The Crystal Structure of Ammonium Hexasulphito-ferrate(III), $(NH_4)_9[Fe(SO_3)_6]$

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The crystal structure of ammonium hexasulphitoferrate(III) $(NH_4)_9[Fe(SO_3)_6]$ has been determined from three-dimensional X-ray data measured on an automatic diffractometer. The crystals are hexagonal, space group $P\bar{3}$ (No. 147); $a = 10.2226(33)$ Å, $c = 7.2055(14)$ Å, and $Z = 1$. The final R index is 0.053 for 359 independent reflections. The structure consists of FeO_6 octahedra whose oxygen atoms belong to six different sulphite groups. The $Fe(SO_3)_6$ groups are linked together by ammonium ions. The $Fe-O$ distance is 2.028(6) Å and the average dimensions of the sulphite ion are: $S-O$ distance 1.517 Å, $O-O$ distance 2.399 Å, and $O-S-O$ angle 104.5°.

The crystal structures of several metal sulphites have been studied over a period of some years at this institute by means of X-ray methods. A survey of the results obtained has recently been given by Kierkegaard et al.[1] In all the sulphites studied except in sodium sulphite, the sulphite group is coordinated to a metal atom through the sulphur atom. Because iron has a lower affinity for sulphur than for oxygen it could be expected that in iron sulphites the ferric ion would be bonded to oxygen atoms. In $(NH_4)_9[Fe(SO_3)_6]$ the dimensions of the sulphite group would be affected by (a) hydrogen bonds between ammonium ions and sulphite oxygen atoms and (b) the lone electron pair of sulphur. Thus, the crystal structure investigation of this compound was started in order to obtain additional information on these effects.

Ammonium hexasulphitoferrate(III) was first synthesized by Erämetsä[2] who found, by microscopic investigation, that the crystals were hexagonal. This conclusion was later confirmed by X-ray powder diffractometric studies.[3,4] This article describes the determination and refinement of the crystal structure of $(NH_4)_9[Fe(SO_3)_6]$ from three-dimensional X-ray single crystal data.

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EXPERIMENTAL

Preparation of crystals. The crystals were prepared according to Erämetsä.[2] In order to avoid oxidation all preparations were carried out in nitrogen atmosphere. The obtained crystals were orange brown hexagonal prisms which had a tendency to form cross shaped twins.

Data collection and reduction. The accurate unit cell dimensions were calculated, by a least squares program, from a powder photograph obtained in a Guinier-Hägg focusing camera of 80 mm diameter with strictly monochromatized $CuK\alpha_1$ radiation

Table 1. X-ray powder data of $(NH_4)_9[Fe(SO_3)_6]$. $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

h k l	d_{obs} (Å)	$10^5 \times \sin^2 \theta_{obs}$	$10^5 \times \sin^2 \theta_{calc}$	I_{obs}
1 0 0	8.900	749	756	s
0 0 1	7.294	1115	1123	s
1 0 1	5.627	1874	1880	m
1 1 0	5.126	2258	2270	m
1 1 1	4.183	3391	3394	s
2 0 1	3.783	4146	4151	w
0 0 2	3.632	4497	4495	w
2 1 0	3.347	5297	5298	s
2 1 1	3.039	6424	6422	m
1 1 2	2.961	6766	6766	s
3 0 0	2.949	6823	6812	s
2 0 2	2.806	7537	7523	w
3 0 1	2.735	7931	7936	w
2 1 2 3 1 0 }	2.458	9819	{ 9794 9840	w
0 0 3	2.452	9868	10115	w
2 2 1	2.421	10123	10207	vw
1 0 3	2.338	10852	10872	vw
3 1 1	2.324	10981	10964	w
3 0 2	2.289	11324	11308	w
4 0 0	2.225	11989	12111	s
1 1 3	2.187	12404	12386	m
4 0 1	2.115	13258	13235	w
2 2 2	2.090	13578	13579	m
3 1 2 3 2 0 }	2.033	14359	{ 14336 14382	m
2 1 3	1.960	15438	15414	w
3 2 1	1.953	15560	15506	vw
4 1 0	1.930	15934	15896	w
4 0 2	1.888	16637	16607	w
4 1 1	1.863	17091	17020	w
0 0 4	1.816	17984	17982	w
3 2 2	1.770	18938	18878	w
2 2 3	1.755	19273	19198	w

