The Crystal Structure of Ferric Ammonium Sulfate Trihydrate, FeNH$_4$(SO$_4$)$_2$.3H$_2$O

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The structure of ferric ammonium sulfate trihydrate, FeNH$_4$(SO$_4$)$_2$.3H$_2$O, has been determined. The crystals are monoclinic, mauve-colored prisms, space group $P2_1/c$, $Z=4$, $a=9.982\pm0.005$, $b=10.156 \pm0.005$, $c=9.504\pm0.005$ Å, and $\beta=94.95\pm0.05°$. The iron atom is octahedrally coordinated to four sulfate oxygen atoms and two water oxygen atoms. The third water molecule is held in the structure by hydrogen bonds. Fe–O distances average 1.997 ± 0.003 Å. S–O distances average 1.464 ± 0.003 Å when oxygen is not bonded to a second atom, and 1.492 ± 0.003 Å when the oxygen atom is bonded to both sulfur and iron. The structure has infinite chains of alternating iron atoms and sulfate group running parallel to **c**. A crystallographically distinct sulfate group forms a bridge between the parallel chains. The structure was refined to a final R index of 0.038 for 1504 reflections measured on a diffractometer.

Introduction

Large crystalline lumps of ferric ammonium alum, FeNH$_4$(SO$_4$)$_2$.12H$_2$O, obtained from a bottle labeled 'Analytical Reagent' for the purpose of preparing standard solutions of ferric ion, were observed to be encrusted with a granular material. When the alum was dissolved in water the granular material remained as a residue. Microscopic examination revealed that it consisted of a mixture of faintly mauve prisms and colorless, hexagonal plates. The optical properties of these two types of crystals were determined, but did not lead to the identification of either one. An X-ray powder pattern of the hexagonal crystals was found to agree with that recorded for ferric ammonium sulfate. The powder pattern of the prismatic crystals did not agree with any of the powder data available to us.

Chemical analysis proved that the prismatic crystals contained iron. Because of our general interest in coordination chemistry, we decided to determine the structure of this previously unreported iron salt. The results of this determination, presented in this paper, prove that the prismatic crystals are FeNH$_4$(SO$_4$)$_2$.3H$_2$O.

Experimental

Crystals suitable for X-ray analysis were prepared by washing the mixed crystalline residue with dilute sulfuric acid, then rinsing with water. After drying the crystalline mass in air, it was shaken on a 100-mesh screen to remove small particles. The fraction remaining on the sieve was suspended in a liquid of density 2·25 g.cm^{-3}. The prismatic crystals floated, while the heaxgonal plates sank to the bottom. The prismatic crystals

were removed, washed in acetone, and dried. The optical properties of the prismatic crystals were determined and have been published separately (Jones, Palmer & Young, 1967).

Weissenberg photographs were used to determine the space group and preliminary values of unit-cell dimensions. The only systematic absences observed were $h0l$, $l\neq2n$ and $0k0$, $k\neq2n$, which is unique for space group $P2_1/c$. Unit-cell dimensions were refined and intensity data were obtained with a single-crystal spectrometer equipped with a manual quarter-circle goniostat, a scintillation counter, and a single-channel pulse-height analyzer. Molybdenum radiation ($\lambda = 0.71069$ Å), filtered with a thin sheet of reactor grade zirconium (0·002″ thick) was used. The crystal was mounted with **a*** parallel to the φ axis of the goniostat. Dimensions of the reciprocal cell were obtained from 2θ measurements for $h00$, $0k0$, $00l$, $h0l$, and $h0\bar{l}$ reflections. Crystallographic data for FeNH$_4$(SO$_4$)$_2$.3H$_2$O are summarized in Table 1.

Table 1. *Crystal data for* FeNH$_4$(SO$_4$)$_2$.3H$_2$O

$a = 9.982\pm0.005$ Å	F.W.	320·08
$b=10.156\pm0.005$	Space group	$P2_1/c$
$c = 9.504\pm0.005$		
$\beta=94.95\pm0.05°$	$F(000)=642.54$	
λ Mo $K\alpha=0.71069$ Å	$\varrho_m = 2.197$ g.cm^{-3}	
$Z=4$	$\varrho_c = 2.213$ g.cm^{-3}	

Intensity data were obtained by the stationary-crystal stationary-counter method at a 4° take-off angle. A counting time of 10 sec was used for both the peak and background. The background was taken as the minimum between the Mo $K\alpha$ and Mo $K\beta$ peaks. A total of 1690 independent reflections were measured between zero and 50° 2θ. Of these reflections 139 had zero intensity. An additional 47 reflections had $I<\sigma(I)$ and were given zero weight in the least-squares refinement. Net intensities I were calculated from the expression:

$I = I(\text{gross}) - B$, where B is the number of counts for the background. When an intensity was measured more than once, the intensities were averaged and $\sigma(I)$, the standard deviation of the mean, was calculated from $\sigma_L(I)$ equal to the larger of $[\sum (I_i - I)^2]^{1/2}/(n-1)$ and $[\sum \sigma^2(I)]^{1/2}/n$ by using the relationship $\sigma^2(I) = \sigma_L^2(I) + (PI)^2$, where P, a constant, was set equal to 0·05 to reduce the weight of the intense reflections.
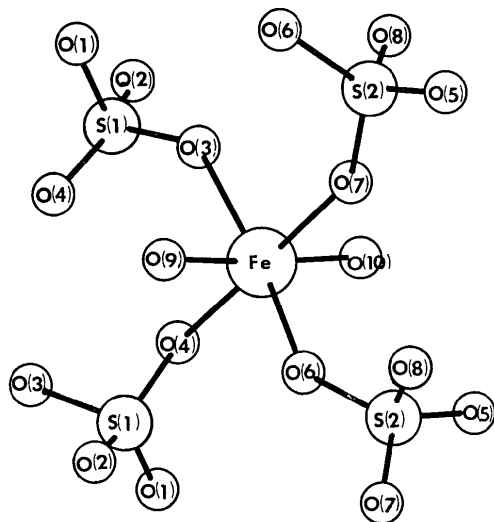

Fig. 1. Coordination of four sulfate and two water oxygen atoms around an iron atom. Numbering system used is shown.

The crystal dimensions were approximately 0·15mm ×0·176mm×0·21 mm parallel to [011], [001], and [100], respectively. Lorentz and polarization corrections were applied to the observed intensities, but no correction was made for absorption ($\mu = 2·08$ cm^{-1}). Atomic scattering factors were taken from the tables published by Cromer & Waber (1965). The real and imaginary dispersion corrections for Fe^{3+} are 0·37 and 0·92e, respectively; for sulfur they are 0·13 and 0·16 respectively (Cromer, 1965).

A full-matrix least-squares program was used to minimize the function $\sum w(\Delta F)^2/\sum wF_o^2$, where $\Delta F = |F_o| - |F_c|$, F_o, and F_c are the observed and calculated structure factors, and w is a weighting factor taken equal to $1/\sigma^2(F)$. The value of $\sigma(F)$ was calculated by the expression $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$ when $I > \sigma(I)$; w was set equal to zero when $I \le \sigma(I)$. The least-squares program accomodates both real and imaginary dispersion corrections.

