atomes Sb(2), Sb(3), O(2) et O(11) ainsi que la valeur des deux angles Sb···O(2)···O(11) reportées sur la figure impliquent une liaison O(2)—H(8) presque alignée sur l'axe O(2)—O(11). On peut comparer ce groupe OH pontant deux atomes Sb à celui que nous avons mis en évidence dans $Sb_2(OH)_2(SO_4)_2.2H_2O$ (Douglade *et al.*, 1978) dans lequel les deux liaisons Sb—OH ont des longueurs de 2,04 et 2,17 Å comparables aux deux liaisons (2,10 Å) de ce composé.

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Disorder of Ammonium Ions in Diammonium Tetrachlorocuprate Dihydrate, $(NH_4)_2CuCl_4.2H_2O$: A High-Precision Neutron Diffraction Study

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Abstract

A least-squares refinement of the crystal structure of $(NH_4)_2CuCl_4.2H_2O$ [space group $P4_2/mnm$, a = 7·596 (4), c = 7·976 (4) Å, $Z = 2$] has been carried out using the intensities of 484 three-dimensional single-crystal neutron reflections (203 independent) with $(\sin\theta)/\lambda \leq 0{\cdot}56$ Å^{-1}. The final R index on F is 0·023. The Cu atom has a distorted octahedral coordination consisting of two H_2O molecules at 1·954 (3) Å, two Cl(2) atoms at 2·271 (1) Å and two Cl(1) atoms at 2·971 (1) Å. The water molecule is trigonally coordinated and forms two equivalent O—H···Cl(1) hydrogen bonds with an H···Cl(1) length of 2·186 (2) Å and H—O···Cl(1) angle of 4·75 (18)°. The O—H distance in the water molecule is 0·965 (3) Å (uncorrected for thermal motion) and the H—O—H angle is 108·96 (40)°. The ammonium ions are orientationally disordered between two available tetrahedral configurations with occupancies of 0·64 (2) and 0·36. In the more favourable orientation, the NH_4^+ is hydrogen bonded to Cl(1) atoms at 3·357 (1) Å while in the other orientation, it is bonded to Cl(2) atoms at 3·370 (1) Å. The respective N—H distances (uncorrected for thermal motion) are 1·011 (6) Å and 1·021 (11) Å, and the bending angles H—N···Cl are 3·40 (32)° and

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0·95 (64)° respectively. No disorder has been observed for water-molecule H atoms. The results are compared with the results obtained from earlier studies on this salt and the energetics of the hydrogen bonding of the disordered ammonium ion are discussed.

Introduction

The compound $(NH_4)_2CuCl_4.2H_2O$ is a member of an isomorphous family of compounds $X_2CuY_4.2H_2O$ (X = K, NH_4, Rb, Cs; Y = Cl, Br) with the space group D_{4h}^{14}. Of all these compounds, $(NH_4)_2CuCl_4.2H_2O$ is known to undergo an order/disorder phase transition at 200·50 K. Specific-heat measurements by Suga, Sorai, Yamanaka & Seki (1965) denote a broad λ anomaly between 120–200 K, with ΔS_{tr} = 1·945 e.u. and $C_{p,tr}$ = 55·42 J deg^{-1} mol^{-1}. They associate this anomaly with the orientational ordering of ammonium ions in the salt.

The crystal structure of $(NH_4)_2CuCl_4.2H_2O$ was studied at room temperature by Hendricks & Dickinson (1927) and Chrobak (1934) using X-ray diffraction, and deduced by Narasimhamurthy & Premaswarup (1964) using electron paramagnetic resonance studies. The heavy-atom positions were determined approximately in these investigations. The directions of the *p–p* vectors of the water molecule were obtained in an NMR study by Itoh, Kusaka, Yamagata, Kiriyama & Ibamoto (1953) and more recently by Klaassen, Looyestijn & Poulis (1973). Matković, Peterson & Willett (1969), from a two-dimensional neutron diffraction study at room temperature, reported ordered hydrogens for the NH_4^+ ions. Using these results as a guideline, Oxton & Knop (1977) interpreted their infrared spectra between 5 and 300 K. They reported the existence of two phase transitions, one discontinuous (at 240 K) and the other continuous (between 77 and 5 K). According to them, both the NH_4^+ and water protons are ordered above 240 K, but the water molecule H atoms become disordered below 240 K and then are progressively ordered between 77 and 5 K while the NH_4^+ ion H atoms remain unchanged.