($\lambda = 1.54050$ Å). Potassium chloride ($a = 6.29228$ Å)[5] was used as internal standard. The powder photograph was measured and interpreted to $\sin^2 \theta = 0.48$. The cell dimensions (see Table 1) at 25°C are:

$$a = 10.2226 \pm 33 \text{ Å}; \quad c = 7.2055 \pm 14 \text{ Å}; \quad \gamma = 120°.$$

The powder data are in agreement with the results obtained by Erämetsä [3] ($a = 10.15$, $c = 7.24$ Å) and by Erämetsä and Valkonen [4] ($a = 10.177$, $c = 7.247$ Å).

The observed density 1.77 g cm⁻³ determined by loss of weight in benzene corresponds to one formula unit in the unit cell (calculated density 1.78 g cm⁻³).

During the collection of the single crystal data it was found that the crystals are very unstable under the influence of X-rays and usually decompose within 30 min. Even if the crystals were coated with three layers of shellac they lasted a maximum of two days. Therefore a new crystal was used for each layer line during the collection of film data with a Weissenberg camera. Complete data were collected but in the course of the structure determination and refinement it became evident that the quality of the film data obtained was unsatisfactory because of decomposition of the crystals. New intensity data were therefore collected on a diffractometer.

Three crystals, with dimensions $0.076 \times 0.040 \times 0.040$ mm³, $0.066 \times 0.026 \times 0.026$ mm³, and $0.118 \times 0.017 \times 0.017$ mm³, respectively, were used in the data collection. The crystals were coated with shellac and three test reflections were used to check for possible decomposition during the data collection.

The X-ray intensity data were measured on a Philips PW 1100 computer controlled four circle diffractometer. Graphite monochromatized CuK radiation and a scintillation counter with pulse height discrimination were used. The $\theta - 2\theta$ scan technique was employed with a scan range of 1°. The background intensities were calculated as averages of the intensities at each end of the scan interval. All 1805 reflections with $\theta < 55°$ were measured, but only the 1238 reflections with $\sigma(I_{net})/I_{net} < 0.25$ were used for further data reduction. The net intensity, I_{net}, was calculated as $I_{tot} - I_{back}$ and its standard deviation, $\sigma(I_{net})$, was estimated as $(I_{tot} + I_{back})^{1/2}$ where I_{tot} and I_{back} are the number of counts for the total intensity and background intensity, respectively.

The data were corrected by application of Lorenz and polarization factors. Absorption correction was made by the method of Coppens et al. [6] The crystals were defined by eight faces, and the linear absorption coefficient, $\mu = 98.4$ cm⁻¹, was calculated from the mass absorption values given in the International Tables. [7]

After averaging of the intensities of symmetry related reflections the data were reduced to 404 independent reflections. However, a comparison of intensities measured on the three crystals revealed that a partial decomposition of the second crystal had taken place rather rapidly. This decomposition was not apparent from the test reflections chosen. The unreliable data obtained from crystal two were discarded, and the remaining 390 independent reflections measured on crystals one and three were used in the subsequent calculations.

Computer programs. All calculations were performed on the IBM 1800 and IBM 360/75 computers using the following programs:

PIRUM. Indexing of powder photographs and least squares refinement of unit cell parameters. Written by P.-E. Werner, Stockholm, Sweden.

DATAP1/DATAP2. Lp- and absorption corrections. Originally written by P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel. Modified by O. Olofsson and M. Elfström, Uppsala, Sweden, and by B. G. Brandt, S. Åsbrink and A. G. Nord, Stockholm, Sweden.

