Berman density balance, using bromoform, as 4·60 ± 0·01 g.cm^{-3}. With the above values of axial lengths and the angle β ($V = 1871$ Å^3), the molecular weight ($M = 648$ for Fe_7S_8) and the observed density, the number of formula units per unit cell is calculated to be 8 ($Z = 7{\cdot}998$), and the calculated density is 4·602 g.cm^{-3}.

The rotation and Weissenberg photographs and the 15° oscillation photographs about [010] and [001] of a crystal fragment, detached from hexagonal platelets (off an ore sample from level-16), showed superstructure characteristics having a hexagonal supercell $a = 6{\cdot}88$, $c = 22{\cdot}90 \pm 0{\cdot}02$ Å; the high angle reflexions did not show any separation characteristic of the monoclinic system. The conditions limiting possible reflexions are: $hh\overline{2h}l$ only with $l = 2n$; $h\bar{h}0l$ only with $l = 2n$; and $hkil$ with no conditions except $l = 2n$; indicating the space group as one of $P6/mcc$ (D^2_{6h}), $P6cc$ (C^2_{6v}). The presence of a number of weak reflexions in the patterns could be explained as being due to the monoclinic phase (see above) which was a minor intergrowth with the hexagonal phase in the crystal fragment. The density for the same crystals was determined as 4·58 ± 0·01 g.cm^{-3} and the number of formula units per unit cell was calculated to be 4 ($Z = 3{\cdot}998$) from the above values of axial lengths ($V = 939$ Å^3), the observed density and the molecular weight [$M = 648$ for Fe_7S_8 although the composition might have a slight excess of iron (Desborough & Carpenter, 1965)]; the calculated density is 4·582 g.cm^{-3}.

The monoclinic and hexagonal pyrrhotites (superstructure types) were found to be associated mainly with chalcopyrite and pyrite in the ores of different levels (Mukherjee, 1968); the monoclinic phase was predominant in the pyrrhotite-rich ores containing pyrite as a minor constituent, and the hexagonal phase was predominant in the pyrrhotite-poor ores containing chalcopyrite and pyrite as major constituents.

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The Structure of Copper Ammonium Sulfate Hexahydrate from Neutron-Diffraction Data[*]

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The structure parameters of the Tutton salt $Cu(NH_4)_2(SO_4)_2.6H_2O$ have been refined by the method of least squares from three-dimensional neutron-diffraction data. The e.s.d.'s of the atomic coordinates are from 0·0010 to 0·0023 Å for the N, S, O atoms and 0·0025 to 0·0053 Å for the H atoms. The value derived for f_S, the coherent scattering amplitude of sulfur, is 0·283(4), significantly different from the value 0·31 in Bacon's table; values derived for f_O and f_N are also slightly different from the tabulated values. Although the heavy-atom coordinates differ significantly in a purely statistical sense from those of the three-dimensional X-ray analysis of Montgomery & Lingafelter, the two descriptions of the heavy-atom structure agree quite well from the point of view of molecular geometry. The hydrogen-bonding pattern from the X-ray study is confirmed.

Introduction

In the last half decade there has been much interest shown, in a number of laboratories, in the crystal structures of Tutton's salts, a well-known series of isomorphous double sulfates with the general formula $XY_2(SO_4)_2.6H_2O$. In an accurate redetermination by X-ray analysis of the structure of $Mg(NH_4)_2(SO_4)_2.6H_2O$, Margulis & Templeton (1962) were able to locate the hydrogen atoms approximately and to deduce the pattern of hydrogen bonding, after first revising the coordinates of the oxygen atoms from incorrect values reported from the original X-ray determination (Hofmann, 1931). At about the same time and independently, Chidambaram & Rao (1963) con-

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cluded from a proton magnetic resonance (p.m.r.) study of $ZnK_2(SO_4)_2.6H_2O$ and $MgK_2(SO_4)_2.6H_2O$ that the oxygen coordinates of Hofmann required revision to allow the assignment of a rational hydrogen-bonding pattern in these salts. There was very satisfying agreement (Templeton, Zalkin & Margulis, 1963) between the orientations of the *p–p* vectors as determined in the p.m.r. study and in the structure analysis of Margulis & Templeton. The crystal structure of $Mg(NH_4)_2(SO_4)_2.6H_2O$ was also determined independently by Montgomery & Lingafelter (1964*b*), who reported slightly different coordinates for the hydrogen atoms. Now X-ray crystal-structure analyses have been reported for 9 other Tutton's salts, and the complete list of salts analyzed is as follows:

$Mg(NH_4)_2(SO_4)_2.6H_2O$	Margulis & Templeton (1962); Montgomery & Lingafelter (1964*b*)
$Zn(NH_4)_2(SO_4)_2.6H_2O$	Montgomery & Lingafelter (1964*a*)
$Ni(NH_4)_2(SO_4)_2.6H_2O$	Grimes, Kay & Webb (1963); Montgomery & Lingafelter (1964*b*)
$Cu(NH_4)_2(SO_4)_2.6H_2O$	Webb, Kay & Grimes (1965); Montgomery & Lingafelter (1966*a*)
$Cd(NH_4)_2(SO_4)_2.6H_2O$	Montgomery & Lingafelter (1966*b*)
$Mn(NH_4)_2(SO_4)_2.6H_2O$	Montgomery, Chastain & Lingafelter (1966)
$V(NH_4)_2(SO_4)_2.6H_2O$ $Fe(NH_4)_2(SO_4)_2.6H_2O$ $Co(NH_4)_2(SO_4)_2.6H_2O$	Montgomery, Chastain, Natt, Witkowska & Lingafelter (1967)
$MgK_2(SO_4)_2.6H_2O$	Kannan & Viswamitra (1965)

The results of all these studies are in good general agreement, with slight variations from one salt to another in the structure of the ion $X(H_2O)_6^{2+}$. It is rather interesting (see Kannan & Viswamitra, 1965) that the tetragonal axis of the *g*-tensor for each of various Tutton's salts as determined by electron spin resonance (e.s.r.) studies matches one or the other of the vectors $X \rightarrow O$ in the new structure for Tutton's salts but shows no correlation with the Hofmann structure. This fact went unnoticed by the e.s.r. workers for a decade.

We undertook the neutron-diffraction analysis of the structure of $Cu(NH_4)_2(SO_4)_2.6H_2O$ to determine precisely the coordinates of the hydrogen atoms in order to examine in detail the structural parameters of the water molecules, the ammonium ion, and the hydrogen bonds. Soon after we started our study, the results of a two-dimensional X-ray analysis of this salt were published by Webb, Kay & Grimes (1965), and we also came to know of the three-dimensional analysis that was later published by Montgomery & Lingafelter (1966*a*). Consequently, the comparison of the heavy-atom parameters from our neutron analysis with those from X-ray work became an additional aim of our study.

Experimental

Crystal specimens of appropriate size were grown by slow evaporation from aqueous solution. A crystal in its natural habit weighing 49·9 mg was carefully examined by X-ray precession photography and found to be a single crystal. Approximate cell parameters were obtained from the precession photographs, and the space group symmetry $P2_1/a$ was verified. For the measurements of intensity, the crystal was mounted on a goniometer head with the *b* axis parallel to the spindle axis.

The recording of the intensity data on the Oak Ridge automatic neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) and the preliminary data processing, by which the raw data were converted to a set of values of observed structure-factor squares and their standard errors, followed the procedures that were used in a recent refinement of the structure of K_2NbF_7 (Brown & Walker, 1966). The same general procedures (Brown & Levy, 1964*b*) have been used recently in a number of other neutron analyses of crystal structures in this laboratory (chloral hydrate, Brown & Levy, 1964*a*; sucrose, Brown & Levy, 1963; α-D-glucose, Brown & Levy, 1965; potassium hydrogen chloromaleate, Ellison & Levy, 1965).

A total of 2250 observations were made in the range $2\theta \leq 111°$ (the limit of the instrument) at a neutron wavelength of 1·078 Å. These included regularly scheduled observations of reference reflections and a few duplicate observations. The number of independent observations was 2032. The few negative values of F_o^2 were replaced by zero values.

For calculation of corrections for absorption (Busing & Levy, 1957; Wehe, Busing & Levy, 1962) the coordinates of the 19 corners of the crystal were measured with a toolmaker's microscope, and the equations of the 12 face planes were calculated. The value 2·2 cm^{-1} for the linear absorption coefficient was determined experimentally. The absorption correction factors were in the range 1·52 to 1·80.

An empirical correction term $(0·03F_o^2)^2$ was added to the statistical variance of each observation F_o^2 to obtain the variance $\sigma^2(F_o^2)$ to be used in computing the weight of the observation in least-squares refinement. The extra term makes allowance for instability in the instrument, deficiencies of the structure model, and so forth (see Peterson & Levy, 1957*a*). The F_o^2 values for 1627 of the 2032 independent reflections were greater than their corrected $\sigma(F_o^2)$ values.

In the course of the collection of the intensity data, the unit-cell parameters were refined, together with three parameters defining the orientation of the crystal on the diffractometer, by the method of least-squares from the observations of the 2θ positions of the centroids of the diffraction peaks (Busing & Levy, 1967). After our structure refinement was complete, we were provided (Montgomery & Lingafelter, 1966*c*) with more precise parameters as follows:* $a=9{\cdot}2105$ (14), $b=12{\cdot}3795$ (17), $c=6{\cdot}3016$ (13) Å, $\beta=106{\cdot}112$ (18)°. These parameters and standard errors were obtained from a least-squares fit to the 2θ values of 17 reflections determined on a diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å).

Location of hydrogen atoms and refinement

At the time our data collection was finished, the results of the two-dimensional X-ray analysis of the structure by Webb, Kay & Grimes (1965) had become available. It was clear from these results† that the pattern of hydrogen bonding in the copper ammonium Tutton salt is the typical one that already had been established by the work on the corresponding magnesium, nickel, and zinc salts. Since in this pattern every hydrogen atom of the water molecules and of the ammonium ion is involved in a hydrogen bond to a sulfate oxygen, it was easy to calculate approximate coordinates for the hydrogen atoms. Thus, the structure of Webb *et al.* provided a complete set of starting coordinates for least-squares refinement. Of course, starting coordinates could have been taken equally well from the structure of the magnesium, zinc, or nickel salt.

The neutron coherent scattering amplitudes originally used (Bacon, 1962) were as follows (all in units of 10^{-12} cm): Cu, 0·79; S, 0·31; O, 0·577; N, 0·94; H, −0·378. The structural parameters were refined to convergence (final parameter shift was less than one tenth of the standard error for every parameter) in seven cycles with these scattering factors held fixed. In the last few cycles, anisotropic thermal parameters were optimized. The factor S scaling the $|F_c|$ values to the $|F_o|$ values was also adjusted. In the full-matrix least-squares refinement (Program XFLS, no. 389 in *World List of Crystallographic Computer Programs*, 1966) the quantity minimized was $\Sigma\, w(F_o^2-S^2F_c^2)^2$, where w is the weight of a particular observation F_o, calculated as $1/\sigma^2(F_o^2)$, and the summation is taken over all symmetrically independent reflections.

Early in the refinement procedure it was clear that many of the F_o^2 values corresponding to observations of high intensity were low because of the effects of extinction, and eventually the 153 observations of highest intensity were omitted from the refinement. Another 81 observations were omitted because their phase signs were indeterminate; these were all reflections with very small F_o^2 and F_c^2 values.

The value of the scale factor and the values of the usual goodness-of-fit measures at this stage are shown in Table 1. The discrepancy indices $R(F^k)$ are defined by the equation $R(F^k)\equiv \Sigma\, ||F_o^k|-S^k|F_c^k||/\Sigma\, |F_o^k|$, and the index $R_w(F^2)$ is defined by $R_w(F^2)\equiv[\Sigma\, w(F_o^2-S^2F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$. The σ_1 is the standard deviation of an observation of unit weight, defined by the equation $\sigma_1=\Sigma\, w(F_o^2-S^2F_c^2)^2/(n-p)$, where w is the weight of an observation F_o^2, n is the total number of observations, and p is the number of parameters fitted to the data. Unit value is expected for σ_1 at convergence when the observational errors are randomly distributed and correctly estimated and the model is correct.

In two additional cycles, the values of the scattering factors of copper, sulfur, oxygen, and nitrogen were refined to convergence, along with the scale, positional, and thermal parameters. The scattering factor of hydrogen was held at $-0{\cdot}378\times10^{-12}$ cm. The values of the scattering factors derived and their standard errors

Table 1. *Scale factors and measures of goodness of fit at convergence in refinement of the structure of* $Cu(NH_4)_2(SO_4)_2.6H_2O$

See text for definitions.

	Scale factor S	$R(F)$	$R(F^2)$	$R_w(F^2)$	σ_1
Scattering factors not refined*	1·032	0·0865	0·0841	0·0917	1·175
Scattering factors refined, final parameters*	1·022	0·0854	0·0823	0·0896	1·149
Final parameters, data corrected for extinction†	1·022	0·0548	0·0581	0·0765	1·286

* Measures of fit tabulated include only contributions from reflections given non-zero weights in least-squares refinement.
† Measures of fit tabulated include contributions for all reflections observed.

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* Here and elsewhere in this paper the numbers in parentheses, which correspond to the least significant digits of the adjacent parameters, are the standard errors of the parameters.

