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The Positions of Hydrogen Atoms in $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ by Neutron Diffraction

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The structure of $(NH_4)_2\,CuCl_4 \cdot 2\,H_2O$ has been determined from two-dimensional neutron data. The *R* index is 5.6% when unobserved reflections are omitted. Two water oxygen atoms with the Cu—O distance of 1.98 Å and two chlorine atoms with the Cu—Cl distance of 2.30 Å form a planar $Cu(OH_2)_2Cl_2$ grouping. Each copper atom also forms two long Cu—Cl bonds of 3.03 Å with the other two chlorine atoms and so completes its distorted octahedral configuration. The structure consists of distorted $[Cu(OH_2)_2Cl_2]Cl_2$ octahedra connected by hydrogen bonds and NH_4 tetrahedra which occupy holes between the three-dimensional network of octahedra.

INTRODUCTION

Structural studies on diammonium copper(II) tetrachloride dihydrate, $(NH_4)_2CuCl_4 \cdot 2\,H_2O$, were carried out be Hendricks and Dickinson (1927)[1], and by Chrobak (1929)[2]. The similar manganese compound, $(NH_4)_2MnCl_4 \cdot 2\,H_2O$, was investigated by Greenberg and Walden (1940)[3]. The crystal structure of $K_2MnCl_4 \cdot 2\,H_2O$ was published recently by Jensen (1968)[4]. The structural studies of above mentioned compounds were investigated by X-ray diffraction methods. The obtained results may be summarized as follows:

(1) Compounds with the common formula $R_2CuCl_4 \cdot 2\,H_2O$ (where R = = ammonium, potassium or rubidium) are isomorphous; $(NH_4)_2CuBr_4 \cdot 2\,H_2O$ belongs to this series too[5]. The crystal isomorphism between $(NH_4)_2MnCl_4 \cdot 2\,H_2O$ and $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ was suggested[3]. $K_2MnCl_4 \cdot 2\,H_2O$ has close structural relationship[4] with this group of compounds.

(2) Central atoms are surrounded by for chlorine and two water oxygen atoms forming discrete octahedra, defined by formula $[M(OH_2)_2Cl_2]Cl_2^{2-}$, where M = Cu or Mn; M—Cl bonds are equal only in $K_2MnCl_4 \cdot 2\,H_2O$ [4], the other compounds have two short and two long M—Cl bonds[5]. R^+ ions (R = NH_4, K, Rb) occupy holes between the three-dimensional network of octahedra.

It was of interest to determine by neutron diffraction the positions of hydrogen atoms in either of these compounds which contain NH_4 groupings. This work reports such an investigation on $(NH_4)_2CuCl_4 \cdot 2\,H_2O$.

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EXPERIMENTAL

The single crystals of $(NH_4)_2CuCl_4 \cdot 2\,H_2O$ were prepared by slow evaporation of a saturated aqueous solution, as described previously[1]. The crystallographic data are very close to those obtained by Hendricks and Dickinson[1]. They are listed in Table I along with the data for compounds mentioned before. The unit cell dimensions were obtained from oscillation and Weissenberg X-ray photographs and corrected from single crystal axial reflections (recorded by neutron diffractometer). Absences for $P4_2/mnm$ space group were checked and confirmed.

TABLE I

Crystal Data

	a (Å)	c (Å)	Space group	Z	Reference
$(NH_4)_2CuCl_4 \cdot 2\,H_2O$	7.64 ± 0.01	7.98 ± 0.01	$P4_2/mnm$	2	This work
$K_2CuCl_4 \cdot 2\,H_2O$	7.45	7.88	,,	,,	5
$Rb_2CuCl_4 \cdot 2\,H_2O$	7.81	8.00	,,	,,	,,
$(NH_4)_2CuBr_4 \cdot 2\,H_2O$	7.98	8.41	,,	,,	,,
$K_2MnCl_4 \cdot 2\,H_2O$	7.415 ± 0.005	8.220 ± 0.005	$I4/mmm$ or $I\bar{4}2m$	,,	4