DRF. Fourier summations and structure factor calculations. Originally written by A. Zalkin, Berkeley, USA. Modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Further modified by O. Lindgren, Gothenburg, Sweden, and by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations. Originally written by A. Zalkin, Berkeley, USA, and modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

LALS. Full matrix least squares refinement. Originally written by P. K. Gentzel, R. A. Sparks and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, Berkeley, USA, and by J.-O. Lundgren, R. Liminga and C. I. Brändén, Uppsala, Sweden. Further modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

ORTEP. Crystal structure illustrations. Originally written by C. K. Johnson, Oak Ridge, USA. Modified by I. Carlbom and A. G. Nord, Stockholm, Sweden.

THE STRUCTURE DETERMINATION

The X-ray photographs showed trigonal symmetry and no systematically absent reflections were found. Among the several possible space groups, P$\bar{3}$ (No. 147) was chosen as a starting point for the structure determination. The position of the iron atom was chosen to be (0,0,0). A three-dimensional Patterson synthesis gave the position of the sulphur atom. The oxygen and nitrogen positions were found from a three-dimensional Fourier synthesis phased on the iron and sulphur atoms.

The structure was refined by the full matrix least squares technique. Atomic scattering factors [7] for neutral atoms were used except for iron which was taken as Fe^{3+}. With isotropic temperature factors the discrepancy index $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 10.2 %. At this stage the temperature factors were allowed to change anisotropically and the R-value was further reduced to 7.5 %. An inspection of the intensity data revealed that for about 31 weak reflections, F_o was several times higher than F_c. For these reflections a strong independent reflection with the same $\sin^2 \theta$ value could be found. It was therefore assumed that diffraction from crystalline powder on the crystals had caused the higher observed intensities for these reflections. An inspection of the Weissenberg photographs also showed the existence of faint powder lines. A least squares refinement with these reflections excluded gave a final R-value of 5.3 %. A weighting scheme $1/w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)$

Table 2. Fractional atomic coordinates with estimated standard deviations.

Atom	Position	x	y	z
Fe	1(a)	0	0	0
S	6(g)	0.7140(3)	0.6820(3)	0.1386(3)
O(1)	6(g)	0.5704(6)	0.6740(7)	0.2070(10)
O(2)	6(g)	0.7507(7)	0.5972(7)	0.2774(9)
O(3)	6(g)	0.8352(6)	0.8499(7)	0.1702(8)
N(1)	6(g)	0.6131(10)	0.9570(10)	0.3488(11)
N(2)	2(d)	1/3	2/3	−0.0117(20)
N(3)	1(b)	0	0	1/2

Table 3. Anisotropic thermal parameters and their standard deviations. The temperature factor is given by exp $\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]\}$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0056(3)	0.0056(3)	0.0086(10)	0.0055(3)	0	0
S	0.0042(3)	0.0060(4)	0.0089(7)	0.0038(6)	0.009(7)	−0.0004(7)
O(1)	0.0040(9)	0.0079(10)	0.0259(22)	0.0062(16)	0.0040(21)	0.0038(22)
O(2)	0.0099(11)	0.0097(10)	0.0208(19)	0.0121(18)	0.0043(22)	0.0087(23)
O(3)	0.0069(9)	0.0071(14)	0.0073(14)	0.0040(15)	0.0029(18)	0.0013(18)
N(1)	0.0103(14)	0.0165(16)	0.0129(19)	0.0196(27)	0.0039(27)	−0.0034(29)
N(2)	0.0039(10)	0.0039(10)	0.0214(41)	0.0048(20)	0	0
N(3)	0.0223(30)	0.0323(30)	0.0135(64)	0.0312(30)	0	0

Table 4. Observed and calculated structure factors of $(NH_4)_9[Fe(SO_3)_6]$. The reflections marked with one asterisk were rejected by the least squares refinement program and reflections marked with two asterisks were rejected before the refinement due to the decomposition of crystal two. F_o and F_c values listed in the table have been multiplied by 10.0.