Determination of the structure

A three-dimensional Patterson function was interpreted in a straightforward way and led to approximate positions for the iron and four oxygen atoms. Least-squares refinement, interspersed with Fourier difference calculations, led to the evaluation of the parameters of all 15 heavy atoms in the asymmetric unit. With isotropic temperature factors, the R index, defined as $\sum|\Delta F|/\sum|F_o|$, was 0·143. The assignment of anisotropic temperature factors led to an R index of 0·065. At this stage of

Table 2. *Positional and thermal parameters* (Å^2) *and their standard deviations for ferric ammonium sulfate trihydrate*

Numbers in parentheses are the standard deviations of the least significant digit(s). Anisotropic temperature factor has the form $T = \exp[-\frac{1}{4} \sum \sum B_{ij} h_i h_j/(b_i b_j)]$ where h_i is the ith Miller index, b_i is the ith reciprocal axis length, and i and j are cycled 1 through 3. Isotropic temperature factor has the form $T = \exp[-\beta(\sin \theta/\lambda)^2]$.

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0·21452 (5)	0·11412 (5)	0·51446 (5)	1·22 (2)	1·32 (3)	1·01 (2)	−0·15 (2)	0·12 (2)	−0·04 (2)
S(1)	−0·01120 (9)	0·0135 (1)	0·27380 (9)	1·29 (4)	1·44 (4)	0·96 (4)	−0·33 (3)	0·08 (3)	0·09 (3)
S(2)	0·39227 (9)	0·25657 (9)	0·2833 (1)	1·13 (4)	1·72 (4)	1·09 (4)	−0·01 (3)	0·13 (3)	0·23 (3)
O(1)	0·0363 (3)	−0·0553 (3)	0·1544 (3)	2·2 (1)	2·4 (1)	1·4 (1)	−0·5 (1)	0·44 (9)	−0·6 (1)
O(2)	−0·0362 (3)	0·1522 (3)	0·2432 (3)	1·8 (1)	1·7 (1)	2·2 (1)	−0·0 (1)	0·2 (1)	0·5 (1)
O(3)	−0·1382 (3)	−0·0488 (3)	0·3116 (3)	1·4 (1)	2·5 (1)	1·3 (1)	−0·8 (1)	−0·01 (9)	0·3 (1)
O(4)	0·0914 (3)	−0·0008 (3)	0·3959 (3)	1·4 (1)	1·7 (1)	1·3 (1)	−0·35 (9)	−0·10 (9)	−0·09 (9)
O(5)	0·5011 (3)	0·1603 (4)	0·2840 (3)	2·0 (1)	4·1 (2)	2·4 (1)	1·4 (1)	0·5 (1)	1·5 (1)
O(6)	0·2730 (3)	0·1922 (3)	0·3363 (3)	1·4 (1)	2·4 (1)	1·3 (1)	−0·5 (1)	0·15 (9)	0·4 (1)
O(7)	0·3554 (3)	0·2905 (3)	0·1326 (3)	1·5 (1)	2·3 (1)	1·2 (1)	0·5 (1)	0·18 (9)	0·4 (1)
O(8)	0·4287 (4)	0·3732 (3)	0·3626 (3)	3·6 (2)	3·2 (2)	2·3 (1)	−1·6 (1)	0·3 (1)	−0·7 (1)
O(9)	0·0904 (3)	0·2675 (3)	0·5190 (4)	2·6 (1)	2·5 (1)	1·3 (1)	1·3 (1)	0·1 (1)	0·2 (1)
O(10)	0·3434 (3)	−0·369 (3)	0·5068 (4)	2·1 (1)	1·8 (1)	1·9 (1)	0·5 (1)	−0·7 (1)	−0·2 (1)
O(11)	−0·2887 (4)	0·2395 (4)	0·1328 (5)	1·9 (2)	3·5 (2)	4·2 (2)	0·1 (1)	0·4 (2)	1·7 (2)
N	0·3060 (5)	−0·0222 (6)	0·0690 (7)	2·4 (2)	3·1 (2)	4·0 (3)	0·1 (2)	0·5 (2)	0·2 (2)
H(1)	0·305 (6)	−0·075 (7)	−0·015 (7)	4·8 (16)					
H(2)	0·352 (8)	−0·026 (8)	0·134 (9)	6·3 (24)					
H(3)	0·320 (8)	0·047 (9)	0·043 (9)	6·9 (24)					
H(4)	0·212 (8)	0·004 (7)	0·086 (7)	5·9 (17)					
H(5)	0·326 (5)	−0·094 (5)	0·460 (6)	2·6 (13)					
H(6)	0·380 (7)	−0·047 (7)	0·566 (7)	4·0 (18)					
H(7)	0·044 (5)	0·294 (6)	0·456 (6)	2·9 (13)					
H(8)	0·058 (7)	0·289 (7)	0·583 (8)	6·2 (21)					
H(9)	−0·251 (8)	0·252 (8)	0·198 (8)	6·1 (25)					
H(10)	−0·342 (6)	0·230 (6)	0·190 (6)	3·1 (14)					

Table 3. *Observed and calculated structure factors* (×4) *for ferric ammonium sulfate trihydrate*

FCA (0,0,0) = 2570. Asterisk indicates zero-weighted data.

