

Table 4 (*cont.*)

Th ₂ N ₂ Sb	2.39*	3.56*
Th ₂ (N _{1/2} O _{1/2}) ₂ Sb	2.35*	3.49*
Th ₂ N ₂ Te	2.38	3.54
Th ₂ N ₂ Bi	2.41*	3.58*
Th ₂ (N, O) ₂ Bi (oxygen saturated)	2.40*	3.57*

* Limits of uncertainties in bond distances are of the order of two to three times that of the compound U₂N₂Sb.

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Neutron Diffraction Refinement of the Crystal Structure of Potassium Copper Chloride Dihydrate, K₂CuCl₄·2H₂O

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A refinement of the crystal structure of K₂CuCl₄·2H₂O (space group $P4_2/mnm$; $a = 7.477$, $c = 7.935$ Å) has been carried out using the intensities of 201 independent three-dimensional single-crystal neutron reflexions with $\sin \theta/\lambda \leq 0.57$ Å⁻¹. The final R index on F is 0.039. The copper atom has a distorted octahedral coordination consisting of two H₂O molecules at 1.971 Å, two Cl atoms at 2.285 Å and two Cl atoms at 2.895 Å. The water molecule is trigonally coordinated and forms two equivalent O—H---Cl bonds at distances of 3.116 Å with H—O---Cl angles of 4.7°. The O—H distance in the water molecule is 0.955 Å (uncorrected for thermal motion) and the H—O—H angle is 109.7°.

Introduction

The crystal structure of K₂CuCl₄·2H₂O has been studied using X-rays by Hendricks & Dickinson (1927) and Chrobak (1934) (see also Wyckoff, 1965). The heavy-atom positions have been determined approximately in these investigations. The proton magnetic resonance in a single crystal of this compound has been studied by Itoh, Kusaka, Yamagata, Kiriyaama & Ibamoto (1953) and by McGrath & Silvidi (1961); the length and orientation of the interproton vector determined by the latter have also been used recently by El Saffar (1968) to predict the hydrogen positions.

Experimental

The preliminary analysis of the crystal structure was carried out on the basis of 53 hll intensities collected at 1.17 Å from a cylindrical sample with its axis parallel

to [01 $\bar{1}$] in the neutron diffractometer at the Philippine Research Reactor (PRR-1) near Manila. The final refinement was based on three-dimensional data collected in the neutron diffractometer 3D-FAD (Momin, Sequeira & Chidambaram, 1969) at the CIRUS reactor in Trombay. The crystal used was a rectangular parallelepiped (weight = 46 mg) with its longest edge of 3.7 mm parallel to [11 $\bar{1}$]. A total of 201 independent reflexions were measured at 1.406 Å up to $\sin \theta/\lambda = 0.57$ Å⁻¹.

The space group extinctions for $P4_2/mnm$ were confirmed.* Using the 2θ values of 26 reflexions, the unit-cell constants were refined and found to be $a = 7.477(13)$

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* The systematic extinctions are also consistent with the non-centrosymmetric space groups $P4_2n2$ and $P4_2nm$, in view of which one of the referees has suggested that the authors should re-examine the space group determination. In anisotropic least-squares refinements these space groups would involve 8 and 17 additional parameters respectively. To reject $P4_2/mnm$ in favour of either of these at a significance level of 0.005 would require an improvement in the R index by ratios of 1.08 and 1.12 respectively (Hamilton, 1964). In view of the fact that (a) the structure refined in the space group $P4_2/mnm$ to an R index of 0.039, (b) there were no anomalous thermal parameters or bond lengths in this refinement and (c) since at worst only small deviations from this are likely to arise in the refinements in the non-centrosymmetric space groups which would become highly non-linear in consequence, we have not considered it worth while to attempt such refinements in the space groups $P4_2n2$ and $P4_2nm$.

Table 1. *Positional and thermal parameters in K₂CuCl₄·2H₂O*

The expression for the temperature factor is

$$\exp [-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$$

The least-squares standard errors are given in parentheses.