(Reflections are listed in reading order: first column group top-to-bottom, then the next, etc. A dash (–) in the FO column indicates an unobserved value.)

H	K	L	FO	FC
1	1	-7	–	-52
2	1	-7	–	145**
1	2	-7	–	7
2	2	-7	120	120
1	1	-6	204	-188**
2	1	-6	–	-33
3	1	-6	212	131**
4	1	-6	–	-31
5	1	-6	–	23
1	2	-6	–	-44
2	2	-6	215	189**
3	2	-6	–	-40
4	2	-6	170	-163**
1	3	-6	158	185**
2	3	-6	–	219**
3	3	-6	–	83
1	4	-6	–	-95
2	4	-6	191	148**
1	5	-6	–	-23
2	5	-6	–	14
1	1	-5	–	-261**
2	1	-5	–	-90
3	1	-5	–	3
4	1	-5	–	5
5	1	-5	137	109
6	1	-5	–	-31
1	2	-5	190	168**
2	2	-5	–	94
3	2	-5	–	-182**
4	2	-5	216	167**
5	2	-5	141	142**
1	3	-5	130	270**
2	3	-5	–	-69
3	3	-5	–	97
4	3	-5	337	350
5	3	-5	–	20
1	4	-5	–	-9
2	4	-5	–	32
3	4	-5	235	221
4	4	-5	–	-24
1	5	-5	191	199**
2	5	-5	123	-20*
3	5	-5	293	315
1	6	-5	101	113
1	1	-4	143	83*
2	1	-4	198	-190
3	1	-4	–	55
4	1	-4	–	-14
5	1	-4	139	-136
6	1	-4	282	289
7	1	-4	379	368
1	2	-4	–	130**
2	2	-4	218	216
3	2	-4	168	170
4	2	-4	123	118
5	2	-4	113	96
6	2	-4	136	108**
1	3	-4	–	23
2	3	-4	233	232
3	3	-4	338	355
4	3	-4	186	172
5	3	-4	–	276**
6	3	-4	160	-129
1	4	-4	219	-221
2	4	-4	255	250
3	4	-4	126	54*
4	4	-4	239	239
5	4	-4	–	62
1	5	-4	170	123
2	5	-4	205	205
3	5	-4	252	240
4	5	-4	195	219
5	5	-4	142	126
1	6	-4	129	125
1	7	-4	–	–
1	1	-3	278	287
2	1	-3	496	491
3	1	-3	–	21
4	1	-3	348	350
5	1	-3	165	137
6	1	-3	358	-376
7	1	-3	–	98
8	1	-3	176	151
1	2	-3	283	253
2	2	-3	214	223
3	2	-3	–	130**
4	2	-3	421	413
5	2	-3	122	107
6	2	-3	134	155
7	2	-3	275	282
1	3	-3	–	121**
2	3	-3	–	48
3	3	-3	193	190
4	3	-3	–	68
5	3	-3	173	163
6	3	-3	191	193
1	4	-3	328	335
2	4	-3	164	-83*
3	4	-3	186	-167
4	4	-3	116	112
5	4	-3	135	43*
1	5	-3	169	157
2	5	-3	–	-38
3	5	-3	184	205
4	5	-3	377	377
1	6	-3	139	-37*
2	6	-3	–	65
3	6	-3	203	209
1	7	-3	127	101
2	7	-3	148	-123
1	8	-3	187	191
1	1	-2	1457	1489
2	1	-2	195	190
3	1	-2	393	392
4	1	-2	645	653
