Single-Crystal Neutron Diffraction Study of Diammonium Hexaaquacopper Disulfate at 15 and 293 K. Investigation of Anharmonic Thermal Motion

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Iversen, B. B., Larsen, F. K., Reynolds, P. A. and Figgis, B. N., 1994. Single-Crystal Neutron Diffraction Study of Diammonium Hexaaquacopper Disulfate at 15 and 293 K. Investigation of Anharmonic Thermal Motion. – Acta Chem. Scand. 48: 800–809 © Acta Chemica Scandinavica 1994.

Crystal data: $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$, $M_r = 419.96$, monoclinic, $P2_1/a$. 15 K: $a = 9.386(3)$, $b = 12.647(7)$, $c = 6.055(2)$ Å, $\beta = 107.17(3)°$, $V = 686.8(5)$ Å^3, $Z = 2$, $D_n = 2.031(2)$ g cm^{-3}, neutron $\lambda = 1.013$ Å, $\mu = 0.39$ cm^{-1}, $F(000) = 44.270 \times 10^{-14}$ m (87.8%$_o$ deuterated), $T = 15.0(5)$ K, $R_F = 0.018$, $R_F^2 = 0.018$ for 1457 unique reflections at 0 σ level. 293 K: $a = 9.302(4)$, $b = 12.519(9)$, $c = 6.188(3)$ Å, $\beta = 106.46(4)°$, $V = 691.07$ Å^3, $D_n = 2.018$ g cm^{-3}, $R_F = 0.029$, $R_F^2 = 0.043$ for 1585 unique reflections at 3 σ level.

Single-crystal neutron diffraction studies of copper Tutton salt at 15 and 293 K are reported. The Cu^{2+} ion of the structure has a strongly Jahn–Teller distorted octahedral surrounding of water molecules. It is shown that at temperatures near absolute zero the atomic potentials become close to harmonic, whereas at room temperature the ammonium ion, especially, exhibits considerable anharmonic motion. Anharmonicity is also found at two of the sulfate oxygen positions. This anharmonicity is related to the switching of the Jahn–Teller minima when going from the deuterated to the hydrated structure. Earlier studies show that within some approximation the CuO_6 chromophore can be thought of as a fluxional system increasingly populating higher-energy minima with increasing temperature, leading to an apparent strong temperature dependence for the Cu–O bond lengths. Assuming the fluxional model, a value of $\Delta E = 224 \pm 16$ cm^{-1} between the two lowest minima is calculated from the diffraction measurements at 15 and 293 K.

The diammonium hexaaquametal disulfate salts are excellent compounds for the study of metal–water bonding as well as hydrogen bonding. The copper complex, especially, has attracted considerable attention. This is because the Cu–O$_6$ chromophore shows a strong Jahn–Teller distortion (Fig. 1) with a temperature-dependent geometry of fluxional behaviour.[1] The Cu^{2+} ion is located on a center of inversion, and for the $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ compound at 293 K,[2] Cu–O7 = 2.228(2) Å, Cu–O8 = 2.078(2) Å and Cu–O9 = 1.968(2) Å. Furthermore, the Jahn–Teller distortion of the copper–oxygen system has an interesting isotope effect.[3] Deuteration of the compound leads to a switch in the long axis of the distorted $Cu(D_2O)_6^{2+}$ octahedron; Cu–O7 = 2.081(6) Å, Cu–O8 = 2.242(7) Å and Cu–O9 = 1.927(6) Å. Very recently it has been shown that this
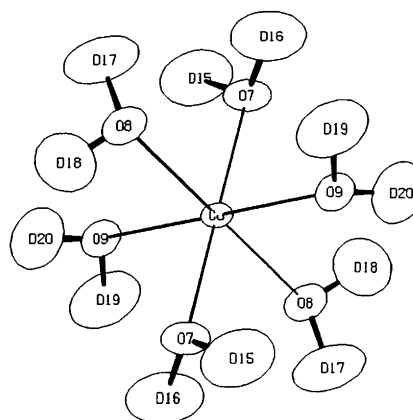

Fig. 1. ORTEP[23] drawing of the CuO$_6$ chromophore at 15 K showing the atom-numbering scheme and 50% ellipsoids.

switch may be triggered by increasing the hydrostatic pressure on the deuterated sample.[4]

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In an earlier paper we presented a combined X–N study of the electron density distribution of $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ at 9 K.[5] In that paper it was shown that quenching of anharmonic thermal motion and reduction in thermal diffuse scattering (TDS) is essential in order to extract high-resolution electron density distributions. Results of the present neutron diffraction study were used in developing the model for analyzing the 9 K X-ray diffraction data. Positions and thermal parameters for deuterium atoms of the neutron study were used, and by introducing extra radial flexibility for the nitrogen and oxygen atoms, thermal parameters determined by the parallel studies agreed closely. The 9 K study was originally initiated because certain features in an 85 K X-ray study of the same compound were not well resolved.[6] This had been suggested to be due to anharmonic motion at the copper site, but correlation with electron deformation parameters had made the 85 K study indecisive in this respect.

In the present paper we examine in more detail the fluxional and anharmonic behaviour of the structure based on comparisons of the results of refinements of 15 and 293 K single-crystal neutron diffraction measurements. We find the temperature dependence of the $Cu(D_2O)_6$ geometry to be $Cu-O7 = 2.007(21)$ Å, $Cu-O8 = 2.298(7)$ Å, $Cu-O9 = 1.959(3)$ Å at 15 K and $Cu-O7 = 2.090(30)$ Å, $Cu-O8 = 2.227(7)$ Å, $Cu-O9 = 1.958(1)$ Å at 293 K. Using anharmonic expansions of the atomic thermal parameters we show that a competition between two oxygen atoms (O3 and O4) for es-

tablishing a hydrogen bond can lead to considerable anharmonic motion of the atoms involved. Contrary to expectation we do not find significant anharmonic parameters for the copper atom either at 15 K or even at 293 K and, even though considerable ammonium ion libration is observed at room temperature, the structure is described well. The diffraction measurements at two different temperatures allow us to estimate the energy difference between the two lowest Jahn–Teller energy minima.

Experimental

In Table 1 experimental details of the study are listed. The considerable and markedly anisotropic changes in lattice parameters with temperature caused the first crystal to fracture during fairly rapid cooling from 293 to 15 K in 1.5 h. Consequently a second crystal was allowed to cool more slowly to 15 K during a period of 10 h. It was mounted on the cold station of the Displex *in vacuo* in order to prevent frosting. The crystal was wrapped in aluminium foil to reduce loss of water of hydration during initial pump-down at room temperature.