† We ignored the conclusion of Webb *et al.* that there is no hydrogen bond from $H_2O(1)$ to O(4), or, in our system of numbering, from O(8) to O(4′). Webb *et al.* concluded that the distance 2·54 Å which they calculated for O(8)···O(4′) is too short for a hydrogen bond and that there is repulsion between O(8) and O(4′). According to them the resultant strain is probably the reason that the copper salt is more liable to dehydration than the corresponding nickel salt. Actually the distance O(8)···O(4′) was incorrectly calculated, as were most of the other distances and angles given in their paper; the correct distance corresponding to their coordinates and cell parameters is 2·64 Å. The much more precise X-ray analysis of Montgomery & Lingafelter gave 2·725 (10) Å, a normal value for an O–H···O hydrogen bond. Our neutron analysis has subsequently yielded the distance 2·707(2) Å and has unambiguously shown that there is a hydrogen bond O(8)···O(4′). The erroneous conclusion of Webb *et al.* emphasizes that one should be cautious in making inferences about the existence of a hydrogen bond when the hydrogen atom has not been located, and especially cautious when the structural parameters have not been carefully refined.

Table 2. *Observed neutron structure factors (corrected for absorption but not for extinction) and calculated neutron structure factors for* $Cu(NH_4)_2(SO_4)_2.6H_2O$

For each reflection, identified by the indices *H* and *K* of a subheading and the running index *L*, the values $|F_o|$ and F_o are given, in units of 10^{-14} cm. The standard error $\sigma(F_o)$, calculated as $\sigma(F_o^2)/2|F_o|$, is given (same units) under the heading SG, except that for each reflection marked *W*, for which $|F_o|^2 < \sigma(F_o^2)$, the standard error $\sigma(F_o^2)$ is given, in units of 10^{-26} cm. The reflections marked *X* and *U* were excluded from the final refinement (see text).