5	1	-2	253	249
6	1	-2	–	-65
7	1	-2	–	88
8	1	-2	190	193
1	2	-2	216	249
2	2	-2	143	154
3	2	-2	406	429
4	2	-2	386	388
5	2	-2	140	141
6	2	-2	157	122
7	2	-2	368	380
1	3	-2	249	239
2	3	-2	205	140
3	3	-2	187	185
4	3	-2	186	-160
5	3	-2	215	-239
6	3	-2	–	66
7	3	-2	–	23
1	4	-2	375	333
2	4	-2	146	66*
3	4	-2	222	221
4	4	-2	–	63
5	4	-2	143	55*
6	4	-2	–	12
1	5	-2	112	84
2	5	-2	136	100
3	5	-2	213	214
4	5	-2	295	305
5	5	-2	140	139
1	6	-2	130	-156
2	6	-2	206	-226
3	6	-2	146	138
4	6	-2	–	128
1	7	-2	138	40*
2	7	-2	169	173
1	8	-2	230	-184
1	1	-1	841	851
2	1	-1	145	48*
3	1	-1	181	171
4	1	-1	190	209
5	1	-1	215	240
6	1	-1	395	406
7	1	-1	179	186
8	1	-1	121	111
1	2	-1	401	410
2	2	-1	199	215
3	2	-1	144	162
4	2	-1	335	341
5	2	-1	–	72
6	2	-1	218	-222
7	2	-1	226	239
8	2	-1	147	168
1	3	-1	181	-177
2	3	-1	–	93
3	3	-1	199	201
4	3	-1	117	-31*
5	3	-1	453	-442
6	3	-1	–	30
7	3	-1	165	127
1	4	-1	230	245
2	4	-1	255	272
3	4	-1	181	161
4	4	-1	–	86
5	4	-1	–	80
6	4	-1	222	223
1	5	-1	373	365
2	5	-1	118	138
3	5	-1	175	99*
4	5	-1	–	82
5	5	-1	–	97
1	6	-1	197	-162
2	6	-1	171	-162
3	6	-1	185	172
4	6	-1	110	-65*
1	7	-1	–	79
2	7	-1	167	174
3	7	-1	287	277
1	8	-1	144	133
2	8	-1	126	134
1	0	0	456	456
2	0	0	–	56
3	0	0	981	1001
4	0	0	–	65
5	0	0	–	75
6	0	0	389	392
7	0	0	391	400
8	0	0	–	-34
9	0	0	–	53
1	1	0	259	-263
2	1	0	530	538
3	1	0	378	376
4	1	0	152	122
5	1	0	178	158
6	1	0	566	581
7	1	0	309	307
8	1	0	–	-25
1	2	0	217	122*
2	2	0	176	-181
3	2	0	148	-116
4	2	0	176	-24*
5	2	0	–	18
6	2	0	117	-87
7	2	0	165	-159
8	2	0	–	18
1	3	0	306	-257
2	3	0	109	-108
3	3	0	338	344
4	3	0	169	146
5	3	0	114	-81
6	3	0	–	74
7	3	0	122	120
1	4	0	325	338
2	4	0	500	515
3	4	0	304	304
4	4	0	126	119
5	4	0	117	78
6	4	0	352	348
1	5	0	224	196
2	5	0	166	151
3	5	0	–	-4
4	5	0	176	-196
5	5	0	147	142
1	6	0	202	-35*
2	6	0	192	185
3	6	0	147	168
4	6	0	134	-42*
1	7	0	130	58*
2	7	0	285	288
3	7	0	151	145
1	8	0	–	-76
