

Powder Diffraction Studies on Dicopper(II) Paraperiodate Hydrates

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The crystal structure of dicopper(II) paraperiodate dihydrate, $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$, has been determined by full profile analysis of a Guinier-Hägg powder diffraction record. The pattern was indexed by a monoclinic unit cell with $a=10.3976(10)$, $b=5.1140(5)$, $c=6.4416(6)$ Å, $\beta=114.974(7)^\circ$ found by a trial-and-error indexing program, TREOR. The structure consists of infinite chains of corner-sharing square CuO_4 groups parallel to the b axis. The CuO_4 squares are distorted and crosslinked by periodate octahedra. The copper atoms may also be described as five-coordinated forming irregular square pyramids with longer apical bonds to crystal water.

The unit cell dimensions of the monohydrate, $\text{Cu}_2\text{HIO}_6 \cdot \text{H}_2\text{O}$, have also been determined by the TREOR program. The monoclinic unit cell dimensions are $a=10.465(7)$, $b=5.110(2)$, $c=9.665(3)$ Å, $\beta=91.66(4)^\circ$. Thus, the b axis is not changed by the dehydration.

Earlier interpretation of thermal and spectroscopic measurements on dicopper(II) paraperiodate dihydrate, $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$, has been based on rather incomplete structural information.^{1–2} We therefore decided to determine the structure of the compound. Because of the great difficulties to obtain single crystals of the substance,³ the study was performed by full profile analysis of a Guinier-Hägg powder diffraction photograph. It was found that the structure could be determined, albeit with limited accuracy, from the powder data.

In order to facilitate a comparison between the mono- and dihydrates, the unit cell dimensions of the dicopper(II) paraperiodate monohydrate, $\text{Cu}_2\text{HIO}_6 \cdot \text{H}_2\text{O}$, have also been determined from a powder pattern.

EXPERIMENTAL

The copper(II) paraperiodate dihydrate used in the present study was prepared as described by Näsänen *et al.*⁴ Copper(II) oxide was dissolved in dilute perchloric acid. Sodium periodate and carbonate-free sodium hydroxide were added to pH=4. The monohydrate was obtained by heating the dihydrate to about 160 °C.³

X-Ray powder diffraction photographs were taken in a focussing camera, 80 mm in diameter, of Guinier-Hägg type with subtraction geometry and

Table 1. Crystal data.

$\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$, FW = 387.03

Space group: $P2_1$

Unit cell used in the structure determination:

$a = 10.3976(10)$, $b = 5.1140(5)$, $c = 6.4416(6)$ Å
 $\beta = 114.974(7)^\circ$

Reduced unit cell:

$a = 9.6461(9)$, $b = 5.1140(5)$, $c = 6.4416(6)$ Å
 $\beta = 102.281(9)^\circ$
 $V = 310.49 \text{ \AA}^3$, $Z = 2$, $F(000) = 344$
 $D_x = 4.139 \text{ g cm}^{-3}$
 $D_m = 4.0 \text{ g cm}^{-3}$ (floatation technique).²
 $M_{20} = 33$

$\text{Cu}_2\text{HIO}_6 \cdot \text{H}_2\text{O}$, FW = 369.02

$a = 10.456(7)$, $b = 5.110(2)$, $c = 9.665(3)$ Å
 $\beta = 91.66(4)^\circ$
 $V = 516.65 \text{ \AA}^3$
 $M_{20} = 15$

Table 2. Observed and calculated 2θ values for the powder pattern of $\text{Cu}_2\text{HfO}_6 \cdot 2\text{H}_2\text{O}$. Calculated data are given for multiple-indexed lines up to the 40th observed line. $\Delta 2\theta = 2\theta_{\text{obs}} - 2\theta_{\text{calc}}$. Indices for the reduced cell can be derived from hkl in the table by multiplication by the matrix $(-1\ 0\ -1, 0\ 1\ 0, 0\ 0\ 1)$.