For collecting neutron diffraction data, a cylinder 2.0 mm in diameter weighing 31 mg was cut from a larger crystal and shaped with the a crystal axis coinciding with the cylinder axis; another cylinder 3.25 mm in diameter weighing 213 mg was cut and shaped with the c crystal axis coinciding with the cylinder axis. The crystals were then oriented for collecting of $hk0$ and $0kl$ data, and a total of 101 independent intensities in these zones were measured on a two circle Picker diffractometer. The wave length used was 1.362 Å. Absorption corrections ($\mu = 2.84$ cm^{-1}) were applied and the observed structure factors were placed on a near absolute scale in the usual way by calibration with the 400 reflection of NaCl. Signs were attached to these structure factors on the basis of Hendricks and Dickinson's parameters[1], and the Fourier projections were calculated. From these projections it was possible to locate the hydrogen atoms. Further parameter refinement was subsequently carried out by means of a weighted least squares refinement by the ORFLS program[6]. The reflections were assigned weights according to the formula already described[7]. The anisotropic temperature factors were calculated only for coefficients β_{11}, β_{22} and β_{33}, because the attempts to vary all possible coefficients were unsuccessful, probably because of small number of reflections. Since temperature factor refinement from projection data is usually unreliable, the coefficients listed are not likely to have more than qualitative significance. After the last least-squares refinement the R_1 factor (including unobserved reflections at half minimum observed value) was reduced to 7.6% and R_2 factor (omitting unobserved reflections) to 5.6%. The definitions of R_1 and R_2 and the final parameters are listed in Table II. The parameters obtained before for similar compounds are listed in Table III. Tables II and III have the same notation. The observed and calculated structure factors are listed in Table IV. Interatomic distances and bond angles are listed in Table V along with their standard errors. They were computed using ORFFE, Fortran function and error program[8].

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

It is obvious from Tables II and III that the atomic coordinates are similar in all of these compounds, and consequently, so are their atomic arrangements. The main difference between the $K_2MnCl_4 \cdot 2\,H_2O$ structure and the others, as mentioned in Introduction, is that manganese-chlorine bonds are equal, and copper atoms in the other mentioned compounds have two short and two long bonds with the chlorine atoms.

TABLE II

Fractional Coordinates for $(NH_4)_2CuCl_4 \cdot 2\,H_2O$

Notation of atom coordinates is the same as in Table III, for comparison. The thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$. $\beta_{22} = \beta_{11}$ for all the atoms except H (2). Standard errors are given in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}
Cu (a) mmm	0	0	0	0.0071 (0.0023)	0.0071 (0.0023)	0.0064 (0.0034)
N (d) $\bar{4}$	0	1/2	1/4	0.0113 (0.0005)	0.0113 (0.0005)	0.0073 (0.0253)
Cl (1) (f) mm	0.2125 (0.0015)	0.2125 (0.0015)	0	0.0101 (0.0009)	0.0101 (0.0009)	0.0055 (0.0018)
Cl (2) (g) mm	0.2195 (0.0013)	0.2195 (0.0013)	1/2	0.0098 (0.0009)	0.0098 (0.0009)	0.0094 (0.0017)
O (e) mm	0	0	0.2480 (0.0052)	0.0177 (0.0023)	0.0177 (0.0023)	0.0067 (0.0516)
H (1) (j) m	0.0673 (0.0011)	0.0673 (0.0011)	0.3275 (0.0060)	0.0145 (0.0009)	0.0145 (0.0009)	0.0003 (0.0083)
H (2) (k)	0.0708 (0.0015)	0.4137 (0.0015)	0.1832 (0.0056)	0.0247 (0.0023)	0.0184 (0.0018)	0.0263 (0.0057)

$R_1 = \Sigma_{hkl} \,||\, F_o \,| - |\, F_c \,||\, / \Sigma_{hkl} \,|\, F_o \,| = 0.076$ (including unobserved reflections)

$R_2 = \Sigma_{hkl} \,||\, F_o \,| - |\, F_c \,||\, / \Sigma_{hkl} \,|\, F_o \,| = 0.056$ (omitting unobserved reflections)

TABLE III

Atomic Coordinates for Compounds with Close Structural Relationship

Notation of chlorine coordinates is as in Wyckoff[5].

