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X-ray Studies on the Partially Dehydrated Phases of some Paramagnetic Tutton Salts

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Thermal dehydration study of some paramagnetic Tutton salts, $Co(KSO_4)_2.6H_2O$, $Cu(KSO_4)_2.6H_2O$ and $Cu(NH_4SeO_4)_2.6H_2O$, revealed the formation of lower hydrates, *viz.* $Co(KSO_4)_2.2H_2O$, $Cu(KSO_4)_2.2H_2O$ and $Cu(NH_4SeO_4)_2.2H_2O$. Powder photographs of these phases have been indexed by the methods of Ito and Lipson. $Co(KSO_4)_2.2H_2O$ has been found to be monoclinic with cell dimensions $a=7{\cdot}31$, $b=13{\cdot}25$, $c=5{\cdot}68$ Å, $\beta=97°35'$, and space group $P2_1/a$. The other two dihydrates are orthorhombic with cell-dimensions $a=14{\cdot}58$, $b=11{\cdot}90$, $c=10{\cdot}40$ Å for $Cu(KSO_4)_2.2H_2O$ and $a=14{\cdot}83$, $b=12{\cdot}39$, $c=10{\cdot}31$ Å for $Cu(NH_4SeO_4)_2.2H_2O$. The probable space groups in both cases are $Pmn2_1$ or $Pmnm$. The probable natures of the structures of these dihydrates are discussed.

In a programme of study of thermal dehydration of paramagnetic Tutton salts and X-ray study of the lower hydrates so obtained – some results of which have been reported earlier (Bhowmik, 1961; Ray, 1965) – the dehydration of the following six Tutton salts was studied: $Cu(KSO_4)_2.6H_2O$, $Cu(NH_4SeO_4)_2.6H_2O$, $Co(KSO_4)_2.6H_2O$, $Co(NH_4SO_4)_2.6H_2O$, $Ni(KSO_4)_2.6H_2O$, $Ni(NH_4SO_4)_2.6H_2O$. The dehydration curves for these six salts fall into two distinct categories. Those of the nickel salts and the cobalt ammonium salt show direct transformation to the anhydrous phase, but each of the three other salts shows the formation of a dihydrate at temperatures given in Table 1.

Table 1. *Dehydration data for the six Tutton salts*

Salt	Temperature of transition to Dihydrate phase	Anhydrous phase
$Cu(KSO_4)_2.6H_2O$	50°C	115°C
$Cu(NH_4SeO_4)_2.6H_2O$	70	102
$Co(KSO_4)_2.6H_2O$	92	130
$Co(NH_4SO_4)_2.6H_2O$	—	78
$Ni(KSO_4)_2.6H_2O$	—	110
$Ni(NH_4SO_4)_2.6H_2O$	—	98

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The lower hydrates were highly unstable, having a tendency to reconversion to the hexahydrate forms on exposure to the atmosphere. They could not be obtained as single crystals in spite of many attempts. Thus, information regarding the structure of these phases had to be obtained only from powder photographs. The samples for powder analysis were prepared in the following way: powdered hexahydrate was packed in a glass capillary with both ends open and heated above the transition temperature in an oven for 24 hours; this treatment was found sufficient for complete conversion into the dihydrate. The capillary was then sealed at both ends before removal from the oven so that risk of reconversion into the hexahydrate was avoided. X-ray photographs were taken with a Unicam 19 cm camera. The powder photographs thus obtained were ascertained to be due to the respective dihydrates only.

$Co(KSO_4)_2.2H_2O$

The pattern could not be indexed in terms of a cubic, tetragonal or hexagonal cell, and an attempt to apply Lipson's (1949) method failed, showing that the structure is probably either monoclinic or triclinic. However,

the pattern could be indexed by applying Ito's (1950) method as shown below.

Assuming the first three lines to be due to pinacoidal reflexions, the indices 020, 001 and 200 could be assigned to them by trial. Higher orders of these reflexions were also present, and provisional values of a^*, b^* and c^* were obtained.