L	FOB	FCA
H,K= 0, 0		
2	143	143
4	426	415
6	247	235
8	268	273
10	117	111
H,K= 0, 1		
1	501	353
2	18	17
3	191	176
4	319	302
5	395	384
6	79	77
7	8	11*
8	202	199
9	238	236
10	46	46
11	29	32
H,K= 0, 2		
0	57	52
1	16	17
2	183	176
3	331	297
4	60	63
5	74	74
6	52	51
7	162	159
8	0	7*
9	109	108
10	0	15*
11	107	102
H,K= 0, 3		
1	81	82
2	158	136
3	108	111
4	22	50
5	31	32
6	276	277
7	168	171
8	44	45
9	101	106
10	64	69
H,K= 0, 4		
0	290	315
1	240	218
2	331	336
3	9	3*
4	131	126
5	33	32
6	206	215
7	110	113
8	73	77
9	0	11*
10	0	6*
H,K= 0, 5		
1	130	141
2	17	23
3	443	436
4	0	4*
5	125	135
6	164	162
7	121	117
8	73	71
9	18	17
10	104	104
H,K= 0, 6		
0	13	27
1	28	27
2	165	161
3	71	72
4	47	52
5	98	101
6	171	176
7	87	84
8	0	3*
9	110	118
H,K= 0, 7		
1	99	101
2	89	87
3	50	53
4	115	113
5	125	125
6	56	58
7	52	59
8	141	142
9	125	123
H,K= 0, 8		
0	342	348
1	126	130
2	48	52
3	126	121
4	240	241
5	118	116
6	25	31
7	21	21
8	144	141
H,K= 0, 9		
1	139	142
2	42	43
3	104	110
4	56	54
5	65	60
6	77	75
7	87	88
H,K= 0, 10		
0	17	22
1	17	13
2	127	130
3	62	63
4	0	6*
5	0	7*
6	37	32
H,K= 0, 11		
1	45	43
2	15	18*
3	70	72
4	22	22
H,K= 0, 12		
0	0	12*
1	74	71
H,K= 1, 0		
-10	58	65
-8	257	251
-6	130	129
-4	513	447
-2	31	33
0	250	187
2	24	23
4	81	82
6	180	176
8	119	117
10	100	96
H,K= 1, 1		
-11	54	55
-10	23	24
-9	217	216
-8	152	151
-7	8	7*
-6	20	19
-5	94	99
-4	317	305
-3	177	175
-2	16	22
-1	181	152
0	607	495
1	64	63
2	242	207
3	0	6*
4	90	97
5	41	39
6	398	383
7	230	226
8	13	12*
9	22	19
10	161	158
11	132	136
H,K= 1, 2		
-11	46	43
-10	47	45
-9	95	99
-8	0	6*
-7	55	57
-6	48	44
-5	239	241
-4	204	182
-3	134	139
-2	333	310
-1	492	402
0	570	532
1	361	311
2	850	772
3	148	157
4	113	122
5	206	212
6	226	234
7	256	258
8	37	38
9	42	40
10	0	10*
H,K= 1, 3		
-10	91	96
-9	30	37
-8	0	4*
-7	154	157
-6	269	269
-5	13	13
-4	0	15*
-3	358	333
-2	201	200
-1	0	7*
0	64	60
1	143	133
2	222	216
3	0	4*
4	165	161
5	128	137
6	34	38
7	216	214
8	157	158
9	166	168
10	0	6*
H,K= 1, 4		
-10	146	148
-9	20	20
-8	9	10*
-7	78	78
-6	157	163
-5	137	140
-4	80	73
-3	37	37
-2	117	121
-1	83	77
0	98	95
1	106	101
2	11	11
3	148	146
4	80	76
5	0	12*
6	60	62
7	0	5*
8	48	47
9	53	59
10	91	92
H,K= 1, 5		
-10	19	16
-9	0	12*
-8	47	48
-7	289	284
-6	189	191
-5	80	83
-4	24	30
-3	223	228
-2	169	172
-1	115	117
0	114	124
1	22	24
2	317	315
3	13	10
4	36	33
5	66	68
6	23	26
7	50	50
8	106	109
9	142	141
10	0	11*
H,K= 1, 6		
-9	103	112
-8	54	49
-7	105	105
-6	149	150
-5	103	104
-4	16	23
-3	402	397
-2	223	221
-1	172	174
0	151	162
1	150	164
2	223	236
3	319	314
4	150	152
5	328	323
6	171	176
7	65	67
8	135	132
9	144	140
H,K= 1, 7		
-9	94	93
-8	161	158
-7	86	85
-6	0	6*
-5	18	15
-4	333	333
-3	62	62
-2	144	155
-1	89	87
0	263	271
1	160	162
2	281	284
3	8	10*
4	211	215
5	32	36
6	167	162
7	14	20*
8	75	74
9	0	1*
H,K= 1, 8		
-8	175	169
-7	160	156
-6	25	20
-5	25	25
-4	173	176
-3	141	144
-2	20	24
-1	91	89
0	31	42
1	131	134
2	107	109
3	35	37
4	21	21
5	107	110
6	70	72
7	58	54
8	61	53
H,K= 1, 9		
-7	0	14*
-6	26	30
-5	96	98
-4	80	76
-3	23	25
-2	64	65
-1	108	110
0	0	7*
1	45	43
2	16	19
3	80	82
4	64	60
5	32	35
6	0	4*
7	93	92
H,K= 1, 10		
-6	0	4*
-5	48	50
-4	94	94
-3	34	35
-2	33	29
-1	204	203
0	100	94
1	17	20
2	61	59
3	155	153
4	74	72
5	11	7*
6	112	108
H,K= 1, 11		
-4	31	34
-3	0	11*
-2	158	148
-1	21	25
0	98	97
1	90	87
2	98	97
3	15	18*
4	119	112
H,K= 1, 12		
0	0	7*
H,K= 2, 0		
-10	25	26
-8	16	21
-6	88	90
-4	258	240
-2	789	568
0	20	26
2	919	852
4	280	264
6	607	572
8	51	53
10	183	179
H,K= 2, 1		
-11	95	98
-10	147	150
-9	40	39
-8	30	29
-7	224	222
-6	184	191
-5	10	12*
-4	101	97
-3	361	326
-2	815	628
-1	250	209
0	118	116
1	281	251
2	250	249
3	43	56
4	142	132
5	245	240
6	58	59
7	389	383
8	0	4*
9	53	54
10	88	82
H,K= 2, 2		
-11	152	143
-10	131	131
-9	141	141
-8	133	141
-7	115	116
-6	128	134
-5	476	446
-4	254	229
-3	45	41
-2	435	417
-1	321	294
0	163	155
1	106	101
2	167	170
3	163	167
4	93	97
5	120	119
6	72	73
7	26	28
8	56	57
9	38	38
10	11	14*
H,K= 2, 3		
-10	161	164
-9	89	88
-8	130	135
-7	0	15*
-6	123	130
-5	61	68
-4	197	206
-3	19	20
-2	24	21
-1	362	356
0	290	290
1	209	205
2	124	126
3	56	61
4	151	156
5	167	170
6	57	57
7	13	7*
8	114	114
9	129	128
10	19	18
H,K= 2, 4		
-10	122	121
-9	0	3*
-8	0	7*
-7	139	141
-6	246	246
-5	97	99
-4	148	144
-3	22	22
-2	119	120
-1	204	203
0	212	225
1	215	204
2	260	247
3	77	68
4	509	504
5	57	56
6	51	48
7	72	75
8	217	218
9	0	6*
10	65	69
H,K= 2, 5		
-10	31	35
-9	120	124
-8	64	61
-7	0	7*
-6	20	20
-5	142	141
-4	184	184
-3	53	57
-2	173	183
-1	190	197
0	45	43
1	301	308
2	51	51
3	211	217
4	83	83
5	196	201
6	85	86
7	13	13*
8	57	57
9	205	202
H,K= 2, 6		
-9	117	120
-8	159	157
-7	195	192
-6	147	147
-5	17	13
-4	186	191
-3	107	118
-2	216	222
-1	156	158
0	234	238
1	95	101
2	59	66
3	11	6*
4	111	112
5	43	47
6	36	36
7	0	9*
8	48	46
9	53	53
H,K= 2, 7		
-9	74	70
-8	184	180
-7	74	73
-6	90	88
-5	78	76
-4	82	82
-3	144	152
-2	208	210
-1	63	66
0	38	38
1	45	43
2	89	89
3	89	90
4	83	87
5	13	10*
6	40	39
7	109	105
8	47	51
H,K= 2, 8		
-8	44	43
-7	28	26
-6	39	45
-5	17	25
-4	58	65
-3	129	133
-2	193	191
-1	150	150
0	17	18
1	89	92
2	248	247
3	108	108
4	0	8*
5	62	65
6	226	220
7	132	131
8	27	24
H,K= 2, 9		
-7	70	67
-6	116	111
-5	62	60
-4	118	118
-3	162	161
-2	191	191
-1	192	193
0	16	13
1	31	31
2	67	66
3	173	174
4	28	34
5	123	126
6	37	42
7	151	139
H,K= 2, 10		
-6	94	93