hkl	$2\theta_{\text{obs}}$ (°)	$\Delta 2\theta$ (°)	d_{obs} (Å)	l/l_0	hkl	$2\theta_{\text{obs}}$ (°)	$\Delta 2\theta$ (°)	d_{obs} (Å)	l/l_0
$\bar{1}11$	14.027	-0.032	6.308	1000	$\bar{2}04$	57.633	0.002	1.5981	18
200	18.182	-0.003	4.713	211	600	58.724	-0.004	1.5710	27
110	19.739	0.004	4.494	74	402	59.903	-0.004	1.5429	72
101	21.010	0.008	4.225	16	$\bar{3}14$	60.264	0.002	1.5345	52
$\bar{1}11$	22.383	0.001	3.9688	7	$\bar{3}31$	60.573	-0.007	1.5274	7
011	23.109	0.008	3.8457	411	$\bar{1}32$	61.611	0.000	1.5041	64
$\bar{2}11$	25.469	-0.002	3.4945	5	$\bar{2}32$	61.860	0.011	1.4987	76
$\bar{3}01$	25.897	0.002	3.4377	399	231	62.159	-0.004	1.4922	107
111	27.345	0.000	3.2589	7	$\bar{5}23$	63.620	0.006	1.4614	75
$\bar{1}12$	33.028	0.006	2.7099	400	123	64.061	-0.008	1.4524	44
$\bar{2}12$		0.040			$\bar{5}14$	64.663	0.001	1.4403	33
310	33.444	-0.002	2.6771	368	431	65.420	-0.004	1.4255	118
211	33.916	0.008	2.6410	327	303	66.252	-0.002	1.4096	80
020	35.075	0.009	2.5563	75	521	68.988	0.008	1.3602	63
012	35.393	0.021	2.5341	48	620	70.260	-0.009	1.3386	28
120	36.394	0.017	2.4667	6	$\bar{2}33$	70.454	-0.023	1.3354	15
$\bar{3}12$		-0.051			422	71.348	0.004	1.3209	38
402	37.576	0.016	2.3917	38	512	72.563	-0.016	1.3017	8
$\bar{1}21$	37.962	0.011	2.3683	228	305	73.581	0.008	1.2862	21
021	38.416	0.016	2.3413	12	033	73.817	-0.020	1.2827	11
411	38.842	0.004	2.3166	87	040	74.057	-0.042	1.2791	8
112		0.027			431	74.320	-0.001	1.2752	6
220	40.063	-0.025	2.2488	182	140	74.863	-0.030	1.2673	21
311	41.867	0.024	2.1560	12	530	75.054	-0.015	1.2646	31
410	42.188	-0.005	2.1403	58	204	75.874	0.000	1.2529	18
202	42.743	0.010	2.1138	23	323	77.230	0.008	1.2343	63
$\bar{3}21$	44.102	-0.001	2.0518	110	413	77.932	0.006	1.2249	47
$\bar{2}13$	45.794	-0.003	1.9798	294	$\bar{6}31$	79.366	0.036	1.2063	30
$\bar{3}22$	48.047	-0.017	1.8921	6	$\bar{3}41$	80.038	0.033	1.1979	31
413	49.759	0.011	1.8309	24	$\bar{8}04$	80.146	-0.017	1.1966	24
013	50.068	-0.036	1.8204	10	340	81.155	-0.001	1.1842	7
411	50.713	0.004	1.7987	15	241	81.411	-0.001	1.1811	22
$\bar{5}03$	51.262	0.012	1.7807	23	800	81.656	-0.002	1.1782	9
510	51.647	0.012	1.7684	136	$\bar{3}34$	82.329	-0.027	1.1703	9
422	52.322	-0.001	1.7471	183	$\bar{3}25$	84.226	0.039	1.1487	7
602	53.220	-0.026	1.7197	7	425	84.328	-0.001	1.1476	8
130	54.673	0.001	1.6774	7	015	85.146	-0.005	1.1386	5
222		0.006			$\bar{4}42$	86.188	0.012	1.1275	29
$\bar{6}12$	56.432	0.005	1.6292	50	341	86.314	0.002	1.1262	35
$\bar{3}23$		0.047			$\bar{9}12$	86.480	-0.016	1.1244	50
$\bar{6}11$	56.755	-0.004	1.6207	166	$\bar{7}32$	86.972	-0.005	1.1193	18
501		0.018			$\bar{9}01$	87.314	0.011	1.1158	8
$\bar{2}31$	57.320	-0.011	1.6061	71	$\bar{1}25$	88.483	0.022	1.1041	9

with strictly monochromatized $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405981$ Å). Finely powdered silicon ($a = 5.430880(35)$ Å at 25°C) was added as internal theta standard.⁵ To avoid simultaneous appearance of front-layer and back-layer profiles and to diminish the background, single-coated film, CEA Reflex 15, was used.

All measurements of the films were made by means of a computer-controlled microdensitometer, recently described by Johansson *et al.*⁶ The slit opening of the collimator was 0.040×2.0 mm,² and the corresponding theta step length was $\sim 0.0143^\circ$.