Scaled squared structure-factor amplitudes and their variances were estimated by the profile analysis program COLL5N.[7] The amplitudes were corrected for absorption and incoherent scattering using a Gaussian integration approximation[8] in the program DATAP.[9] The hydrogen content was determined by full-matrix least-squares structural refinements, including the deuterium scattering lengths as fitting parameters. The deuterium percentage

Table 1. Experimental data for $(ND_4)_2Cu(SO_4)_4 \cdot 6D_2O$.

Unit cell	Monoclinic, $P2_1/a$, $Z = 2$. 15 K: $a = 9.386(3)$, $b = 12.647(7)$, $c = 6.055(2)$ Å, $\beta = 107.17(3)°$ 293 K: $a = 9.302(4)$, $b = 12.519(9)$, $c = 6.188(3)$ Å, $\beta = 106.46(4)°$
Crystal preparation	Recrystallization of the protonated compound in D_2O. Deuteration: 15 K crystal 88%, 293 K crystal 89%.
Crystal dimensions	15 K: Rectangular crystal bounded by faces $\pm(110)$ (2 mm between planes), $\pm(1\bar{1}0)$ and $\pm(001)$ (max. 5.2 mm between planes). Volume = 56.1 mm³. 293 K: Rectangular, bounded by same set of faces as 15 K crystal (max. 5.4 mm between planes). Volume = 73.5 mm³.
Data collection	Type 512 Huber four-circle diffractometer fitted with type CS201 Displex at beamline TAS2, reactor DR3, Research Establishment RISØ, Denmark. $\lambda = 1.013$ (002 planes from Be monochromator). Lattice parameters from 25 medium range reflections $(15 < \theta < 34°)$. Low-temperature study: 3 week data colection. 3018 reflections measured. $T = 15.0 \pm 0.5$ K. $0° < 2\theta < 90°$. At least two equivalent reflections. Above $2\theta = 50°$ the data set is not complete. High-order reflections evenly distributed in reciprocal space. Room temperature study: 3 week data collection. 2440 reflections measured. One quadrant. $0 < 2\theta < 90°$. $\omega/2\theta$ scan mode. Two standards every 50 reflections (negligible change).
Internal agreement factors	15 K: $R_I = \Sigma \lvert F^2 - F^2_{av} \rvert / \Sigma F^2 = 0.018$ [$R_I = 0.016$ for 1750 reflections with $F^2/$ $\sigma(F^2) > 50$ and $R_I = 0.02$ for 174 reflections with $5 > F^2/\sigma(F^2) > 3$]. 293 K: $R_I = 0.059$ for 2380 reflections.

(87.8%) was then incorporated in the effective absorption coefficient. Since deuteration was not complete the effective absorption coefficient was estimated by adding to the absorption coefficient contributions of incoherent scattering from hydrogen.[10,11] The resulting transmission factors varied from 0.813 to 0.914. A few months after the data collection the degree of deuterium substitution was estimated from solid-state ^{1}H MAS NMR at 1.1 T to be 84%. This value was obtained by comparing the integrated intensity for the ^{1}H center band and spinning side bands in ^{1}H MAS NMR spectra of the deuterated and non-deuterated samples.

Multiple scattering and TDS corrections

Initial plotting of the profiles of systematically absent reflections revealed a significant intensity in most cases for both the 15 and 293 K studies. A total of 70 systematically absent reflections evenly distributed throughout reciprocal space were measured during the data collection in the 15 K study and 96 in the room-temperature study. The integrated intensities are plotted vs. θ in Fig. 2. Obviously they tend to be positive definite. However, we could not reliably fit these observations to a curve of the expected angular dependence for such multiple scattering events.[12] We therefore simply calculated the average from the, respectively, 70 and 96 systematically absent reflections. This average was then subtracted from every reflection before least-squares refinements. $(I_{multiple})^{1/2}$ was added to the standard deviations of the measured intensities. On dealing with multiple scattering this way, we observed a considerable improvement of the least-squares fits of the data.

In a recent neutron diffraction study of cobalt phthalocyanine[13] it was concluded that for this compound even at 115 K TDS corrections are essential if one wants to extract charge information from X-ray experiments using the X–N procedure. Because of a lack of knowledge of the elastic constants we have not been able to apply a TDS correction in the present study, but based on the results of our combined X–N study of copper Tutton salt[5] it seems likely that at 15 K we have succeeded in cooling the system to a point where the TDS effects are not a serious factor. However, the room-temperature data set is likely to suffer from TDS effects, and this may account in part for the poorer R-factors obtained in refinements of those data.

Harmonic refinements

Full-matrix least-squares refinements using the harmonic approximation for thermal vibrations were performed using the program LINEX[9] minimizing $\Sigma w(F^2_o - k^2 F^2_c)^2$. Weights were $w = \sigma(F^2_o)^{-2}$ in the room-temperature study, but in the 15 K study a term in F^2 was added in final refinements to give $\sigma = \sigma + 0.005\ F^2$.
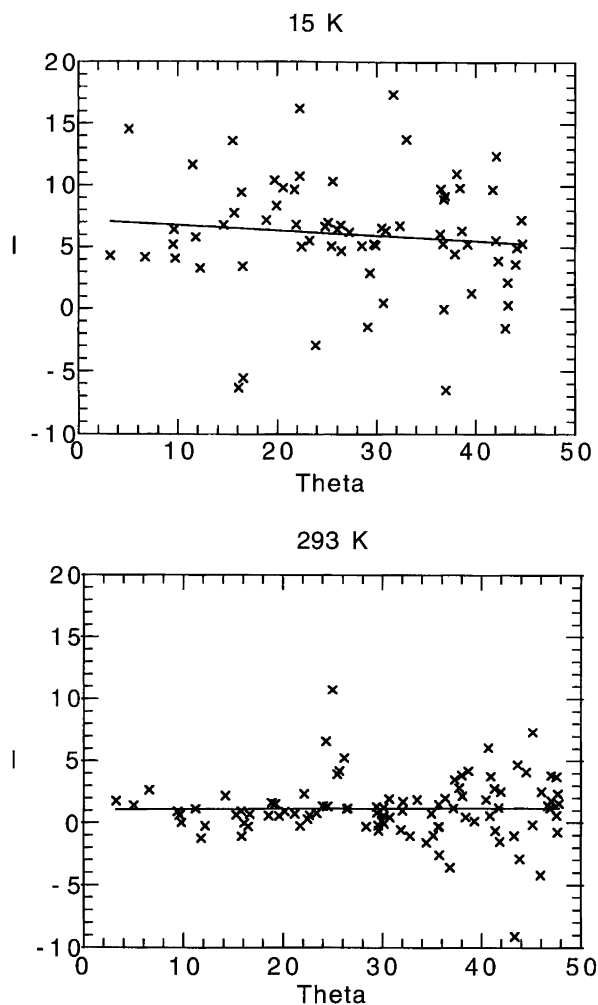

Fig. 2. Net integrated intensities of systematically absent reflections as a function of θ (a) at 15 K and (b) at 293 K.