To determine the reciprocal cell angles α^* β^* γ^*, pairs of observed Q's were searched for in such a manner, that if they were assumed to have indices $h0l$ and $h0\bar{l}$, relations of the following type were satisfied:

$$\frac{Q_{h0l}+Q_{h0\bar{l}}}{2} = h^2a^{*2}+l^2c^{*2} = Q'_{h0l}$$

(Similar relations for Q'_{hk0} and Q'_{0kl} hold good).

For several pairs of h and k, Q'_{hk0} coincided with observed Q values, and for several pairs of k and l, Q'_{0kl} coincided with observed Q values. Thus $\alpha^*=\gamma^*=90°$ so that in the process of indexing, without using any intermediate triclinic cell, a monoclinic cell was directly arrived at. To find β^*, a pair of observed Q values were assumed to be Q_{201} and $Q_{20\bar{1}}$ and the values of β^* obtained therefrom could index several other pairs like Q_{131} and $Q_{13\bar{1}}$, Q_{221} and $Q_{22\bar{1}}$ *etc.* The whole pattern could thus be indexed by the following parameters.

$a^*=0{\cdot}13802$ $\quad$ $\alpha^*=90°$
$b^*=0{\cdot}0755$ $\quad$ $\beta^*=82°25'$
$c^*=0{\cdot}17748$ $\quad$ $\gamma^*=90°$

The real cell dimensions as deduced from above are $a=7{\cdot}31$, $b=13{\cdot}25$, $c=5{\cdot}68$ Å, $\beta=97°35'$.

Since these values satisfy the condition (Buerger, 1957)

$$|ac\cos\beta| \le a^2/2 \le c^2/2\,,$$

the cell cannot be reduced further. Hence the cell is primitive monoclinic. The experimentally determined value of the density was 2·31 g.cm^{-3}, and the number of formula units per unit cell calculated therefrom was 2·07. The density calculated on the basis of $Z=2$ was 2·22 g.cm^{-3}.

Table 2. *Observed and calculated values of* $1/d^2$ *of* $Co(KSO_4)_2.2H_2O$ *with the indices*

Serial no.	Intensity	d (Å)	$1/d^2$(obs)	$1/d^2$(calc)	Index
1	*s*	6·605	0·0229	0·0228	020
2	*vs*	5·634	0·0315	0·0315	001
3	*w*	3·627	0·0760	0·0762	200
4	*s*	3·554	0·0792	0·0799	121
5	*ms*	3·320	0·0907	0·0912	040
6	*vs*	3·259	0·0942	0·0947	20$\bar{1}$
				0·0952	13$\bar{1}$
7	*w*	3·046	0·1078	0·1084	131
8	*s*	3·003	0·1109	0·1103	140
9	*w*	2·907	0·1183	0·1175	22$\bar{1}$
10	*w*	2·875	0·1210	0·1207	201
11	*s*	2·645	0·1430	0·1435	221
12	*w*	2·547	0·1541	0·1549	12$\bar{2}$
13	*vw*	2·473	0·1635	0·1638	112
14	*vvw*	2·411	0·1720	0·1720	231
15	*s*	2·317	0·1863	0·1866	15$\bar{1}$
				0·1859	24$\bar{1}$

Table 2 (*cont.*)

Serial no.	Intensity	d (Å)	$1/d^2$(obs)	$1/d^2$(calc)	Index
16	*vw*	2·268	0·1944	0·1940	320
17	*w*	2·240	0·1992	0·1993	22$\bar{2}$
18	*vw*	2·208	0·2051	0·2052	060
19	*vw*	2·186	0·2093	0·2094	132
20	*vvw*	2·148	0·2168	0·2172	042
21	*w*	2·051	0·2377	0·2372	25$\bar{1}$
				0·2367	061
22	*vw*	2·022	0·2446	0·2452	321
23	*w*	1·909	0·2744	0·2738	331
				0·2747	34$\bar{1}$
24	*w*	1·880	0·2829	0·2835	003
25	*w*	1·813	0·3041	0·3048	400
26	*w*	1·753	0·3257	0·3260	35$\bar{1}$
				0·3259	261
27	*ms*	1·733	0·3330	0·3331	42$\bar{1}$
28	*ms*	1·660	0·3630	0·3623	401
				0·3633	162
				0·3632	241
29	*vvw*	1·616	0·3839	0·3844	41$\bar{2}$
				0·3839	180
30	*vw*	1·556	0·4130	0·4133	143
				0·4136	431
31	*w*	1·538	0·4226	0·4219	181
32	*w*	1·519	0·4337	0·4334	262
33	*vw*	1·490	0·4504	0·4500	233
34	*vvw*	1·457	0·4707	0·4700	44$\bar{2}$
35	*vvw*	1·439	0·4830	0·4828	402
36	*vvw*	1·323	0·5713	0·5719	124