L	OBS	CAL	SG
*** 0 0 L ***			
1X	220	223	4
2	128	-135	3
3X	358	380	5
4	46	78	21
5X	675	741	11
6UW	40	-2	24
7U	68	-4	23
8	282	269	7
*** 0 1 L ***			
1X	350	372	6
2	157	-151	5
3	149	155	6
4	176	-190	7
5	385	382	7
6 W	0	16	23
7	239	-230	6
8	62	90	27
*** 0 2 L ***			
0X	228	245	3
1X	254	256	4
2	71	-57	9
3	99	-113	9
4X	474	480	8
5	116	114	11
6	146	163	9
7	200	186	9
8	120	131	14
*** 0 3 L ***			
1	216	219	4
2	192	-189	5
3X	503	-539	8
4	78	72	13
5	96	-101	13
6	240	-236	7
7	252	-244	8
8	169	-169	10
*** 0 4 L ***			
0 W	0	-34	11
1	72	-66	9
2	298	295	6
3	86	75	11
4 W	0	-33	21
5	216	-213	7
6	83	-65	14
7	181	170	9
8 W	0	-11	29
*** 0 5 L ***			
1X	611	705	9
2X	711	-814	11
3	108	111	9
4 W	5	31	22
5	442	-447	8
6	220	218	9
7	86	-64	19
8 W	0	42	28
*** 0 6 L ***			
0	212	-205	6
1	194	192	6
2	279	276	6
3X	467	479	8
4	159	-161	8
5	155	-140	9
6	193	196	10
7	134	-126	8
8 W	0	3	27
*** 0 7 L ***			
1 W	0	36	18
2X	553	567	9
3	95	102	12
4 W	48	48	24
5	384	378	7
6	170	175	10
7	334	332	8
*** 0 8 L ***			
0	238	243	6
1	95	64	11
2	329	327	7
3	70	58	18
4	76	102	17
5	459	448	8
6	196	193	9
7	140	139	12
*** 0 9 L ***			
1X	539	-567	9
2X	446	461	8
3 W	0	-1	24
4	157	-166	9
5	195	200	9
6	180	-177	10
7	143	-149	11
*** 0 10 L ***			
0	230	-216	7
1X	485	474	8
2	225	224	7
3	174	-190	8
4	330	335	6
5	84	57	19
6	135	146	13
7	135	150	11
*** 0 11 L ***			
1	310	-309	7
2	188	-181	8
3	90	84	14
4 W	0	71	34
5	187	-193	6
6	127	-110	13
*** 0 12 L ***			
0	266	281	7
1 W	0	-31	25
2	90	88	14
3	280	266	8
4	68	-35	22
5	96	93	18
6 W	35	26	29
*** 0 13 L ***			
1	73	-74	14
2 W	0	-57	34
3	71	34	21
4U	64	9	27
5 W	0	-73	34
*** 0 14 L ***			
0	266	241	9
1	181	-162	10
2	179	-171	10
3	144	152	13
4 W	44	36	22
5	64	80	23
*** 0 15 L ***			
1 W	0	49	43
2 W	59	82	37
3	106	-109	17
4	159	-153	10
*** 0 16 L ***			
0	156	158	12
1	158	156	12
2	97	-36	18
3 W	0	27	30
*** 0 17 L ***			
1	233	227	8
2U	98	-30	16
*** 1 1 L ***			
-8	74	75	22
-7	315	321	8
-6	163	-159	8
-5 W	42	26	23
-4	244	-248	6
-3X	497	-542	8
-2X	420	458	7
-1	52	50	7
0	56	-50	2
1X	395	421	6
2	121	116	6
3	314	320	6
4X	688	757	11
5	58	67	21
6	275	270	7
7	206	223	8
8UW	45	6	31
*** 1 2 L ***			
-8	125	118	14
-7	197	178	9
-6	232	239	7
-5 W	0	16	23
-4	277	-266	6
-3	197	200	6
-2	192	190	5
-1X	418	446	7
0X	264	-261	4
1X	456	-491	7
2X	330	-341	6
3	313	307	6
4 W	0	11	20
5X	492	-498	8
6	129	-118	7
7	176	-174	9
8 W	0	1	28
*** 1 3 L ***			
-8	161	167	10
-7	125	107	13
-6	241	234	7
-5	112	106	12
-4X	509	547	8
-3X	829	1041	13
-2 W	0	48	13
-1X	373	390	6
0X	482	544	8
1	64	-80	9
2	238	250	5
3X	475	501	8
4	392	-388	7
5 W	29	23	24
6	79	-66	18
7	126	119	16
8	131	136	11
*** 1 4 L ***			
-8	337	-343	8
-7	165	184	11
-6	172	164	8
-5	365	-375	7
-4	378	385	7
-3UW	33	-4	18
-2	124	112	7
-1	254	250	5
0	196	186	5
1	303	311	5
2	233	242	5
3	63	-30	15
4X	551	576	9
5	347	354	7
6	180	-172	10
7	192	183	9
8	87	85	16
*** 1 5 L ***			
-8 W	0	22	32
-7 W	37	-34	30
-6	60	84	23
-5	110	83	12
-4	404	412	7
-3	126	126	9
-2X	360	-359	6
-1 W	36	-27	14
0	136	-127	6
1	248	-243	5
2	83	-74	11
3	358	-363	7
4	184	-182	7
5 W	48	-62	24
6	72	45	22
7 W	0	20	33
*** 1 6 L ***			
-8	222	-222	8
-7 W	37	19	33
-6	243	230	8
-5	236	-235	7
-4	146	131	10
-3	149	-135	8
-2X	562	-620	9
-1	42	19	20
0X	464	-495	8
1	88	105	10
2	127	-126	8
3X	725	-806	11
4	289	286	7
5	60	45	20
6	171	-180	10
7 W	0	125	37
*** 1 7 L ***			
-7 W	0	24	34
-6	168	158	10
-5	397	399	8
-4	85	-34	14
-3	243	-236	7
-2X	432	446	7
-1	104	87	9
0 W	0	18	18
1X	443	451	7
2	252	240	6
3	272	-276	7
4	199	196	7
5	381	375	7
6 W	34	43	29
7 W	42	-54	33
*** 1 8 L ***			
-7 W	46	-45	33
-6	223	-234	9
-5	284	300	7
-4	350	-334	7
-3	158	-158	9
-2	194	191	7
-1X	407	-416	7
0	272	259	6
1	157	-157	5
2	252	-249	6
3	306	305	7
4X	525	-544	9
5	86	-74	19
6	153	157	6
7	185	-193	10
*** 1 9 L ***			
-7 W	0	-37	33
-6	379	405	8
-5 W	0	-2	33
-4 W	22	-10	24
-3	213	234	8
-2	183	188	8
-1X	500	516	8
0	331	326	7
1	359	372	7
2	349	341	7
3	322	311	7
4	226	209	7
5	381	402	8
6	177	187	10
7 W	47	-59	29
*** 1 10 L ***			
-7	179	-174	9
-6	134	-123	13
-5 W	0	-31	34
-4 W	0	11	24
-3	246	257	8
-2	173	163	9
-1	316	308	7
0	248	251	7
1	60	64	20
2X	500	508	8
3	322	323	7
4	88	-47	19
5 W	15	33	30
6	139	127	8
*** 1 11 L ***			
-6 W	52	-35	33
-5U	95	19	16
-4	228	-225	9
-3	166	171	10
-2	185	-195	9
-1	142	-128	10
0	307	290	7
1	301	-286	7
2	94	113	14
3	215	223	7
4	86	80	19
5	166	166	11
6	125	90	13
*** 1 12 L ***			
-6	64	-25	23
-5	134	85	13
-4	125	153	14
-3	106	101	16
-2	66	88	24
-1	197	-189	8
0	75	-48	19
1	111	-122	12
2	154	-143	9
3 W	0	45	34
4	149	-156	11
5 W	41	-40	21
*** 1 13 L ***			
-5	138	137	13
-4	352	370	8
-3	61	-21	28
-2	439	442	8
-1 W	0	22	34
0	191	-185	7
1	457	446	9
2	109	-96	16
3	124	121	14
4	100	120	17
5	263	-278	8
*** 1 14 L ***			
-5	138	139	11
-4	63	-61	28
-3U	94	26	18
-2	102	-135	18
-1	74	-61	23
0	98	68	17
1 W	0	-56	35
2	75	-76	21
3 W	35	28	22
4	85	43	20
*** 1 15 L ***			
-4	85	60	18
-3	240	232	9
-2	93	97	17
-1 W	0	25	27
0	137	142	15
1 W	34	-35	36
2	145	125	13
3	97	54	18
4 W	22	-13	30
*** 1 16 L ***			
-3	270	-270	8
-2 W	0	9	36
-1	57	42	20
0 W	0	-28	36
1 W	0	25	36
2U	60	-14	29
3	89	66	17
*** 1 17 L ***			
-2	106	-129	15
-1	92	94	17
0	151	152	11
1 W	41	-23	31
*** 2 0 L ***			
-8	198	201	9
-7	186	188	10
-6 W	0	20	23
-5	401	-391	7
-4X	405	414	7
-3X	581	628	9
-2	268	-268	5
-1X	600	718	9
0X	503	579	8
1	130	-143	5
2X	364	385	6
3	92	-63	10
4	126	119	9
5	153	141	8
6	437	-438	8
7	250	247	8
8 W	0	11	29
*** 2 1 L ***			
-8	207	-205	9
-7 W	27	21	31
-6	446	-455	8
-5	315	-300	7
-4X	414	425	7
-3	208	198	5
-2 W	0	32	12
-1	140	-140	4
0X	348	352	6
1	114	113	6
2X	526	568	8
3	56	-33	16
4UW	34	-5	21
5	285	295	7
6	108	-104	15
7 W	56	58	33
8	57	86	25
*** 2 2 L ***			
-8	121	-125	9
-7	230	228	8
-6	163	-160	9
-5	208	-202	7
-4	384	386	7
-3	232	-225	6
-2	45	-52	17
-1	129	116	4
0	194	205	4
1X	418	440	7
2	260	-272	5
3	282	281	6
4X	426	434	7
5 W	0	-7	23
6	317	288	8
7 W	35	100	34
8	128	94	11
*** 2 3 L ***			
-8	150	-132	11
-7	69	-67	23
-6	185	171	8
-5X	627	-672	10
-4	305	297	6
-3X	692	803	11
-2X	331	-343	6
-1	44	37	13
0UW	23	-6	12
1	228	231	5
2X	639	698	10
3 W	32	43	19
4	61	80	19
5	215	207	7
6 W	0	60	34
7 W	37	86	34
*** 2 4 L ***			
-8	114	117	15
-7	143	135	8
-6	225	220	7
-5X	574	606	9
-4	122	126	10
-3	270	267	6
-2	108	95	8
-1	220	-230	5
0	278	286	5
1	126	116	7
2	181	181	6
3 W	42	23	20
4 W	44	45	24
5	131	141	10
6	267	262	8
7	112	113	15
*** 2 5 L ***			
-8 W	0	-58	33
-7UW	32	-2	29
-6X	500	510	9
-5 W	0	-17	24
-4X	733	-804	11
-3X	623	666	10
-2	229	-224	6
-1X	575	-625	9
0X	430	452	7
1X	376	-368	6
2	52	-29	17
3	291	286	6
4X	456	-474	8
5	264	259	7
6	69	-55	24
7	137	-135	13
*** 2 6 L ***			
-8	169	160	9
-7	146	133	13
-6	444	448	8
-5	333	330	7
-4	305	303	7
-3	154	161	8
-2X	433	454	7
-1X	424	441	7
0	296	-293	6
1 W	34	51	18
2X	468	495	8
3 W	49	-45	24
4	341	-343	7
5	196	194	8
6 W	33	-39	29
7 W	40	-50	32
*** 2 7 L ***			
-8	85	-97	17
-7 W	7	-35	18
-6	166	167	11
-5 W	0	-61	24
-4 W	23	-40	24
-3	290	-278	7
-2	115	-121	10
-1	90	76	11
0	102	-87	10
1	82	60	12
2	336	-326	7
3X	446	-452	8
4	154	143	9
5	162	-167	11
6	126	-115	7
7 W	39	-56	28
*** 2 8 L ***			
-7	262	-270	8
-6 W	0	-20	33
-5U	58	3	21
-4X	628	-668	10
-3	65	-54	18
-2	261	259	6
-1	220	228	5
0	133	-142	10
1	214	-201	6
2	386	385	7
3	237	235	7
4	230	225	7
5	232	236	8
6	68	65	25
7	98	98	15
*** 2 9 L ***			
-7	211	194	9
-6	311	-314	8
-5	257	251	8
-4	425	440	8
-3	415	-422	8
-2	294	298	7
-1	152	153	8
0	237	-227	7
1 W	0	54	23
2	333	-332	6
3	83	-92	15
4	133	129	10
5	154	-166	11
6 W	23	-22	33
*** 2 10 L ***			
-7 W	0	5	29
-6U	67	14	25
-5	156	160	11
-4	187	-188	9
-3	147	152	10
-2X	538	553	9
-1	322	-320	7
0	259	267	7
1	309	296	7
2	256	-260	7
3	355	350	7
4	122	133	15
5	75	-38	27
6	254	259	8
*** 2 11 L ***			
-6	171	-163	10
-5	155	154	11
-4 W	13	15	33
-3U	71	-12	17
-2	79	82	17
-1	151	144	9
0 W	0	18	25
1	65	-49	19
2	68	62	18
3	332	342	8
4U	81	12	19
5	143	-125	12
6	154	137	10
*** 2 12 L ***			
-6	232	227	8
-5	78	97	14
-4	383	387	8
-3	350	345	8
-2	94	-94	15
-1	159	149	9
0	211	221	7
1	282	282	7
2	112	123	16
3	100	-87	17
4 W	0	56	36
5	104	62	16
*** 2 13 L ***			
-5	78	85	22
-4	86	-42	20
-3	207	-174	9
-2	118	114	8
-1	125	132	15
0	93	69	18
1	140	123	13
2	185	179	9
3	218	222	9
4 W	49	51	34
5 W	14	14	29
*** 2 14 L ***			
-5 W	23	25	30
-4	299	311	8
-3 W	0	-36	36
-2	190	-193	10
-1	224	233	9
0	189	170	10
1	133	126	14
2	178	144	12
3 W	0	-30	36
4	186	181	10
*** 2 15 L ***			
-4	83	99	19
-3	163	-164	12
-2	132	-74	14
-1	96	58	19
0	170	-148	11
1	62	-41	18
2 W	19	-28	35
3	201	-195	6
*** 2 16 L ***			
-3 W	54	27	31
-2	141	134	13
-1	121	110	15
0	116	100	15
1	118	112	15
2	112	-95	10
*** 2 17 L ***			
-1	107	-101	15
0 W	0	-5	31
1	119	-120	13
*** 3 1 L ***			
-8	73	51	22
-7	130	144	13
-6	66	52	18
-5	209	-202	7
-4	103	105	10
-3X	543	575	9
-2 W	34	33	14
-1	127	116	5
0	151	154	5
1X	498	-521	8
2 W	26	-19	17
3X	433	435	7
4U	53	-11	22
5UW	28	3	24
6 W	0	18	32
7	80	63	13
*** 3 2 L ***			
-8	263	-284	8
-7	312	-315	8
-6	102	92	12
-5 W	39	-22	23
-4	342	-343	7
-3	143	121	7
-2X	454	-478	7
-1	302	-315	5
0	52	-55	12
1	144	-144	6
2	192	164	6