Table 3. Observed and calculated 2θ values for the powder pattern of $\text{Cu}_2\text{HIO}_6 \cdot \text{H}_2\text{O}$ up to $2\theta = 60^\circ$. $\Delta 2\theta = 2\theta_{\text{obs}} - 2\theta_{\text{calc}}$.

<i>hkl</i>	$2\theta_{\text{obs}}$ ($^\circ$)	$\Delta 2\theta$ ($^\circ$)	d_{obs} (\AA)	<i>l/l</i> ₀	<i>hkl</i>	$2\theta_{\text{obs}}$ ($^\circ$)	$\Delta 2\theta$ ($^\circ$)	d_{obs} (\AA)	<i>l/l</i> ₀
200	16.934	-0.005	5.232	1000	313	42.556	-0.018	2.1227	68
002	18.363	0.012	4.828	150	222	43.381	-0.008	2.0842	86
111	21.515	-0.001	4.127	320	105		0.044		
202	24.720	0.016	3.5986	397	511	48.138	-0.003	1.8887	187
112	26.579	-0.013	3.3510	8	420	49.861	0.003	1.8274	11
311	32.637	0.009	2.7415	364	115	51.004	0.000	1.7891	81
113	33.761	-0.004	2.6527	389	421		-0.001		
113	34.188	0.005	2.6206	365	323	52.243	-0.001	1.7496	49
020	35.091	-0.001	2.5552	91	404		-0.011		
312	36.700	0.022	2.4468	44	422	53.173	-0.009	1.7212	183
004	37.199	0.004	2.4151	5	602		0.004		
402		0.007			131	55.473	-0.002	1.6551	81
410	38.650	0.004	2.3277	47	414		-0.005		
220	39.193	-0.016	2.2967	196	315	56.665	-0.016	1.6231	181
022	39.909	0.027	2.2571	22	006	57.154	-0.005	1.6104	60
313	41.560	0.033	2.1712	50	132	57.977	0.027	1.5894	8
204		-0.044			603		0.042		
104	42.009	-0.003	2.1490	47	206	59.554	0.023	1.5511	16

INDEXING OF THE POWDER PATTERNS

In previous studies of copper(II) periodates different unit cell dimensions have been tried for $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$. Näsänen and coworkers⁴ proposed a hexagonal cell with the dimensions $a = 6.0$, $c = 18.8 \text{ \AA}$ and Uggla³ suggested a triclinic unit cell with $a = 5.52$, $b = 25.78$, $c = 5.56 \text{ \AA}$, $\alpha = 99.5$, $\beta = 119.6$ and $\gamma = 93.8^\circ$. None of these unit cells can be proved from the X-ray data however. The De Wolff figure of merit⁷ M_{20} remains less than 4 for both models. Since the situation is similar for the monohydrate we decided to index both patterns by a trial-and-error program, TREOR, written by one of us (P.-E. W.). The unit cell dimensions and figures of merit found are given in Table 1. The indexed patterns are listed in Tables 2 and 3.

STRUCTURE DETERMINATION

The iodine and copper atom positions could be derived from the Patterson function. However, no oxygen coordinates could be found directly from the integrated intensity data. Application of a Rietveld type profile refinement program⁸ yielded sets of structure factors from which oxygen atom

coordinates could successively be derived by standard Fourier techniques.

Considering the fact that each oxygen contributes about 5% of the total scattering power, one should not expect the oxygen atom coordinates to refine accurately. Moreover, the number of reflexions in the powder pattern is limited (see Fig. 1 and Table 2); a total number of 32 positional coordinates

Table 4. Fractional atomic coordinates for $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$. Estimated standard deviations are given within parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
I	0.253(2)	0	0.257(3)
Cu1	0.384(3)	0.534(5)	0.499(4)
Cu2	0.116(3)	0.504(5)	0.978(4)
O1	0.549(9)	0.382(15)	0.581(13)
O2	0.923(9)	0.656(15)	0.872(13)
O3	0.672(9)	0.750(15)	0.340(13)
O4	0.795(9)	0.290(15)	0.022(13)
O5	0.688(9)	0.358(15)	0.402(13)
O6	0.738(9)	0.772(15)	0.984(13)
O7	0.447(9)	0.617(15)	0.864(13)
O8	0.933(9)	0.716(15)	0.393(13)