	Fractional coordinates ($\times 10^4$)				Thermal parameters ($\times 10^4$)				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu	0	0	0	235 (14)	<i>U</i> ₁₁	159 (17)	-063 (9)	0	0
K	0	5000	2500	404 (26)	<i>U</i> ₁₁	247 (27)	0	0	0
Cl(1)	2161 (3)	<i>x</i>	0	232 (8)	<i>U</i> ₁₁	254 (10)	-068 (6)	0	0
Cl(2)	7262 (3)	- <i>x</i>	0	264 (8)	<i>U</i> ₁₁	240 (10)	060 (6)	0	0
O	0	0	2484 (5)	386 (23)	<i>U</i> ₁₁	171 (21)	-127 (19)	0	0
H	0739 (10)	<i>x</i>	3178 (6)	451 (23)	<i>U</i> ₁₁	353 (26)	-098 (21)	-016 (16)	<i>U</i> ₁₃

and $c=7.935(19)$ Å. There are two formula units in the unit cell. The linear absorption coefficient was calculated and found to be 1.56 cm^{-1} at 1.406 Å; the raw data were reduced to structure factors using the CDC-3600 program *DATARED* (Srikanta, 1968), which includes the absorption-correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine.

Refinement of the structure

Starting with the heavy-atom coordinates as reported by Hendricks & Dickinson (1927) and hydrogen positions as indicated by the proton resonance work of McGrath & Silvidi (1961), the structure was refined by conventional Fourier and least-squares techniques. The observed data F_o^2 were found to be suffering from secondary extinction:

$$\frac{F_o^2}{F_c^2} \approx \left(1 - 0.00155 \frac{F_c^2}{\sin 2\theta}\right)$$

(the reflexion most severely affected was 004 for which $F_o^2/F_c^2=0.687$ and $F_c^2/\sin 2\theta=220$). An error analysis based on the observed structure factors F_o^2 corrected for secondary extinction indicated the suitability of the following weighting scheme:

$$\omega^{-1/2} = \langle |F_o^2 - F_c^2| \rangle_{av} \approx 0.12 + 0.031 \frac{F_c^2}{\sin 2\theta}$$

This scheme was used in the final stages of the refinement (on F^2) which converged at a discrepancy index $R_x \equiv [\sum |F_o^x - F_c^x| / \sum |F_o^x|]$ of 0.0396 for $x=1$. The following scattering amplitudes (in units of 10^{-12} cm) were used up to this stage: H, -0.378 ; Cu, 0.79 ; K, 0.35 ; O, 0.577 and Cl, 0.99 . The intensity data seemed good enough to merit a least-squares refinement of the scattering amplitudes along with other parameters. This was carried out with the scattering amplitude of H held at -0.378 (total number of parameters varied = 28). The refinement converged at $R_1=0.0390$ and led to the following values for the other scattering amplitudes; Cu, $0.794(29)$; K, $0.374(17)$; O, $0.587(19)$ and Cl, $0.961(28)$. The final discrepancy factors were as follows:

	Set 1	Set 2
$x=1$	0.039	0.030
$x=2$	0.053	0.052
Number of data	201	174

Table 2. *K₂CuCl₄·2H₂O: observed and calculated structure factors*

The four columns in each set contain respectively *h*, *l*, $100F_o^2$ and $100F_c^2$.

<i>k</i>	<i>h</i>	<i>l</i>	$100F_o^2$	$100F_c^2$
0	2	4613	5141	7 00 03
4	13455	14568	8 932	966 7 0
6	544	572	2 0	250 237 2 104
8	9046	9697	1 387	382 3 82 84 3 03
1	850	850	2 1049	987 4 42 32 4 2274
5	49	42	3 00	01 8 0 1624 1604 5 52
5	1148	1149	4 535	537 1 26 20 6 205
7	116	105	5 499	496 2 1993 1679 7 0
2	1265	1195	6 215	203 1 114 104 1 214
2	5727	5919	7 71	70 2 0 10424 10500 2 46
4	148	147	8 454	398 1 83 92 3 337
6	5960	6117	3 1 67	61 2 2364 2213 4 65
8	19	02	2 12	12 3 128 142 8 0
3	111	118	3 44	43 4 8914 10214 1 46
3	05	15	4 284	265 5 182 173 1 13
5	152	142	5 108	105 6 731 725 3 0
7	53	42	6 17	03 7 15 00 1 13
4	0	11260	10170	7 06 02 8 5982
2	691	749	8 247	237 3 0 1765 1775 3 630
4	6972	7058	4 0 2837	2919 1 378 397 4 1100
6	754	788	1 177	151 2 68 62 5 90
5	193	200	2 1182	1221 3 268 252 6 305
3	862	900	3 339	345 4 344 333 7 38
5	73	70	4 1452	1427 5 334 334 4 0
7	207	228	5 81	90 6 697 692 1 105
0	722	660	6 1442	1428 7 187 175 2 2270
2	2086	2110	7 128	125 8 03 24 3 212
4	68	62	5 0 1928	1551 4 0 11 09 4 1620
6	357	368	1 24	22 1 22 02 5 97
7	02	00	2 51	39 2 3945 3736 6 308
3	398	306	3 160	174 3 394 396 7 61
5	18	07	4 588	563 4 09 00 3 0 11
8	0	1951	1523	5 04 04 5 36 42 1 137
2	93	95	6 323	315 6 1838 1849 2 319
1	0	08	06	6 0 1824 1887 5 0
1	07	02	1 60	43 1 11 15 5 203
2	523	569	2 2226	2370 2 474 490 6 94
3	37	34	3 938	556 3 187 201 6 0
4	667	737	4 1759	1735 4 154 152 1 48
5	15	07	5 03	05 5 08 04 2 1113