Neutron scattering lengths were taken from Koester.[14] Cu = 0.7718, S = 0.2847, O = 0.5805, N = 0.93, D = 0.65, H = -0.378×10^{-14} m. The scattering lengths of the deuterium/hydrogen atoms were included as parameters in the least-squares refinements. We suspected H/D exchange might occur owing to the lengthy exposure to the atmosphere, and indeed the average degree of substitution was found to be 87.8%. The refined values of scattering length for the individual deuterium/hydrogen atoms were not significantly different. The refinements therefore indicate no isotopic preference in substitution site for hydrogen on either of the ND_4 or D_2O units. In the final refinements the deuterium scattering length was constrained to two parameters, one for deuterium/hydrogen in the ammonium group and one for the water molecules. The deuterium content of the crystal used in the 15 K study refined to 88.7% for the ammonium group and 87.2% for the water molecules. For the larger crystal used in the 293 K study the corresponding numbers were 89.3 and 89.7%.

Initial coordinates and harmonic thermal parameters were taken from our 9 K X-ray study.[5] All reflections

Table 2. Residuals from the various refinements.

T/K	Model	σ-Level	Weights	No. of observations	No. of parameters	R_F	R_{wF}	R_{F^2}	R_{wF^2}	GOF
15	Harmonic	0	$1/(\sigma+0.005F^2)^2$	1457	179	0.018	0.013	0.018	0.024	1.00
293	Harmonic	3	$1/\sigma^2$	1585	179	0.042	0.037	0.064	0.072	2.41
293	1[a]	3	$1/\sigma^2$	1585	384	0.029	0.025	0.043	0.049	1.80
293	2[b]	3	$1/\sigma^2$	1585	274	0.029	0.026	0.043	0.050	1.76

[a] All atoms anharmonic. [b] O3, O4, O7, D11, D12, D13, D14, D19 anharmonic.

were included in the refinements of the 15 K model. Using a 3σ level data cut-off in the low-temperature refinements did not alter the parameters or the fits significantly, indicating a very good description of the weak intensities following the *umweganregung* correction. In the 293 K study a 3σ level data cut-off was used in final refinements.

Isotropic extinction was applied in the final refinements. Use of a six-parameter anisotropic extinction model[15-17] in the 15 K study did not improve the fit. Since the room-temperature data were collected as a unique set, it was not meaningful to examine for anisotropic extinction effects. Owing to the large size of the crystals extinction effects were very pronounced [$g_{15K} = 0.215(5) \times 10^4$, $g_{293K} = 1.44(9) \times 10^4$]. Overall, 91% of the reflections in the 15 K study and 75% of the reflections in the 293 K study have less than 10% ex-

tinction ($y > 0.9$ for $I = yI_{kin}$). The degree of extinction of the strong reflections apparently decreased after applying the multiple scattering correction. These two corrections both decrease the ratio between weak and strong intensities and so are likely to be correlated. However, even after the multiple scattering correction, the extinction effects were severe. We therefore ran a series of refinements with successive removal of the most affected reflections. No improvement of the fits is seen when removing reflections with $y > 0.6$, and this was then chosen as the final level of data removal. We thus see that the isotropic extinction model does well in correcting for the intensity missing due to extinction. Using these considerations we removed six reflections from the 15 K structure factor list and 42 from the 293 K list. As the refined parameters do not change by removal of more reflections, we are

Table 3a. Atomic positional parameters.[a]

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	0.0000	0.0000	0.0000	D11	0.04171(7)	0.34592(5)	0.2318(1)
	0.0000	0.0000	0.0000		0.0505(3)	0.3402(3)	0.2167(4)
	0.0000	0.0000	0.0000		0.0550(6)	0.3396(4)	0.2195(8)
S2	0.3868(1)	0.14367(7)	0.7492(1)	D12	0.20434(7)	0.30588(5)	0.4226(1)
	0.3954(3)	0.1414(2)	0.7422(4)		0.2123(2)	0.3024(6)	0.4069(3)
	0.3955(2)	0.1415(2)	0.7425(3)		0.2068(6)	0.3014(4)	0.3993(9)
O3	0.38031(5)	0.23865(4)	0.60589(8)	D13	0.08243(7)	0.37720(5)	0.5128(1)
	0.3965(2)	0.2357(1)	0.6001(3)		0.0803(4)	0.3564(4)	0.4882(5)
	0.3974(4)	0.2358(3)	0.6020(5)		0.0790(5)	0.3530(4)	0.4839(7)
O4	0.52759(5)	0.08709(4)	0.77544(8)	D14	0.17651(7)	0.43316(5)	0.3508(1)
	0.5354(2)	0.0820(2)	0.7730(4)		0.1706(4)	0.4276(2)	0.3564(6)
	0.5355(3)	0.0820(3)	0.7753(6)		0.1714(7)	0.4220(5)	0.3561(10)
O5	0.26101(5)	0.07336(4)	0.63022(7)	D15	0.19624(7)	0.09331(5)	0.3295(1)
	0.2690(2)	0.0722(1)	0.6246(3)		0.2056(2)	0.0937(2)	0.3247(3)
	0.2690(1)	0.0722(1)	0.6248(2)		0.2055(2)	0.0938(1)	0.3247(3)
O6	0.37316(5)	0.17338(4)	0.97856(7)	D16	0.23106(7)	0.12550(5)	0.0982(1)
	0.3770(2)	0.1747(1)	0.9614(3)		0.2382(2)	0.1258(2)	0.0973(3)
	0.3771(1)	0.1746(1)	0.9614(2)		0.2382(2)	0.1258(1)	0.0977(3)
O7	0.15153(5)	0.10746(4)	0.16484(8)	D17	−0.28278(7)	0.10228(5)	−0.0447(1)
	0.1601(2)	0.1100(2)	0.1674(3)		−0.2780(2)	0.0991(2)	−0.0548(4)
	0.1615(4)	0.1103(3)	0.1693(6)		−0.2782(2)	0.0992(1)	−0.0545(3)
O8	−0.18069(5)	0.11197(4)	0.05041(8)	D18	−0.15740(7)	0.18524(5)	0.0305(1)
	−0.1771(2)	0.1118(1)	0.0397(3)		−0.1552(2)	0.1853(2)	0.0121(4)
	−0.1772(1)	0.1117(1)	0.0397(2)		−0.1552(2)	0.1853(1)	0.0122(3)
O9	0.00999(5)	−0.06612(4)	0.29670(8)	D19	−0.08507(7)	−0.06327(5)	0.3319(1)
	0.0020(2)	−0.0656(1)	0.2883(2)		−0.0942(2)	−0.0613(2)	0.3238(3)
	0.0019(1)	−0.0654(1)	0.2882(2)		−0.0924(4)	−0.0606(3)	0.3256(6)
N10	0.12603(3)	0.36448(2)	0.37800(5)	D20	0.04298(7)	−0.13994(5)	0.3165(1)
	0.1265(1)	0.3545(1)	0.3633(2)		0.0342(2)	−0.1398(1)	0.3127(3)
	0.1263(1)	0.3543(1)	0.3632(2)		0.0344(2)	−0.1398(1)	0.3130(2)