On the other hand, a recent laser–Raman study between 100 and 300 K carried out by Bansal, Sahni & Roy (1979) indicates disordered NH_4^+ and ordered H_2O at room temperature. The contradictory findings on the nature of the NH_4^+ ion orientations prompted us to undertake a high-precision study of this structure, using three-dimensional single-crystal neutron data.

Crystal data

$(NH_4)_2CuCl_4.2H_2O$, M_r = 277·5, Z = 2. Space group: tetragonal, $P4_2/mnm$, $a = b$ = 7·596 (4), c = 7·976 (4) Å, V = 460·17 Å^3, D_m = 2·09, D_c = 2·00 Mg m^{-3}, λ (neutrons) = 1·0358 Å, μ = 0·224 mm^{-1}.

Experimental

The neutron data on $(NH_4)_2CuCl_4.2H_2O$ were recorded at the CIRUS reactor in Trombay, using a TDC-312 computer-controlled four-circle diffractometer (Sequeira *et al.*, 1978) at a mean neutron wavelength of 1·0358 Å. The crystal used was a rectangular parallelepiped (weight = 73·3 mg and dimensions 3·9 × 3·4 × 2·7 mm) with {011} as its bounding faces, and was mounted with its a axis along the φ axis. The intensities of 484 reflections (203 independent) within the limit $(\sin\theta)/\lambda$ = 0·56 Å^{-1} were recorded using the θ–2θ step scanning mode. The space-group extinctions for $P4_2/mnm$ were confirmed. The peak 2θ values of 80 strong reflections were used to obtain the refined cell parameters.

Preliminary examination of the intensities of some of the equivalent reflections indicated the possible existence of secondary extinction in the crystal. Hence the data on strong reflections were recorded for four equivalent sets within a quadrant of reciprocal space. Because of the existence of extinction, the intensities of equivalent reflections were not averaged. The measured intensities of 27 reflections, negative within $\sim 3\sigma$, were set equal to zero. The raw data were reduced to structure factors using the program *DATRED* (Rajagopal, Srikanta & Sequeira, 1973, unpublished) which includes the absorption-correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine. The calculated linear absorption coefficient μ = 0·224 mm^{-1} was used, the absorption factors varying between 0·48 and 0·58.

Refinement of the structure

Of all the isomorphous family of compounds $X_2CuY_4.2H_2O$ (space group $P4_2/mnm$), high-precision neutron diffraction work has been reported so far only on $K_2CuCl_4.2H_2O$ (Chidambaram *et al.*, 1970). Starting with the heavy-atom coordinates reported for the K salt, the H positional parameters were located using a preliminary Fourier map, derived by using the program *FORDAP* (Zalkin, 1962, unpublished) which indicated clear, sharp peaks for the protons of the water molecules. The protons of the ammonium ion, however, showed a smeared negative density around the N, with a broad negative peak towards the four closest chlorines and some residual negative density toward the four distant ones, which was indicative of some orientational disorder in the ammonium ions.

All the structural parameters were refined by the method of least squares using the program *TRXFLS* (Rajagopal & Sequeira, 1977, unpublished) which is a modification of *ORFLS* (Busing, Martin & Levy, 1962). Three distinct models were tried in the refinement, depending on the orientations of the ammonium ions in the distorted cubic surroundings. The environment of the ammonium ion consists of eight chlorine ions, of which four, Cl(1), are closer to the NH_4^+ compared to the other four, Cl(2). The models tested were:

(1) The hydrogens of the NH_4^+ ion are ordered and pointing towards Cl(1).