2	8	0	196	190
0	0	1	805	834
1	0	1	305	311
2	0	1	139	129
3	0	1	268	227
4	0	1	203	-32*
5	0	1	251	252
6	0	1	306	307
7	0	1	220	225
8	0	1	227	213
9	0	1	152	158
0	1	1	265	244
1	1	1	488	-463
2	1	1	220	-192
3	1	1	363	385
4	1	1	–	134
5	1	1	146	-131
6	1	1	379	383
7	1	1	–	86
8	1	1	147	-166
0	2	1	190	-193
1	2	1	315	-315
2	2	1	161	-116
3	2	1	184	-155
4	2	1	431	-425
5	2	1	169	147
6	2	1	328	317
7	2	1	320	-340
8	2	1	–	7
0	3	1	601	634
1	3	1	271	296
2	3	1	325	-319
3	3	1	272	287
4	3	1	223	193
5	3	1	281	289
6	3	1	141	147
7	3	1	–	32
0	4	1	547	541
1	4	1	–	0
2	4	1	305	281
3	4	1	509	507
4	4	1	–	76
5	4	1	–	44
6	4	1	220	223
0	5	1	325	-331
1	5	1	174	-177
2	5	1	277	284
3	5	1	131	-89
4	5	1	138	-149
5	5	1	244	237
0	6	1	280	284
1	6	1	254	271
2	6	1	174	137
3	6	1	–	16
4	6	1	111	69*
0	7	1	281	280
1	7	1	–	103
2	7	1	256	236
3	7	1	–	58
0	8	1	274	-278
1	8	1	–	-54
2	8	1	192	185
0	9	1	–	-4
0	0	2	752	-720
1	0	2	152	166
2	0	2	281	300
3	0	2	288	271
4	0	2	353	360
5	0	2	392	391
6	0	2	236	235
7	0	2	–	15
8	0	2	278	288
9	0	2	160	162
0	1	2	136	130
1	1	2	367	-370
2	1	2	150	-142
3	1	2	172	-45*
4	1	2	215	-196
5	1	2	117	61*
6	1	2	159	-34*
7	1	2	–	-40
8	1	2	–	15
0	2	2	203	194
1	2	2	151	-149
2	2	2	655	662
3	2	2	165	-50*
4	2	2	222	-217
5	2	2	282	294
6	2	2	211	217
7	2	2	–	-75
0	3	2	246	221
1	3	2	463	485
2	3	2	461	457
3	3	2	286	288
4	3	2	255	267
5	3	2	500	488
6	3	2	196	203
7	3	2	–	-12
0	4	2	230	211
1	4	2	249	-244
2	4	2	110	-44*
3	4	2	115	60*
4	4	2	195	192
5	4	2	156	152
6	4	2	–	-24
0	5	2	253	-207
1	5	2	142	-128
2	5	2	268	282
3	5	2	175	-25*
4	5	2	–	50
5	5	2	–	82
0	6	2	–	52
1	6	2	464	475
2	6	2	182	181
3	6	2	–	-3
4	6	2	120	134
0	7	2	–	-104
1	7	2	141	161
2	7	2	–	-15
3	7	2	–	32
0	8	2	147	-126
1	8	2	–	13
0	0	3	396	-412
1	0	3	191	-177
2	0	3	126	125
3	0	3	103	108
4	0	3	–	74
5	0	3	316	321
6	0	3	–	-18
7	0	3	190	-185
8	0	3	253	262
0	1	3	179	-164
1	1	3	263	283
2	1	3	181	191