where set 1 includes all data and set 2 only the data which have $F_o^2 > 2\omega^{-1/2}$ (in the final stages of the refinement all data with $F_o^2 < 2\omega^{-1/2}$ and $F_o^2/\sin 2\theta > 100$ were omitted). Table 1 gives the final positional and thermal parameters and Table 2 compares the observed and calculated squared structure factors. A composite Fourier synthesis of the structure calculated using the program *FORDAP* (Zalkin, 1962) is presented in Fig. 1.

Discussion

Some of the interatomic distances and bond angles calculated by the program *ORFFE** (Busing, Martin

* The CDC 3600 version used incorporates modifications by C. K. Johnson and S. Srikanta.

& Levy, 1964) are shown in Table 3. The distorted octahedral coordination around Cu consists of two close O, two close Cl and two farther Cl contacts. Eight

Cl neighbours, all at about 3.32 Å form a distorted cube around K.

The water molecule has a lone-pair coordination of

Table 3. *Interatomic distances and bond angles*

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

(a) The Cu octahedron			
2 × Cu—O	1.971 (6) Å	O ---Cu---Cl(1)	90.0 (0)°
2 × Cu—Cl(1)	2.285 (3)	O ---Cu---Cl(2)	90.0 (0)
2 × Cu—Cl(2)	2.895 (4)	Cl(1)---Cu---Cl(2)	90.0 (0)
(b) The K polyhedron (cube)			
4 × K—Cl(2)	3.315 (4) Å		
4 × K—Cl(1)	3.325 (4)		
(c) The water molecule and the hydrogen bond			
O—H	0.955 (6)* Å	H—O—H	109.7 (7)°
	0.966 (6)†		
H—H	1.562 (11)*		
	1.580 (11)†	Cl(2)---O---Cl(2)	100.3 (2)°
O---Cl(2)	3.116 (5)	H —O---Cl(2)	4.7 (3)
H---Cl(2)	2.165 (6)		

* Uncorrected for thermal motion.