[a] Line 1 is at 15 K, line 2 is at 293 K using a harmonic model for the thermal vibrations, and line 3 contains the results of model 2.

Table 3b. Atomic thermal parameters.[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.0029(2)	0.0032(2)	0.0031(2)	−0.004(2)	0.0014(1)	0.0000(1)
	0.0151(5)	0.0186(6)	0.0154(6)	−0.0018(4)	0.0033(4)	0.0007(5)
	0.0155(4)	0.0183(4)	0.0167(4)	−0.0021(3)	0.0036(3)	0.0006(3)
S2	0.0030(4)	0.0032(4)	0.0036(3)	−0.0002(3)	0.0021(3)	−0.0001(3)
	0.017(1)	0.021(1)	0.019(1)	−0.0038(9)	0.0045(8)	0.000(1)
	0.0160(7)	0.0212(8)	0.0206(8)	−0.0033(7)	0.0044(6)	−0.0009(7)
O3	0.0074(2)	0.0044(2)	0.0061(2)	−0.0005(2)	0.0022(2)	0.0014(2)
	0.0477(9)	0.0271(7)	0.0284(8)	−0.0111(7)	0.0090(7)	0.0031(6)
	0.0476(7)	0.0269(5)	0.0302(6)	−0.0113(5)	0.0094(5)	0.0026(5)
O4	0.0038(2)	0.0070(2)	0.0075(2)	0.0012(2)	0.0022(1)	0.0002(2)
	0.0213(7)	0.049(1)	0.047(1)	0.0059(7)	0.0052(5)	−0.0063(8)
	0.0210(5)	0.0490(8)	0.0500(8)	0.0061(5)	0.0052(5)	−0.0063(6)
O5	0.0045(2)	0.0053(2)	0.0059(2)	−0.0017(2)	0.0019(1)	−0.0010(1)
	0.0223(6)	0.0290(7)	0.0268(7)	−0.0092(5)	0.0061(5)	−0.0042(6)
	0.0223(4)	0.0294(5)	0.0284(5)	−0.0094(4)	0.0062(11)	−0.0042(4)
O6	0.0066(2)	0.0065(2)	0.0046(2)	−0.0004(2)	0.0028(1)	−0.0009(1)
	0.0391(8)	0.0349(8)	0.0215(7)	−0.0046(6)	0.0097(6)	−0.0047(6)
	0.0387(6)	0.0339(6)	0.0230(5)	−0.0037(5)	0.0100(4)	−0.0045(4)
O7	0.0054(2)	0.0073(2)	0.0059(2)	−0.0019(2)	0.0019(2)	−0.0001(2)
	0.0284(7)	0.0415(9)	0.0228(7)	−0.0057(6)	0.0054(6)	0.0027(6)
	0.0285(6)	0.0416(6)	0.0244(6)	−0.0056(5)	0.0062(5)	0.0023(5)
O8	0.0055(2)	0.0062(2)	0.0083(2)	0.0006(2)	0.0026(2)	0.0002(2)
	0.0267(8)	0.0301(8)	0.0337(8)	−0.0011(6)	0.0056(6)	0.0060(6)
	0.0267(6)	0.0298(6)	0.0364(6)	−0.0022(5)	0.0057(5)	0.0059(5)
O9	0.0057(2)	0.0054(2)	0.0054(2)	0.0005(2)	0.0028(2)	0.0008(1)
	0.0239(6)	0.0238(7)	0.0197(6)	0.0002(5)	0.0081(5)	0.0026(5)
	0.0242(5)	0.0231(6)	0.0210(5)	0.0003(4)	0.0086(4)	0.0027(4)
N10	0.0065(1)	0.0068(1)	0.0067(1)	0.0001(1)	0.0027(1)	0.0003(1)
	0.0292(5)	0.0344(5)	0.0284(5)	0.0012(4)	0.0107(4)	0.0033(4)
	0.0300(4)	0.0335(5)	0.0304(5)	0.0012(4)	0.0110(4)	0.0029(4)
D11	0.0154(3)	0.0218(3)	0.0132(3)	−0.0025(2)	0.0012(2)	−0.0024(2)
	0.0571(14)	0.0812(20)	0.0400(12)	−0.0195(14)	0.0051(11)	−0.0041(12)
	0.0598(12)	0.0816(15)	0.0405(10)	−0.0209(11)	0.0046(9)	−0.0053(9)
D12	0.0162(3)	0.0141(3)	0.0224(3)	0.0063(2)	0.0061(2)	0.0024(2)
	0.0541(14)	0.0496(14)	0.0834(19)	0.0149(12)	0.0236(13)	0.0082(13)
	0.0600(14)	0.0504(11)	0.0863(17)	0.0182(11)	0.0272(12)	0.0103(11)
D13	0.0177(3)	0.0229(3)	0.0143(3)	.0006(2)	0.0097(2)	−0.0011(2)
	0.0609(15)	0.1447(35)	0.0513(15)	0.0363(20)	0.0325(13)	0.0285(19)
	0.0598(12)	0.1164(26)	0.0516(11)	0.0235(14)	0.0301(10)	0.0211(14)
D14	0.0192(3)	0.0142(3)	0.0213(3)	−0.0041(2)	0.0071(2)	0.0031(2)
	0.0769(19)	0.0411(13)	0.0757(19)	−0.0116(13)	0.0007(15)	0.0084(13)
	0.0802(15)	0.0498(17)	0.0753(14)	−0.0129(13)	0.0002(12)	0.0093(12)
D15	0.0145(3)	0.0180(3)	0.0089(3)	−0.0020(2)	0.0022(2)	0.0006(2)
	0.0374(9)	0.0448(11)	0.0260(9)	−0.0047(8)	0.0049(7)	0.0005(8)
	0.0383(7)	0.0443(8)	0.0274(7)	−0.0045(6)	0.0056(5)	0.0008(6)
D16	0.0129(3)	0.0186(3)	0.0149(3)	−0.0036(2)	0.0074(2)	0.0001(2)
	0.0381(9)	0.047(1)	0.0349(9)	−0.0104(8)	0.0142(8)	−0.0002(8)
	0.0382(7)	0.0466(9)	0.0366(7)	−0.0099(6)	0.0134(6)	0.0005(6)
D17	0.0090(3)	0.0175(3)	0.0168(3)	−0.0012(2)	0.0017(2)	−0.0006(2)
	0.0280(9)	0.047(1)	0.040(1)	−0.0014(8)	0.0079(7)	0.0000(9)
	0.0282(6)	0.0459(8)	0.0415(7)	−0.0010(6)	0.0078(5)	0.0004(7)
D18	0.0172(3)	0.0101(3)	0.0213(3)	−0.019(2)	0.0070(2)	0.0004(2)
	0.042(1)	0.033(1)	0.044(1)	−0.0025(8)	0.0146(8)	0.0017(8)
	0.0412(7)	0.0336(8)	0.0467(8)	−0.0025(6)	0.0146(6)	0.0012(6)
D19	0.0123(3)	0.0178(3)	0.0175(3)	0.0022(2)	0.0093(2)	0.0024(2)
	0.0352(9)	0.0386(9)	0.0323(9)	0.0047(7)	0.0174(7)	0.0050(7)
	0.0363(7)	0.0384(7)	0.0350(7)	0.0048(6)	0.0188(6)	0.0052(5)
D20	0.0155(3)	0.0098(3)	0.0163(3)	0.0027(2)	0.0063(2)	0.0020(2)
	0.0358(8)	0.0274(8)	0.0308(8)	0.0049(7)	0.0105(6)	0.0043(7)
	0.0356(6)	0.0279(6)	0.0324(6)	0.0047(5)	0.0107(5)	0.0051(5)