		$P4_2/mnm$	$I4/mmm$
Cu or Mn	2 (*a*)	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2};$	the same
K, Rb or N	4 (*d*)	$0, \frac{1}{2}, \frac{1}{4};\ \frac{1}{2}, 0, \frac{1}{4};\ 0, \frac{1}{2}, \frac{3}{4};\ \frac{1}{2}, 0, \frac{3}{4};$	the same
Cl (1) or Br (1)	4 (*f*)	$\pm\left(u, u, 0;\ u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}\right)$	Cl in 8 (*h*), eightfold position, the same coordinates with $v = 1/2 - u$
Cl (2) or Br (2)	4 (*g*)	$\pm\left(v, v, \frac{1}{2};\ v+\frac{1}{2}, \frac{1}{2}-v, 0\right)$	
O	4 (*e*)	$\pm\left(0, 0, w;\ \frac{1}{2}, \frac{1}{2}, w+\frac{1}{2}\right)$	the same
H	8 (*h*)	$\pm\left(x, x, z;\ -x, -x, z;\ \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}+z;\ \frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}+z\right)$	
			H in 16 (*m*), the same coordinates plus $\pm\left(-x, x, z;\ x, -x, z;\ \frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}+z;\ \frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}+z\right)$

	u	v	w	Space group	Reference
$K_2CuCl_4 \cdot 2\,H_2O$	0.220	0.220	0.250	$P4_2/mnm$	5
$Rb_2CuCl_4 \cdot 2\,H_2O$	0.213	0.217	0.330	,,	,,
$(NH_4)_2CuBr_4 \cdot 2\,H_2O$	0.218	0.222	0.250	,,	,,
$K_2MnCl_4 \cdot 2\,H_2O$	0.2414	0.2586	0.2647	$I4/mmm$	4

(Water hydrogens in $K_2MnCl_4 \cdot 2\,H_2O$ were placed at x, x, z with $x = 0.0634$, $z = 0.3134$ and a statistical distribution was supposed.)

TABLE IV

Observed an Calculated Structure Factors for $(NH_4)_2CuCl_4 \cdot 2H_2O$

(An asterisk before F_o indicates an unobserved reflection. The numerical value is the estimated minimum observable value.)

h k 0	F_o	F_c	h k 0	F_o	F_c	h 0 l	F_o	F_c
2 0 0	4.44	—4.53	4 3 0	1.39	—1.54	0 0 2	6.38	8.61
4 0 0	12.06	12.60	4 4 0	8.04	7.31	0 0 4	14.51	15.41
6 0 0	7.29	7.46	4 5 0	3.39	2.93	0 0 6	2.23	—2.17
8 0 0	5.16	5.24	4 6 0	2.69	2.34	0 0 8	12.99	13.10
1 1 0	2.59	2.47	4 7 0	*0.48	—0.40	1 0 1	2.93	2.96
1 2 0	1.88	—2.11	4 8 0	1.95	2.24	1 0 3	1.16	—0.97
1 3 0	1.21	—1.20	5 1 0	*0.48	—0.20	1 0 5	3.76	3.34
1 4 0	5.78	6.26	5 2 0	*0.48	—0.60	1 0 7	*0.38	1.94
1 5 0	*0.48	—0.20	5 3 0	2.99	—2.97	1 0 9	*0.38	—1.16
1 6 0	4.33	—4.26	5 4 0	3.45	2.93	2 0 0	4.49	—4.53
1 7 0	1.33	—1.43	5 5 0	4.12	4.32	2 0 2	7.77	—7.34
1 8 0	4.16	3.89	5 6 0	0.96	—1.12	2 0 4	1.42	1.29
1 9 0	*0.48	0.95	5 7 0	2.87	—2.99	2 0 6	11.11	—11.30
2 1 0	1.80	—2.11	6 1 0	4.40	—4.26	2 0 8	2.00	2.25
2 2 0	9.56	10.33	6 2 0	8.30	8.33	3 0 1	1.13	1.19
2 3 0	4.01	3.82	6 3 0	5.27	5.37	3 0 3	*0.38	0.65
2 4 0	3.70	3.17	6 4 0	2.59	2.34	3 0 5	1.03	1.06
2 5 0	*0.48	—0.61	6 5 0	1.07	—1.12	3 0 7	0.75	0.65
2 6 0	8.86	8.33	6 6 0	1.76	1.80	4 0 0	12.36	12.60
2 7 0	*0.48	—0.11	6 7 0	*0.48	0.19	4 0 2	*0.38	—0.21
2 8 0	4.64	5.11	7 1 0	1.48	—1.43	4 0 4	9.20	9.33
3 1 0	1.27	—1.21	7 2 0	*0.48	—0.11	4 0 6	1.44	1.43
3 2 0	4.07	3.82	7 3 0	2.76	2.82	4 0 8	6.35	6.27
3 3 0	2.04	2.11	7 4 0	*0.46	—0.40	5 0 1	1.33	1.02
3 4 0	1.42	—1.34	7 5 0	3.00	—2.99	5 0 3	3.02	2.88
3 5 0	3.06	—2.97	7 6 0	*0.46	0.19	5 0 5	*0.38	0.84
3 6 0	5.39	5.37	8 1 0	4.29	3.89	5 0 7	1.31	1.18
3 7 0	2.75	2.82	8 2 0	4.81	5.11	6 0 0	7.53	7.46
3 8 0	3.17	—3.06	8 3 0	2.97	—3.06	6 0 2	7.31	—6.34
4 1 0	5.78	6.26	8 4 0	2.03	2.24	6 0 4	2.55	2.34
4 2 0	3.61	3.17	9 1 0	*0.45	0.95	6 0 6	*0.38	—0.84
			9 2 0	*0.48	0.22	7 0 1	0.96	0.61
						7 0 3	1.65	1.97
						7 0 5	*0.38	0.08
						8 0 0	5.07	5.24
						8 0 2	3.51	—3.37
						8 0 4	1.90	2.18
						9 0 1	*0.38	0.49