(2) The hydrogens of the NH_4^+ ion are disordered and shared between Cl(1) and Cl(2) in the ratio 0·5:0·5.

(3) The hydrogens of NH_4^+ are partially disordered and are shared between Cl(1) and Cl(2) in the ratio $x:(1-x)$ where x is variable.

Initial refinements were carried out using isotropic temperature factors and an isotropic extinction correction (Zachariasen, 1967). The function minimized was $\sum w(F_o^2 - |F_c|^2)$ with initial weights $w = [\sigma^2_{\rm count} + (0{\cdot}02F_o^2)^2]^{-1}$. The R values at the end of the isotropic refinement are given in Table 1. It was possible to eliminate models 1 and 2 in favour of model 3 on the basis of the R values and the reasonableness of the proton B values. The refinement was, however, continued for all the three models using anisotropic temperature factors and the resulting R values confirmed the rejection of models 1 and 2 in favour of model 3. Table 1 gives the subsequent R values.

A comparison of the observed and calculated structure factors for model 3 at this stage was strongly indicative of the presence of anisotropic extinction effects in the data. Hence the refinement was continued further by applying the anisotropic extinction correction in both type I and type II forms (Coppens & Hamilton, 1970). The type II correction resulted in a marginally lower R value compared to the type I correction as shown in Table 1. An error analysis carried out on $|\Delta F^2|$ in the last stages of refinement indicated that the weighting scheme using errors based on counting statistics only, $\sigma_{\rm count}(F_o^2)$, was the best. This weighting scheme was used in the final cycles of refinement, in which reflections with intensities less than $\sigma_{\rm count}$ and 11 strong reflections with F_o^2/F_c^2 values less than 0·6 were also omitted. The final R value so obtained was 0·023. The particle-size tensor values (in units of 10^6 mm^{-2}), obtained in the final refinement, were:

$$W_{11} = 8{\cdot}33\ (0{\cdot}87),\quad W_{22} = 5{\cdot}12\ (0{\cdot}59),$$
$$W_{33} = 9{\cdot}04\ (1{\cdot}27),\quad W_{12} = 0{\cdot}36\ (0{\cdot}47),$$
$$W_{13} = 0{\cdot}91\ (0{\cdot}67),\quad W_{23} = 0{\cdot}87\ (0{\cdot}51),$$

where, W defines the anisotropic particle size, $r(\mathbf{N}) = [\hat{\mathbf{N}}\mathbf{W}\mathbf{N}]^{-1/2}$, $\hat{\mathbf{N}}$ being the unit vector normal to the incident beam and lying in the scattering plane. The scattering amplitudes used in these calculations were $\bar{b}_{\rm H} = -3{\cdot}74$, $\bar{b}_{\rm Cu} = 7{\cdot}6$, $\bar{b}_{\rm Cl} = 9{\cdot}6$, $\bar{b}_{\rm N} = 9{\cdot}4$, $\bar{b}_{\rm O} = 5{\cdot}8$ fm. Attempts at refining the scattering amplitude of N in the final cycles did not indicate any significant change in the original value. The final positional and thermal parameters are listed in Table 2.*

Table 1. *R-factor table for various refinement models*

		Model 1 (ordered protons of NH_4^+)	Model 2 (0·5:0·5 disorder)	Model 3 ($x:1-x$) disorder)
(*a*) Isotropic thermal parameters (isotropic extinction)	$R(F)$	11·18%	7·72%	7·36%
(*b*) Anisotropic thermal parameters (isotropic extinction)	$R(F)$	3·48	3·10	3·02
(*c*) Anisotropic thermal parameters and anisotropic extinction, type I	$R(F)$* $R(F)$†			2·30 2·35
(*d*) Anisotropic thermal parameters and anisotropic extinction, type II	$R(F)$* $R(F)$†			2·29 2·34

(*a*) and (*b*): $w = [\sigma^2_{\rm count} + (0{\cdot}02F_o^2)^2]^{-1}$.
(*c*) and (*d*): $w = [\sigma^2_{\rm count}]^{-1}$.

