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Bonding effects and the crystal structures of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ and its $H_2{}^{18}O$ substituted form at 9.5 K

Brian N. Figgis,[a]* Alexandre N. Sobolev,[a] Charles J. Simmons,[b] Michael A. Hitchman,[c] Horst Stratemeier[c] and Mark J. Riley[d]

[a]School of Chemistry, University of Western Australia, Nedlands, WA 6097, Australia, [b]Division of Natural Sciences, University of Hawaii at Hilo, Hawaii, 200 West Kawili Street, Hawaii 96720-4091, USA, [c]School of Chemistry, University of Tasmania, Box 252-75, Hobart, Tasmania 7001, Australia, and [d]Department of Chemistry, University of Queensland, St Lucia, Queensland 4072, Australia

Correspondence e-mail:
bnf@crystal.uwa.edu.au

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The crystal structures of the Tutton salts $(NH_4)_2$-$[Cu(H_2O)_6](SO_4)_2$, diammonium hexaaquacopper disulfate, formed with normal water and isotopically substituted $H_2{}^{18}O$, have been determined by X-ray diffraction at 9.5 K and are very similar, with Cu—O(7) the longest of the Cu—O bonds of the Jahn–Teller distorted octahedral $[Cu(H_2O)_6]^{2+}$ complex. It is known that structural differences accompany deuteration of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, the most dramatic of which is a switch to Cu—O(8) as the longest such bond. The present result suggests that the structural differences are associated with hydrogen-bonding effects rather than with increased mass of the water ligands affecting the Jahn–Teller coupling. The Jahn–Teller distortions and hydrogen-bonding contacts in the compounds are compared with those reported for other Tutton salts at ambient and high pressure.

1. Introduction

The Jahn–Teller theorem provides the basic framework within which the stereochemistry and spectroscopic properties of a number of Cu^{2+} complexes are interpreted (Hathaway, 1984; Reinen & Atanasov, 1991). Interest in this area has recently increased with the suggestion that Jahn–Teller coupling may play a role in the mechanism underlying the behaviour of high-temperature superconductors (Fil *et al.*, 1992, and references therein; Reinen *et al.*, 1995). An unusual feature of copper(II) stereochemistry is the fact that the geometry and electronic structure of many complexes vary as a function of temperature and/or pressure (Simmons, 1993; Hitchman, 1994). These characteristics are particularly well developed in the copper(II) Tutton salts of the general formula $M_2{}^{I}[Cu(H_2O)_6](SO_4)_2$. The fluxional behaviour of the $[Cu(H_2O)_6]^{2+}$ group present when Cu^{2+} is doped into the zinc(II) Tutton salts formed with a range of cations has been studied by EPR spectroscopy (Silver & Getz, 1974; Riley *et al.*, 1987). Similar dynamic behaviour occurs for undiluted $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ and its deuterated analogue (Alcock *et al.*, 1984; Hathaway & Hewat, 1984), although there the temperature dependence of the crystal structure and EPR spectrum suggest that significant cooperative interactions occur (Hitchman *et al.*, 1999).

The ammonium copper(II) Tutton salt is especially interesting because it exists in two distinct forms. Upon deuteration it adopts a structure (form *A*), in which the long axis of the distorted $Cu(D_2O)_6{}^{2+}$ cation is directed to the pair of O(8) water molecules, whereas in the hydrogenous salt (form *B*) this direction is to the O(7) waters. This change in direction is accompanied by slight alterations in the dispositions of, and hydrogen-bonding interactions with, the ammonium and

Table 1
Experimental details.