-5	144	140
-4	15	18*
-3	15	14*
-2	147	148
-1	99	99
0	93	93
1	17	19
2	0	10*
3	36	41
4	113	112
5	0	7*
H,K= 2, 11		
-4	134	132
-3	24	30
-2	22	21
-1	60	56
0	93	92
1	15	13*
2	11	11*
3	0	10*
4	81	77
H,K= 3, 0		
-10	244	246
-8	127	128
-6	311	307
-4	228	204
-2	322	306
0	434	425
2	274	275
4	66	64
6	35	36
8	33	35
10	36	38
H,K= 3, 1		
-11	171	169
-10	42	40
-9	0	9*
-8	0	4*
-7	134	137
-6	48	47
-5	54	56
-4	71	71
-3	177	174
-2	211	212
-1	68	64
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1	269	255
2	94	106
3	122	116
4	102	100
5	0	10*
6	232	231
7	48	45
8	60	57
9	118	118
10	15	18*
H,K= 3, 2		
-10	15	16*
-9	0	15*
-8	107	107
-7	91	88
-6	90	87
-5	59	64
-4	0	16*
-3	211	205
-2	95	89
-1	304	294
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1	381	371
2	187	173
3	177	183
4	355	359
5	242	254
6	202	204
7	198	199
8	148	147
9	147	146
10	54	50
H,K= 3, 3		
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-9	200	200
-8	25	19
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-6	101	105
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-3	126	133
-2	56	57
-1	114	95
0	442	457
1	218	215
2	313	303
3	155	151
4	285	286
5	95	95
6	91	94
7	148	156
8	208	214
9	142	147
10	125	120
H,K= 3, 4		
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-9	52	51
-8	332	335
-7	0	17*
-6	50	50
-5	74	74
-4	283	285
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-2	100	90
-1	94	92
0	494	519
1	67	66
2	35	37
3	88	91
4	140	145
5	37	36
6	45	48
7	30	33
8	72	75
9	42	44
H,K= 3, 5		
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-9	172	177
-8	74	76
-7	175	177
-6	142	144
-5	251	247
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-3	15	24
-2	85	83
-1	241	247
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1	107	106
2	116	116
3	112	115
4	326	322
5	107	106
6	90	90
7	39	37
8	119	120
9	52	50
H,K= 3, 6		
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-7	91	94
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-5	66	70
-4	41	43
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-2	19	17
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1	123	122
2	45	43
3	196	201
4	214	217
5	56	55
6	141	147
7	170	168
8	85	84
9	101	101
H,K= 3, 7		
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0	59	63
1	38	37
2	187	189
3	61	59
4	105	112
5	23	24
6	126	122
7	59	61
8	62	60
H,K= 3, 8		
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-7	0	3*
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-5	105	107
-4	71	72
-3	35	36
-2	353	356
-1	187	184
0	15	6
1	9	6*
2	65	67
3	130	132
4	22	23
5	68	70
6	59	62
7	85	82
H,K= 3, 9		
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-6	81	83
-5	85	85
-4	42	42
-3	220	221
-2	19	19
-1	75	74
0	85	84
1	80	79
2	100	102
3	91	92
4	20	16
5	40	39
6	65	63
H,K= 3, 10		
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-3	95	96
-2	105	101
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1	180	176
2	76	74
3	30	26
4	32	32
5	140	138
H,K= 3, 11		
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-2	19	22
-1	19	24
0	150	148
1	31	31
2	63	63
3	64	63
H,K= 4, 0		
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-6	27	21
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-2	15	8
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2	82	76
4	261	264
6	35	41
8	176	165
10	56	53
H,K= 4, 1		
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-9	80	81
-8	25	23
-7	141	143
-6	145	146
-5	228	227
-4	171	162
-3	128	131
-2	75	69
-1	103	95
0	318	312
1	131	131
2	47	42
3	288	294
4	101	100
5	128	129
6	65	66
7	39	41
8	138	136
9	155	149
10	38	41
H,K= 4, 2		
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-9	167	166
-8	97	99
-7	161	165
-6	122	125
-5	251	252
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-3	550	507
-2	122	131
-1	70	61
0	149	166
1	376	367
2	181	196
3	177	181
4	209	212
5	127	134
6	60	60
7	0	8*
8	17	22
9	18	25
10	30	34
H,K= 4, 3		
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-9	92	89
-8	287	287
-7	20	19
-6	107	114
-5	73	73
-4	355	348
-3	92	100
-2	198	212
-1	248	247
0	352	354
1	172	172
2	285	297
3	35	40
4	50	53
5	99	102
6	239	243
7	187	189
8	68	70
9	18	27
H,K= 4, 4		
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-9	103	106
-8	34	30
-7	38	38
-6	103	103
-5	29	32
-4	124	127
-3	51	52
-2	161	165
-1	175	177
0	280	296
1	23	18
2	138	141
3	24	27
4	216	216
5	112	116
6	302	306
7	10	10*
8	88	89
9	0	5*
H,K= 4, 5		
-9	93	95
-8	159	162
-7	134	132
-6	0	6*
-5	103	100
-4	118	125
-3	172	175
-2	131	132
-1	134	133
0	44	29
1	165	176
2	93	98
3	167	170
4	19	17
5	22	19
6	49	47
7	221	213
8	18	18
9	109	100
H,K= 4, 6		
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-8	0	17*
-7	129	127
-6	107	106
-5	82	80
-4	204	209
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-2	306	313
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0	[illegible]	189
1	[illegible]	16*
2	[illegible]	59
3	[illegible]	96
4	104	[illegible]
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6	103	102
7	31	33
8	50	52
H,K= 4, 7		
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-7	0	4*
-6	240	236
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-4	60	66
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-2	227	228
-1	67	63
0	124	122
1	15	6
2	84	90
3	81	79
4	180	177
5	31	32
6	49	52
7	26	25
8	86	86
H,K= 4, 8		
