9781 (4)	679.52 (8)	0.333
(V) <sup>e</sup>	N	15	0	42 (2)	2.281 (1)	2.007 (1)	1.975 (1)	677.2 (5)	0.336
(VI) <sup>d</sup>	N	15	0	0	2.2834 (5)	2.0077 (5)	1.9792 (5)	680.44 (11)	0.336
(VII) <sup>b</sup>	N	15	150	100 <sup>f</sup>	2.290 (2)	2.014 (2)	1.988 (3)	686.4 (2)	0.335

Notes: (a) this work; (b) Simmons *et al.* (1993); (c) Figgis *et al.* (2000); (d) Dobe *et al.* (2003); (e) Henning *et al.* (2000); (f) nominal value, not refined; (g) Jahn–Teller radius  $\rho = [2\Sigma(\Delta d_i)^2]^{1/2}$ , where  $\Delta d_i = d_i - d_{\text{mean}}$ .

### Crystal data

$(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$   
 $M_r = 417.13$   
 Monoclinic,  $P2_1/a$   
 $a = 9.0806$  (17)  $\text{\AA}$   
 $b = 12.1903$  (17)  $\text{\AA}$   
 $c = 6.3424$  (12)  $\text{\AA}$   
 $\beta = 106.379$  (16) $^\circ$   
 $V = 673.6$  (2)  $\text{\AA}^3$   
 $Z = 2$   
 $D_x = 2.057$   $\text{Mg m}^{-3}$

White-beam radiation  
 $\lambda = 0.7\text{--}4.2$   $\text{\AA}$   
 Cell parameters from 2615 reflections  
 $\mu = 0.86 + 0.188\lambda$   $\text{cm}^{-1}$   
 $T = 20$  (2) K  
 Prism, blue  
 $2.5 \times 2.5 \times 2.5$  mm

### Data collection

IPNS single-crystal diffractometer  
 Time-of-flight Laue analysis  
 Absorption correction: Gaussian  
 (IPNS ANVRED; local program)  
 $T_{\text{min}} = 0.698$ ,  $T_{\text{max}} = 0.797$   
 2162 measured reflections  
 1636 independent reflections

1499 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.066$   
 $h = -12 \rightarrow 12$   
 $k = -17 \rightarrow 5$   
 $l = -2 \rightarrow 9$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.089$   
 $S = 1.17$   
 1636 reflections  
 179 parameters

$w = 1/[\sigma^2(F_o^2) + 6.3927P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.008$   
 $\Delta\rho_{\text{max}} = 0.94$   $\text{fm \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.93$   $\text{fm \AA}^{-3}$

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu1—O7	2.2663 (17)	Cu1—O9	1.9774 (17)
Cu1—O8	2.0041 (17)		
O9—Cu1—O8	88.74 (7)	O8—Cu1—O7	89.10 (7)
O9—Cu1—O7	90.67 (7)		

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N10—D11...O6 <sup>i</sup>	1.025 (3)	1.910 (3)	2.882 (2)	157.3 (2)
N10—D12...O3	1.019 (3)	2.010 (3)	2.972 (2)	156.5 (2)
N10—D13...O3 <sup>ii</sup>	1.024 (3)	1.871 (3)	2.886 (2)	170.7 (2)
N10—D14...O5 <sup>iii</sup>	1.022 (3)	1.820 (3)	2.837 (2)	173.0 (2)
O7—D15...O5	0.971 (3)	1.881 (3)	2.836 (3)	166.8 (3)
O7—D16...O6 <sup>iv</sup>	0.960 (3)	1.889 (3)	2.824 (3)	164.2 (2)
O8—D17...O4 <sup>v</sup>	0.985 (3)	1.684 (3)	2.669 (3)	179.1 (2)
O8—D18...O6 <sup>i</sup>	0.976 (3)	1.737 (3)	2.712 (2)	176.6 (3)
O9—D19...O5 <sup>vi</sup>	0.982 (3)	1.758 (3)	2.730 (3)	169.7 (2)
O9—D20...O3 <sup>vii</sup>	0.973 (3)	1.718 (3)	2.680 (2)	169.6 (3)

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$ ; (iv)  $x, y, z - 1$ ; (v)  $x - 1, y, z - 1$ ; (vi)  $-x, -y, -z + 1$ ; (vii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ .

Three-dimensional reciprocal-space histograms were measured using the IPNS SCD instrument (Schultz *et al.*, 1984). Indexing and integration were performed using *ISAW* (Chatterjee *et al.*, 2002). Initial atomic coordinates were taken from the known structure of other Tutton salts. Refinement was first performed using *GSAS* (Larson & Von Dreele, 2004), and then the extinction-corrected data were input to *SHELXL97* (Sheldrick, 1997) for final refinement. H atoms were refined anisotropically.

Data collection: IPNS SCD data acquisition system (Hammonds *et al.*, 2002); cell refinement: *LATCON* (local program); data reduction: *ANVRED* (local program); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2004) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1122). Services for accessing these data are described at the back of the journal.

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