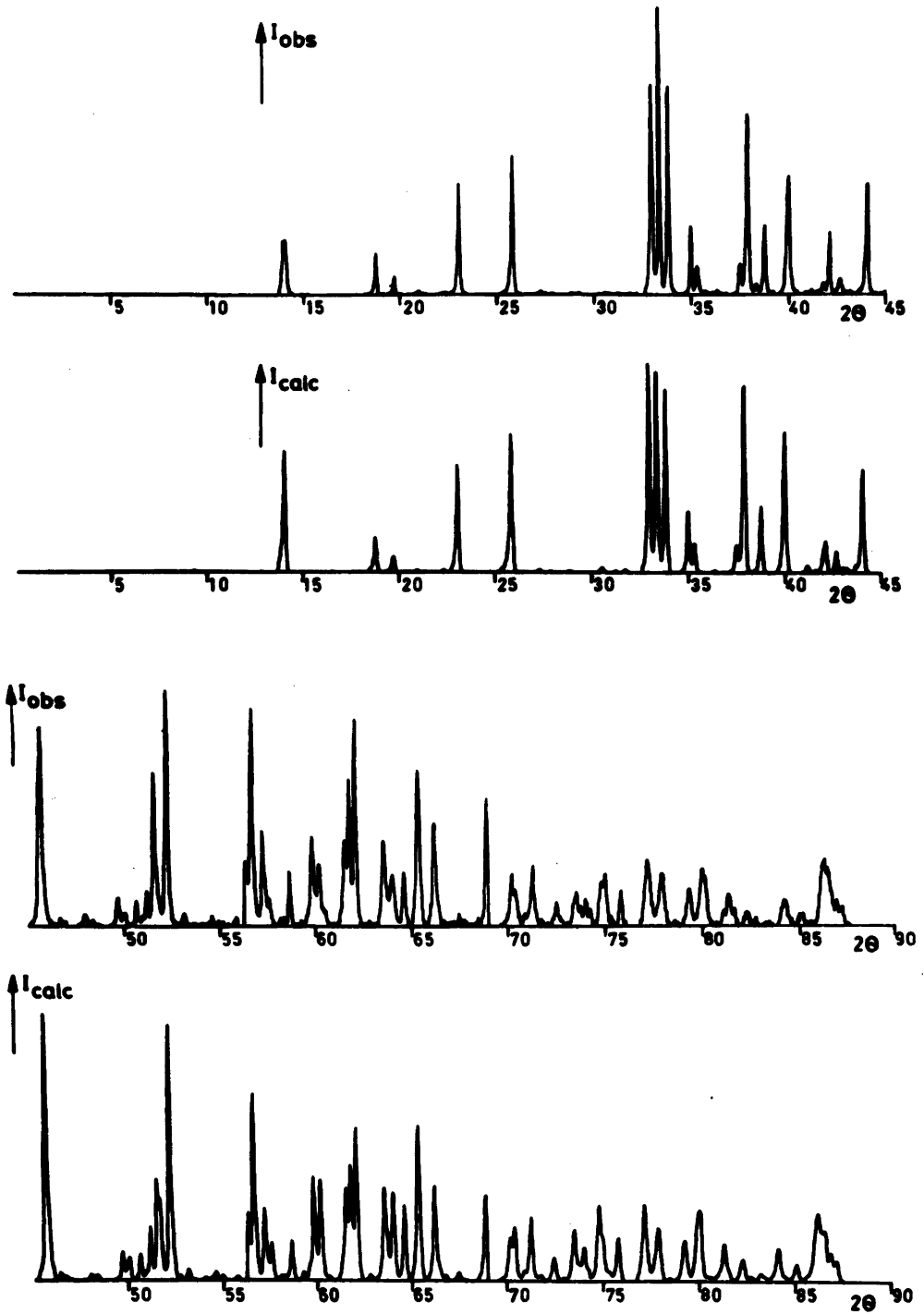


Fig. 1. Observed and calculated intensities for the Guinier-Hägg powder pattern of $\text{Cu}_2\text{HfO}_6 \cdot 2\text{H}_2\text{O}$ corrected for Lorentz and polarization effects.

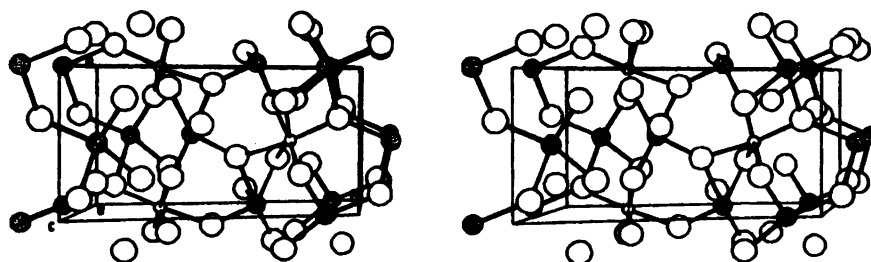


Fig. 2. A stereoscopic pair of drawings showing the content of a unit-cell of $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$. The c axis points towards the reader, a to the right, and b upwards. Large circles represent O, shaded Cu, and small I.