Fig. 1 represents the projection of the $(NH_4)_2CuCl_4 \cdot 2\ H_2O$ structure on a plane normal to [001]. The closest neighbours of the copper atom are two water-oxygen (Cu—O = 1.979 Å) and two chlorine atoms (Cu—Cl (1) = 2.296 Å). They form a $Cu(OH_2)_2Cl_2$ planar grouping. Each copper atom completes its distorted octahedral configuration by forming two long copper-chlorine bonds (Cu—Cl (2) = 3.031 Å). The water-hydrogen atoms (H (1)) were found to be 0.965 Å from oxygen and 2.14 Å from the chlorine (Cl (2)) atoms. The chlorine--hydrogen-oxygen (Cl (2) . . . H (1) — O) distance of 3.109 Å indicates hydrogen bonds between the chlorine atoms (Cl (2)) from one octahedral group and water-oxygens which belong to other octahedra. Nitrogen atoms are surrounded by four hydrogen atoms in tetrahedral coordination and in outer coordination by eight chlorine atoms which are located at the corners of a slightly distorted

TABLE V

Selected Interatomic Distances and Angles in $(NH_4)_2CuCl_4 \cdot 2H_2O$

Standard errors are given in parentheses

Within octahedron in Å

Cu—O = 1.979 (42)
Cu—Cl(1) = 2.296 (8)
Cu—Cl(2) = 3.031 (7)
Cl(1)—O = 3.031 (30)
Cl(2)—O = 3.620 (30)
Cl(1)—Cl(2) = 3.802 (10)

Outside octahedron in Å

O—Cl(2) = 3.109 (29)
N—Cl(2) = 3.374 (5)
N—Cl(1) = 3.382 (5)
N—O = 3.820 (35)
Cl(1)—Cl(2) = 3.991 (11)

Other distances in Å

O—H(1) = 0.965 (45) in H_2O
N—H(2) = 1.006 (25) in NH_4
Cl(2)—H(1) = 2.144 (31)
Cl(1)—H(2) = 2.381 (30)
H(1)—H(2) = 2.886 (19)

Angles

O—H(1)—Cl(2) = 179° (4°)
N—H(2)—Cl(1) = 173° (3°)
H(1)—O—H(1) = 98° (6°)