The conditions limiting possible reflexions as observed in the indices are

hkl: no condition
$h0l$: $h=2n$
$0k0$: $k=2n$.

So the space group $P2_1/a$ may be assigned to this phase.

$Cu(KSO_4)_2.2H_2O$ and $Cu(NH_4SeO_4)_2.2H_2O$

The photographs of these two hydrates showed some striking resemblances. On analysis, both were found to be orthorhombic by the application of Lipson's method. Tables 3 and 4 show the indexing of these patterns. For $Cu(KSO_4)_2.2H_2O$, the values of the constants $A=\lambda^2/4a^2$, $B=\lambda^2/4b^2$ and $C=\lambda^2/4c^2$ are 0·0028, 0·0042 and 0·0055 respectively, whence the cell-dimensions are, $a=14{\cdot}58$, $b=11{\cdot}90$, $c=10{\cdot}40$ Å. From the value of the experimentally observed density, which is 2·65 g.cm^{-3}, the number of formula units per unit cell comes out as 7·79. The density calculated on the basis of $Z=8$ was 2·72 g.cm^{-3}.

Table 3. *Observed and calculated* $\sin^2\theta$ *values of* $Cu(KSO_4)_2.2H_2O$ *with the indices*

Serial no.	Intensity	d (Å)	$\sin^2\theta$(obs)	$\sin^2\theta$(calc)	Index
1	*s*	7·771	0·0098	0·0097	011
2	*vs*	6·057	0·0164	0·0168	020
3	*vw*	5·451	0·0200	0·0196	120
4	*w*	5·202	0·0220	0·0220	002
5	*w*	4·709	0·0268	0·0262	012
6	*w*	4·400	0·0307	0·0307	301

Table 3 (*cont.*)

Serial no.	Intensity	d (Å)	$\sin^2\theta$(obs)	$\sin^2\theta$(calc)	Index
7	*vs*	4·192	0·0338	0·0335	221
				0·0332	202
8	*w*	4·013	0·0369	0·0374	212
9	*s*	3·766	0·0418	0·0416	122
10	*s*	3·735	0·0426	0·0420	320
11	*w*	3·614	0·0455	0·0448	400
12	*w*	3·539	0·0474	0·0475	321
13	*w*	3·502	0·0484	0·0490	410
				0·0490	230
14	*w*	3·306	0·0544	0·0545	231
				0·0545	411
15	*vs*	3·166	0·0593	0·0598	032
16	*s*	3·075	0·0629	0·0626	132
				0·0630	330
17	*s*	3·011	0·0656	0·0663	023
				0·0649	213
18	*vs*	2·964	0·0677	0·0672	040
				0·0671	421
19	*vw*	2·864	0·0725	0·0727	041
20	*w*	2·716	0·0805	0·0797	511
21	*w*	2·601	0·0879	0·0880	004
22	*ms*	2·437	0·1001	0·1004	242
23	*ms*	2·388	0·1049	0·1050	610
24	*ms*	2·260	0·1164	0·1162	250
				0·1160	224
25	*w*	2·196	0·1232	0·1228	602
				0·1237	513
26	*s*	2·105	0·1341	0·1340	442
27	*vw*	2·037	0·1432	0·1427	701
28	*vw*	2·029	0·1443	0·1445	115
29	*ms*	1·964	0·1540	0·1540	160
30	*vw*	1·884	0·1675	0·1679	261
				0·1680	640
				0·1669	315
31	*vw*	1·853	0·1730	0·1732	062
32	*w*	1·799	0·1836	0·1844	262
33	*w*	1·742	0·1958	0·1958	154
				0·1960	460
34	*s*	1·712	0·2028	0·2035	163
35	*s*	1·663	0·2149	0·2141	171
36	*ms*	1·633	0·2229	0·2232	306
37	*vw*	1·590	0·2352	0·2358	036
38	*vvw*	1·507	0·2618	0·2610	336
39	*s*	1·633	0·2734	0·2737	017
				0·2740	662
40	*w*	1·456	0·2805	0·2800	280
41	*w*	1·273	0·3669	0·3660	646