[a]Line 1 is at 15 K, line 2 is at 293 K using a harmonic model for the thermal vibrations, and line 3 contains the results of model 2.

confident that the subtle thermal features presented in this article are trustworthy and are not artefacts of a de-

fective extinction model. Final residuals for the harmonic refinements are given in Table 2, and corresponding

positional and thermal parameters are given in Tables 3a and 3b.

Anharmonic refinements

In a previous X-ray study of copper Tutton salt at 85 K[6] the Cu atom appeared to vibrate anharmonically. It has also been observed that the ammonium ion libration increases very much with temperature, suggesting that the atomic potentials are not well described in the harmonic approximation, except perhaps at the lowest temperatures. We therefore carried out refinements using an anharmonic model. If anharmonicities are not too large then a good description can be obtained by using expansions of the harmonic model.[18] In the Gram–Charlier expansion the harmonic displacement factor expression is replaced by

$$T(H) = (1 - 4i\pi^3/3 C^{jkl} h_j h_k h_l$$
$$+ 2\pi^4/3 D^{jklm} h_j h_k h_l h_m) \, T_{\text{harmonic}}(H)$$

with

$$T_{\text{harmonic}}(H) = \exp(-P^{ij} h_i h_j)$$

The anharmonic refinements were carried out with the program MOLLY.[19] The Cu atom sits on a special position having an inversion center, so only even orders of the expansion are symmetry-allowed in that case. In order not to over-parametrise the refinement in a first model, we chose to terminate the Gram–Charlier expansion at third order for all atoms except Cu, which was continued to fourth order. Thus each N, D, S and O atom, which are all located at general positions, receives 10 third-order anharmonic thermal parameters. Cu was allowed 15 fourth-order thermal parameters; thus there

Table 4. Anharmonic thermal parameters.[a]