-7	49	51
-6	54	52
-5	121	120
-4	31	32
-3	13	17*
-2	65	63
-1	110	112
0	65	60
1	0	4*
2	88	88
3	156	155
4	166	168
5	76	77
6	21	16
7	25	26
H,K= 4, 9		
-6	0	5*
-5	92	94
-4	0	5*
-3	14	18*
-2	0	3*
-1	103	104
0	157	158
1	132	122
2	84	83
3	92	92
4	65	62
5	238	234
6	0	0*
H,K= 4, 10		
-5	106	103
-4	130	125
-3	160	160
-2	64	67
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0	133	129
1	149	145
2	0	11*
3	26	26
4	162	156
H,K= 4, 11		
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-2	88	88
-1	0	18*
0	72	71
1	0	6*
2	164	156
H,K= 5, 0		
-10	128	120
-8	141	137
-6	176	176
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-2	243	233
0	235	244
2	55	53
4	300	307
6	80	82
8	147	139
H,K= 5, 1		
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-9	173	171
-8	115	114
-7	43	44
-6	110	113
-5	340	328
-4	32	36
-3	204	195
-2	272	274
-1	110	124
0	0	12*
1	157	160
2	129	129
3	247	259
4	137	141
5	55	59
6	75	79
7	36	37
8	128	120
9	53	52
H,K= 5, 2		
-10	29	30
-9	78	77
-8	114	114
-7	41	47
-6	0	8*
-5	96	93
-4	17	19
-3	70	66
-2	79	80
-1	19	23
0	66	66
1	203	209
2	73	72
3	209	215
4	84	89
5	128	132
6	134	139
7	166	169
8	31	29
9	125	121
H,K= 5, 3		
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-9	0	15*
-8	82	84
-7	216	218
-6	127	134
-5	19	15
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-3	222	221
-2	76	75
-1	145	149
0	98	103
1	80	89
2	201	212
3	181	184
4	110	105
5	65	69
6	190	191
7	152	155
8	88	91
9	25	29
H,K= 5, 4		
-9	19	21
-8	191	193
-7	84	85
-6	191	196
-5	0	10*
-4	30	31
-3	16	26
-2	507	507
-1	218	218
0	139	147
1	31	33
2	433	438
3	114	117
4	116	114
5	20	21
6	218	218
7	94	95
8	21	24
9	53	60
H,K= 5, 5		
-9	75	76
-8	47	45
-7	185	184
-6	107	108
-5	38	36
-4	57	61
-3	223	234
-2	206	209
-1	192	190
0	118	120
1	103	107
2	62	61
3	48	52
4	181	185
5	116	118
6	203	204
7	75	75
8	73	74
H,K= 5, 6		
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-7	58	54
-6	47	50
-5	35	37
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-3	20	27
-2	79	79
-1	15	17
0	106	107
1	69	69
2	0	5*
3	44	49
4	0	5*
5	146	144
6	18	19
7	18	13
8	43	49
H,K= 5, 7		
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-7	41	41
-6	20	21
-5	114	110
-4	25	30
-3	28	30
-2	73	74
-1	158	155
0	94	98
1	98	103
2	35	39
3	13	22*
4	133	132
5	129	131
6	52	51
7	41	43
H,K= 5, 8		
-7	33	40
-6	134	126
-5	34	34
-4	212	212
-3	0	12*
-2	40	39
-1	84	84
0	236	237
1	105	107
2	63	63
3	14	15*
4	230	223
5	111	114
6	22	24
H,K= 5, 9		
-6	95	91
-5	158	159
-4	123	124
-3	121	118
-2	156	156
-1	164	163
0	23	18
1	123	119
2	21	26
3	98	96
4	75	75
5	141	138
H,K= 5, 10		
-4	89	89
-3	19	24
-2	55	59
-1	48	47
0	50	48
1	11	13*
2	89	92
3	127	124
H,K= 6, 0		
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-8	193	192
-6	174	173
-4	159	155
-2	0	15*
0	0	14
2	295	294
4	0	10
6	0	9
8	169	171
H,K= 6, 1		
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-9	158	156
-8	122	118
-7	66	69
-6	100	101
-5	326	316
-4	208	209
-3	59	57
-2	42	43
-1	45	48
0	205	215
1	62	62
2	186	191
3	77	83
4	25	24
5	36	32
6	27	24
7	74	72
8	26	32
9	0	15
H,K= 6, 2		
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-9	114	117
-8	92	90
-7	158	157
-6	141	144
-5	189	194
-4	154	159
-3	150	157
-2	137	144
-1	286	291
0	239	249
1	159	163
2	72	77
3	221	227
4	249	252
5	69	67
6	119	118
7	154	154
8	94	94
9	51	50
H,K= 6, 3		
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-8	0	11
-7	115	117
-6	178	180
-5	148	151
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-3	49	49
-2	378	388
-1	96	91
0	69	71
1	51	51
2	277	281
3	27	30
4	174	176
5	118	122
6	36	39
7	54	57
8	113	110
H,K= 6, 4		
-9	35	34
-8	0	7
-7	60	64
-6	131	133
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-4	0	6
-3	46	49
-2	14	8
-1	35	41
0	53	56
1	18	24
2	37	37
3	15	11
4	72	72
5	21	21
6	176	177
7	47	47
8	92	89
H,K= 6, 5		
-9	36	38
-8	30	41
-7	109	111
-6	168	173
-5	83	85
-4	16	20
-3	18	12
-2	154	153
-1	139	138
0	24	10
1	50	53
2	143	142
3	88	87
4	97	97
5	190	192
6	78	76
7	36	32
8	62	60
H,K= 6, 6		
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-7	72	71
-6	29	28
-5	117	116
-4	82	83
-3	196	195
-2	91	96
-1	214	219
0	176	182
1	152	153
2	121	124
3	41	41
4	265	263
5	217	217
6	73	76
7	0	5
H,K= 6, 7		
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-6	63	64
-5	102	106
-4	243	241
-3	66	69
-2	0	13
-1	0	12
0	305	309
1	92	94
2	60	58
3	20	17
4	110	108
5	0	3*
6	149	150
H,K= 6, 8		
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-5	48	46
-4	84	85
-3	120	122
-2	62	62
-1	36	41
0	72	74
1	142	141
2	62	59
3	45	48
4	56	57
5	102	96
H,K= 6, 9		
-5	57	57
-4	0	19*
-3	34	33
-2	26	29
-1	49	49
0	38	38
1	97	93
2	0	3*
3	69	72
4	0	3*
H,K= 6, 10		
-3	39	46
-2	38	36
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0	0	11*
1	22	20
2	116	115
H,K= 7, 0		
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-6	83	80
-4	327	314
-2	224	215
0	119	126
2	506	510
4	68	68
6	236	226
8	27	28
H,K= 7, 1		
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-8	102	100
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-6	28	29
-5	41	43
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-3	294	288
-2	201	202
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0	236	241
1	264	272
2	62	62
3	157	160
4	154	155
5	82	79
6	17	9
7	113	109
8	102	102
H,K= 7, 2		
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-8	33	36