Crystal data		
Chemical formula	$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$	$(NH_4)_2[Cu(H_2{}^{18}O)_6](SO_4)_2$
Chemical formula weight	399.84	411.84
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a (Å)	9.0964 (9)	9.0921 (6)
b (Å)	12.2225 (11)	12.2195 (8)
c (Å)	6.3447 (7)	6.3442 (5)
β (°)	106.295 (7)	106.277 (5)
V (Å^3)	677.07 (12)	676.59 (8)
Z	2	2
D_x (Mg m^{-3})	1.961	2.022
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	12	12
θ range (°)	20.75–23.35	20.79–23.41
μ (mm^{-1})	1.994	1.995
Temperature (K)	9.5 (2)	9.5 (2)
Crystal form	Plate	Prism
Crystal size (mm)	0.57 × 0.50 × 0.20	0.70 × 0.53 × 0.40
Crystal colour	Light blue	Light blue
Data collection		
Diffractometer	Huber 512	Huber 512
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	Gaussian	Gaussian
$T_{\min}$	0.3363	0.4047
$T_{\max}$	0.7129	0.5170
No. of measured reflections	4295	4102
No. of independent reflections	1988	1986
No. of observed reflections	1930	1949
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0389	0.0127
$\theta_{\max}$ (°)	30.07	30.07
Range of h, k, l	$-12 \rightarrow h \rightarrow 12$ $-17 \rightarrow k \rightarrow 17$ $0 \rightarrow l \rightarrow 8$	$0 \rightarrow h \rightarrow 12$ $-17 \rightarrow k \rightarrow 17$ $-8 \rightarrow l \rightarrow 8$
No. of standard reflections	3	3
Frequency of standard reflections	Every 100 reflections	Every 100 reflections
Intensity decay (%)	0.5	0.5
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0213	0.0199
$wR(F^2)$	0.0597	0.0540
S	1.122	1.184
No. of reflections used in refinement	1988	1986
No. of parameters used	129	129
H-atom treatment	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0310P)^2 + 0.2280P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 0.3880P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.001	<0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.652	0.490
$\Delta\rho_{\min}$ (e Å^{-3})	−0.665	−0.460
Extinction method	*SHELX*97 (Sheldrick, 1997)	*SHELX*97 (Sheldrick, 1997)
Extinction coefficient	0.0162 (18)	0.050 (2)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	Local diffractometer control software	Local diffractometer control software
Cell refinement	Local diffractometer control software	Local diffractometer control software
Data reduction	*PROFIT* (Streltsov & Zavodnik, 1989)	*PROFIT* (Streltsov & Zavodnik, 1989)
Structure solution	*SHELX*97 (Sheldrick, 1997)	*SHELX*97 (Sheldrick, 1997)
Structure refinement	*SHELX*97 (Sheldrick, 1997)	*SHELX*97 (Sheldrick, 1997)
Preparation of material for publication	*SHELX*97 (Sheldrick, 1997)	*SHELX*97 (Sheldrick, 1997)

sulfate ions (Alcock *et al.*, 1984; Simmons *et al.*, 1993). However, upon raising the pressure from ambient to 150 MPa (1.5 kbar) at 15 K, the deuterated compound switches to form *B* (Simmons *et al.*, 1993). This change exhibits hysteresis when the pressure is decreased (Schultz *et al.*, 1997). The deuterated compound, form *A*, has been the subject of charge-density analyses at 85 K (Figgis *et al.*, 1992) and 9 K (Figgis *et al.*, 1993).

A major point of interest is the origin of the structural difference between the hydrogenous and deuterated salts and the reason for the change in the latter at high pressure. One possibility is that deuteration affects the hydrogen bonding interactions in the lattice through its lower zero-point vibrational energy, and that this changes the relative energies of the two orientations of the $[Cu(H_2O)_6]^{2+}$ group by altering the lattice strain interactions acting upon the copper(II) complex ion (Simmons *et al.*, 1993). An alternative suggestion is that deuteration affects the structure through its effect on the mass of the H_2O ligand, because the Jahn–Teller distortion depends on coupling with a vibration. The ligand mass might influence the Jahn–Teller coupling constant and thus the geometry of a Cu^{2+} complex, and this could underlie the structural difference (Rauw *et al.*, 1996).

To investigate these possibilities we prepared samples of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ using normal water and $H_2{}^{18}O$, and report here their crystal structures determined accurately at 9.5 K. If the change in form is due to the change in mass of the ligand, then a similar structural switch to that observed on deuteration should occur in the ^{18}O complex. The fact that the