Third order

Atom	C^{111}	C^{222}	C^{333}	C^{112}	C^{122}	C^{113}	C^{133}	C^{223}	C^{233}	C^{123}
S2	0.01(3)	−0.02(3)	−0.03(3)	0.09(5)	0.10(5)	−0.06(5)	−0.02(5)	−0.01(5)	0.00(5)	0.03(7)
O3	−0.10(3)	0.01(2)	−0.03(3)	−0.02(4)	0.02(4)	−0.32(4)	−0.09(4)	−0.03(3)	0.02(3)	0.24(5)
	−0.11(2)	0.00(2)	−0.03(2)	0.00(4)	0.01(3)	−0.32(4)	−0.11(4)	−0.02(3)	0.02(3)	0.24(5)
O4	−0.03(2)	−0.06(3)	−0.11(3)	0.06(3)	−0.12(4)	−0.06(4)	0.03(4)	−0.10(5)	0.16(5)	0.05(6)
	−0.02(2)	−0.07(3)	−0.12(3)	0.05(3)	−0.11(4)	−0.05(3)	0.02(4)	−0.13(5)	0.16(5)	0.07(5)
O5	−0.01(2)	−0.02(2)	0.03(3)	0.00(3)	0.05(3)	0.01(3)	−0.04(3)	0.04(3)	0.00(3)	−0.04(4)
O6	−0.02(2)	0.00(2)	−0.01(2)	−0.11(4)	0.00(4)	0.06(4)	0.01(3)	0.04(3)	−0.03(3)	−0.02(5)
O7	−0.07(2)	−0.01(2)	−0.03(2)	−0.01(4)	−0.20(3)	−0.14(4)	−0.06(4)	−0.12(3)	−0.07(4)	−0.11(5)
	−0.07(2)	−0.02(2)	−0.03(2)	−0.02(3)	−0.20(3)	−0.15(3)	−0.06(4)	−0.12(3)	−0.08(4)	−0.11(5)
O8	0.00(3)	0.11(3)	−0.02(2)	0.09(4)	0.03(4)	−0.01(5)	−0.06(4)	0.02(4)	0.09(4)	−0.01(6)
O9	−0.01(2)	−0.03(2)	−0.02(3)	0.00(4)	0.00(4)	0.05(3)	−0.01(3)	0.02(3)	−0.03(3)	0.03(4)
N10	0.03(2)	0.00(2)	−0.03(2)	0.07(3)	0.02(3)	−0.03(4)	−0.03(3)	−0.12(3)	−0.02(3)	0.00(5)
D11	−0.37(5)	−0.01(6)	−0.05(4)	0.56(10)	−0.82(10)	−0.21(9)	−0.06(8)	−0.55(9)	0.20(8)	0.43(13)
	−0.36(5)	0.00(5)	−0.07(4)	0.51(9)	−0.76(9)	−0.09(7)	−0.01(7)	−0.45(8)	0.09(7)	0.29(11)
D12	0.38(6)	−0.03(4)	0.47(7)	0.70(8)	0.36(7)	0.65(10)	0.76(11)	0.35(8)	0.23(9)	0.96(15)
	0.40(5)	−0.05(4)	0.48(9)	1.00(13)	0.47(10)	0.89(17)	1.05(18)	0.47(11)	0.29(13)	1.07(13)
D13	0.02(5)	0.45(13)	0.06(4)	0.84(12)	1.19(18)	0.48(9)	0.39(9)	1.78(17)	0.57(12)	1.71(20)
	0.03(4)	0.47(8)	0.10(4)	0.75(9)	0.86(12)	0.40(7)	0.39(9)	1.38(12)	0.50(9)	1.23(15)
D14	0.09(6)	0.57(8)	0.06(6)	0.77(11)	−0.80(12)	−0.10(10)	0.02(10)	0.50(12)	0.61(11)	−0.46(15)
	0.08(6)	0.46(6)	0.05(6)	0.91(10)	−0.77(10)	−0.19(9)	0.07(9)	0.37(10)	0.76(9)	−0.69(13)
D15	0.00(3)	−0.07(3)	0.01(3)	−0.07(4)	−0.04(5)	−0.02(5)	−0.03(5)	0.04(4)	−0.05(5)	−0.07(7)
D16	0.05(3)	0.01(3)	0.01(3)	−0.01(5)	−0.04(5)	−0.01(5)	0.03(5)	−0.04(5)	0.01(4)	−0.04(7)
D17	0.01(3)	−0.04(3)	0.00(3)	0.00(5)	0.05(4)	0.06(6)	0.04(5)	0.00(5)	−0.02(5)	−0.01(7)
D18	0.01(3)	0.06(4)	−0.04(3)	0.06(5)	0.08(6)	0.01(5)	0.05(5)	−0.04(6)	0.12(5)	0.07(5)
D19	−0.10(3)	−0.04(3)	−0.05(2)	−0.10(5)	−0.09(4)	−0.21(5)	−0.19(4)	−0.06(4)	−0.09(4)	−0.22(6)
	−0.10(3)	−0.04(2)	−0.05(2)	−0.12(4)	−0.08(4)	−0.23(4)	−0.19(4)	−0.06(4)	−0.07(4)	−0.19(6)
D20	0.03(2)	−0.07(3)	−0.01(2)	−0.03(4)	0.04(5)	0.04(4)	0.06(4)	−0.08(4)	−0.01(4)	−0.03(6)

[a] Line 1 is from model 1, line 2 from model 2.

Fourth order

Atom	D^{1111}	D^{2222}	D^{3333}	D^{1112}	D^{1113}	D^{1122}	D^{1123}	D^{1133}	D^{1222}	D^{1223}	D^{1233}	D^{1333}	D^{2223}	D^{2233}	D^{2333}
Cu[b]	−0.02 (2)	−0.04 (2)	0.02 (2)	0.06 (3)	0.01 (4)	−0.10 (4)	0.05 (6)	0.02 (5)	0.02 (4)	−0.03 (6)	0.04 (6)	0.05 (4)	−0.01 (4)	−0.01 (4)	0.02 (4)
D13[c]	−0.05 (3)	−1.12 (9)	0.03 (3)	−0.14 (12)	−0.21 (10)	−0.63 (20)	−0.57 (26)	−0.23 (13)	−1.73 (20)	−2.31 (33)	−0.84 (25)	−0.02 (9)	−1.58 (20)	−1.03 (19)	−0.33 (11)

[a] The values in the table are connected with the parameters in the temperature factor expression by C^{jkl} (Table 4) = $C^{jkl} 4\pi^3/3 \, a_j^* a_k^* a_l$ and D^{jklm} (Table 4) = $D^{jklm} 2\pi^4/3 \, a_j^* a_k^* a_m^*$. [b] Model 1. [c] Model 2.

are a total of 384 parameters to be varied. This first an-harmonic model indicated that significant anharmonicity is only present at O3, O4, O7, D11, D12, D13, D14 and D19 (Table 4). Examination of the anharmonicity found in this general model inspired a second model in which O3, O4, O7, D11, D12, D14 and D19 were allowed third-order thermal parameters, whereas the expansion was extended to fourth order for D13. For Cu only harmonic parameters were included. This model has 274 parameters, and results are given in Table 4. As can be seen, the R-factor for model 2 is identical to that of model 1 even though it has 110 parameters less. This supports the procedure of model 2 of using only the significant anharmonic parameters.

Discussion

For the structure, Tables 5–7 list selected bond lengths, angles and important intermolecular contacts as well as standard deviations calculated by the program ORFFE.[20]

The positional parameters compare well with those obtained in the 9 K X-ray study. A thorough comparison was made in our combined X-N paper.[5] Anharmonic refinements of the 15 K data reveal, as expected, no significant anharmonic parameters. There is therefore no reason to include these parameters in the fit, and the discussion of the 15 K data is based on the results of the harmonic refinement. In the present study the anharmonic refinements of the 293 K data did not reveal significant anharmonic motion of the Cu atom. Significant anharmonic parameters were only found for O3, O4, O7, D11, D12, D13, D14 and D19. Hathaway and Hewat[3] conducted neutron diffraction experiments on the deuterated compound at temperatures ranging from 5 K to

Table 6. Selected angles (in °) with e.s.d.s in parentheses.