3	195	181	7
4	302	-292	7
5	336	327	7
6	99	113	16
7U	82	-26	19
*** 3 3 L ***			
-8	70	56	23
-7	312	320	8
-6	353	359	7
-5	117	-103	11
-4X	476	485	8
-3	41	51	16
-2X	454	-473	7
-1X	467	511	7
0	87	67	9
1	129	-122	7
2	318	325	6
3	163	-164	8
4U	57	7	21
5U	73	-7	16
6	89	-88	19
7	197	196	6
*** 3 4 L ***			
-8	112	-103	15
-7 W	46	-62	33
-6 W	0	13	24
-5	372	365	7
-4 W	26	-16	21
-3	116	115	6
-2X	512	546	8
-1	219	-223	5
0X	678	786	10
1X	502	664	9
2	383	-394	7
3	80	91	14
4	341	341	7
5 W	25	-14	24
6	97	-96	15
7	106	-93	15
*** 3 5 L ***			
-8 W	0	-31	33
-7	84	68	18
-6	60	52	20
-5	388	404	7
-4	72	71	15
-3	264	-260	6
-2X	531	574	9
-1	280	282	6
0X	593	657	9
1X	866	1014	13
2	281	261	6
3X	444	474	8
4	447	468	8
5	354	353	7
6	382	398	8
7 W	40	74	32
*** 3 6 L ***			
-8	97	107	17
-7	121	98	18
-6	173	164	10
-5	145	-131	10
-4	328	-338	7
-3U	52	-5	20
-2	289	283	6
-1	332	-339	6
0	146	143	7
1	128	112	8
2X	706	-772	11
3 W	15	-41	24
4	303	300	7
5	256	-285	8
6	69	-75	27
7	98	-81	15
*** 3 7 L ***			
-8	289	290	7
-7	231	-230	8
-6 W	0	-55	33
-5X	493	500	9
-4	354	-352	7
-3	310	299	7
-2X	493	505	8
-1	383	-381	7
0	89	81	12
1X	443	448	8
2	67	30	17
3	142	-132	9
4	146	132	9
5	211	209	9
6	161	182	11
7 W	46	-55	28
*** 3 8 L ***			
-7	58	45	18
-6	225	203	9
-5	130	-132	7
-4	252	-251	7
-3	317	302	7
-2	290	-287	7
-1 W	0	-3	21
0	186	-184	7
1X	598	-607	10
2	197	191	7
3 W	27	30	24
4	329	-341	7
5	156	148	10
6 W	0	-33	23
*** 3 9 L ***			
-7	136	128	8
-6 W	0	-61	31
-5	94	86	18
-4	342	339	7
-3	167	-158	9
-2	306	311	7
-1	193	-194	7
0X	593	-612	10
1	106	95	13
2	105	-119	12
3	211	-209	8
4	185	-171	10
5 W	61	-71	39
6 W	37	-31	33
*** 3 10 L ***			
-7 W	0	-20	29
-6 W	37	12	18
-5	58	-34	29
-4X	495	522	9
-3 W	50	-54	25
-2	90	-93	15
-1	338	355	7
0	309	-316	7
1	206	205	7
2X	478	482	8
3	55	-46	23
4U	66	-9	25
5	77	-57	21
6	165	170	10
*** 3 11 L ***			
-6	150	162	12
-5	53	72	17
-4	59	72	28
-3	84	65	15
-2	122	-82	11
-1	457	476	8
0	151	131	9
1 W	46	-56	26
2	419	418	8
3	136	139	13
4	211	220	9
5	113	94	15
*** 3 12 L ***			
-6	405	-410	8
-5	70	42	24
-4	109	90	14
-3	339	-346	8
-2	130	-115	11
-1	84	-80	15
0	94	-84	14
1 W	0	-2	25
2	138	126	12
3	68	-38	23
4 W	24	30	34
5 W	0	-30	29
*** 3 13 L ***			
-5	185	186	10
-4 W	0	-21	36
-3	98	105	19
-2	189	186	10
-1 W	0	44	35
0	365	372	7
1	81	82	21
2	98	-102	21
3	236	219	8
4 W	0	8	34
*** 3 14 L ***			
-5	143	-114	11
-4	93	117	20
-3 W	0	-13	36
-2	74	-78	22
-1	373	384	9
0 W	0	-13	31
1	110	-76	20
2 W	0	40	31
3U	74	-4	14
4 W	24	-12	29
*** 3 15 L ***			
-4	142	132	11
-3	326	336	8
-2 W	40	-19	35
-1	212	211	10
0	179	183	11
1	89	74	20
2	181	170	10
3 W	0	12	30
*** 3 16 L ***			
-3	119	125	13
-2	188	187	10
-1 W	0	5	36
0	163	170	12
1	148	-143	12
2 W	49	21	30
*** 4 0 L ***			
-8	331	338	8
-7	277	274	8
-6	154	153	9
-5	183	181	7
-4X	846	969	13
-3	211	213	6
-2X	505	-541	8
-1X	374	-370	6
0X	451	-484	7
1	252	254	6
2	95	111	11
3	368	-370	7
4	90	44	13
5	190	-162	8
6	126	114	13
7	279	282	6
*** 4 1 L ***			
-8	181	175	10
-7	85	80	19
-6 W	41	-34	24
-5X	588	616	10
-4 W	0	-29	20
-3	300	-301	6
-2	317	336	5
-1X	366	-383	6
0	233	240	5
1	246	249	6
2	256	-262	6
3	215	-217	7
4 W	0	2	21
5	122	-144	12
6 W	0	-47	30
7UW	42	1	31
*** 4 2 L ***			
-8 W	28	-15	21
-7	240	234	8
-6	147	-151	9
-5	102	80	12
-4	63	52	23
-3	312	311	6
-2 W	37	-18	16
-1X	368	-387	6
0X	655	756	10
1	75	-31	12
2	137	-130	8
3X	469	499	8
4	119	-120	11
5	143	127	8
6	129	148	15
7 W	46	-23	26
*** 4 3 L ***			
-8	195	-179	9
-7	70	57	21
-6	55	51	22
-5	60	-73	20
-4	1,7	-180	8
-3X	447	-460	8
-2	158	151	5
-1X	509	-524	8
0X	548	-609	9
1X	596	637	9
2	380	-368	7
3	394	-406	7
4	184	173	8
5	230	-232	9
6	109	97	12
7	93	90	15
*** 4 4 L ***			
-8	61	64	26
-7 W	0	-42	30
-6	327	326	7
-5	242	-238	7
-4	314	-313	7
-3X	529	545	9
-2 W	0	-8	18
-1X	651	741	10
0X	679	753	11
1	44	40	21
2	98	113	11
3	345	338	7
4	340	332	7
5	188	192	10
6	150	150	7
7U	55	2	26
*** 4 5 L ***			
-8	252	-246	8
-7 W	0	20	30
-6	182	184	9
-5X	459	-450	8
-4	349	-355	7
-3X	579	617	9
-2	180	181	7
-1	201	-196	6
0X	453	-482	8
1	122	134	9
2	238	228	7
3	277	-275	7
4	131	134	11
5	113	105	15
6	214	-210	9
*** 4 6 L ***			
-8	63	27	22
-7	170	154	12
-6	152	145	11
-5	316	312	7
-4	232	238	7
-3	395	-394	7
-2X	752	853	12
-1X	435	444	7
0	381	-372	7
1	405	410	7
2	200	206	7
3 W	0	-20	21
4	250	252	7
5	92	95	18
6 W	55	45	33
*** 4 7 L ***			
-8	79	58	18
-7	117	116	9
-6	162	152	11
-5	93	98	14
-4	340	346	7
-3	379	376	7
-2X	557	590	9
-1	129	122	9
0	253	257	6
1	271	261	6
2	113	-100	10
3	275	267	7
4	150	145	11
5	155	-154	10
6 W	0	-35	33
*** 4 8 L ***			
-7	191	-193	9
-6	134	136	12
-5	324	329	7
-4	83	101	16
-3	193	-199	8
-2	339	338	7
-1	299	288	7
0X	583	-608	9
1	122	130	11
2X	516	522	9
3	155	-148	9
4	111	135	16
5U	62	-8	27
6 W	0	-35	29
*** 4 9 L ***			
-7	191	-176	9
-6	228	-229	8
-5	197	209	10
-4	167	-160	9
-3	243	-246	7
-2	437	-469	8
-1UW	26	-1	25
0	432	444	8
1	304	-304	7
2	55	45	22
3	254	258	7
4 W	35	-17	33
5 W	49	78	35
6	84	87	17
*** 4 10 L ***			
-7	90	80	16
-6	162	158	11
-5	178	182	10
-4 W	0	65	36
-3	221	233	8
-2	93	-96	14
-1 W	15	-28	25
0	118	83	11
1	93	-82	15
2	143	148	10
3 W	0	45	33
4	172	-160	10
5	215	213	6
*** 4 11 L ***			
-6 W	0	30	34
-5	114	-86	15
-4	92	66	18
-3	302	-298	7
-2X	495	-522	9
-1	212	215	8
0	67	62	18
1	306	-296	7
2U	60	16	28
3 W	0	-52	30
4	218	-207	9
5	148	141	10
*** 4 12 L ***			
-6 W	0	-7	30
-5 W	49	-25	34
-4	130	120	13
-3 W	39	31	33
-2	69	61	25
-1 W	34	39	25
0	173	164	11
1	178	162	10
2 W	0	-36	33
3 W	0	-18	18
4	119	110	13
*** 4 13 L ***			
-5	67	70	26
-4	55	59	20
-3	116	116	18
-2 W	0	40	35
-1	122	112	14
0 W	0	10	34
1	215	-198	9
2 W	37	21	34
3	98	-83	18
4	142	-154	11
*** 4 14 L ***			
-5	58	58	26
-4UW	58	18	34
-3	94	92	19
-2	172	173	11
-1	113	105	15
0	290	272	9
1	218	219	6
2	67	80	27
3	212	195	8
*** 4 15 L ***			
-4 W	0	-7	31
-3 W	37	-62	34
-2	182	197	7
-1 W	37	-71	32
0	110	-110	17
1UW	40	12	35
2 W	33	-24	31
*** 4 16 L ***			
-2U	60	-1	18
-1	126	-87	13
0	347	328	7
1 W	49	48	31
*** 5 1 L ***			
-8 W	37	-21	29
-7	293	302	8
-6	253	257	7
-5	235	233	7
-4	174	182	7
-3	218	221	6
-2 W	41	21	18
-1	331	322	6
0X	582	635	9
1X	437	441	7
2 W	0	-10	21
3	306	304	7
4	397	394	7
5 W	46	-65	32
6 W	39	-62	34
*** 5 2 L ***			
-8	219	-226	8
-7	144	142	12
-6	209	219	7
-5X	501	-516	8
-4	152	-151	8
-3	299	-289	6
-2	291	-284	6
-1	313	315	6
0	316	-312	6
1	280	277	6
2	93	-79	13
3X	598	-612	10
4	261	263	7
5	330	325	8
6	145	-130	12
*** 5 3 L ***			
-8	67	67	15
-7	153	170	11
-6	90	-92	14
-5	196	-201	8
-4	208	210	7
-3	243	-248	5
-2	286	290	6
-1	174	-176	7
0	251	-243	6
1 W	34	28	20
2	326	-319	7
3	139	135	10
4	228	225	7
5	144	-137	12
6	256	256	9
*** 5 4 L ***			
-8 W	0	-10	32
-7	149	-132	11
-6	371	371	7
-5	194	187	8
-4X	443	-437	8
-3	129	124	9
-2	204	-208	7
-1X	551	-603	9
0	271	279	6
1	307	-307	6
2X	520	-535	9
3	428	-431	8
4 W	0	49	25
5U	73	10	20
6	265	-258	6
*** 5 5 L ***			
-8 W	8	37	32
-7 W	0	24	30
-6 W	37	28	32
-5 W	0	37	24
-4	63	-35	19
-3X	533	557	9
-2	252	246	6
-1	176	182	7
0	94	121	12
1	300	-303	7
2	386	386	7
3	182	202	8
4	99	-115	17
5	277	272	8
6	127	119	13
*** 5 6 L ***			
-8	125	-118	11
-7	235	-243	8
-6	104	118	16
-5	76	64	16
-4	116	119	11
-3	357	349	6
-2 W	48	87	24
-1	107	-97	11
0	141	137	9
1	391	401	7
2	138	139	7
3	311	296	7
4	232	229	9
5 W	0	23	26
6 W	25	30	32
*** 5 7 L ***			
-8	203	200	8
-7	173	-189	11
-6	392	390	8
-5	111	118	12
-4	109	117	12
-3	344	339	7
-2	335	-330	7
-1	300	291	7
0 W	0	15	45
1	112	113	13
2X	518	521	9
3	205	-195	8
4	166	-149	11
5	394	394	8
6 W	0	4	28
*** 5 8 L ***			
-7	59	58	18
-6	159	-161	12
-5 W	0	-73	34
-4	174	169	9
-3	95	67	14
-2	196	198	6
-1	334	326	7
0	165	-144	6
1	186	190	8
2X	539	542	9
3 W	0	-3	33
4UW	45	11	30
5	137	116	13
*** 5 9 L ***			
-7 W	0	24	34
-6U	97	-25	17
-5X	501	522	9
-4	89	84	16
-3	234	-228	7
-2	255	263	7
-1	166	-163	9
0	147	157	10
1	354	335	7
2	190	203	8
3	84	-70	20
4	164	-157	13
5	191	176	10
*** 5 10 L ***			
-7	226	215	8
-6 W	56	-75	35
-5 W	49	58	31
-4UW	30	2	33
-3	296	-294	6
-2	208	209	8
-1U	58	13	25
0	116	-110	11
1	188	-179	8
2	298	-297	8
3U	57	-17	26
4	279	-283	8
5	201	-192	8
*** 5 11 L ***			
-6	133	106	12
-5	187	182	10
-4	159	151	11
-3	95	81	18
-2	402	406	8
-1	468	469	8
0UW	41	6	25
1	251	266	8
2	237	217	9
3	139	148	12
4	218	211	6
*** 5 12 L ***			
-6	101	-98	14
-5	160	167	11
-4	246	-251	10
-3 W	46	30	30
-2	121	-107	14
-1	82	-115	22
0	197	208	10
1	263	-269	8
2	161	-150	6
3	291	287	8
4	76	-56	19
*** 5 13 L ***			
-5	83	-76	20
-4 W	33	-45	21
-3 W	45	34	34
-2	73	72	22
-1 W	23	-22	32
0	74	90	23
1	141	-141	13
2	95	-86	19
3	234	236	9
*** 5 14 L ***			
-4	239	253	9
-3	171	-172	11
-2	117	-93	15
-1U	69	-12	16
0	165	-160	11
1 W	0	-15	36
2 W	0	-27	34
*** 5 15 L ***			
-3 W	0	24	32
-2	78	-81	14
-1UW	55	9	36
0	70	30	24
1	146	143	11
*** 5 16 L ***			
-1	140	138	12
0 W	0	-18	31
*** 6 0 L ***			
-8	81	-37	20
-7 W	24	-25	29
-6	275	272	7
-5	205	-201	7
-4	72	-24	16
-3	142	130	9
-2X	424	441	7
-1	200	-201	7
0X	572	588	9
1X	795	899	12
2	185	-177	8
3	74	-106	18
4	307	311	7
5UW	23	1	30
6	776	272	8
*** 6 1 L ***			
-8	230	239	6
-7	119	-119	13
-6	364	380	7
-5	206	206	8
-4X	467	-463	8