Table 4. *Observed and calculated* $\sin^2\theta$ *values of* $Cu(NH_4SeO_4)_2.2H_2O$ *with the indices*

Serial no.	Intensity	d (Å)	$\sin^2\theta$(obs)	$\sin^2\theta$(calc)	Index
1	*vvw*	8·266	0·0087	0·0083	101
2	*vvw*	7·442	0·0107	0·0108	200
3	*ms*	6·271	0·0151	0·0155	020
				0·0147	210
4	*vs*	5·635	0·0187	0·0182	120
5	*vvw*	5·433	0·0201	0·0203	211
6	*ms*	5·157	0·0224	0·0224	002
7	*vvw*	4·786	0·0260	0·0263	220
				0·0263	012
8	*vvw*	4·594	0·0282	0·0282	310
9	*ms*	4·541	0·0289	0·0290	112
10	*vw*	4·446	0·0301	0·0299	301
11	*vs*	4·330	0·0317	0·0319	221
12	*vw*	4·238	0·0331	0·0332	202
13	*ms*	4·021	0·0368	0·0371	212

Table 4 (*cont.*)

Serial no.	Intensity	d (Å)	$\sin^2\theta$(obs)	$\sin^2\theta$(calc)	Index
14	*vs*	3·799	0·0412	0·0406	122
				0·0405	031
15	*ms*	3·712	0·0431	0·0432	400
16	*ms*	3·488	0·0488	0·0487	222
17	*ms*	3·419	0·0509	0·0506	312
18	*vvw*	3·330	0·0536	0·0531	103
19	*vw*	3·272	0·0548	0·0543	013
20	*s*	3·140	0·0603	0·0602	132
21	*vvw*	3·032	0·0647	0·0643	421
				0·0647	140
22	*w*	2·966	0·0675	0·0683	232
23	*ms*	2·903	0·0705	0·0703	141
24	*ms*	2·866	0·0724	0·0731	501
				0·0728	240
25	*w*	2·719	0·0804	0·0811	422
26	*vvw*	2·669	0·0834	0·0836	431
				0·0830	520
27	*w*	3·580	0·0893	0·0896	004
28	*w*	2·513	0·0941	0·0938	512
				0·0935	014
29	*ms*	2·464	0·0976	0·0969	050
				0·0972	600
30	*vw*	2·418	0·1018	0·1025	051
31	*ms*	2·259	0·1164	0·1159	224
32	*ms*	2·211	0·1215	0·1214	513
33	*w*	2·164	0·1269	0·1276	442
34	*w*	2·123	0·1318	0·1323	630
35	*w*	1·982	0·1512	0·1515	613
				0·1516	044
36	*vw*	1·943	0·1574	0·1577	161
37	*vvw*	1·874	0·1692	0·1698	325
38	*vvw*	1·854	0·1730	0·1728	800
				0·1726	524
				0·1730	731
39	*w*	1·787	0·1862	0·1868	552
40	*ms*	1·754	0·1932	0·1926	460
41	*ms*	1·717	0·2017	0·2016	006
				0·2014	515
42	*ms*	1·675	0·2118	0·2124	206
43	*w*	1·662	0·2150	0·2150	462
				0·2148	553
44	*vw*	1·631	0·2234	0·2226	9,1,0
45	*w*	1·614	0·2282	0·2279	226
46	*w*	1·597	0·2329	0·2324	535
47	*ms*	1·550	0·2474	0·2480	080
48	*ms*	1·522	0·2567	0·2566	922
				0·2563	181
				0·2570	734
49	*vw*	1·501	0·2638	0·2632	571
50	*ms*	1·483	0·2703	0·2703	10,0,0
51	*vvw*	1·450	0·2827	0·2821	165
52	*w*	1·414	0·2970	0·2974	735
53	*w*	1·397	0·3046	0·3051	10,3,0
				0·3042	536
54	*w*	1·356	0·3233	0·3227	383
55	*vvw*	1·328	0·3371	0·3378	716
56	*vvw*	1·239	0·3969	0·3866	318
57	*ms*	1·229	0·3933	0·3927	1,10,0