should be difficult to refine from the 80 observed intensity peaks. It was thus found that a full-matrix refinement of all parameters involved could not be made to converge. The variables, 40 in total, are those shown in Table 4 plus three half-width, and, one asymmetry parameter, one scale factor and three formal thermal parameters. The thermal parameters account for absorption effects as well as thermal vibration phenomena. The parameters for the oxygen positions oscillated about one standard deviation in the final refinement cycles. In Table 4 the atomic coordinates are given with standard

deviations estimated as twice the average STD calculated for the various stom types in the last refinement cycle. The least-squares refinement ended with a reliability factor

$$R = \frac{\sum_{hkl} |\sqrt{I_{\text{obs}}} - \sqrt{I_{\text{calc}}}|}{\sum_{hkl} \sqrt{I_{\text{obs}}}} = 0.115,$$

the sums taken over 260 reflections.

The observed and calculated intensity curves are shown in Fig. 1. Although the scale reduces the resolution of the curves it should be emphasized that they represent the complete data set from which the structure shown in Fig. 2 is derived.

Table 5. Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses.

The I polyhedron

I—O1	1.97(8)	O1—I—O3	80(3)	O1—I—O2	172(4)
—O2	1.85(8)	O1—I—O4	97(4)	O3—I—O4	175(3)
—O3	2.70(8)	O2—I—O3	93(3)	O5—I—O6	153(3)
—O4	1.97(8)	O2—I—O4	90(4)		
—O5	2.14(8)				
—O6	2.12(8)				

The Cu1 square pyramid

Cu1—O1	1.74(9)	O1—Cu1—O1'	94(2)
—O1'	2.06(8)	O1'—Cu1—O3	89(4)
—O3	2.01(8)	O1—Cu1—O5	65(4)
—O5	2.03(8)	O3—Cu1—O5	102(4)
—O7 ^a	2.20(8)		

The Cu2 square pyramid

Cu2—O2	1.99(9)	O2—Cu2—O2'	97(2)
—O2'	2.15(8)	O2'—Cu2—O4	97(4)
—O4	1.72(8)	O2—Cu2—O6	73(4)
—O6	1.85(8)	O4—Cu2—O6	98(4)
—O8 ^a	2.66(8)		

^a Crystal water oxygen.

DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

Selected interatomic distances and bond angles of $\text{Cu}_2\text{HIO}_6\cdot 2\text{H}_2\text{O}$ are listed in Table 5. The structure consists of chains of corner-sharing square-coordinated CuO_4 groups parallel to the b axis. Thus, two infinite copper-oxygen chains $-\text{Cu}1-\text{O}1-\text{Cu}1'-\text{O}1'-$ and $-\text{Cu}2-\text{O}2-\text{Cu}2'-\text{O}2'-$ link the structure in the $[010]$ direction. The CuO_4 squares are distorted and crosslinked by periodate octahedra. Each oxygen in a CuO_4 square is also coordinated to iodine, *i.e.* it is member of a periodate ion. The remaining oxygen atoms, O7 and O8, are not included in the polyhedra discussed above; they belong to the crystal water in the structure. These oxygen atoms form weaker bonds to copper (*cf.* Table 5). The copper atoms may therefore also be described as five-coordinated, forming irregular square pyramids with longer apical bonds to the crystal water.

The degree of distortion in each coordination polyhedron can hardly be meaningfully discussed because of the limited accuracy in the structure determination. It seems likely, however, that there must be distortions due to the crosslinking in the structure.

It has been observed by Uggla *et al.*² that the removal of a water molecule from the dihydrate by heating does not alter the magnetic properties significantly. They concluded that both hydrates form infinite chains of hydroxy-bridged copper atoms. It is not possible from the present study to determine the hydrogen bonding scheme, although O7 and O8 can be identified as crystal water oxygen. The fact that the b axis is not altered by dehydration to the monohydrate, however, indicates that the hydrogen bonds are most frequently parallel to the a c -plane.

From the assumption that the unit cell of the monohydrate contains four formula units it follows that the volume is reduced by 28.3 \AA^3 for each crystal water molecule lost by the dehydration.

Acknowledgements. The authors wish to thank Prof. P. Kierkegaard for his kind interest in this work. Thanks are also due to Mr. Lars Göthe and Mrs. Stina Nord for their skilful technical assistance.

This investigation has received financial support from the Swedish Natural Science Research Council.

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Received April 14, 1981.