Table 2 (*cont.*)

L	OBS	CAL	SG
*** 6 1 L ***			
-3X	565	585	9
-2 W	0	35	21
-1	202	195	7
0	182	184	5
1X	653	-707	10
2	123	121	11
3	54	19	22
4	150	-145	11
5	64	46	23
6	105	-98	10
*** 6 2 L ***			
-8 W	34	40	32
-7	290	287	8
-6	243	247	7
-5	51	45	23
-4	311	298	7
-3X	686	751	11
-2	54	-26	19
-1	314	321	6
0X	440	435	8
1	186	159	7
2	262	276	7
3 W	48	53	24
4	139	118	12
5	110	102	18
6 W	42	-77	37
*** 6 3 L ***			
-8 W	26	-49	32
-7 W	36	-34	29
-6	198	206	9
-5	112	-109	12
-4	415	-419	7
-3	251	248	7
-2X	539	572	9
-1	119	-129	10
0	66	-59	16
1	169	-133	8
2	87	-88	15
3	290	268	7
4	174	-161	10
5 W	0	69	39
6	85	-78	17
*** 6 4 L ***			
-8 W	0	18	31
-7	171	159	10
-6 W	56	73	32
-5	204	-209	7
-4X	474	495	8
-3	87	71	13
-2X	433	-437	8
-1	218	206	7
0	379	-372	7
1	300	-284	7
2	162	139	9
3	222	215	7
4	116	119	15
5UW	54	15	33
6	71	-29	20
*** 6 5 L ***			
-8	127	-99	11
-7	120	-99	14
-6	86	102	19
-5	189	-203	8
-4	293	-283	7
-3	144	144	9
-2	129	114	10
-1	395	-398	7
0	177	-165	8
1X	531	532	9
2	170	175	8
3	144	-145	10
4	208	207	9
5 W	16	25	21
6	68	-75	21
*** 6 6 L ***			
-8	214	211	8
-7	157	-160	11
-6	234	-238	8
-5	447	447	8
-4X	463	-475	8
-3X	472	-479	8
-2	324	314	7
-1X	471	-488	8
0 W	0	11	24
1	171	-189	8
2 W	35	-41	17
3	253	243	8
4	86	-74	18
5	154	155	12
*** 6 7 L ***			
-7 W	0	1	33
-6 W	42	51	30
-5	260	253	8
-4 W	48	-35	24
-3 W	0	-41	24
-2	57	-59	23
-1	338	-324	7
0	120	114	11
1	127	114	10
2 W	48	-56	24
3	72	-69	23
4	91	-72	17
5 W	16	39	33
*** 6 8 L ***			
-7 W	40	36	32
-6	273	279	9
-5X	540	553	9
-4	61	-25	20
-3 W	0	-30	24
-2X	691	744	11
-1X	552	589	9
0	201	195	8
1	408	412	8
2	114	127	13
3	123	127	14
4 W	59	29	38
5	96	81	15
*** 6 9 L ***			
-7	196	-195	8
-6	118	-112	14
-5 W	52	59	30
-4	138	136	12
-3	129	-124	11
-2	148	-144	9
-1	317	317	7
0 W	0	-27	31
1	155	-161	9
2 W	11	-51	33
3 W	0	-27	30
4 W	19	-9	34
5UW	43	-13	28
*** 6 10 L ***			
-6	117	89	14
-5	97	133	22
-4	210	211	9
-3	114	104	15
-2	150	128	10
-1	419	432	8
0	240	230	8
1	64	58	26
2	253	243	8
3	79	74	21
4	81	101	13
*** 6 11 L ***			
-6	206	-202	8
-5 W	26	14	34
-4	320	333	8
-3	165	-190	11
-2	69	99	25
-1	244	233	9
0	91	-64	19
1 W	34	-33	33
2	131	-139	16
3 W	47	-20	34
4	157	131	10
*** 6 12 L ***			
-5	101	-41	16
-4	200	199	9
-3	115	117	15
-2 W	0	-7	18
-1	89	-100	18
0	66	-74	24
1	157	135	13
2 W	53	66	35
3 W	0	39	33
*** 6 13 L ***			
-5	80	-64	18
-4	180	175	10
-3 W	0	-25	34
-2	150	-163	13
-1 W	0	71	36
0UW	46	8	35
1U	79	-12	14
2 W	0	-35	35
3 W	0	-10	29
*** 6 14 L ***			
-4	84	97	18
-3	243	236	8
-2 W	0	70	36
-1 W	27	-61	36
0 W	58	-36	35
1	164	166	11
2	88	94	17
*** 6 15 L ***			
-3 W	0	26	30
-2	153	-149	10
-1 W	0	-12	31
0	128	149	12
*** 7 1 L ***			
-8	86	40	20
-7	123	129	13
-6	276	277	8
-5 W	30	33	24
-4	68	26	18
-3	360	360	7
-2 W	29	52	24
-1	351	349	7
0	412	415	7
1	238	-235	7
2	284	-284	7
3	213	216	5
4	295	307	8
5	99	106	17
*** 7 2 L ***			
-8	188	178	9
-7	186	167	11
-6	305	-305	8
-5	347	337	7
-4X	513	527	9
-3	143	141	9
-2X	733	809	11
-1	235	-218	7
0 W	0	2	24
1X	635	664	10
2U	54	-15	22
3 W	45	20	24
4	179	184	10
5 W	13	18	34
*** 7 3 L ***			
-8	101	103	14
-7	73	-52	25
-6	193	169	9
-5	126	133	10
-4	85	-86	15
-3	303	288	7
-2U	50	7	23
-1	290	-286	7
0X	561	586	9
1	200	190	8
2	178	182	8
3	325	342	8
4 W	17	16	31
5	116	107	14
*** 7 4 L ***			
-8U	93	2	15
-7	67	-45	27
-6	149	136	11
-5	83	90	15
-4	131	-134	11
-3	186	184	8
-2	102	-112	13
-1U	64	-19	19
0	66	-53	18
1	106	100	12
2 W	43	-28	25
3	294	-269	8
4 W	33	29	30
5	67	72	25
*** 7 5 L ***			
-8	132	142	11
-7	167	166	11
-6UW	57	4	32
-5	200	192	8
-4	229	216	7
-3 W	23	-24	25
-2	88	106	15
-1	99	-83	13
0	331	-345	7
1	336	333	7
2	266	268	7
3	154	-164	11
4	185	-185	10
5	97	-90	17
*** 7 6 L ***			
-7	144	-133	12
-6	78	58	19
-5	97	39	16
-4	300	-307	7
-3	286	-281	7
-2 W	18	23	25
-1	167	-173	9
0	170	170	9
1	165	175	9
2	213	-204	8
3	81	-90	21
4	95	-78	20
5	84	72	18
*** 7 7 L ***			
-7	154	155	11
-6	124	-88	15
-5 W	9	30	33
-4	404	404	8
-3	277	-269	7
-2	402	410	7
-1X	493	500	8
0	442	-439	7
1	399	405	8
2	280	259	8
3	113	-116	16
4	259	259	8
5 W	39	56	28
*** 7 8 L ***			
-7 W	49	-69	29
-6	61	-70	28
-5	67	26	22
-4	116	-116	15
-3	208	-207	8
-2 W	0	-7	25
-1	73	-81	17
0	194	-202	8
1 W	45	73	35
2 W	0	-59	33
3	71	-84	24
4	160	171	11
*** 7 9 L ***			
-7 W	0	-27	28
-6 W	33	-33	34
-5	165	159	6
-4 W	25	-51	34
-3	73	86	23
-2	282	270	6
-1	198	204	8
0	217	204	9
1 W	0	33	34
2	245	247	5
3	174	179	11
4	149	150	10
*** 7 10 L ***			
-6	92	-53	17
-5 W	0	-71	34
-4	91	109	19
-3U	70	21	23
-2 W	55	-25	34
-1UW	34	6	33
0	145	-169	12
1	305	-305	8
2 W	37	66	35
3	150	163	12
*** 7 11 L ***			
-6	199	208	8
-5	95	63	16
-4	156	186	12
-3	124	110	14
-2UW	48	4	31
-1	63	71	25
0 W	29	15	31
1 W	10	11	35
2 W	0	36	35
3	58	64	26
*** 7 12 L ***			
-5	153	-140	10
-4	181	183	10
-3	374	364	8
-2	133	-135	13
-1	420	450	8
0	184	161	7
1	226	-226	9
2	323	331	8
*** 7 13 L ***			
-4	112	124	13
-3	165	145	11
-2	114	-107	16
-1	96	126	19
0	226	203	6
1 W	57	-32	34
2	144	161	11
*** 7 14 L ***			
-3	118	-110	13
-2	74	48	20
-1 W	0	0	22
0	116	116	13
*** 8 0 L ***			
-8 W	10	-44	28
-7	54	43	19
-6	81	-65	20
-5	356	-343	7
-4	288	-285	7
-3	341	328	7
-2	136	126	10
-1X	600	-629	10
0UW	44	1	25
1	186	182	8
2 W	0	12	24
3	387	398	8
4	218	227	9
5	195	174	8
*** 8 1 L ***			
-8	197	-192	8
-7 W	30	-22	36
-6	89	77	19
-5	255	-254	7
-4 W	0	43	24
-3	240	-248	7
-2	216	-223	7
-1	321	327	7
0X	619	-668	10
1	95	59	14
2	357	373	7
3	150	-162	12
4	114	84	15
5U	66	9	21
*** 8 2 L ***			
-8	234	235	7
-7	238	229	8
-6 W	0	-6	33
-5	175	152	9
-4	94	70	13
-3	205	211	8
-2	207	207	7
-1	145	-133	9
0 W	0	38	24
1	191	199	8
2	54	28	18
3	107	111	16
4	113	136	16
5 W	0	-28	28
*** 8 3 L ***			
-8	156	-132	9
-7	160	157	11
-6U	75	11	20
-5	209	193	9
-4	91	82	13
-3	93	-63	14
-2	408	406	8
-1	107	106	12
0	298	-297	7
1	177	176	8
2	368	373	8
3 W	36	-43	30
4	74	41	20
5	96	52	15
*** 8 4 L ***			
-7	197	210	10
-6	86	81	19
-5	330	328	8
-4X	478	497	8
-3	166	-176	9
-2	278	269	7
-1X	462	479	8
0	227	221	7
1	335	343	7
2 W	0	-52	33
3 W	13	-4	31
4 W	37	34	33
*** 8 5 L ***			
-7	78	35	21
-6	133	145	13
-5U	63	9	26
-4	62	22	14
-3	96	81	14
-2	340	344	7
-1U	72	-17	25
0 W	0	-40	24
1	157	166	10
2	260	-246	8
3	104	-103	9
4	161	193	11
*** 8 6 L ***			
-7	259	-256	8
-6	342	357	8
-5	206	188	9
-4	81	-38	20
-3	332	326	7
-2	97	-97	14
-1	392	399	7
0	406	400	8
1	109	-80	15
2	308	293	8
3	64	-60	26
4 W	48	43	33
*** 8 7 L ***			
-7 W	0	38	28
-6	98	-88	17
-5	204	-197	9
-4	287	-283	8
-3	189	-201	10
-2	222	-201	6
-1	112	-108	9
0	109	-129	16
1	275	-259	8
2	170	-177	10
3	161	-145	11
4 W	0	-23	29
*** 8 8 L ***			
-7	64	84	22
-6	221	220	9
-5 W	31	43	33
-4 W	24	76	34
-3	115	89	15
-2	75	97	23
-1	164	140	11
0	110	-117	16
1	121	-120	13
2	195	183	10
3	93	84	19
*** 8 9 L ***			
-6	65	60	25
-5 W	0	2	34
-4	119	143	15
-3	65	67	25
-2	140	-137	13
-1	166	171	11
0	62	58	24
1 W	0	48	31
2	237	233	8
3U	75	3	22
*** 8 10 L ***			
-6	101	-106	15
-5 W	36	-52	33
-4	78	80	14
-3	168	-168	10
-2	56	-43	27
-1	283	282	8
0	163	-155	11
1	89	-63	19
2	237	234	9
3	80	116	18
*** 8 11 L ***			
-5	200	192	8
-4 W	15	55	34
-3	143	143	8
-2 W	0	-12	35
-1	160	-186	12
0	304	319	8
1	120	96	15
2 W	0	12	30
*** 8 12 L ***			
-4	74	67	20
-3 W	15	54	34
-2	66	98	27
-1 W	0	6	35
0	241	245	9
1	123	108	12
*** 8 13 L ***			
-3U	86	-12	17
-2 W	45	-97	31
-1	88	-64	18
0	119	120	13
*** 9 1 L ***			
-7	108	104	15
-6	166	-148	10
-5 W	33	90	34
-4	160	159	9
-3	258	-255	7
-2	75	41	18
-1 W	0	-8	24
0	117	-110	11
1	284	273	8
2 W	50	-43	33
3UW	10	1	21
4	304	295	7
*** 9 2 L ***			
-7	320	-329	8
-6 W	48	-37	38
-5	61	34	27
-4	127	-125	14
-3	86	54	15
-2	291	-294	7
-1	356	-356	7
0	302	303	7
1	151	169	12
2	67	42	22
3	156	-143	11
4	98	-98	11
*** 9 3 L ***			
-7	188	162	9
-6	221	213	9
-5	106	-84	16
-4	319	321	8
-3	271	282	7
-2U	59	-8	21
-1	443	459	8
0	367	363	7
1	100	89	17
2	120	139	15
3	66	27	25
4	144	139	11
*** 9 4 L ***			
-7 W	0	-6	20
-6 W	53	49	33
-5	247	-247	8
-4 W	0	17	33
-3 W	15	27	25
-2	171	-166	9
-1 W	17	-28	24
0	62	-129	28
1	288	290	8
2	207	212	9
3	151	-167	12
4	138	134	11
*** 9 5 L ***			
-7	103	110	14
-6	307	310	8
-5	249	252	8
-4 W	55	-39	32
-3	387	387	8
-2	189	193	7
-1	83	93	20
0	224	218	9
1 W	0	-46	33
2	112	109	18
3	70	83	15
*** 9 6 L ***			
-7	206	204	8
-6	171	181	7
-5 W	51	-39	39
-4 W	0	35	33
-3	168	190	11
-2 W	55	49	33
-1 W	0	30	34
0	148	-156	12
1	164	-165	11
2 W	24	11	18
3	138	-140	12
*** 9 7 L ***			
-6	82	57	13
-5	294	288	6
-4	97	-104	16
-3UW	25	1	33
-2	445	447	8
-1	197	-184	9
0	99	-81	16
1	120	121	8
2	104	101	11
3	310	300	7
*** 9 8 L ***			
-6	73	66	20
-5	117	116	15
-4 W	35	60	34
-3 W	0	34	31
-2	147	128	11
-1	75	89	24
0	101	95	16
1	138	-142	11
2	112	-123	15
3	83	89	18
*** 9 9 L ***			
-6 W	0	45	29
-5UW	55	10	32
-4 W	46	-56	34
-3	223	226	9
-2 W	26	-64	41
-1 W	32	17	26
0	105	68	18
1	76	-67	23
2	309	305	7
*** 9 10 L ***			
-5	172	145	9
-4	81	-55	20
-3	204	-202	8
-2 W	24	48	36
-1	64	59	28
0	141	136	12
1 W	0	2	34
2UW	51	6	29
*** 9 11 L ***			
-4	192	185	8
-3UW	55	2	32
-2 W	0	-33	22
-1 W	46	69	25
0 W	51	61	34
1 W	47	80	30
*** 9 12 L ***			
-3	172	-184	9
-2U	71	-23	21
-1	96	69	16
0	207	-196	8
***10 0 L ***			
-7	320	311	7
-6	159	142	11
-5UW	32	3	30
-4	424	428	8
-3	470	471	9
-2	119	116	14
-1	163	161	11
0	225	200	9
1	177	185	9
2	201	202	9
3	117	-116	14
***10 1 L ***			
-7 W	0	-24	28
-6	133	-131	12
-5	66	-64	23
-4	209	-196	9
-3	286	-282	8
-2	159	153	11
-1UW	44	-8	32
0	132	-141	13
1	161	173	11
2	123	-100	14
3	63	-37	25
***10 2 L ***			
-7 W	0	-15	28
-6	155	150	11
-5	74	-60	20
-4 W	0	-4	33
-3	267	255	8
-2	88	-91	19
-1	71	43	23
0UW	54	0	33
1	64	-24	23
2	116	126	15
3 W	42	26	29
***10 3 L ***			
-7	81	-92	18
-6	85	94	22
-5 W	54	47	34
-4	379	-396	8
-3	85	-57	20
-2 W	0	46	34
-1	83	-62	20
0	109	106	16
1	69	-90	13
2	108	-93	14
3UW	40	-11	28
***10 4 L ***			
-7	107	103	13
-6U	79	-18	20
-5	187	197	10
-4 W	23	-60	31
-3	125	-108	13
-2	300	308	8
-1U	60	14	27
0	169	156	10
1 W	0	7	38
2 W	50	41	37
3	355	351	7
***10 5 L ***			
-6	269	259	8
-5 W	36	-54	34
-4 W	17	-62	31
-3	194	200	9
-2 W	55	-25	33
-1	107	-55	14
0	205	212	9
1	121	-162	15
2 W	46	-48	24
***10 6 L ***			
-6	138	116	11
-5	134	114	13
-4	217	227	9
-3	59	21	25
-2	77	93	23
-1	342	354	8
0	172	158	11
1	248	243	6
2	125	125	13
***10 7 L ***			
-6	132	-113	11
-5 W	0	32	21
-4 W	53	21	33
-3	146	134	12
-2	118	107	15
-1U	94	15	18
0 W	0	-71	35
1	59	61	18
2	130	122	11
***10 8 L ***			
-5	172	178	9
-4 W	45	52	21
-3	92	-112	19
-2UW	42	9	34
-1	107	-105	16
0 W	0	20	34
1	186	181	7
***10 9 L ***			
-5	55	40	25
-4	283	276	8
-3	171	-150	10
-2	142	141	13
-1	51	28	21
0	240	-253	8
1	207	193	8
***10 10 L ***			
-4	83	81	17
-3U	89	27	16
-2	280	275	6
-1 W	9	42	30
0 W	0	11	29
***10 11 L ***			
-2	257	-263	7
-1 W	0	9	29
***11 1 L ***			
-6	219	219	8
-5	267	275	9
-4	84	91	20
-3	260	263	8
-2 W	0	22	31
-1	136	-115	12
0	426	433	8
1	85	100	20
2	145	-157	11
***11 2 L ***			
-6	177	176	9
-5 W	41	-44	21
-4U	69	21	24
-3 W	0	-26	18
-2	91	-77	16
-1 W	59	-37	39
0	130	-143	9
1	175	-181	7
2	77	-82	19
***11 3 L ***			
-6	151	-162	10
-5 W	45	31	33
-4	223	238	9
-3 W	39	-44	37
-2 W	0	23	40
-1	189	162	9
0	60	31	28
1 W	41	69	30
2 W	0	35	28
***11 4 L ***			
-6 W	53	-75	29
-5	97	-93	17
-4 W	43	-31	33
-3	104	87	16
-2	172	169	10
-1	203	-206	8
0	82	-75	21
1	295	293	6
2	114	-104	13
***11 5 L ***			
-5	182	-177	10
-4 W	31	18	33
-3 W	53	-20	33
-2	98	111	18
-1	228	243	9
0	153	-142	12
1	120	118	14
***11 6 L ***			
-5 W	42	-24	29
-4 W	41	39	32
-3	113	115	10
-2	128	113	14
-1	178	-188	10
0	106	55	15
1	268	268	7
***11 7 L ***			
-5	167	164	9
-4	145	-128	11
-3	116	107	9
-2	334	340	6
-1	63	54	26
0 W	19	-32	30
***11 8 L ***			
-4	132	106	11
-3 W	0	-48	29
-2	126	-141	14
-1	190	179	9
0 W	0	15	29
***11 9 L ***			
-3	88	89	16
-2 W	39	68	29
-1	289	279	7
***12 0 L ***			
-5	246	226	7
-4	190	186	9
-3 W	0	0	33
-2	247	248	8
-1	207	200	9
0	130	126	13
1	150	160	10
***12 1 L ***			
-5	67	62	21
-4 W	12	9	20
-3	46	71	23
-2	204	200	9
-1 W	55	-25	32
0 W	10	14	32
***12 2 L ***			
-5	148	-127	10
-4	158	166	11
-3 W	0	33	33
-2	90	91	19
-1	130	140	8
0	65	34	22
***12 3 L ***			
-5	60	-81	23
-4	90	-80	20
-3 W	29	25	32
-2 W	0	-21	33
-1	84	38	19
0	126	-125	12
***12 4 L ***			
-4U	54	-11	26
-3	190	220	10
-2 W	0	-9	29
-1 W	10	-53	33
0 W	23	43	28
***12 5 L ***			
-4	94	64	15
-3	117	-110	12
-2	135	-141	11
-1	132	143	11
***12 6 L ***			
-3 W	37	46	29
-2 W	52	56	28
-1	70	70	21

are: $f_{\rm Cu}=0{\cdot}785\pm0{\cdot}007$; $f_{\rm S}=0{\cdot}283\pm0{\cdot}004$; $f_{\rm O}=0{\cdot}588\pm0{\cdot}003$; $f_{\rm N}=0{\cdot}957\pm0{\cdot}006$. The R-factor ratio test (Hamilton, 1965) shows that the accompanying slight improvement (see Table 1) in the agreement between calculated and observed F^2 values is significant ($\mathscr{R}=1{\cdot}024$, $\mathscr{R}_{4,1618,0{\cdot}005}=1{\cdot}005$, probability $>0{\cdot}995$).* The new value of $f_{\rm Cu}$ is not significantly different from the tabulated one, but we believe that the new values for $f_{\rm S}$, $f_{\rm O}$, and $f_{\rm N}$ are to be preferred over the values tabulated by Bacon. The new value $f_{\rm S}$ is clearly significantly different from the old.