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(a) $(NH_4)_2[(Cu(H_2O)_6](SO_4)_2$				
Cu	0	0	0	0.00280 (8)
S1	0.41985 (3)	0.13459 (2)	0.74317 (4)	0.00309 (8)
O3	0.42991 (9)	0.22753 (7)	0.59587 (14)	0.00541 (15)
O4	0.55809 (9)	0.06696 (7)	0.78323 (14)	0.00638 (16)
O5	0.28391 (9)	0.06777 (6)	0.63161 (13)	0.00535 (16)
O6	0.40174 (9)	0.17903 (7)	0.95209 (14)	0.00577 (15)
O7	0.18660 (10)	0.11856 (7)	0.17780 (15)	0.00650 (16)
O8	−0.15738 (9)	0.10924 (7)	0.02938 (14)	0.00562 (16)
O9	−0.00600 (9)	−0.06422 (7)	0.28289 (14)	0.00563 (15)
N1	0.14204 (11)	0.34170 (8)	0.35777 (17)	0.00646 (18)
H11	0.085 (2)	0.3280 (17)	0.227 (4)	0.011 (4)
H12	0.221 (2)	0.3020 (19)	0.391 (4)	0.018 (5)
H13	0.087 (2)	0.3260 (19)	0.443 (4)	0.018 (5)
H14	0.167 (3)	0.414 (2)	0.377 (4)	0.024 (5)
H15	0.220 (2)	0.0935 (19)	0.305 (4)	0.019 (5)
H16	0.244 (3)	0.1235 (19)	0.118 (4)	0.023 (6)
H17	−0.239 (3)	0.095 (2)	−0.051 (4)	0.024 (5)
H18	−0.136 (2)	0.1668 (19)	0.003 (4)	0.016 (5)
H19	−0.084 (3)	−0.055 (2)	0.309 (4)	0.024 (5)
H20	0.018 (3)	−0.128 (2)	0.313 (4)	0.023 (5)
(b) $(NH_4)_2[Cu(H_2{}^{18}O)_6](SO_4)_2$				
Cu	0	0	0	0.00300 (8)
S1	0.41999 (3)	0.13461 (2)	0.74317 (4)	0.00333 (8)
O3	0.43010 (9)	0.22763 (7)	0.59597 (13)	0.00560 (15)
O4	0.55825 (9)	0.06705 (7)	0.78309 (14)	0.00667 (16)
O5	0.28403 (9)	0.06783 (6)	0.63190 (13)	0.00544 (16)
O6	0.40192 (9)	0.17916 (7)	0.95197 (13)	0.00589 (15)
O7	0.18678 (10)	0.11864 (7)	0.17781 (15)	0.00661 (16)
O8	−0.15725 (10)	0.10919 (7)	0.02927 (14)	0.00568 (16)
O9	−0.00620 (10)	−0.06428 (7)	0.28256 (14)	0.00572 (15)
N1	0.14189 (12)	0.34172 (8)	0.35758 (17)	0.00676 (18)
H11	0.088 (2)	0.3284 (17)	0.221 (3)	0.014 (4)
H12	0.215 (3)	0.2988 (19)	0.385 (3)	0.021 (5)
H13	0.081 (2)	0.3250 (18)	0.443 (3)	0.018 (5)
H14	0.162 (3)	0.414 (2)	0.367 (4)	0.026 (5)
H15	0.219 (2)	0.0963 (18)	0.299 (4)	0.019 (5)
H16	0.248 (2)	0.1212 (17)	0.124 (4)	0.016 (5)
H17	−0.238 (3)	0.0957 (19)	−0.047 (4)	0.020 (5)
H18	−0.139 (2)	0.1732 (19)	0.005 (3)	0.017 (5)
H19	−0.087 (3)	−0.057 (2)	0.313 (4)	0.029 (6)
H19	−0.087 (3)	−0.057 (2)	0.313 (4)	0.029 (6)

Table 3
Selected geometric parameters (Å^2, °).