Angle	15 K	293 K All atoms harmonic	293 K Model 2 anharmonic
O7–Cu–O8	87.7(5)	88.7(5)	88.8(7)
O7–Cu–O9	89.8(1.1)	90.2(1.5)	90.0(1.5)
O8–Cu–O9	88.8(1.1)	88.8(1.5)	88.8(1.5)
O3–S–O4	109.9(9)	109.2(1.2)	109.4(1.2)
O3–S–O5	108.3(1.1)	108.4(1.4)	108.8(1.4)
O3–S–O6	110.2(1)	110.1(2)	110.0(1)
O4–S–O5	108.8(6)	108.8(9)	108.9(9)
O4–S–O6	110.2(1.5)	110.9(2.0)	110.3(2.0)
O5–S–O6	109.3(1.1)	109.6(1.4)	109.6(1.4)
D11–N–D12	111.9(9)	115.5(1.4)	111.4(1.4)
D11–N–D13	109.5(3)	111.2(3)	111.35(5)
D11–N–D14	109.2(2)	108.5(4)	108.9(4)
D12–N–D13	109.3(2)	107.2(1.1)	107.3(1.0)
D12–N–D14	109.0(1)	107.4(4)	107.2(3)
D13–N–D14	107.8(5)	106.6(7)	110.6(6)
O7–D15···O5	174.4	172.2	172.6
O7–D16···O6	173.9	172.0	172.2
O8–D17···O4	178.7	177.4	177.6
O8–D18···O6	175.9	177.3	177.2
O9–D19···O5	172.1	172.1	171.0
O9–D20···O3	170.4	170.7	171.3

room temperature. They observed a considerable increase of the ammonium thermal parameters with rising temperature, which made them challenge the fluxional picture and instead propose that a second-order phase transition was about to take place above 293 K. This transition was thought to be from an elongated octahedral CuO_6 system at low temperature to a compressed octahedral system at high temperature. To test this hypothesis we have carried out DTA and DSC measurements from 100 to 400 K. We do not detect any phase transitions below 330 K. At this temperature the salt starts to loose water. It seems

Table 5. Selected bond lengths (in Å) with e.s.d.s in parentheses.

Bond	15 K, Deu. Harmonic model[a]	293 k, Deu. Harmonic model[a]	293 K, Deu. Model 2[a]	14 K, 1.4 kbar, Hyd.[b]	293 K, Hyd.[c]
Cu–O7	2.007(21)	2.075(30)	2.090(30)	2.272(2)	2.228(2)
Cu–O8	2.298(7)	2.229(8)	2.227(7)	2.005(2)	2.078(2)
Cu–O9	1.959(3)	1.959(2)	1.958(1)	1.979(2)	1.968(2)
O7–D15	0.977(12)	0.968(17)	0.955(17)	0.967(4)	0.962(5)
O7–D16	0.975(9)	0.968(13)	0.960(13)	0.973(3)	0.965(5)
O8–D17	0.969(17)	0.968(23)	0.969(23)	0.983(5)	0.976(4)
O8–D18	0.968(1)	0.968(3)	0.970(2)	0.989(4)	0.980(4)
O9–D19	0.977(6)	0.980(8)	0.971(8)	0.979(3)	0.977(5)
O9-D20	0.980(2)	0.975(3)	0.977(2)	0.982(4)	0.974(4)
S–O3	1.473(2)	1.474(3)	1.470(1)	1.489(4)	1.480(4)
S–O4	1.470(4)	1.463(7)	1.464(7)	1.466(4)	1.459(3)
S–O5	1.484(17)	1.476(23)	1.477(23)	1.476(4)	1.475(4)
S–O6	1.480(4)	1.475(7)	1.472(6)	1.486(4)	1.479(4)
N–D11(H)	1.026(20)	0.996(26)	0.964(25)	1.018(4)	0.988(5)
N–D12(H)	1.022(6)	1.007(9)	0.976(7)	1.017(4)	0.994(6)
N–D13(H)	1.028(10)	0.986(14)	0.969(14)	1.026(3)	1.004(7)
N–D14(H)	1.026(2)	1.009(3)	0.952(1)	1.039(4)	1.004(6)

[a]This study. [b]Ref. 4. [c]Ref. 2.

Table 7. Selected intermolecular contacts (in Å).

Bond	15 K, Deu. Harmonic model[a]	293 k, Deu. Harmonic model[a]	293 K, Deu. Model 2[a]	14 k, 1.4 Kbar, Hyd.[b]	293 K, Hyd.[c]
O7–D15···O5	2.734	2.763	2.752	2.831	2.821
D15–O5	1.760	1.801	1.802	1.881	
O7–D16···O6	2.771	2.797	2.791	2.827	2.820
D16–O6	1.800	1.834	1.836	1.879	
O8–D17···O4	2.771	2.741	2.735	2.658	2.708
D17–O4	1.802	1.774	1.766	1.675	
O8–D18···O6	2.819	2.787	2.790	2.722	2.744
D18–O6	1.852	1.820	1.821	1.734	
O9–D19···O5	2.709	2.724	2.723	2.727	2.734
D19–O5	1.738	1.749	1.760	1.760	
O9–D20···O3	2.673	2.681	2.677	2.690	2.682
D20–O3	1.702	1.715	1.707	1.718	
N–D11···O6	2.885	2.903	2.902	2.872	2.901
D11–O6	1.866	1.921	1.956	1.906	
N–D12···O3	2.862	2.929	2.938	2.971	2.979
D12–O3	1.898	1.975	2.033	2.011	
N–D13···O3	3.287	3.127	3.126	2.885	3.014
D13–O3	2.587	2.324	2.307	1.870	
N–D13···O4	2.887	2.998	3.012	3.209	3.116
D13–O4	1.866	2.072	2.119	2.524	
N–D14···O5	2.852	2.887	2.890	2.846	2.896
D14–O5	1.860	1.889	1.954	1.811	
O7···N	3.532	3.341	3.332	3.077	3.153
O8···N	3.072	3.098	3.099	3.178	3.188
O9···N	3.514	3.655	3.660	3.591	3.692

[a]This study. [b]Ref. 4. [c]Ref. 2.

that even though the motion of the ammonium group becomes quite anharmonic at higher temperatures the same structure is intact between 9 and 330 K. Based on the low decomposition temperature of the substance we would expect the water groups to vibrate anharmonically at room temperature. Only O7 shows a weak anharmonicity, which will be discussed below. The lack of anharmonicity for the other atoms in the water groups can probably be attributed to the strong hydrogen-bonding network.