Detailed analysis of the structure at this point showed no abnormal features. It seemed desirable, however, to perform a final check by computing (Program *XFOUR*, no. 391 in *World List*, 1966) a Fourier map and a difference map. The $|F_o|$ values in error because of extinction effects were first corrected by the empirical procedure used by Brown & Walker (1966) at the corresponding stage of the work on K_2NbF_7. The measures of fit of the final calculated F_c^2 values to the corrected F_o^2 values are shown in Table 1. The difference map showed no interpretable features. The maximum excursion of density on each side of zero was 0·11 in units of 10^{-12} cm.Å^{-3}. For comparison, the peak heights in the Fourier map were 5·98 for the copper atom, 5·27 for the nitrogen atom, 2·66 to 3·73 for the oxygen atoms, 1·96 for the sulfur atom, $-0{\cdot}96$ to $-1{\cdot}05$ for the hydrogen atoms of the ammonium ion, and $-1{\cdot}54$ to $-1{\cdot}83$ for the hydrogen atoms of the water molecules.

The observed structure-factor magnitudes $|F_o|$, not corrected for extinction, and the calculated structure factors F_c are listed in Table 2. For each reflection for which $|F_o|^2$ is equal to or greater than $\sigma(F_o^2)$, the standard error $\sigma(F_o)$ is given (computed as $\sigma(F_o^2)/2|F_o|$); for the other reflections, marked W in the table, $\sigma(F_o^2)$ is given. The reflections marked X are the reflections

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* $\mathscr{R}_{4,1618,0{\cdot}005}$ is the value from Hamilton's tables of the R-factor ratio for an hypothesis of dimension 4 (corresponding to the 4 scattering amplitudes adjusted) for the 1618 degrees of freedom in our determination and the probability level 0·005.

Table 3. *Final atomic coordinates and thermal parameters (with standard errors in parentheses) of the crystal structure of* $Cu(NH_4)_2(SO_4)_2.6H_2O$

The thermal parameters β_{ij} are the coefficients of the index products in the temperature factor:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

The second line associated with each heavy atom contains, for each parameter, the values Δ, defined as the X-ray parameter value minus the neutron value, and $|\Delta|/\sigma$ (see text). Each coordinate Δ is expressed in units Å × 10^{-3}; each Δ for the parameters β_{ij} is on the same scale as the β_{ij}.

	Fractional coordinates × 10^5			Thermal parameters × 10^5					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0 (—)	0 (—)	0 (—)	438 (13)	252 (08)	1054 (29)	0 (07)	207 (14)	31 (10)
	—	—	—	156 9·4	92 10·2	796 13·8	−6 0·8	73 3·7	19 1·5
S(2)	41069 (24)	13898 (19)	74517 (36)	435 (26)	299 (16)	1177 (60)	−37 (14)	208 (27)	−72 (21)
	−17 7·0	6 2·1	4 1·6	−32 1·2	−60 3·6	193 2·3	−13 0·9	−14 0·5	28 1·2
O(3)	41576 (18)	23173 (11)	60057 (23)	1184 (19)	376 (08)	1721 (33)	−198 (10)	514 (20)	−3 (13)
	−7 2·0	4 1·1	2 0·4	−34 0·7	−54 2·9	139 0·9	7 0·3	−25 0·4	9 0·3
O(4)	54888 (16)	7580 (14)	78118 (30)	595 (15)	604 (11)	3296 (53)	104 (10)	221 (22)	−215 (19)
	−9 2·7	7 1·8	4 0·8	−27 0·7	−51 2·1	−116 0·7	−13 0·6	0 0·0	−24 0·5
O(5)	28057 (13)	7032 (11)	63349 (21)	605 (13)	390 (08)	1747 (31)	−137 (08)	291 (16)	−122 (12)
	−4 1·5	−2 0·6	−3 0·7	2 0·0	−41 2·2	−157 1·2	−9 0·5	48 1·0	56 1·6
O(6)	39147 (17)	17862 (12)	95686 (21)	1152 (19)	420 (08)	1376 (29)	−47 (09)	437 (19)	−105 (12)
	−9 2·4	−10 2·8	−2 0·4	−62 1·4	−14 0·7	154 1·1	−3 0·2	−50 0·9	−6 0·2
O(7)	17658 (16)	11673 (12)	17726 (23)	789 (16)	541 (10)	1559 (35)	−31 (10)	290 (19)	61 (14)
	−14 4·2	−22 5·9	2 0·4	−34 0·9	5 0·2	121 0·8	24 1·0	47 0·9	91 2·3
O(8)	−16392 (15)	10892 (12)	3043 (23)	687 (15)	385 (09)	1892 (34)	−24 (09)	278 (18)	92 (13)
	−4 1·4	9 2·8	11 2·6	4 0·1	−48 2·5	408 2·9	−34 1·7	−5 0·1	58 1·6
O(9)	−531 (14)	−6534 (10)	28210 (19)	737 (14)	332 (08)	1309 (27)	28 (08)	405 (15)	112 (11)
	0 0·0	15 5·1	−1 0·2	−92 2·7	−11 0·6	451 3·4	30 1·6	11 0·2	−12 0·4
N(10)	13458 (10)	34786 (08)	35953 (14)	861 (12)	448 (07)	1845 (26)	5 (07)	485 (12)	6 (09)
	−10 2·7	−2 0·6	2 0·5	−103 2·3	−48 2·1	415 2·2	22 1·0	−76 1·2	81 2·0
H(11)	6554 (46)	33321 (38)	20966 (60)	1964 (61)	1334 (40)	2694 (99)	−526 (40)	361 (63)	−226 (49)
H(12)	22515 (43)	29916 (31)	40162 (76)	1565 (51)	801 (27)	5929 (167)	365 (30)	1439 (74)	371 (53)
H(13)	7617 (49)	33427 (42)	46879 (68)	2018 (59)	1573 (45)	3549 (108)	681 (44)	1712 (71)	870 (61)
H(14)	16861 (49)	42467 (30)	36184 (66)	2068 (62)	586 (22)	4149 (125)	−105 (30)	119 (68)	140 (41)
H(15)	22103 (31)	9620 (25)	32899 (41)	1220 (34)	717 (20)	1796 (68)	−31 (20)	193 (37)	103 (27)
H(16)	25555 (31)	12868 (24)	10680 (45)	1150 (33)	731 (20)	2523 (72)	−184 (21)	725 (40)	−62 (29)
H(17)	−26718 (26)	9535 (22)	−5970 (43)	794 (28)	600 (18)	2610 (70)	−12 (16)	292 (35)	8 (28)
H(18)	−14202 (28)	18405 (21)	217 (44)	1113 (32)	423 (16)	2690 (72)	−24 (17)	597 (38)	81 (25)
H(19)	−10271 (28)	−5877 (21)	31563 (41)	1039 (31)	596 (17)	2341 (65)	131 (17)	848 (35)	147 (26)
H(20)	2457 (27)	−14082 (19)	30950 (38)	1055 (28)	431 (16)	2138 (59)	99 (17)	523 (32)	155 (23)

omitted in the final refinement because of extinction errors. The reflections marked *U* are the ones omitted because it is considered that their signs are undetermined.

The final atomic parameters and their standard errors appear in Table 3. A drawing (Program *ORTEP*, no. 387 in *World List*, 1966) of the crystal structure viewed in the direction of $-\mathbf{c}$ is shown in Fig. 1.

Discussion

Comparison of neutron and X-ray parameters

Because of the possibility of learning something about the effects of chemical bonding on atomic electron distributions (see Dawson, 1964, 1965; Coppens & Coulson, 1967; Coppens, 1967), we consider it desirable to make a detailed comparison of the parameters from our neutron analysis with those from the three-dimensional X-ray analysis of Montgomery & Lingafelter (hereafter abbreviated to M. & L.). We therefore present in Table 3 the differences between the M. & L. heavy-atom coordinates and thermal parameters and ours. Each difference Δ in the table, X-ray parameter minus neutron parameter, is accompanied by the ratio of its magnitude to its standard error σ, where σ is computed as $[\sigma^2_{\text{neutron}}+\sigma^2_{\text{X-ray}}]^{1/2}$. Our Table 4 of bond lengths and angles* involving the heavy atoms only includes for comparison the corresponding values from the M. & L. X-ray work. For the hydrogen atoms, the parameters of which M. & L. do not claim to be accurate, we note only that the positions are different by from 0·05 Å to 0·4 Å (average difference 0·24 Å).

From the point of view of molecular geometry only, the descriptions of the hydrated copper ion and the sulfate ion are in reasonable agreement with those of M. & L. (see Table 4). In particular, the copper–oxygen framework of the cation clearly does have approximate orthorhombic symmetry rather than the essentially te-

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* All our bond lengths and angles and functions of thermal parameters, shown in Table 4 and subsequent tables, were computed with Program *ORFFE* II, modified by Dr C. K. Johnson from *ORFFE* (no. 363 in *World List*, 1966). The full least-squares covariance matrix was used in computing standard errors.

Table 4. *Bond lengths and angles not involving the hydrogen atoms in the crystal structure of* $Cu(NH_4)_2(SO_4)_2.6H_2O$

The corresponding bond lengths and angles from the X-ray work of Montgomery & Lingafelter are shown for comparison. Bond lengths marked with asterisks are 'corrected' values ('riding' model, see text).

Atoms	Bond length (Å) or angle (°)	
	This work	M. & L.†
Cu(1)–O(7)	2·2300 (14) 2·2369*	2·209 (5)
Cu(1)–O(8)	2·0725 (14) 2·0871*	2·084 (5)
Cu(1)–O(9)	1·9660 (11) 1·9710*	1·960 (5)
S(2)—O(3)	1·475 (3) 1·489*	1·479 (5)
S(2)—O(4)	1·457 (3) 1·481*	1·463 (5)
S(2)—O(5)	1·479 (3) 1·486*	1·476 (5)
S(2)—O(6)	1·477 (3) 1·490*	1·465 (5)
O(7)–Cu(1)–O(8)	88·90 (05)	88·89 (15)
O(7)–Cu(1)–O(9)	90·65 (05)	90·35 (15)
O(8)–Cu(1)–O(9)	88·99 (05)	88·61 (15)
O(3)–S(2)—O(4)	109·8 (2)	109·4 (2)
O(3)–S(2)—O(5)	108·3 (2)	108·4 (2)
O(3)–S(2)—O(6)	109·4 (2)	110·1 (2)
O(4)–S(2)—O(5)	108·9 (2)	108·5 (2)
O(4)–S(2)—O(6)	110·9 (2)	110·5 (2)
O(5)–S(2)—O(6)	109·7 (2)	110·2 (2)

† The bond lengths and angles in this column are slightly different from those given in the M. & L. (1966*a*) paper, which were calculated before the revised unit-cell parameters (M. & L., 1966*c*) were available.

tragonal symmetry reported by Webb *et al.* from the two-dimensional X-ray analysis. From the point of view of physical statistics, however, we conclude that the small differences between the two sets of heavy-atom coordinates are significant. By application of the *R*-factor ratio test (Hamilton, 1965) the hypothesis that the X-ray heavy-atom coordinates fit the neutron data is most decisively rejected* ($\mathcal{R}=1\cdot275$, $\mathcal{R}_{27,1618,0\cdot005}=1\cdot015$, probability $\leqslant 0\cdot005$). This result implies either that the differences are real effects related to bonding and electron distributions or that in one or the other, or both, of the two determinations data have been included which are affected by systematic errors.

Several considerations suggest that the differences are mainly the results of errors. First, we note that for the x direction in the crystal all of the non-zero Δ values except one have the same sign. Neither this fact nor the apparently random signs of the differences in bond lengths is explicable on the basis of bonding effects on electron distributions.