(a) $(NH_4)_2[(Cu(H_2O)_6](SO_4)_2$			
Cu—O9^{i}	1.9737 (9)	O7—H15	0.83 (2)
Cu—O9	1.9737 (9)	O7—H16	0.73 (3)
Cu—O8^{i}	2.0042 (8)	O8—H17	0.79 (2)
Cu—O8	2.0042 (8)	O8—H18	0.76 (2)
Cu—O7	2.2758 (9)	O9—H19	0.78 (3)
Cu—O7^{i}	2.2758 (9)	O9—H20	0.81 (2)
S1—O4	1.4662 (8)	N1—H11	0.87 (2)
S1—O6	1.4839 (8)	N1—H12	0.84 (2)
S1—O5	1.4853 (8)	N1—H13	0.85 (2)
S1—O3	1.4900 (8)	N1—H14	0.91 (2)
O9^{i}—Cu—O9	180.00 (5)	O4—S1—O3	109.75 (5)
O9^{i}—Cu—O8^{i}	88.72 (4)	O6—S1—O3	108.85 (5)
O9—Cu—O8^{i}	91.28 (4)	O5—S1—O3	108.05 (5)
O9^{i}—Cu—O8	91.28 (4)	Cu—O7—H15	105.2 (15)
O9—Cu—O8	88.72 (4)	Cu—O7—H16	109.8 (18)
O8^{i}—Cu—O8	180.00 (6)	H15—O7—H16	114 (2)
O9^{i}—Cu—O7	89.45 (3)	Cu—O8—H17	111.0 (18)
O9—Cu—O7	90.55 (3)	Cu—O8—H18	111.2 (16)
O8^{i}—Cu—O7	91.00 (3)	H17—O8—H18	108 (2)
O8—Cu—O7	89.00 (3)	Cu—O9—H19	113.2 (18)
O9^{i}—Cu—O7^{i}	90.55 (3)	Cu—O9—H20	121.2 (17)
O9—Cu—O7^{i}	89.45 (3)	H19—O9—H20	107 (2)
O8^{i}—Cu—O7^{i}	89.00 (3)	H11—N1—H12	112 (2)
O8—Cu—O7^{i}	91.00 (3)	H11—N1—H13	105.5 (18)
O7—Cu—O7^{i}	180.00 (6)	H12—N1—H13	109 (2)
O4—S1—O6	110.87 (5)	H11—N1—H14	112 (2)
O4—S1—O5	109.36 (5)	H12—N1—H14	111 (2)
O6—S1—O5	109.92 (5)	H13—N1—H14	107 (2)
(b) $(NH_4)_2[Cu(H_2{}^{18}O)_6](SO_4)_2$			
Cu—O9	1.9724 (8)	O7—H15	0.79 (2)
Cu—O9^{i}	1.9724 (8)	O7—H16	0.73 (2)
Cu—O8	2.0019 (8)	O8—H17	0.78 (2)
Cu—O8^{i}	2.0019 (8)	O8—H18	0.82 (2)
Cu—O7^{i}	2.2769 (9)	O9—H19	0.82 (3)
Cu—O7	2.2769 (9)	O9—H20	0.83 (2)
S1—O4	1.4655 (8)	N1—H11	0.89 (2)
S1—O6	1.4832 (8)	N1—H12	0.82 (2)
S1—O5	1.4843 (8)	N1—H13	0.90 (2)
S1—O3	1.4902 (8)	N1—H14	0.90 (3)
O9—Cu—O9^{i}	180.00 (7)	O4—S1—O3	109.72 (5)
O9—Cu—O8	88.74 (3)	O6—S1—O3	108.75 (5)
O9^{i}—Cu—O8	91.26 (3)	O5—S1—O3	108.10 (5)
O9—Cu—O8^{i}	91.26 (3)	Cu—O7—H15	106.5 (16)
O9^{i}—Cu—O8^{i}	88.74 (3)	Cu—O7—H16	110.8 (17)
O8—Cu—O8^{i}	180.00 (5)	H15—O7—H16	110 (2)
O9—Cu—O7^{i}	89.39 (3)	Cu—O8—H17	112.2 (17)
O9^{i}—Cu—O7^{i}	90.61 (3)	Cu—O8—H18	115.3 (15)
O8—Cu—O7^{i}	91.00 (3)	H17—O8—H18	107 (2)
O8^{i}—Cu—O7^{i}	89.00 (3)	Cu—O9—H19	115.4 (17)
O9—Cu—O7	90.61 (3)	Cu—O9—H20	117.6 (16)
O9^{i}—Cu—O7	89.39 (3)	H19—O9—H20	104 (2)
O8—Cu—O7	89.00 (3)	H11—N1—H12	106.2 (19)
O8^{i}—Cu—O7	91.00 (3)	H11—N1—H13	106.6 (18)
O7^{i}—Cu—O7	180.00 (6)	H12—N1—H13	109 (2)
O4—S1—O6	110.90 (5)	H11—N1—H14	107.0 (19)
O4—S1—O5	109.40 (5)	H12—N1—H14	118 (2)
O6—S1—O5	109.91 (5)	H13—N1—H14	109 (2)

Symmetry code: (i) $1 - x, -y, -z$.

structures of the two samples are the same suggests that the ligand mass is not the driving force for the change in form, and that deuteration influences the structure *via* changes in the hydrogen-bonding interactions. Comparison of the structure of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ with those reported for this salt at high pressure and upon deuteration allow these aspects to be evaluated.