* Reflections having $I < \sigma_{\rm count}$ omitted from the refinement.

† Reflections having $I < \sigma_{\rm count}$ and $F_o^2/F_c^2 < 0{\cdot}6$ omitted from the refinement.

Table 2. *Positional and thermal parameters in* $(NH_4)_2CuCl_4.2H_2O$

The equivalent value of the anisotropic temperature factor, $U_{\rm eq}$, is expressed as: $(\frac{1}{6}\pi^2)(\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j)$. The least-squares standard errors are given in parentheses, those on $U_{\rm eq}$ are calculated by the method of propagation of errors.

	Relative occupancy	Fractional coordinates (×10⁴) x	y	z	$U_{\rm eq}$ (Å^2) (×10⁴)
Cu	1	0	0	0	185 (5)
N	1	0	5000	2500	266 (4)
H(1)	0·64 (2)	0740 (7)	4196 (8)	3224 (9)	609 (25)
H(2)	0·36	0659 (15)	4130 (11)	1753 (15)	579 (51)
Cl(1)	1	7235 (1)	−7235 (1)	0	228 (4)
Cl(2)	1	2114 (1)	2114 (1)	0	211 (4)
O	1	0	0	2450 (3)	305 (6)
H*w*	1	0731 (3)	0731 (3)	3153 (4)	408 (8)

Results and discussion

The structural study of $(NH_4)_2CuCl_4.2H_2O$ shows that the crystal lattice essentially comprises three sub-units, NH_4^+, Cl^- and $CuCl_2.2H_2O$. Thus the framework of the present crystal can be considered similar to that of NH_4Cl diluted by $CuCl_2.2H_2O$ groups, chains of NH_4Cl alternating with chains of $CuCl_2.2H_2O$ running parallel to the c axis. The inter-ammonium distance within a chain is 3·99 Å as compared to 5·37 Å in the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35556 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane perpendicular to the chains, the octupolar interaction between the ammonium tetrahedra being weakened in two dimensions. Thus $(NH_4)_2CuCl_4.2H_2O$ is an assembly of very weakly-coupled chains of NH_4^+ ions running along the *c* axis. This pseudo one-dimensional nature of the ammonium-ion framework in the salt is also evident from specific-heat results (Suga *et al.*, 1965), susceptibility measurements at low temperatures (Miedema, Van Kempen & Huiskamp, 1963) and a laser–Raman scattering study of the evolution of order parameter with temperature (Roy, Sahni & Bansal, 1979). The interest in this salt is enhanced by its pseudo one-dimensional characteristics. Our study of the salt is restricted to the room-temperature structure of the compound in general, and the disorder in ammoniums in particular.

Table 3. *Interatomic distances and bond angles in* $(NH_4)_2CuCl_4.2H_2O$ *and* $K_2CuCl_4.2H_2O$, *for comparison*

The standard deviations are given in parentheses and include cell-parameter errors.