We note on careful examination of the fit of the calculated to the observed structure factors in the structure-factor table of M. & L. that for by far the most of the reflections included in the refinement having $|F_o|\geqq 40$ the quantity $|F_o|-|F_c|$ is negative, often by as much as 10% of $|F_c|$. This fact might suggest more pervasive effects of extinction than were recognized by M. & L. However, even in the case of the 12 reflections

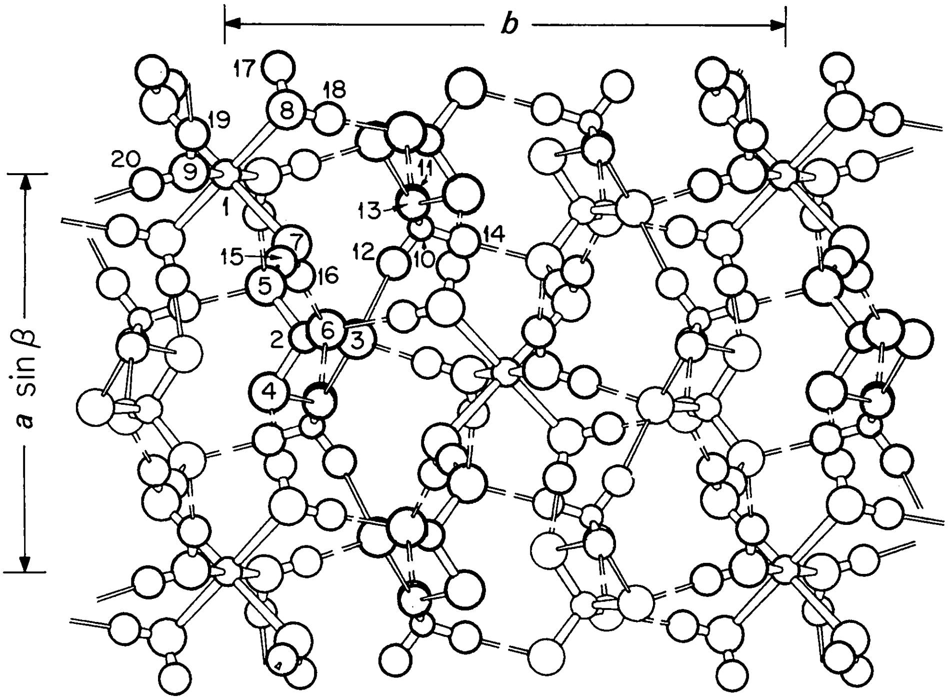

Fig. 1. The crystal structure of $Cu(NH_4)_2(SO_4)_2.6H_2O$, viewed in projection in the direction of $-\mathbf{c}$. The atoms of the reference asymmetric unit are numbered as in Table 3. Identification of atoms: 1, Cu; 2, S; 3–9, O; 10, N; 11–20, H.

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* Our thermal parameters were used with the X-ray coordinates in the structure-factor calculation required for determining $\mathcal{R}$.

assumed to be affected by extinction and omitted from the refinement, there is not the expected correlation of the magnitude of $|F_o|-|F_c|$ with the calculated intensity, some of the largest discrepancies being associated with reflections of only moderate intensity. We believe that systematic errors of some other kind may be involved as well and that these other errors in the data may account for the main differences between the X-ray and neutron coordinates. M. & L. do not in fact claim great accuracy in their structure determination.

We cannot assert, of course, that our results are entirely free of the effects of systematic errors. However, most of our standard errors in the coordinates are only about half as large as M. & L.'s and some are about one third as large. Only for the sulfur atom, for which the neutron scattering factor is relatively small and the X-ray scattering factor is moderately large, are the X-ray standard errors smaller (one half to one third of the neutron errors); our errors for this atom are smaller than the X-ray errors for any other atom.

In contrast to the case of copper ammonium sulfate hexahydrate, it has been found in this laboratory (El Saffar & Brown, 1968) that the heavy-atom coordinates from the X-ray determination of structure of $MnCl_2.4H_2O$ (counter data, Mo $K\alpha$ radiation, Zalkin, Forrester & Templeton, 1964) fit the neutron data as well as the neutron coordinates do, according to the R-factor ratio test, the probability of significant difference in fit being $\sim 0{\cdot}5$. In the comparison for $MnCl_2.4H_2O$, the average and maximum values of $|\Delta|$ for the 21 heavy-atom coordinates are only 0·0021 Å and 0·0039 Å, and the average and maximum $|\Delta|/\sigma$ values are 0·8 and 1·9.

Even without the effects of systematic errors, any attempts at interpreting the thermal parameters of M. & L. would be expected to be difficult because the X-ray data for the layers recorded in Weissenberg photography (five layers hkl with $l=0$ to 4) were not relatively scaled, except approximately, before the least-squares refinement. Therefore, concerning the comparison of neutron and X-ray thermal parameters (Table 4) we only remark that the agreement is surprisingly good, except for the three β_{ii} parameters of copper, for each of which Δ/σ is ~ 10. These large errors are clearly the result of the fact that the dispersion correction $\Delta f'$ ($-2{\cdot}1$ electrons for the Cu atom and Cu $K\alpha$ radiation) was not used in the X-ray analysis. We have found after performing three more cycles of refinement with the dispersion correction and the published X-ray data that the Δ values of the Cu β_{ii} parameters are reduced approximately to the level of the Δ values of the remaining thermal parameters. There was no accompanying significant improvement in the agreement for other parameters.

Thermal motion

Principal-axis transformations were performed on the thermal-parameter ellipsoids. Table 5 gives the principal root-mean-square vibrational displacements and the orientations of the principal axes in the cell. For the oxygen and hydrogen atoms the orientation of each principal axis is specified with respect to the vector $X \rightarrow A$, where X is the heavier atom to which the given lighter atom A (oxygen or hydrogen) is attached. The root-mean-square displacements of X and A in the direction $X \rightarrow A$ are also given.

The data in Table 5 for O(7), O(8), and O(9) are relevant to consideration of the problem of correcting the Cu–O bond lengths for thermal motion. There is a correlation between the looseness of binding of oxygen to copper as measured by the length of the Cu–O bond and the looseness as measured by the difference between the r.m.s. displacements of the two atoms along the bond direction. The most tightly bound oxygen atom, O(9), is the only one of the three water oxygens for which the principal axis of smallest r.m.s. displacement lies close to the Cu–O bond direction. The orientations of the ellipsoids from the M. & L. X-ray structure are close to those of Table 5. The situation is different from that found in the X-ray study of the magnesium Tutton salt (Margulis & Templeton, 1962) in which the principal axis of smallest displacement of each water oxygen lies close to the Mg–O bond direction. Table 5 includes 'corrected' bond lengths for the Cu–O bonds, calculated as the mean Cu–O separations on the assumption that the oxygen atoms 'ride' the copper atom (Busing & Levy, 1964). The corrected bond-length Cu–O(9) is probably reliable, but the others may not be. Fortunately, the desired corrections are probably small and of little significance in any case.

We judge from the relevant data in the last three columns of Table 5 that the riding model is probably a good approximation for calculating corrected S–O bond lengths. It is interesting that the corrections we calculate are almost identical with the riding corrections for the S–O bonds calculated by Margulis & Templeton (1962) in their X-ray study of the isomorphous magnesium ammonium sulfate hexahydrate. No bond or angle difference between our sulfate ion and that in the magnesium compound is greater than one standard deviation (theirs) and almost every one is considerably less. Our average values of 1·473 Å and 1·486 Å for the uncorrected and corrected S–O bonds are nearly identical with theirs.

Water molecules, ammonium ion, and hydrogen bonding

It is convenient to discuss the water molecules and the ammonium ion in relation to the hydrogen bonding. Our results confirm the pattern of hydrogen bonding in $Cu(NH_4)_2(SO_4)_2.6H_2O$ as found by Montgomery & Lingafelter (1966*a*) and at the same time furnish a much more precise description of the bonding. Table 6 shows the interatomic distances and angles which describe the water molecules, the ammonium ion, and the hydrogen bonding. The hydrogen bonding is nearly symmetrical on the two sides of each water molecule.

Table 5. *Description of atomic thermal-parameter ellipsoids of* $Cu(NH_4)_2(SO_4)_2.6H_2O$: *orientations of the principal axes and root-mean-square displacements* (*r.m.s.d.*)

The orientations of the principal axes (p.a.) are specified with respect to the unit vectors of a Cartesian coordinate system and to interatomic vectors $X\rightarrow A$. The vector **i** is along the crystal vector **a**; **j** is along **b**; **k** is along **c***. Atom X is the heavier atom to which a given listed atom A is attached.

Atom		R.m.s.d.	Angle (°) between p.a. and reference axis				R.m.s.d. (Å) of X and A along $X\rightarrow A$	
A	p.a.	(Å)	**i**	**j**	**k**	$X\rightarrow A$	X	A
Cu(1)	1	0·130 (2)	15 (13)	79 (10)	99 (10)			
	2	0·136 (2)	75 (13)	132 (10)	46 (10)			
	3	0·144 (2)	91 (06)	44 (09)	46 (09)			
S(2)	1	0·129 (4)	21 (11)	74 (08)	77 (10)			
	2	0·142 (4)	70 (12)	122 (09)	140 (09)			
	3	0·160 (4)	96 (05)	37 (08)	127 (08)			
O(3)	1	0·151 (2)	61 (01)	33 (02)	105 (03)	25 (2)	0·157 (4)	0·162 (2)
	2	0·177 (2)	86 (02)	110 (03)	160 (02)	72 (3)		
	3	0·229 (2)	29 (01)	116 (01)	77 (01)	107 (1)		
O(4)	1	0·149 (2)	19 (01)	104 (01)	77 (01)	19 (1)	0·143 (4)	0·157 (2)
	2	0·209 (2)	96 (01)	151 (02)	118 (02)	72 (1)		
	3	0·264 (2)	108 (01)	115 (02)	32 (01)	85 (1)		
O(5)	1	0·138 (2)	38 (02)	56 (02)	75 (02)	167 (2)	0·132 (4)	0·140 (2)
	2	0·175 (2)	58 (02)	115 (03)	137 (04)	78 (2)		
	3	0·193 (2)	108 (03)	44 (03)	129 (04)	85 (2)		
O(6)	1	0·152 (2)	101 (01)	69 (02)	23 (02)	11 (1)	0·143 (4)	0·154 (2)
	2	0·183 (2)	105 (02)	157 (02)	73 (02)	87 (2)		
	3	0·215 (2)	19 (02)	101 (02)	75 (01)	101 (1)		
O(7)	1	0·169 (2)	95 (11)	101 (03)	12 (07)	73 (9)	0·139 (2)	0·187 (2)
	2	0·176 (2)	167 (05)	101 (03)	98 (11)	140 (6)		
	3	0·207 (2)	102 (03)	15 (02)	81 (02)	55 (3)		
O(8)	1	0·162 (2)	34 (10)	56 (10)	90 (07)	105 (9)	0·136 (2)	0·179 (2)
	2	0·170 (2)	62 (11)	134 (09)	57 (03)	139 (6)		
	3	0·195 (2)	108 (03)	63 (03)	33 (03)	53 (3)		
O(9)	1	0·139 (2)	66 (03)	61 (03)	141 (02)	170 (2)	0·136 (2)	0·140 (2)
	2	0·161 (2)	48 (04)	137 (04)	96 (04)	88 (4)		
	3	0·179 (2)	52 (04)	61 (04)	51 (02)	80 (2)		
N(10)	1	0·171 (1)	37 (02)	91 (03)	127 (02)			
	2	0·186 (2)	86 (06)	173 (09)	84 (07)			
	3	0·193 (1)	54 (02)	83 (09)	37 (03)			
H(11)	1	0·214 (4)	71 (03)	73 (02)	26 (04)	173 (2)	0·191 (1)	0·216 (4)
	2	0·259 (4)	140 (03)	119 (02)	65 (04)	91 (4)		
	3	0·351 (5)	124 (02)	34 (02)	94 (02)	83 (1)		
H(12)	1	0·200 (4)	142 (03)	52 (03)	91 (02)	167 (2)	0·185 (1)	0·209 (4)
	2	0·262 (4)	125 (03)	137 (03)	68 (02)	85 (3)		
	3	0·342 (5)	78 (02)	72 (02)	22 (02)	78 (1)		
H(13)	1	0·189 (4)	46 (02)	88 (02)	136 (02)	171 (1)	0·171 (1)	0·196 (4)
	2	0·249 (4)	54 (03)	126 (01)	57 (03)	88 (3)		
	3	0·394 (6)	66 (01)	36 (01)	64 (01)	98 (1)		
H(14)	1	0·210 (4)	83 (03)	9 (02)	95 (03)	13 (4)	0·186 (2)	0·214 (4)
	2	0·254 (4)	123 (03)	91 (04)	147 (03)	101 (4)		
	3	0·327 (5)	34 (03)	99 (02)	123 (03)	84 (2)		
H(15)	1	0·179 (4)	79 (03)	98 (02)	13 (02)	8 (3)	0·170 (2)	0·180 (4)
	2	0·225 (3)	147 (08)	123 (08)	85 (03)	85 (3)		
	3	0·242 (3)	121 (08)	34 (08)	78 (02)	95 (2)		
H(16)	1	0·185 (3)	32 (03)	71 (03)	114 (04)	11 (3)	0·175 (2)	0·187 (3)
	2	0·218 (3)	103 (04)	117 (04)	149 (04)	84 (4)		
	3	0·252 (3)	118 (02)	35 (04)	108 (04)	99 (2)		
H(17)	1	0·177 (3)	19 (03)	87 (03)	71 (03)	163 (3)	0·168 (2)	0·182 (3)
	2	0·216 (3)	90 (06)	172 (15)	82 (15)	85 (5)		
	3	0·225 (3)	109 (03)	82 (15)	20 (07)	107 (3)		
H(18)	1	0·178 (4)	76 (05)	18 (05)	101 (03)	1 (3)	0·167 (2)	0·178 (4)
	2	0·206 (3)	160 (06)	73 (05)	79 (06)	90 (5)		
	3	0·226 (3)	76 (06)	82 (03)	16 (05)	88 (3)		
H(19)	1	0·163 (3)	33 (02)	96 (03)	122 (03)	160 (2)	0·159 (2)	0·172 (3)
	2	0·201 (3)	76 (03)	143 (03)	57 (03)	101 (3)		
	3	0·239 (3)	61 (02)	53 (03)	50 (03)	107 (2)		
H(20)	1	0·172 (3)	101 (06)	29 (03)	116 (05)	163 (5)	0·157 (2)	0·175 (4)
	2	0·192 (3)	141 (05)	82 (06)	52 (06)	102 (7)		
	3	0·217 (3)	53 (05)	62 (03)	49 (04)	101 (3)		