Similarly for $Cu(NH_4SeO_4)_2.2H_2O$, the values of the constants A, B, C are 0·0027, 0·0039 and 0·0056, from which the real cell dimensions come out as $a=14·83$, $b=12·39$, $c=10·31$ Å. The number of formula units per unit cell, as calculated from the observed density 2·89 g.cm^{-3}, is 7·82. The density calculated on the basis of $Z=8$ is 2·96 g.cm^{-3}.

Table 5. *Comparison of the crystallographic data for the dihydrates*

	$Cu(NaSO_4)_2.2H_2O$ (kröhnkite) Monoclinic	$Co(KSO_4)_2.2H_2O$ Monoclinic	$Cu(NH_4SO_4)_2.2H_2O$ Orthorhombic	$Cu(KSO_4)_2.2H_2O$ Orthorhombic	$Cu(NH_4SeO_4)_2.2H_2O$ Orthorhombic
a(Å)	5·78	7·31	14·84	14·58	14·83
b(Å)	12·58	13·25	12·52	11·90	12·39
c(Å)	5·48	5·68	10·69	10·40	10·31
β	108°30′	97°35′			
Space group	$P2_1/c$	$P2_1/a$	*Pmnm* or $Pmn2_1$	*Pmnm* or $Pmn2_1$	*Pmnm* or $Pmn2_1$
Number of formula units per cell	2	2	8	8	8

Tables 3 and 4 show that in both these compounds the conditions limiting possible reflexions are same. They are as follows:

hkl: no condition
$0kl$: no condition
$hk0$: no condition
$h0l$: $h+l$ even
$h00$: $(h=2n)$
$0k0$: no condition
$00l$: $(l=2n)$.

The conditions agree with both the space groups $Pmn2_1$ and *Pmnm*.

It is interesting to compare the crystallographic data of the above dihydrates with those of the mineral kröhnkite, $Cu(NaSO_4)_2.2H_2O$, which has been shown to bear some structural relationship with the Tutton salts (Dahlman, 1952). Such a comparison is made in Table 5, which appears to suggest a close structural relationship between the three dihydrates and kröhnkite. The (100) projection of kröhnkite (Fig. 1) shows how the octahedral coordination of the paramagnetic ion is completed by sharing four oxygen atoms with two SO_4 tetrahedra, and a system of octahedron–tetrahedron chains is formed, in the interstices of which the monovalent metal ions are accomodated. It is quite probable that the structures of the three dihydrates consist of similar basic features.

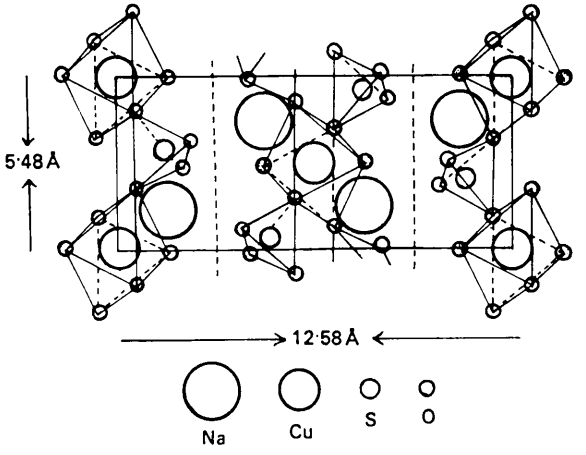

Fig. 1. (100) projection of kröhnkite (after Dahlman).

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