2. Experimental

2.1. Preparation of the compound

A finely ground sample of 0.3534 g of $(NH_4)_2$-$[Cu(H_2O)_6](SO_4)_2$ was dehydrated by heating in an oven at 390 K for 24 h; the weight loss (0.0951 g) indicated that all the water was removed. The anhydrous compound was dissolved in 1.0 ml of $H_2{}^{18}O$ (95% isotopic purity, obtained from Sigma Aldrich Co.) at a temperature of 355 K. On cooling to ∼290 K, pale blue crystals of $(NH_4)_2[Cu(H_2{}^{18}O)_6](SO_4)_2$ formed. The isotopic substitution was checked by determining the mass spectrum of water driven off from the sample on heating. Using a Kratos Concept ISQ mass spectrometer operating at 70 eV, the ^{18}O content was found to be > ∼90%.

Table 4
Independent metal–oxygen bond lengths and Jahn–Teller radii, ρ (Å), determined by low-temperature single-crystal X-ray or neutron diffraction for $(NH_4)_2[M(H_2O)_6](SO_4)_2$, M = Cu or Cr, under different pressures (P) and conditions of isotopic substitution .

Deuteration is specified by (ND_4) and substitution of the water by ^{18}O is specified by ($H_2{}^{18}O$).

	Form *B*				Form A		
	$(NH_4)Cu(H_2{}^{18}O)^{(a)}$	$(NH_4)Cu(H_2O)^{(a)}$	$(NH_4)Cu(H_2O)^{(b)}$	$(ND_4)Cu(D_2O)^{(b)}$	$(ND_4)Cu(D_2O)^{(b)}$	$(ND_4)Cr(D_2O)^{(c)}$	$(NH_4)Cr(H_2O)^{(d)}$
Method	X-ray	X-ray	Neutron	Neutron	Neutron	Neutron	X-ray
Temperature (K)	9.5	9.5	14	15	15	4.3	84
P (kPa)	100	100	140 000	150 000	100	100	100
M—O(7)	2.2769 (9)	2.2758 (8)	2.272 (2)	2.290 (2)	2.022 (2)	2.0802 (9)	2.0792(5)
M—O(8)	2.0019 (8)	2.0042 (8)	2.005 (2)	2.014 (2)	2.310 (2)	2.389 (1)	2.3889 (5)
M—O(9)	1.9724 (8)	1.9737 (9)	1.979 (2)	1.988 (3)	1.966 (3)	2.054 (1)	2.0532 (5)
ρ	0.336 (2)	0.333 (2)	0.324 (5)	0.335 (5)	0.369 (5)	0.373 (2)	0.374 (1)

References: (*a*) present work; (*b*) Simmons *et al.* (1993); (*c*) Figgis *et al.* (1991); (*d*) Figgis *et al.* (1990).

2.2. X-ray structure determination

A hemisphere of data was collected at the University of Western Australia on a crystal of each of the normal and the ^{18}O-substituted salts using a diffractometer with type 512 Huber circles and a DE-202 Displex refrigerator following the design of Larsen (1995). Mo $K\alpha$ radiation was employed. The collection procedures have been described elsewhere (Figgis *et al.*, 1993). Three standard reflections were collected after every 100 reflections. Data analysis was performed with the profile-fitting program *PROFIT* (Streltsov & Zavodnik, 1989). Initial models for the structures were taken from Figgis *et al.* (1992) and the refinements were carried out with *SHELX*97 (Sheldrick, 1997). Neutral atomic scattering factors were taken from *International Tables for Crystallography* (1992). The models were refined on data $F^2 > 2\sigma(F^2)$, minimizing the quantity $\Sigma w(F_{\rm obs}{}^2 - F_{\rm calc}{}^2)/\Sigma wF_{\rm obs}{}^2$, with $w = [\sigma^2(F_{\rm obs}{}^2) + (AP)^2 + BP]$, where $P = (F_{\rm obs}{}^2 + 2F_{\rm calc}{}^2)/3$, using the full matrix. Corrections for absorption and extinction [secondary, with $F_{\rm calc}{}^* = kF_{\rm calc}(1 + 0.001\chi F_{\rm calc}{}^2\lambda^3/\sin 2\theta)^{1/4}$, where χ is an extinction coefficient] were carried out. The values of R factors, $R = \Sigma||F_{\rm obs}| - |F_{\rm calc}||/\Sigma|F_{\rm obs}|$, goodness-of-fit parameters GOOF = $\{\Sigma[w(F_{\rm obs}{}^2 - F_{\rm calc}{}^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined; other coefficients are listed in Table 1.