The lone-pair coordination of the water molecules is of type *J* in the classification scheme of Chidambaram, Sequeira & Sikka (1964); that is, one of the lone pairs of electrons on each water molecule is directed approximately toward a polyvalent metal ion and the other lone pair is not specifically directed. The two-lone pair orbitals and the two OH bonds are considered to make approximately regular tetrahedral angles one with another (Coulson, 1957). The O–H bond lengths before correction are all in the range 0·961–0·980 Å, the shortest two being in the water molecule which has the weakest hydrogen bonding. The corrected bond lengths range from 0·982 to 1·003 Å, averaging 0·991 Å. The riding model does not actually apply exactly here, and consequently the corrections are probably over-corrections. The valence angle 105·9 (3)° for the water molecule H(17)–O(8)–H(18) and the angle 105·7 (3)° for molecule H(19)–O(9)–H(20) are close to the value 104·52 (5)° reported for water vapor (Benedict, Gailar & Plyler, 1956; for earlier values see references in *Tables of, Interatomic Distances* 1958), but the angle 109·3 (3)° for molecule H(15)–O(7)–H(16) is distinctly higher.

The water molecule with the largest valence angle, H(15)–O(7)–H(16), is the one having the largest associated O···O···O angle (118·04°), the weakest (that is, longest) hydrogen bonds, and the longest Cu–O coordination distance. The large O···O···O angle suggests that some part of the increase of the valence angle H–O–H from the vapor value of 104·5° must result from the forces exerted on the hydrogen atoms along the lines H···O. However, most of the deformation of the valence angle must be attributed to some other cause, since Chidambaram (1962) has shown that bending of the O–H···O bonds is energetically much more favorable than distortion of the H–O–H angle. If the O···O···O angle were an important factor, one would think that the water molecule H(19)–O(9)–H(20)

Table 6. *Distances and angles which describe the water molecules, the ammonium ion, and the hydrogen bonding in* $Cu(NH_4)_2(SO_4)_2.6H_2O$

The bond lengths *X–H* in the table marked with asterisks are 'corrected' values ('riding' model, see text). The atom number marked with asterisks indicate atoms related to the atoms of the asymmetric unit by symmetry transformations, which are specified in the paper of Montgomery & Lingafelter (1966*a*).

Hydrogen bond	Distances (Å)			Angles (°)		
X–H···O	*X*–H	H···O	*X*···O	*X*–H···O	H···O–S	H–O–Cu
O(7)—H(15)···O(5)	0·964 (3) 0·982*	1·871 (3)	2·826 (2)	170·1 (3)	111·0 (2)	112·1 (2)
O(7)—H(16)···O(6*)	0·963 (3) 0·983*	1·871 (3)	2·821 (2)	168·7 (3)	127·7 (2)	114·1 (2)
O(8)—H(17)···O(4*)	0·978 (3) 0·993*	1·730 (3)	2·707 (2)	178·1 (3)	133·5 (2)	116·8 (2)
O(8)—H(18)···O(6*)	0·978 (3) 0·993*	1·765 (3)	2·743 (2)	177·5 (3)	122·4 (2)	114·2 (2)
O(9)—H(19)···O(5*)	0·981 (3) 0·991*	1·760 (3)	2·732 (2)	170·4 (3)	129·2 (2)	114·5 (2)
O(9)—H(20)···O(3*)	0·976 (3) 1·002*	1·715 (3)	2·683 (2)	171·3 (2)	125·1 (2)	118·5 (2)
N(10)–H(11)···O(6*)	0·998 (4) 1·061*	1·927 (4)	2·899 (2)	164·1 (4)	116·1 (2)	
N(10)–H(12)···O(3)	1·004 (4) 1·061*	2·032 (4)	2·983 (2)	157·3 (4)	122·1 (2)	
O(3*)		2·055 (4)	3·007 (2)	158·6 (5)	95·2 (2)	
N(10)–H(13)	0·999 (4) 1·070*					
O(4*)		2·335 (5)	3·121 (2)	134·9 (4)	84·6 (2)	
N(10)–H(14)···O(5)	1·000 (4) 1·052*	1·861 (4)	2·860 (2)	176·3 (4)	112·5 (2)	

H–*X*–H angles (°)		Distance H···H (Å)
H(15)–O(7)—H(16)	109·3 (3)	1·572 (4)
H(17)–O(8)—H(18)	105·9 (3)	1·561 (4)
H(19)–O(9)—H(20)	105·7 (3)	1·560 (3)
H(11)–N(10)–H(12)	113·9 (4)	1·678 (6)
H(11)–N(10)–H(13)	107·3 (4)	1·609 (5)
H(11)–N(10)–H(14)	107·5 (4)	1·612 (5)
H(12)–N(10)–H(13)	106·5 (3)	1·604 (5)
H(12)–N(10)–H(14)	109·5 (4)	1·636 (5)
H(13)–N(10)–H(14)	112·1 (4)	1·658 (6)

O···*X*···O angles (°)	
O(5)····O(7)····O(6*)	118·04 (6)
O(4*)···O(8)····O(6*)	104·17 (7)
O(5*)···O(9)····O(3*)	98·98 (6)
O(6*)···N(10)···O(3)	137·87 (5)
O(6*)···N(10)···O(3*)	86·67 (5)
O(6*)···N(10)···O(4*)	117·58 (5)
O(6*)···N(10)···O(5*)	105·29 (5)
O(3)····N(10)···O(3*)	101·18 (4)
O(3)····N(10)···O(4*)	95·82 (5)
O(3)····N(10)···O(5*)	105·15 (4)
O(3*)···N(10)···O(5)	121·77 (4)
O(4*)···N(10)···O(5)	80·09 (5)

should have a valence angle smaller than it actually has, since the associated angle O···O···O is in this case only 98·98° and the hydrogen bonds involved are stronger than those of H(15)–O(7)–H(16).

The bonding of a water molecule to a copper ion may be expected to affect the structure of the water molecule. Thus, Peterson & Levy (1957*b*) have noted that in cupric chloride dihydrate the planarity of the entire grouping $CuCl_2.2H_2O$, including the H atoms, suggests π character in the Cu–O bonds. It also suggests an accompanying increase of *s* character in the O–H bonds, consistent with the observed opening of the H–O–H angle from the vapor value to 108° (Chidambaram, 1963; Chidambaram, Sequeira & Sikka, 1964; see also Pimentel & McClellan, 1960, and Frank, 1958). The lone-pair coordination in $CuCl_2.2H_2O$ is of type *D* in the classification scheme of Chidambaram *et al.* (1964); that is, the bisector of the angle between the directions of the lone pairs is directed toward the cupric ion. For coordination of type *J*, as in our case, the effect on the valence angle would be expected to be smaller than for type *D*, consistent with the angles observed for molecules H(17)–O(8)–H(18) and H(19)–O(9)–H(20) but not with the angle of molecule H(15)–O(7)–H(16). Other hydrates in which rather large H–O–H angles have been found in neutron-diffraction studies are $CuSO_4.5H_2O$ (Bacon & Curry, 1962; see also the nuclear magnetic resonance (n.m.r.) study of El Saffar, 1966) and $MnCl_2.4H_2O$ (El Saffar & Brown, 1968). In the latter hydrate there is a correlation between the coordination types and the H–O–H angles of the four water molecules: two type *D* molecules have angles of 104·3 (0·3)° and 106·4 (0·2)°, and two of type *J* have angles of 112·4 (0·3)° and 111·4 (0·3)°. In $CuSO_4.5H_2O$ the angles 114 (1)° and 109 (1)° of two type *D* molecules are not much different from the angles 111 (1)° and 109 (1)° of two type *J* molecules; the fifth water molecule, which is not coordinated to the copper ion, has the angle 106 (1)°. It is clear that more data are needed for understanding the variations in the shape of the water molecule in hydrates. Also needed is a rational procedure for correcting the valence angle for the effects of thermal motion, which must limit our understanding to some degree at present.

In a comparison of n.m.r. and neutron-diffraction results for twelve crystalline hydrates, El Saffar (1966) has included a comparison of the magnitudes (see Table 6) and orientations of the *p–p* vectors of the water molecules from our study of $Cu(NH_4)_2(SO_4)_2.6H_2O$ with the average values from the two sets of vectors obtained for $K_2Zn(SO_4)_2.6H_2O$ and $K_2Mg(SO_4)_2.6H_2O$ in the n.m.r. study of Chidambaram & Rao (1963). If allowance is made for the fact that the same Tutton salt was not used in the two techniques, the agreement seems quite satisfactory.

The accuracy of the determination of the N–H bond lengths is impaired by the effects of the considerable thermal motion of the hydrogen atoms of the ammonium ion. The average N–H bond length before correction, 1·000 Å, becomes 1·06 Å after application of the riding model correction to the individual bonds, which we judge should be a good approximation in this case. These values are close to the corresponding values from neutron-diffraction studies reported by Schlemper, Hamilton & Rush (1966): 0·985 (7) and 1·064 (7) Å for the uncorrected and corrected values in $(NH_4)_2SiF_6$; 1·06 (1) Å for the mean corrected value in $(NH_4)_2SO_4$ (uncorrected values not given). It is difficult, unfortunately, to assess the accuracy of bond lengths corrected by use of the riding model when the corrections amount to 0·06 to 0·08 Å, as in these cases. The close agreement in the N–H bond lengths from $Cu(NH_4)_2(SO_4)_2.6H_2O$ and $(NH_4)_2SiF_6$ may be fortuitous, especially in view of the disordered arrangement of H atoms which complicated the diffraction study of the latter compound.

Other values reported previously for the N–H bond length in ammonium salts determined by neutron analysis have been consistently lower than 1·06 Å: 1·03 (2) Å in NH_4Cl and ND_4Cl (Levy & Peterson, 1952); 1·026 (2) to 1·037 (2) Å in various forms of ND_4Br (Levy & Peterson, 1953*a*); 1·03 Å in ND_4I (Levy & Peterson, 1953*b*); $1{\cdot}00_4$ Å in $NH_4H_2PO_4$ (Tenzer, Frazer & Pepinsky, 1958); 1·03 (3) Å in $(NH_4)_2BeF_4$ (Kay, Lajzerowicz, Okaya & Pepinsky, 1959); $1{\cdot}02_3$ Å (average) in $(NH_4)_2C_2O_4.H_2O$ (Padmanabhan, Srikantha & Ali, 1965); 1·02 Å and 1·044 Å (corrected), both averages, in HN_3OHCl (Padmanabhan, Smith & Peterson, 1967); 1·03 Å (average) in $LiN_2H_5SO_4$ (Padmanabhan & Balasubramanian, 1967). Most of these neutron determinations were based on a small number of intensity data*, and in most of them the refinements were not so complete as the present one. In general the effects of thermal motion on bond lengths were not taken into account.† It is not clear, however, whether the bond length 1·06 Å from $Cu(NH_4)_2(SO_4)_2.6H_2O$, $(NH_4)_2SiF_6$, and $(NH_4)_2SO_4$ should be regarded as more reliable than values from the other neutron-diffraction studies. It should be noted here that N–H bond lengths of 1·03 to 1·04 Å have been reported from n.m.r. work on NH_4Br and NH_4Cl (Gutowsky, Pake & Bersohn, 1954; Bersohn & Gutowsky, 1954).

The hydrogen bonds N–H···O are, on the average, bent more than the bonds O–H···O. Atom H(13) is the hydrogen involved in what was described by Montgomery & Lingafelter as a bifurcated hydrogen bond. The distance H(13)···O(4) of 2·332 Å indicates a rather weak interaction, and the main strength of the bifurcated hydrogen bond lies in the H(13)···O(3) interaction. There appears to be a rough correlation

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* The NH_3OHCl determination was the only one based on even partial three-dimensional data.

† In the work by Levy & Peterson on the ammonium halides the effects of thermal motion on bond lengths were allowed for explicitly in the structure analysis; however, the structure parameters were determined only by trial calculations.

between the angles H–N–H, which range from 106·5° to 113·9°, and the corresponding angles O···N···O.

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