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

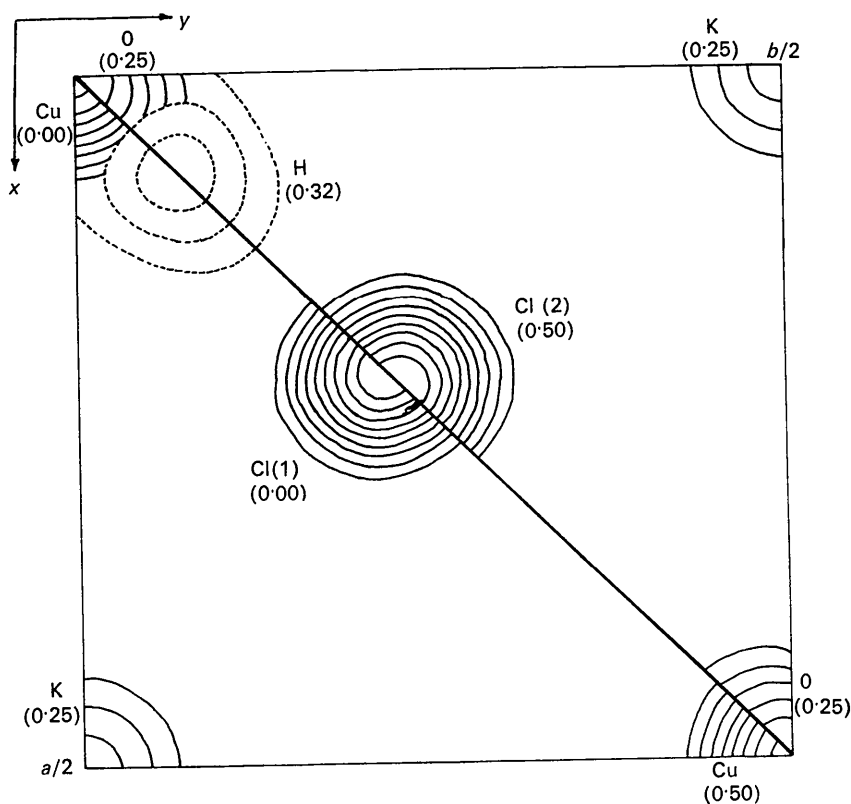


Fig. 1. The composite Fourier synthesis of $K_2CuCl_4 \cdot 2H_2O$. The numbers in parentheses indicate the z coordinates of the various nuclear scattering density sections. For convenience in plotting, the symmetry of the mirror plane indicated by the thick line from the top left hand corner to the bottom right-hand corner is used to show only half the contours for Cu, O, Cl(1) and Cl(2). The contours are at equal arbitrary intervals and the negative contours are shown by broken lines; the zero contours are omitted.

type *D* (Chidambaram, Sequeira & Sikka, 1964) with the bisector of the lone pairs directed toward the divalent copper ion. There are two equivalent bent O—H---Cl(2) hydrogen bonds from the water molecule. The H—O—H angle of $109.7(7)^\circ$ is significantly larger than the value of 104.5° in water vapour. It has been noted earlier also (Chidambaram, Sequeira & Sikka, 1964; Sikka & Chidambaram, 1969; Brown & Chidambaram, 1969) that trigonally coordinated water molecules with lone pair coordination of type *D* show an increased H—O—H angle compared with tetrahedrally coordinated water molecules. The uncorrected H—H distance of $1.562(11)$ Å is less than the distance of $1.61(2)$ Å found in the proton magnetic resonance study by McGrath & Silvidi (1961); this follows the tendency found in other hydrates by El Saffar (1966) and also in Ba(ClO₃)₂·H₂O (Sikka, Momin, Rajagopal & Chidambaram, 1968) and K₂C₂O₄·H₂O (Sequeira, Srikanta & Chidambaram, 1970).

It may be noted that the coordinates of the hydrogen atom in the asymmetric unit derived by El Saffar (1968) from the proton resonance determination of the length and orientation of the interproton vector are 0.076, 0.076, 0.178. The disagreement of the *z* coordinate from the parameter list of Table 1 is due to a different choice of origin (El Saffar, private communication) placing the Cu at $(0, 0, \frac{1}{2})$ rather than at the origin we have chosen following Wyckoff (1965).

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The Crystal Structure of Zr₇O₉F₁₀

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Zr₇O₉F₁₀, a new compound prepared from ZrF₄ and ZrO₂, crystallizes in the orthorhombic space group *Pbam* with the unit-cell dimensions $a = 6.443$, $b = 26.851$, $c = 4.071$ Å. The structure has been refined by the method of least-squares from three-dimensional Weissenberg data. The zirconium atoms are six and seven coordinated and the coordination polyhedra (octahedra and pentagonal bipyramids) are joined by corners and edges in the (001) plane and by corners along the *c* axis. The structure is related to α -UO₃ in much the same way as the orthorhombic U₃O₈ structure. From these similarities a building principle for a series of compounds $(MA)_{2(3n+1)}A_{4(3n+1)-2n}$ in which the composition asymptotically approaches the composition M_3A_8 is discussed.

Introduction

Several zirconium oxide fluorides have been observed by Kolditz & Feltz (1961) in their studies of thermal

decomposition of zirconium tetrafluoride hydrates and zirconium oxide fluoride hydrates. To characterize existing compounds and to determine their structures a reinvestigation of the zirconium oxide fluoride system