-7	76	78
-6	134	137
-5	51	53
-4	183	187
-3	54	55
-2	115	113
-1	12	4*
0	85	82
1	20	15
2	177	181
3	77	77
4	0	10*
5	61	63
6	10	8*
7	72	70
8	55	58
H,K= 7, 3		
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-8	28	31
-7	44	46
-6	22	21
-5	174	175
-4	132	135
-3	24	30
-2	42	44
-1	88	93
0	48	51
1	92	100
2	88	88
3	0	9*
4	0	2*
5	114	115
6	72	71
7	21	18
8	50	49
H,K= 7, 4		
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-7	23	27
-6	157	158
-5	39	43
-4	141	143
-3	101	102
-2	135	140
-1	23	31
0	232	236
1	18	27
2	68	71
3	0	4*
4	294	294
5	133	133
6	34	39
7	38	41
H,K= 7, 5		
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-7	37	34
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-5	206	206
-4	63	60
-3	104	104
-2	13	5*
-1	205	205
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1	61	62
2	99	97
3	106	107
4	57	56
5	187	183
6	28	34
7	55	49
H,K= 7, 6		
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-6	11	15*
-5	105	103
-4	191	194
-3	44	48
-2	13	22*
-1	70	72
0	104	105
1	40	41
2	17	20
3	37	40
4	55	54
5	52	53
6	55	56
H,K= 7, 7		
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-5	0	2*
-4	23	30
-3	107	108
-2	31	33
-1	24	32
0	0	8*
1	153	148
2	14	22*
3	0	4*
4	80	78
5	38	38
H,K= 7, 8		
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-4	108	108
-3	57	56
-2	131	128
-1	33	39
0	83	69
1	0	6*
2	188	183
3	66	66
4	40	39
H,K= 7, 9		
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-3	53	51
-2	67	66
-1	125	124
0	91	95
1	138	136
2	83	80
H,K= 8, 0		
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-6	171	163
-4	80	78
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0	125	126
2	172	169
4	110	112
6	31	30
H,K= 8, 1		
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-7	213	211
-6	20	20
-5	66	65
-4	116	116
-3	206	212
-2	167	169
-1	116	112
0	111	119
1	36	35
2	204	207
3	21	22
4	0	7*
5	36	36
6	169	163
7	31	33
H,K= 8, 2		
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-7	72	73
-6	35	34
-5	89	90
-4	81	82
-3	162	166
-2	160	166
-1	105	104
0	23	14
1	172	176
2	210	214
3	160	161
4	146	148
5	112	110
6	66	62
7	85	83
H,K= 8, 3		
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-7	35	36
-6	80	78
-5	79	75
-4	117	117
-3	56	58
-2	65	66
-1	90	97
0	174	174
1	41	43
2	51	56
3	10	1*
4	230	225
5	58	60
6	0	8*
7	73	75
H,K= 8, 4		
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-7	34	36
-6	27	27
-5	0	11*
-4	182	181
-3	40	37
-2	86	87
-1	0	11*
0	161	164
1	19	23
2	121	124
3	42	45
4	29	30
5	46	48
6	41	39
H,K= 8, 5		
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-6	26	23
-5	169	170
-4	117	117
-3	0	6*
-2	17	13
-1	106	104
0	92	91
1	10	10*
2	0	6*
3	0	12*
4	176	170
5	56	59
6	0	5*
H,K= 8, 6		
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-5	144	143
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-3	108	106
-2	63	61
-1	172	170
0	28	34
1	188	191
2	86	87
3	158	149
4	34	36
5	87	84
H,K= 8, 7		
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-4	55	60
-3	44	42
-2	191	187
-1	67	68
0	84	86
1	70	73
2	237	235
3	0	3*
4	74	74
H,K= 8, 8		
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-3	0	7*
-2	129	123
-1	149	142
0	19	15
1	24	26
2	74	73
3	69	69
H,K= 9, 0		
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-6	46	42
-4	14	16*
-2	376	363
0	100	96
2	132	131
4	245	237
6	116	112
H,K= 9, 1		
-8	22	21
-7	26	29
-6	161	158
-5	194	187
-4	60	60
-3	45	46
-2	105	105
-1	234	242
0	69	72
1	57	56
2	39	40
3	136	133
4	164	165
5	79	76
6	109	106
H,K= 9, 2		
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-6	0	1*
-5	88	87
-4	88	85
-3	149	149
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-1	91	96
0	253	250
1	0	14*
2	158	157
3	79	79
4	154	157
5	0	8*
6	73	71
H,K= 9, 3		
-7	67	68
-6	0	6*
-5	48	48
-4	95	93
-3	110	109
-2	19	21
-1	33	39
0	80	78
1	76	76
2	48	49
3	118	117
4	103	104
5	34	34
6	73	72
H,K= 9, 4		
-7	16	23*
-6	75	77
-5	39	40
-4	115	111
-3	66	64
-2	48	49
-1	22	30
0	124	121
1	92	94
2	164	161
3	0	14*
4	34	35
5	0	21*
H,K= 9, 5		
-6	11	4*
-5	36	35
-4	26	34
-3	108	104
-2	0	4*
-1	0	15*
0	0	22*
1	186	184
2	26	27
3	135	134
4	65	62
H,K= 9, 6		
-5	128	129
-4	27	28
-3	0	7*
-2	133	134
-1	115	109
0	69	67
1	0	5*
2	135	132
3	31	31
4	0	3*
H,K= 9, 7		
-4	11	19*
-3	16	10*
-2	95	90
-1	73	75
0	50	44
1	19	18
2	37	42
H,K= 10, 0		
-6	75	76
-4	136	125
-2	92	92
0	224	220
2	124	119
4	203	198
H,K= 10, 1		
-6	104	102
-5	130	131
-4	75	81
-3	29	29
-2	144	147
-1	147	145
0	0	8*
1	34	37
2	89	86
3	35	33
4	103	100
5	19	15
H,K= 10, 2		
-6	35	37
-5	40	39
-4	21	21
-3	91	90
-2	37	41
-1	117	118
0	0	16*
1	67	65
2	0	6*
3	126	124
4	52	52
H,K= 10, 3		
-6	25	24
-5	19	26
-4	117	113
-3	133	132
-2	33	36
-1	0	16*
0	118	118
1	56	56
2	96	94
3	37	40
4	67	61
H,K= 10, 4		
-5	0	10*
-4	84	83
-3	72	72
-2	122	117
-1	70	71
0	79	70
1	15	25*
2	221	213
3	36	36
H,K= 10, 5		
-4	106	103
-3	129	128
-2	0	4*
-1	65	60
0	91	92
1	110	112
2	55	55
3	22	25
H,K= 10, 6		
-3	71	72
-2	27	27
-1	41	41
0	19	23
1	118	121
H,K= 11, 0		
-4	38	39
-2	40	44
0	32	50
2	41	41
H,K= 11, 1		
-5	22	21
-4	150	149
-3	138	139
-2	0	4*
-1	32	25
0	79	80
1	60	59
2	38	37
3	32	32
H,K= 11, 2		
-4	0	3*
-3	128	124
-2	0	5*
-1	118	121
0	15	15*
1	90	90
2	153	152
H,K= 11, 3		
-4	11	9*
-3	0	2*
-2	193	191
-1	82	81
0	0	11*
1	41	41
2	118	118
H,K= 11, 4		
-2	0	6*
-1	103	99
0	148	146
1	0	7*