The switchable Jahn–Teller distortion has been one of the key interests in earlier studies of copper Tutton salt. Recently it was shown that an interchange of the Cu–O7 and Cu–O8 bond lengths can also be obtained by applying pressure to the deuterated compound.[4] It has been pointed out[2,4] that the change in hydrogen bonding between N10–D13 to either O3 or O4 is the major difference between the switched structures (Fig. 3). A rotation of the ammonium ion accompanies the breaking of the N10–D13···O4 hydrogen bond and the formation of N10–D13···O3 when going from the deuterated to the hydrated-type structure or when sufficient pressure is applied to the deuterated structure. In the hydrated structure O4 only forms the O8–D17····O4 hydrogen bond, which thus is increased in strength compared to the deuterated structure where O4 is involved in two hydrogen bonds. Maslen et al.[2] proposed that hydrogen bonding of the water hydrogens increases the ligating power of that

group, and thus O8 is strengthened as a ligand in the hydrated complex, making Cu–O8 shorter and shifting the long axis of the distortion to Cu–O7. The interaction between D13 and O3/O4 might make the atomic potentials of these atoms highly anharmonic, just as is observed in the present study. It is striking that the two other sulfate oxygen atoms remain close to harmonic at room temperature, whereas O3 and O4 have significant anharmonic contributions in their thermal motion. For
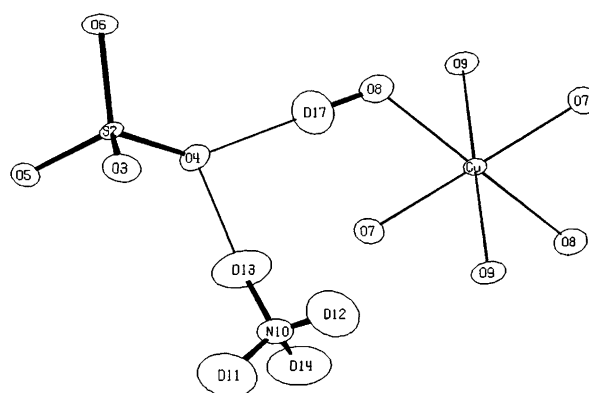

Fig. 3. ORTEP[23] drawing of the ammonium group, the sulfate group and the CuO6 octahedra at 15 K showing the hydrogen bonds important for the position of the Jahn–Teller prolonged Cu–O distance. 50% ellipsoids are shown.

D13 the anharmonicity becomes very pronounced, and even fourth-order anharmonic parameters become highly significant. The transition of the long bond from Cu–O8 to Cu–O7 must be connected to these anharmonic modes of vibration. It seems that the important interactions in the structural transition are also reflected in the atomic anharmonic motions. This is seen as well for the interaction of O7 and O8 with the ammonium group. Maslen *et al.*[2] proposed that interaction between a ligating water and an ammonium ion decreases its ligating strength. In the deuterated compound O8 is closer to an ammonium than is O7 (3.098 Å for N10---O8 vs. 3.341 Å for N10--O7). This corroborates that the hydrogen bonding makes the O8 water the weakest ligand in the deuterated structure. In the hydrated structure O7 has approached N10, and the distances are now similar (3.153 Å for O7 and 3.188 Å for O8). Just as the anharmonic motion of O3 reflected an important interaction in the structural transition from the deuterated to the hydrated structure (formation of a hydrogen bond) O7 also vibrates anharmonically, indicating an important interaction.

It is a puzzle why D19 vibrates quite anharmonically when all the other atoms in the water molecules (except O7 as mentioned above) are close to being harmonic. This is especially true when considering that the O9–D19–D20 water group is the tightest bound ligand in both the hydrated and the deuterated structure. The anharmonic motion may be connected to the decomposition of the substance at 330 K.

Simmons *et al.*[4] (1993) have corroborated that to a good approximation the simple fluxional model developed by Getz and Silver[21] is valid as a simplification of the more complex 'Mexican Hat' potential model of Riley *et al.*[22] In the fluxional model the apparent shortening of the Cu–O8 bond is explained by an increased population of the second energy minimum. The bond length is the Boltzmann-weighted value of the two lowest minima. One can get an estimate of the energy difference between the low-lying minima from diffraction measurements carried out at two or more temperatures. If P_I is the population of the first minimum and P_{II} is the population of a second minimum we have

$$P_I/P_{II} = \exp(\Delta E/kT)$$

Following Alcock *et al.*[1] we define $\delta^{obs} =$ Cu–O7 – Cu–O8 and δ^{max} as the purely static value of Cu–O7 – Cu–O8 (in other words the low-temperature value). The energy difference is then obtained as

$$\Delta E = kT \ln(\delta^{max} + \delta^{obs}/\delta^{max} - \delta^{obs})$$

By conducting the diffraction experiment at several different temperatures one can plot $\ln(\delta^{max} + \delta^{obs}/\delta^{max} - \delta^{obs})$ vs. $1/T$ and obtain an estimate of ΔE. We get $\Delta E = 208$ cm^{-1} when using anharmonic thermal parameters on O7 as in model 2. The harmonic refinement at 293 K gives $\Delta E = 240$ cm^{-1}. We suggest using this interval to define an experimental standard deviation lead-

ing to a value of $\Delta E = 224 \pm 16$ cm^{-1}. Alcock *et al.*[1] found $\Delta E = 160 \pm 20$ cm^{-1} for the hydrated compound using the same procedure. Detailed calculations by Simmons *et al.*[4] gave $\Delta E = 250$ cm^{-1} for the deuterated and $\Delta E = 247$ cm^{-1} for the hydrated structure.

Concluding remarks

In our study of the electron density distribution of ammonium copper Tutton salt it is shown that unbiased knowledge of thermal parameters is of great importance. The neutron diffraction values are essential in the modelling of the charge density. However, apart from being vital in the study of the electronic structure of a compound, the positional and thermal parameters themselves also contain a wealth of chemical information. Structural transitions are accompanied by anharmonic motion, so the description of anharmonic motion is therefore an important task in chemistry. This study is a good example of a structure in which examination of the atomic anharmonicities reveals the important interactions in a structural transition.

Acknowledgement

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