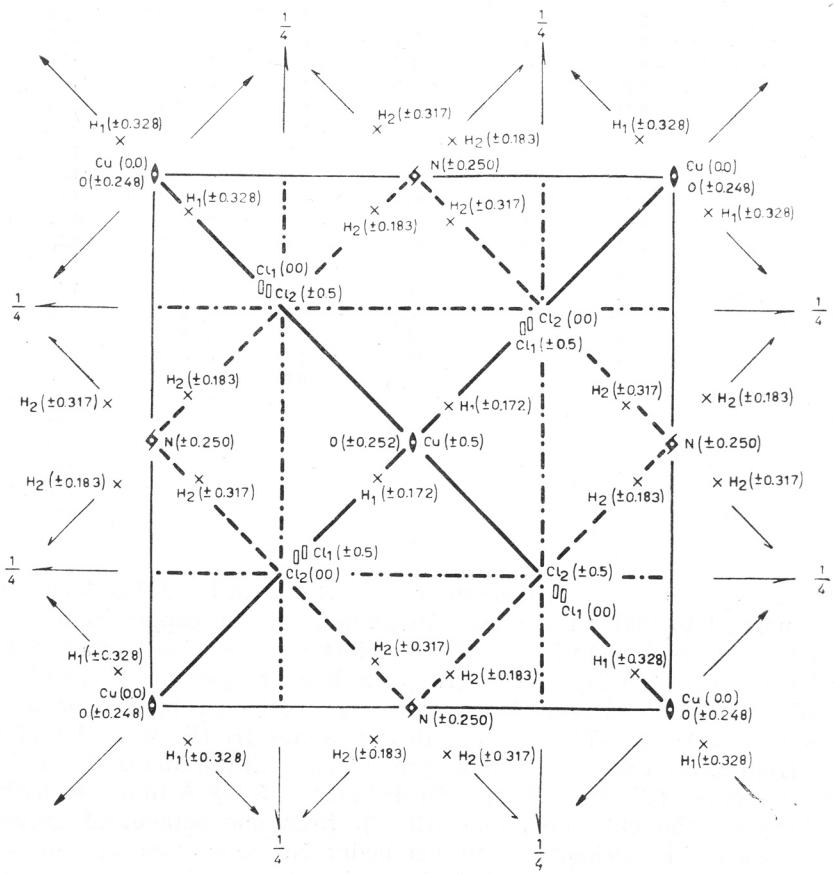

Fig. 1. Contents of the unit cell and symmetry elements projected down the c axis. z coordinates are in parentheses.

cube (N—Cl (2) = 3.374, and N—Cl (1) = 3.382 Å). Hydrogen atoms (H (2)), which belong to NH_4 groupings, are in general position with N—H (2) distance of 1.006 Å. They are directed to chlorine (Cl (1)) atoms, which belong to shorter copper-chlorine (Cu—Cl (1)) bonds. The chlorine-hydrogen (Cl (1) ... H (2)) distance was found to be 2.381 Å. Thus the structure consists of distorted $[Cu(OH_2)_2Cl_2]Cl_2$ octahedra connected by hydrogen bonds and NH_4 tetrahedra, which occupy holes between the octahedra. A view of the unit cell with all atoms is represented in Fig. 2. The unit cell is indicated by broken lines; the chlorine and oxygen atoms, which surround the copper atom, are connected by full lines; dotted lines join chlorine and hydrogen atoms, which are part of Cl (2) ... H (1) —O hydrogen bonds. The closets contact, that between water- and ammonium-hydrogen atoms (H (1) and H (2)), a distance of 2.886 Å, is greater than the expected van der Waals separation. The chlorine-copper--oxygen bond angles are required by symmetry to be 90^0. The bond angle in the water molecule (H (1) —O—H (1)) is 98 ± 6^0. The chlorine-hydrogen-oxygen (Cl (2) —H (1) —O) bond angle is linear within the precision of the measurement, and chlorine-hydrogen-nitrogen (Cl (1) —H (2) —N) angle is observed to be $173^0 \pm 3^0$.