refinement, a Fourier difference map was calculated from which approximate parameters for the 10 hydrogen atoms were determined. Inclusion of the hydrogen atoms in the least-squares refinement, with isotropic temperature factors and no restrictions on their positional parameters, led to an R index of 0·062. A correction for secondary extinction was made (Zachariasen, 1963) by applying the equation $F_{corr}=(1+$ $(EF)\,I)\,F_{obs}$, where I is the net intensity, EF the extinction factor, and F_{corr} and F_{obs} are the corrected and observed structure factors. An extinction factor of $EF=$ 1×10^{-5} resulted in a final R index of 0·038 for 1504 reflections, or $R=0·045$ when all 1690 reflections were included in the least-squares refinement.

Positional and thermal parameters for all atoms and their calculated standard deviations are listed in Table 2. Observed and calculated structure factors are shown in Table 3.

Discussion of the structure

The ferric ion is coordinately bonded to six oxygen atoms which form a slightly distorted octahedron. Four of the six are sulfate oxygen atoms and two are water oxygen atoms. The arrangement of the four sulfate

groups and the two water molecules about the iron atom, as well as the atom numbering system used in this investigation, are shown in Fig. 1. The nitrogen atom and the third water oxygen, O(11), are not shown but can be seen in Fig. 2.

The structure has continous chains composed of alternate iron atoms and the S(2) sulfate groups running parallel to the c axis. A segment of this chain, along with interatomic bond distances and angles, is shown in Fig. 3. The parallel chains are bridged together by the coordinate bonding of the S(1) sulfate group to iron atoms in adjacent chains. This results in the eight-membered ring structure shown in Fig.4.

Complete sets of interatomic bond distances and angles involving the heavy atoms are listed in Tables 4 and 5, respectively. Distances given in column 2 of Table 4 are uncorrected for thermal motion; distances in column 3 are corrected by assuming that the light atom rides on the heavy atom. The six, thermally corrected, Fe–O distances vary between 1·979 and 2·014 Å with an average value of 1·997 Å. This average value agrees well with the average value reported in *International Tables for X-ray Crystallography* (1962) for six-coordinated iron of 2·01 Å, and with the value o
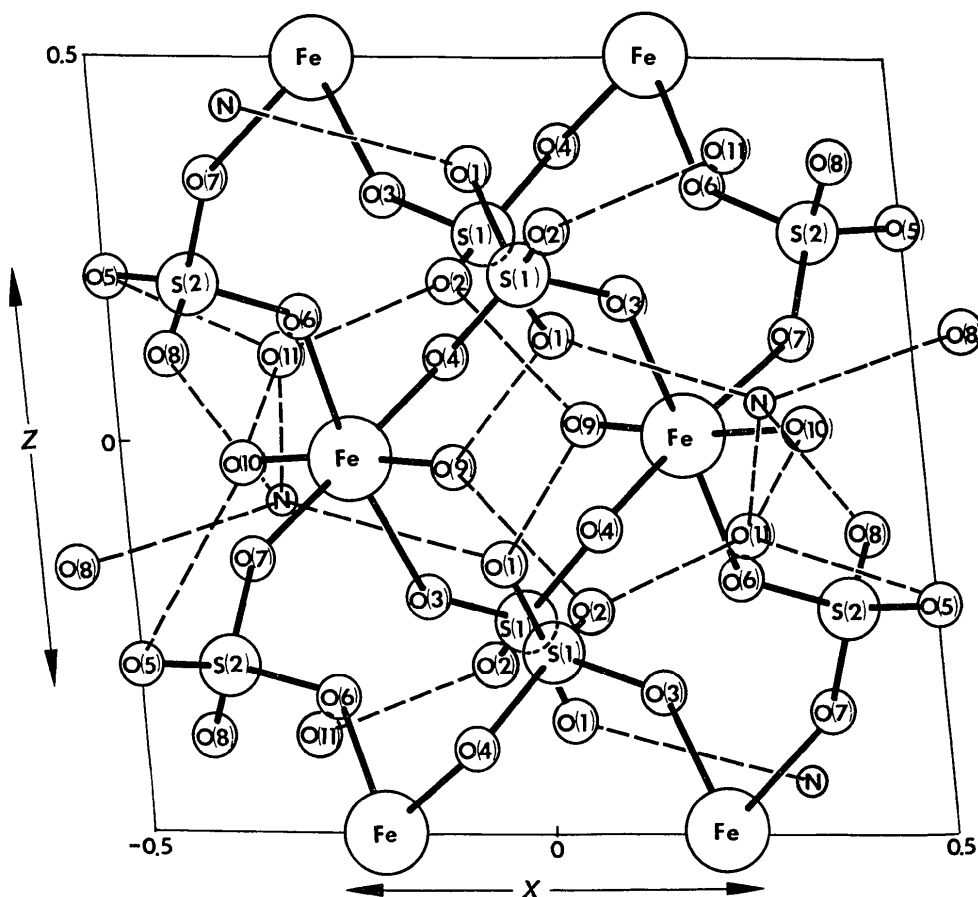

Fig.2. Packing and bonding in $FeNH_4(SO_4)_2.3H_2O$. This is a projection on to the (101) plane. Hydrogen bonds are shown as dashed lines. O(9), O(10), and O(11) are water oxygen atoms.

2·02 Å found by Romers, Rooymans & DeGraaf (1967) for octahedrally coordinated iron in Na₃Fe₅O₉.

Table 4. *Bond distances between heavy atoms*

	Uncorrected	Corrected*
Fe–O(3)	1·993 Å	1·999 Å
–O(4)	1·976	1·979
–O(6)	2·002	2·007
–O(7)	1·976	1·982
–O(9)	1·993	2·003
–O(10)	2·007	2·014
S(1)–O(1)	1·447	1·457
–O(2)	1·455	1·463
–O(3)	1·488	1·495
–O(4)	1·487	1·490
S(2)–O(5)	1·461	1·480
–O(6)	1·484	1·489
–O(7)	1·488	1·492
–O(8)	1·434	1·456

* Distances corrected for thermal motion assume that the light atom is riding on the heavy atom.