	$(NH_4)_2CuCl_4.2H_2O$	$K_2CuCl_4.2H_2O$
(*a*) The Cu octahedron		
2 × Cu—O	1·954 (3) Å	1·971 (6) Å
2 × Cu—Cl(1)	2·971 (1)	2·895 (4)
2 × Cu—Cl(2)	2·271 (1)	2·285 (3)
∠O···Cu···Cl(1)	90°	90°
∠O···Cu···Cl(2)	90	90
(*b*) The *X* polyhedron (cube)	$X = NH_4$	$X = K$
4 × *X*—Cl(1)	3·357 (1) Å	3·315 (4) Å
4 × *X*—Cl(2)	3·370 (1)	3·325 (4)
The hydrogen bond in the NH_4^+ salt	N—H···Cl	
4 × N—H(1)	1·011 (6) Å*	
	1·059 (7)†	
4 × N—H(2)	1·021 (11)*	
	1·063 (11)†	
4 × H(1)···Cl(1)	2·348 (6)	
4 × H(2)···Cl(2)	2·350 (11)	
∠N···H(1)···Cl(1)	175·1 (5)°	
∠N···H(2)···Cl(2)	178·6 (9)	
∠H(1)···N···Cl(1)	3·4 (3)	
∠H(2)···N···Cl(2)	1·0 (6)	
(*c*) The water molecule and the hydrogen bond O—H*w*···Cl		
O—H*w*	0·965 (3) Å*	0·955 (6) Å*
	0·978 (3)†	0·966 (6)†
H*w*—H*w*	1·571 (3)*	1·562 (11)*
	1·595 (3)†	1·580 (11)†
O···Cl(1)	3·146 (2)	3·116 (5)
H*w*···Cl(1)	2·186 (2)	2·165 (6)
∠H*w*···O···H*w*	109·0 (4)°	109·7 (7)°
∠Cl(1)···O···Cl(1)	99·46 (8)	100·3 (2)
∠H*w*···O···Cl(1)	4·7 (2)	4·7 (3)

* Uncorrected for thermal motion.

† Corrected for thermal motion, assuming that the H atom 'rides' on the heavy atom (Busing & Levy, 1964). In calculating the 'corrected' H*w*—H*w* distance, it is assumed that the H*w*···O···H*w* angle remains unchanged.

Some of the interatomic distances and angles calculated using the program *ORFFE* (Busing, Martin & Levy, 1964) are shown in Table 3, along with those of $K_2CuCl_4.2H_2O$. The Cu has a distorted octahedral coordination with two water O atoms, two closer Cl atoms, Cl(2), and two farther Cl atoms, Cl(1). The ammonium ion is coordinated tetrahedrally either to four Cl(1) or to four Cl(2), the eight Cl atoms together forming a distorted cube around NH_4^+. The ammonium ion thus has two energetically comparable orientations available. Disorder is observed between these two sites with occupancies 0·64 (2):0·36 in favour of H atoms being bonded to closer Cl atoms, Cl(1). Fig. 1 shows a view of the surroundings of the ammonium ion. The thermal ellipsoids of all the atoms have been drawn to include 30% probability density. The water molecule is trigonally coordinated, forming two equivalent bent hydrogen bonds [∠H*w*···O···Cl (1) = 4·75°] with the Cl(1) ions belonging to the nearest-neighbour Cu octahedra. Of the two distinct types of Cl atoms, one, Cl(1), is bonded to four ammonium protons and two water protons and is also long-bonded to Cu while the other, Cl(2), is hydrogen-bonded to four ammonium H atoms and is short-bonded to Cu. A stereoscopic projection of the unit cell, given in Fig. 2, clearly shows

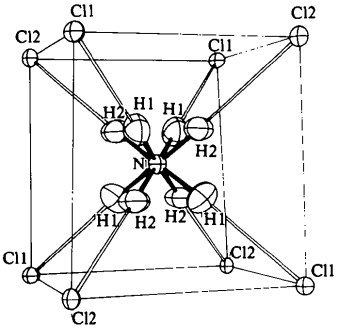

Fig. 1. An illustration of the surroundings of the disordered ammonium ion, occupancies of H(1) and H(2) being 0·64 (2) and 0·36 respectively. The thermal ellipsoids are scaled to include 30% probability.