3. Results and discussion

Fractional atomic coordinates and isotropic atomic displacement parameters are given in Table 2, and bond distances and angles in Table 3. Lists of observed and calculated structure factors, of the anisotropic displacement parameters, and hydrogen-bond distances have been deposited.[1] The $[Cu(OH_2)_6]^{2+}$ cation is shown in Fig. 1; the atomic numbering system is that used by Figgis *et al.* (1992).

From the copper–oxygen bond lengths it may be seen that the geometry and disposition of the $[Cu(H_2O)_6]^{2+}$ ions of the two isotopic forms are very similar and this also applies to the bond lengths and angles in general. The Cu—O bond lengths are compared with those observed for $(NH_4)_2$-$[Cu(H_2O)_6](SO_4)_2$ and the corresponding deuterated salt, both at ~15 K and ~ 150 MPa (1.5 kbar) pressure (Simmons *et al.*, 1993), in Table 4. For all these compounds the longest Cu—O bond is to O(7), a characteristic of form *B*. Also given are the Cu—O bond lengths reported for deuterated ammonium copper(II) sulfate at 15 K and ambient pressure (Simmons *et al.*, 1993), as well as the Cr—O bond lengths for the hydrogenous and deuterated forms of the analogous chromium(II) compound (Figgis *et al.*, 1990, 1991) measured at ambient pressure and very low temperature. For these latter compounds the longest bond occurs to O(8), which is characteristic of form *A*. The chromium(II) complexes are relevant because the $[Cr(H_2O)_6]^{2+}$ ion is subject to the same type of Jahn–Teller distortion as the copper(II) complex, but the ionic radius of Cr^{2+} is ~ 0.09 Å larger than that of Cu^{2+} (Shannon & Prewitt, 1969). Interestingly, both the hydrogenous and deuterated forms of the chromium(II) salt adopt the lower density form *A* structure type at ambient pressure, in marked contrast to the copper(II) salts where the hydrogenous compound adopts form *B*.

The fact that $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ does not switch to form *A* when the mass of water ligands is raised to 20 a.m.u.

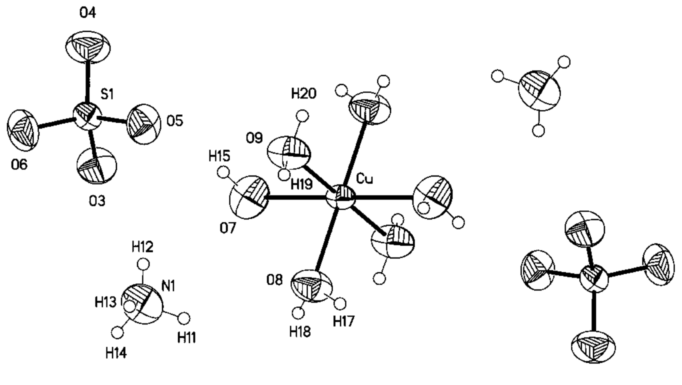

Figure 1
The $Cu(OH_2)_6{}^{2+}$, $NH_4{}^+$ and $SO_4{}^{2-}$ ions in $(NH_4)_2[Cu(OH_2)_6](SO_4)_2$ and its ^{18}O analogue, employing 99% probability thermal ellipsoids.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA0006). Services for accessing these data are described at the back of the journal.

Table 5
Hydrogen bonds for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (^{16}O 100 kPa) and $(NH_4)_2[Cu(H_2{}^{18}O)_6](SO_4)_2$ (^{18}O 100 kPa; Å and °).

Selected values are also shown for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ at 14 K and 140 MPa {H 140 MPa} and $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$ at 15 K and 100 kPa {D 100 kPa}[10]. For each entry: first row, ^{16}O 100 kPa; second row, ^{18}O 100 kPa.