Table 5. *Bond angles between heavy atoms*

O(3)–Fe–O(9)	87·68°	O(1)–S(1)–O(2)	111·88°
O(3)–Fe–O(10)	93·90	O(1)–S(1)–O(3)	109·11
O(3)–Fe–O(4)	90·74	O(1)–S(1)–O(4)	108·32
O(3)–Fe–O(6)	173·66	O(2)–S(1)–O(3)	108·94
O(3)–Fe–O(7)	89·79	O(2)–S(1)–O(4)	110·23
O(4)–Fe–O(9)	96·70	O(3)–S(1)–O(4)	108·28
O(4)–Fe–O(10)	84·09		
O(4)–Fe–O(6)	87·91	O(5)–S(2)–O(6)	108·77
O(4)–Fe–O(7)	172·27	O(5)–S(2)–O(7)	106·36
O(6)–Fe–O(9)	86·32	O(5)–S(2)–O(8)	113·28
O(6)–Fe–O(10)	92·13	O(6)–S(2)–O(7)	106·82
O(7)–Fe–O(9)	91·02	O(6)–S(2)–O(8)	111·12
O(7)–Fe–O(10)	88·18	O(7)–S(2)–O(8)	110·19
O(9)–Fe–O(10)	178·23		
O(6)–Fe–O(7)	92·38	Fe–O(3)–S(1)	137·44
		Fe–O(4)–S(1)	137·72
		Fe–O(6)–S(2)	139·68
		Fe–O(7)–S(2)	139·92

Two of the Fe–O bonds are slightly shorter than the other four. The difference between the average value of the short bonds (1·981 Å) and the average value of the other four (2·006 Å) is 0·025 Å or 8 standard deviations. Two of the six octahedral bonds in Fe(II) complexes also have been observed to be shorter than the other four (Montgomery, Chastain, Natt, Witkowska & Lingafelter, 1967). The O–Fe–O angles (Table 5) indicate that the octahedron of oxygen atoms about the Fe atom is distorted appreciably. A similar distortion was found by Romers *et al.* (1967) for the octahedrally coordinated iron in Na₃Fe₅O₉.

Sulfate groups

There are two crystallographically distinct sulfate groups in the crystal, as shown in Figs. 3 and 4. The S–O distances, uncorrected for thermal motion, appear to be longer when the oxygen atom forms a second bond (column 2, Table 4). After correction for thermal motion, assuming that oxygen rides on sulfur, the difference

between the average value of the four short bonds and the average value of the four long bonds is reduced from 0·038 to 0·028 Å. The value 0·028 Å is equal to 7σ and, therefore, would appear to be significant. A similar difference in S–O bond lengths of the sulfate group was reported by Morimoto & Lingafelter (1970). The average value for all S–O bond lengths found for FeNH₄(SO₄)₂.3H₂O is 1·468 Å, uncorrected for thermal motion, and 1·478 Å after correction. These values compare favorably with those found by Zalkin, Ruben & Templeton (1964): 1·473 Å uncorrected for thermal motion and 1·468 Å after correction.

The Fe–O–S and O–Fe–O bond angles in the eight-membered rings are significantly less than the similar angles in the continous chains involving S(2). On the other hand, the O–S–O– angles vary in the opposite direction. The structure provides no obvious explanation for these differences. Deviation of the O–S–O– angles from the tetrahedral value indicates that the sulfate groups are also distorted.

Packing and bonding

The packing and bonding are illustrated in Fig. 2 which is a projection on to the (101) plane. The nitrogen atom and water molecules form hydrogen bonds as shown by the dashed lines. There are 10 hydrogen bonds in the asymmetric unit; their lengths and angles are listed in Table 6(a). The third water molecule, O(11),
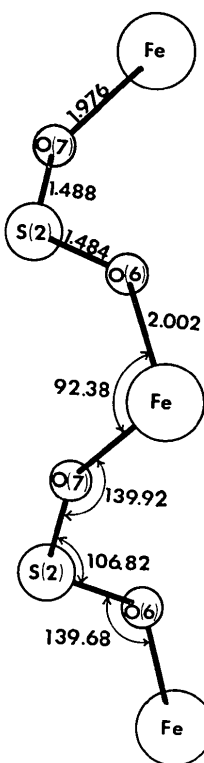

Fig. 3. Chain formed by the iron atoms and S(2) sulfate groups. Interatomic bond distances and angles shown are uncorrected for thermal motion.
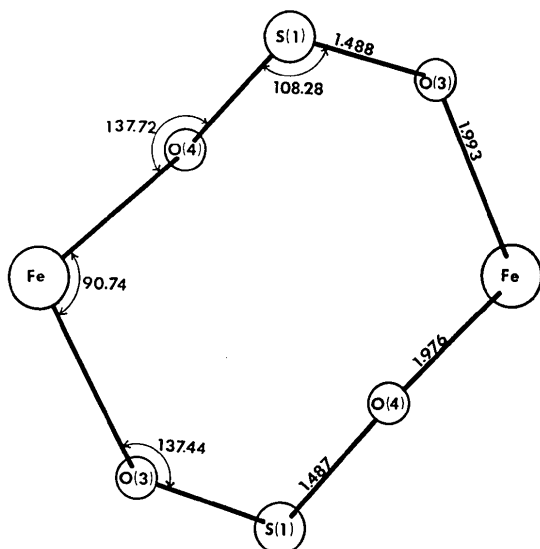
Fig. 4. Eight-membered ring formed by iron atoms and the S(1) sulfate groups which bridge adjacent chains. Interatomic bond distances and angles shown are uncorrected for thermal motion.

is held in the crystal by four hydrogen bonds. It forms a bridge between two sulfate groups, but is also hydrogen-bonded to nitrogen and the water molecule

O(10). The strongest of these bonds appears to be that between the two water molecules, as judged by the distance of 2·663 Å. The two hydrogen bonds, formed by O(9) to two sulfate oxygen atoms, O(1) and O(2), also have relatively short O–O distances.

The nitrogen atom forms four hydrogen bonds with oxygen atoms. N–O distances observed in this investigation (Table 6) agree well with those found in $Fe(NH_4)_2(SO_4)_2.6H_2O$ by Montgomery et al. (1967).

Hydrogen-atom positions were refined by least-squares methods without restricting their positional parameters. But because of incomplete compensation of the electron distribution around the heavy atoms by the assumed form of the anisotropic temperature factor, their final positions are only approximate. Distances involving hydrogen are listed in Table 6(b).

Thermal parameters of the heavy atoms are all quite small. As expected, the magnitude of these parameters is significantly larger for the singly-bonded than for the doubly-bonded sulfate oxygen atoms. Thermal parameters for the water oxygen atoms are only slightly larger than those for the sulfate oxygen atoms, and even O(11) which is held in the structure by hydrogen bonds only, has comparatively small thermal parameters.

Table 6. (a) Hydrogen bond lengths and angles (e.s.d.'s are 0·005 Å and 0·03°, respectively) and (b) distances involving hydrogen atoms (e.s.d.'s are 0·10 Å)

(a)

	Length	Angle
N——H(4)—O(1)	2·898 Å	145·91°
N——H(2)—O(8)	2·875	122·42
N——H(3)—O(8)	2·838	133·78
N——H(1)—O(11)	2·919	157·15
O(9)—H(7)—O(1)	2·682	149·87
O(9)—H(8)—O(2)	2·696	176·82
O(10)–H(6)—O(5)	2·720	154·94
O(10)–H(5)—O(11)	2·663	170·23
O(11)–H(9)—O(2)	2·789	118·86
O(11)–H(10)–O(5)	2·763	160·39

(b)

N——H(1)	0·96 Å	O(9)—H(8)	0·75 Å
N——H(2)	0·74	O(10)–H(5)	0·74
N——H(3)	0·77	O(10)–H(6)	0·65
N——H(4)	1·00	O(11)–H(9)	0·71
O(9)–H(7)	0·78	O(11)–H(10)	0·80

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