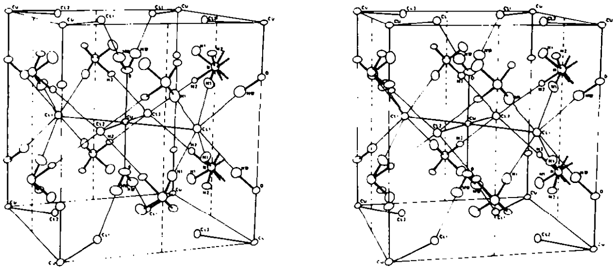

Fig. 2. Stereoscopic illustration of the contents of the unit cell showing the surroundings of Cl(1) [long-bonded to Cu] and Cl(2) [short-bonded to Cu], along with a few representative hydrogen bonds. The thermal ellipsoids have been drawn to include 30% probability, those of NH_4^+ ion H atoms being further scaled by the occupancy factors.

the surroundings of Cl(1) and Cl(2) and also indicates the three-dimensional network of O—H···Cl and N—H···Cl hydrogen bonds which bind the NH_4^+ ions and Cu octahedra together. The details of the hydrogen-bond parameters are given in Table 3.

Comparisons between the K and NH_4 salts show that the introduction of NH_4^+ in place of K^+ has not altered the backbone of the structure. In the ammonium salt, however, due to the hydrogen bonds associated with Cl(1), the latter are perhaps moved away from Cu while the water oxygens and the other Cl atoms, Cl(2), are consequently pulled closer to the Cu.

The two-dimensional neutron diffraction results of Matković *et al.* (1969) have been deduced from *hk*0 and 0*kl* data. On the basis of these projections, it may not be possible to distinguish between the ordered structure, *i.e.* parallel ordering of ammonium tetrahedra along the *c* axis and the disordered structure. The ordered ammonium ions reported by these workers are, in any case, not consistent with our findings. Oxton & Knop (1977) have interpreted their IR spectra using Matković *et al.*'s (1969) structure at room temperature as the starting point. As such, their deductions regarding the NH_3D^+ stretching band may be misleading. An exact analysis of their spectra at low temperatures and the phase transitions therein should await a study of the structure of the title compound at low temperature.

Specific-heat measurements (Suga *et al.*, 1965) on this salt indicated a λ transition at $T_c \sim 200{\cdot}5$ K. On comparison with $K_2CuCl_4.2H_2O$, this anomaly has been attributed to the reorientational motion of ammonium ions in the salt. The authors have estimated the transition entropy from the experimental specific-heat anomaly after correcting for the normal specific heat and the internal vibrations of NH_4^+. The smallness of the estimated transition entropy $\Delta S_{tr} = 1{\cdot}945$ e.u. (using vibrational frequencies of NH_4Cl), compared to $2R \ln 2$ (= 2·76 e.u., assuming complete disorder) has been attributed to residual disorder in the low-temperature phase. However, if the 64:36 disorder at room temperature as observed in the present study is taken into account, the discrepancy between the observed and calculated ΔS_{tr} seems to reduce a little. The discrepancy reduces further when the transition entropy values are recalculated using the vibrational frequencies for NH_4^+ in $(NH_4)_2CuCl_4.2H_2O$ presently available (Bansal, Sahni & Roy, 1979). With these modifications incorporated, the estimated transition entropy is $\Delta S_{tr} = 2{\cdot}12$ e.u. as against the expected value of 2·52 e.u. for $2R(0{\cdot}643 \ln 0{\cdot}643 - 0{\cdot}357 \times \ln 0{\cdot}357)$.

Assuming simple Boltzmann statistics, the energy difference between the two available orientations (with occupancies 0·64 and 0·36) has been calculated and found to be ~1·38 kJ mol^{-1}. The difference in the hydrogen-bond energies [along Cl(1) and Cl(2)] for the two different orientations of NH_4^+, calculated on the basis of the Lippincott–Schroëder formalism for bent bonds (Chidambaram & Sikka, 1968), works out to be approximately 0·67 kJ mol^{-1}. We cannot, however, rule out the role of other interactions involving the ammonium ions.

For a better understanding of the partial-disorder phenomenon in this salt at room temperature, we propose to perform a low-temperature study.

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