	$^{16}O/^{18}O$ 100 kPa				H 140 MPa		D 100 kPa	
A—H···B	$d(A$—H)	d(H···B)	$d(A\cdots B)$	$<(AHB)$	$d(A\cdots B)$	d(H···B)	$d(A\cdots B)$	d(H···B)
N(1)—H(11)···O(6)$^{\rm i}$	0.87 (2)	2.05 (2)	2.883 (1)	162 (2)	2.872 (2)	1.906 (5)	2.907 (3)	1.881 (3)
	0.89 (2)	2.04 (2)	2.881 (1)	158 (2)				
N(1)—H(12)···O(3)	0.84 (2)	2.18 (2)	2.978 (1)	158 (2)	2.971 (2)	2.011 (5)	2.882 (3)	1.918 (3)
	0.82 (2)	2.22 (2)	2.979 (1)	154 (2)				
N(1)—H(13)···O(3)$^{\rm ii}$	0.85 (2)	2.05 (2)	2.891 (1)	169 (2)	2.885 (2)	1.870 (3)	–	–
	0.90 (2)	2.00 (2)	2.889 (1)	171 (2)				
N(1)—H(13)···O(4)	–	–	–	–	–	–	2.911 (4)	1.890 (5)
	–	–	–	–				
N(1)—H(14)···O(5)$^{\rm iii}$	0.91 (2)	1.94 (2)	2.840 (1)	171 (2)	2.846 (2)	1.811 (4)	2.865 (3)	1.869 (3)
	0.90 (3)	1.94 (3)	2.840 (1)	175 (2)				
O(7)—H(15)···O(5)	0.83 (2)	2.02 (2)	2.834 (1)	166 (2)	2.831 (3)	1.881 (4)	2.754 (4)	1.772 (4)
	0.79 (2)	2.06 (2)	2.835 (1)	168 (2)				
O(7)—H(16)···O(6)$^{\rm iv}$	0.73 (3)	2.12 (3)	2.828 (1)	166 (2)	2.827 (2)	1.879 (3)	2.791 (4)	1.813 (4)
	0.73 (2)	2.12 (2)	2.828 (1)	162 (2)				
O(8)—H(17)···O(4)$^{\rm v}$	0.79 (2)	1.88 (2)	2.672 (1)	174 (2)	2.658 (3)	1.675 (4)	2.791 (3)	1.821 (3)
	0.78 (2)	1.90 (2)	2.670 (1)	176 (2)				
O(8)—H(18)···O(6)$^{\rm i}$	0.76 (2)	1.96 (2)	2.716 (1)	173 (2)	2.722 (2)	1.734 (3)	2.839 (3)	1.866 (4)
	0.82 (2)	1.89 (2)	2.714 (1)	179 (2)				
O(9)—H(19)···O(5)$^{\rm vi}$	0.78 (3)	1.97 (3)	2.731 (11)	167 (2)	2.727 (2)	1.760 (3)	2.736 (3)	1.743 (4)
	0.82 (3)	1.92 (3)	2.729 (1)	169 (2)				
O(9)—H(20)···O(3)$^{\rm vii}$	0.81 (2)	1.88 (3)	2.693 (1)	175 (2)	2.690 (2)	1.718 (4)	2.690 (3)	1.720 (3)
	0.83 (2)	1.87 (2)	2.691 (1)	168 (2)				

† 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) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+1$.

using $H_2{}^{18}O$ implies that the $B \rightarrow A$ structural change which occurs on deuteration is not caused by the increase in ligand mass. It was suggested that such an increase should cause the Jahn–Teller radius of the $Cu(H_2O)_6{}^{2+}$ ion to expand slightly and that this might underlie the form change (Rauw *et al.*, 1996). This proposal is invalid, however, because although the coordinates used to describe the potential energy surface in dimensionless units (as presented by Rauw *et al.*, 1996) are dependent on mass, when these are transformed to dimensioned units they become independent of mass. While the isotope mass influences the kinetic energy of the system, it has only a very small effect upon its potential energy and the effect on bond lengths is expected to be many orders of magnitude less than that considered here (Van Vleck, 1936; Cencek *et al.*, 1998). To a good approximation, therefore, the ligand mass is not expected to influence the size of the Jahn–Teller distortion.

The Jahn–Teller radius, ρ, of a distorted six-coordinate copper(II) complex is defined in (1)

$$\rho = (2\delta x^2 + 2\delta y^2 + 2\delta z^2)^{1/2}, \tag{1}$$

where δx, δy and δz are the differences in each independent Cu—O bond length from its mean value. The values of ρ for the various hexahydrate complexes are listed in Table 4. Here, the uncertainties represent the maximum difference in ρ which would result from changes in the bond lengths equal to their standard deviations. It may be seen that substitution of normal water by $H_2{}^{18}O$ causes no significant change in the Jahn–Teller radius, confirming that ligand mass has no influence on this parameter. Increasing the pressure to 140 MPa (1.4 kbar) causes ρ to contract slightly as a result of a slight decrease in the longest Cu—O bond. Interestingly, the *average* Cu—O distance does not alter significantly.