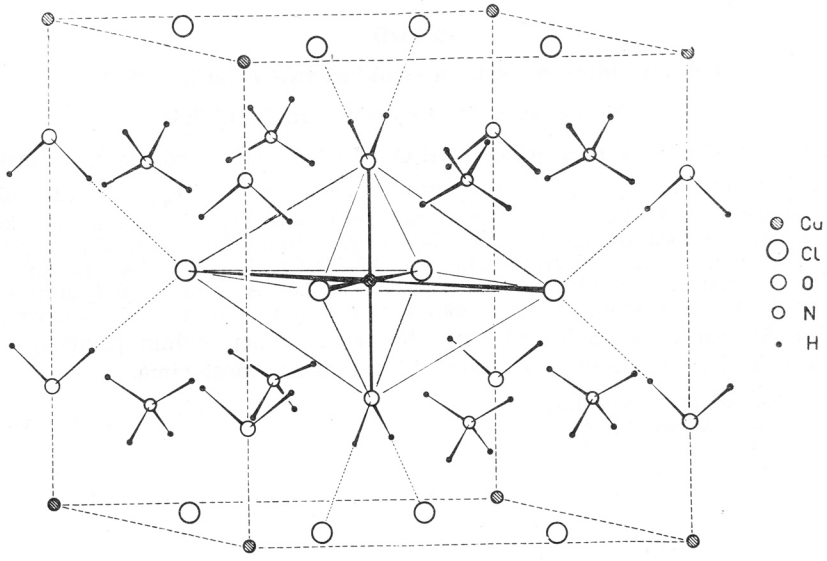

Fig. 2. A view down the unit cell of $(NH_4)_2CuCl_4 \cdot 2H_2O$

The configurations and the values of interatomic distances obtained in this structure are in agreement with those already found. A planar $Cu(OH_2)_2Cl_2$ group with Cu—O = 1.925 Å and Cu—Cl = 2.275 Å was found in the structure of $CuCl_2 \cdot 2 H_2O$[9]. Copper-oxygen octahedral bond lengths (averaged shorter Cu—O distances are 1.956 Å) obtained in $CuMoO_4$ [10], together with copper--oxygen distances cited in the same article[10] for comparison, agree with the values reported in the present paper. $(NH_4)_2CuCl_4$ [11] has a $CuCl_4$ square planar group with four short copper-chlorine bond lengths of 2.300 and 2.332 Å. The

atomic arrangement in $(NH_4)_2CuCl_4$ also has two long (apical) copper-chlorine bonds of 2.793 Å and the configuration around the copper atom is a distorted octahedral. The O—H . . . Cl hydrogen bond of 3.18 Å found in $CuCl_2 \cdot 2H_2O$ [9] is also compatible with present data.

REFERENCES

1. S. B. Hendricks and R. G. Dickinson, *J. Am. Chem. Soc.* **49** (1927) 2149.
2. L. Chrobak, *Bull. Acad. polonaise Sci. Letters,* 1929 A, 361; and *Z. Krist.* **88** (1934) 35.
3. A. L. Greenberg and G. H. Walden, Jr., *J. Chem. Phys.* **8** (1960) 645.
4. S. J. Jensen, *Acta Chem. Scand.* **22** (1968) 647.
5. R. W. G. Wyckoff, *Crystal Structures,* Vol. III, John Wiley & Sons, Inc., New York 1965, p. 617.
6. W. R. Busing, K. O. Martin, and H. A. Levy, *U. S. Atomic Energy Commission Report ORNL-TM-305* (1962).
7. J. E. Worsharm, Jr., H. A. Levy, and S. W. Peterson, *Acta Cryst.* **10** (1957) 319.
8. W. R. Busing, K. O. Martin, and H. A. Levy, *U. S. Atomic Energy Commission Report ORNL-TM-306* (1964).
9. S. W. Peterson and H. A. Levy, *J. Chem. Phys.* **26** (1957) 220.
10. S. C. Abrahams, J. L. Bernstein, and P. B. Jamieson, *J. Chem. Phys.* **48** (1968) 2619.
11. R. D. Willett, *J. Chem. Phys.* **41** (1964) 2243.

IZVOD

Položaj hidrogen-atoma u strukturi $(NH_4)_2CuCl_4 \cdot 2H_2O$

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Kristalna struktura $(NH_4)_2CuCl_4 \cdot 2H_2O$ određena je metodama neutronske difrakcije. Kristali su tetragonski, prostorna grupa $P4_2/mnm$ (D_{4h}^{14}), $Z = 2$. Dobiveni faktor tačnosti iznosi 5,6% (bez neopaženih refleksa). Dva oksigen atoma, koji su udaljeni 1,98 Å od bakrenog atoma, i dva klorova atoma, koji su udaljeni 2,30 Å od istoga bakrenog atoma, stvaraju planarnu $Cu(OH_2)_2Cl_2$ grupaciju. Bakar je još povezan s preostala dva klora duljom vezom od 3,03 Å, i tako upotpunjuje svoju koordinaciju na šest atoma koji su oko njega raspoređeni u obliku deformiranog oktaedra. Struktura se sastoji od NH_4^+ tetraedara i nepravilnih $[Cu(OH_2)_2Cl_2]Cl^{2-}$ oktaedara, koji su međusobno povezani hidrogenskim mostovima.

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