Although ρ is insensitive to isotopic substitution, the average value in form A [0.377 (3) Å] is significantly larger than that in form B [0.332 (2) Å]. This is a trend which is independent of pressure or whether the metal ion is Cu^{2+} or Cr^{2+} and includes the copper(II) Tutton salts with alkali metals as the counter ions, where the Cu—O bonds have the arrangement of form A. There, neutron diffraction studies have shown that ρ is 0.39 (2) Å in the potassium salt at 14 K and 140 MPa (1.4 kbar; Rauw *et al.*, 1996) and 0.379 (1) Å in the rubidium compound at 77 K and ambient pressure (Smith *et al.*, 1975). It thus appears that the lattice interactions in form B favour not only a different O atom for the long bond of the Jahn–Teller distortion, but also a smaller overall distortion from a regular octahedral geometry compared with form A. The average Cu—O bond length is also somewhat smaller in form B, by ~0.011 Å for the Cu^{2+} complexes listed in Table 4, also including the potassium (Rauw *et al.*, 1996) and rubidium (Smith *et al.*, 1975) salts. This is mainly due to a significant contraction of ~0.036 Å in the longest Cu—O bond in form B compared with form A. The smaller volume occupied by the $[Cu(D_2O)_6]^{2+}$ ion in phase B may be one reason why the deuterated copper(II) salt switches to this structure type at high pressure.

It thus appears likely that the structural difference between hydrogenous and deuterated $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ at ambient pressure and very low temperature is due to the influence of the mass of the H atoms on the hydrogen-bonding interactions, possibly through the change in zero-point vibrational energy. The hydrogen-bonding contacts observed for the hydrogenous salt formed using normal water and $H_2{}^{18}O$ are shown in Table 5 and, as expected, these are identical to within approximate experimental uncertainty. The contacts observed for the deuterated salt at ambient pressure (Simmons *et al.*, 1993) are also shown and indicate that the slightly different orientations of the ammonium and sulfate ions in the two forms cause the the hydrogen bond from H(13) to O(3) in form *B* to be replaced by one to O(4) in form *A*. Interestingly, however, the hydrogen-bonding contacts involving the water ligands are relatively unaffected by deuteration at ambient pressure, despite the large difference in the Cu—O(7) and Cu—O(8) bond lengths between the two structures.

Increasing the pressure on $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ to 140 MPa (1.4 kbar) causes no form change (Simmons *et al.*, 1993) and the contacts shown in Table 5 indicate that pressure also has comparatively little effect on the overall distance between the water O atoms and the sulfate O atoms to which they are hydrogen bonded. The actual hydrogen-bond H···O distances shorten somewhat at high pressure, although the effect is small and involves comparison between X-ray and neutron diffraction structure determinations. However, it has been demonstrated that at the very low temperatures involved the two techniques produce atomic positional and displacement parameters almost identical within the errors for several transition metal complexes, including Tutton salts (Figgis *et al.*, 1993; Iversen *et al.*, 1996; Figgis *et al.*, 1998).

The hydrogen bonding contacts to O(8) show a particularly large change, and are considerably shorter than those to O(7) in form *B*. The sensitivity of these interactions to pressure may perhaps be relevant to the form change observed for the deuterated salt, since the long axis of the Jahn–Teller distortion which occurs to O(8) in the low-pressure form *A* switches to O(7) in form *B* at 150 MPa (1.5 kbar; Simmons *et al.*, 1993).

4. Conclusions

The long Cu—O bond in ammonium copper Tutton salts at very low temperatures switches from Cu—O(7) to Cu—O(8) on deuteration of the water molecules, but not on substitution for the water molecules of ^{18}O for ^{16}O. Combined with the fact that the deuterated compound switches back to Cu—O(7) being long at high pressure, this observation suggests that the structural differences involved are determined by the influence of the hydrogen-bonding interactions, not by the mass of the water ligands affecting the Jahn–Teller coupling constant for the $[Cu(OH_2)_6]^{2+}$ ion.

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