Table 4. Continued.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	1	3	169	-146	2	0	4	237	239	3	5	4	206	199	1	5	5	313	315
4	1	3	-	-39	3	0	4	244	-237	3	5	4	191	199	2	5	5	-	20
5	1	3	120	104	4	0	4	-	31	4	5	4	144	132	3	5	5	131	108
6	1	3	313	-318	5	0	4	121	87	0	6	4	-	-1	3	5	5	123	108
7	1	3	113	88	6	0	4	-	-116	1	6	4	-	-65	0	6	5	136	139
8	1	3	205	193	7	0	4	-	-32	2	6	4	-	75	1	6	5	-	-58
0	2	3	177	211	8	0	4	120	73*	3	6	4	159	150	0	0	6	467	457
1	2	3	98	-27*	0	1	4	-	-62	0	7	4	-	0	1	0	6	116	128
2	2	3	674	663	1	1	4	718	698	1	7	4	142	136	2	0	6	-	-45
3	2	3	301	258	2	1	4	225	190	0	8	4	228	229	3	0	6	274	279
4	2	3	140	133	3	1	4	-	49	0	0	5	-	106**	4	0	6	-	-3
5	2	3	267	272	4	1	4	446	454	1	0	5	139	155	5	0	6	-	-60
6	2	3	-	46	5	1	4	-	-17	2	0	5	138	132	0	1	6	282	282
7	2	3	130	117	6	1	4	195	-190	3	0	5	-	-6	1	1	6	291	301
0	3	3	107	-90	7	1	4	195	-190	4	0	5	-	8	2	1	6	167	177
1	3	3	213	203	8	1	4	119	118	5	0	5	-	-83	3	1	6	134	120
2	3	3	633	652	0	2	4	109	111	6	0	5	-	66	4	1	6	149	159
3	3	3	-	25	1	2	4	117	111	0	1	5	114	111	5	1	6	239	248
4	3	3	187	170	2	2	4	439	450	1	1	5	117	111	0	2	6	235	242
5	3	3	370	368	3	2	4	415	417	2	1	5	417	415	1	2	6	-	44
6	3	3	-	100	4	2	4	404	417	3	1	5	159	128	2	2	6	207	-227
0	4	3	167	-165	5	2	4	400	422	4	1	5	403	400	3	2	6	-	30
1	4	3	135	148	6	2	4	421	415	5	1	5	183	169	4	2	6	-	82
2	4	3	239	-226	7	2	4	162	174	6	1	5	-	21	0	3	6	242	217
3	4	3	231	-226	8	2	4	165	174	0	2	5	174	186	1	3	6	142	-139
4	4	3	265	-254	0	3	4	-	72	1	2	5	392	380	2	3	6	-	-84
5	4	3	212	217	1	3	4	181	-170	2	2	5	-	-27	3	3	6	176	177
6	4	3	146	123	2	3	4	181	-170	3	2	5	219	192	0	4	6	198	202
0	5	3	196	195	3	3	4	222	233	4	2	5	297	317	1	4	6	158	163
1	5	3	-	-51	4	3	4	146	105	5	2	5	-	-20	2	4	6	189	192
2	5	3	155	112	5	3	4	129	-95	0	3	5	-	34	0	5	6	169	183
3	5	3	157	143	6	3	4	-	63	1	3	5	-	2	1	5	6	167	147
4	5	3	-	18	7	3	4	-	19	2	3	5	127	-109	0	0	7	333	341
0	6	3	131	-98	0	4	4	128	-84*	3	3	5	-	64	1	0	7	174	111**
1	6	3	236	205	1	4	4	460	450	4	3	5	-	-78	2	0	7	-	-61
2	6	3	242	250	2	4	4	-	-57	5	3	5	152	-157	3	0	7	189	207
3	6	3	-	67	3	4	4	133	-125	5	3	5	156	-157	0	1	7	-	141**
0	7	3	146	-141	4	4	4	143	-125	0	4	5	-	-13	1	1	7	-	16
1	7	3	152	132	5	4	4	-	77	1	4	5	282	269	2	1	7	-	91**
2	7	3	125	-136	6	4	4	-	-15	2	4	5	143	161	0	2	7	-	10
0	8	3	142	126	0	5	4	349	333	3	4	5	-	-60	1	2	7	-	-82
1	8	3	119	-35*	1	5	4	222	236	4	4	5	-	59	0	3	7	-	217**
0	0	4	236	-240	2	5	4	235	236	0	5	5	256	258					
1	0	4	108	108	3	5	4	131	76*										

was used in the refinement, with coefficients $A = 3667.9$, $B = -140.45$, $C = 2.095$ and $D = -0.00558$.

Attempts were also made to refine the structure in space group $P3$ (No. 143). No improvement in R-value was obtained and the isotropic temperature factor for one of the nitrogen atoms became negative. Space group $P\bar{3}$ was therefore considered to be correct for the nonhydrogen atoms. Attempts to locate the hydrogen atoms from the difference Fourier maps were not successful, revealing definitely only the hydrogen atoms around the nitrogen atom at the $2(d)$ position $(1/3, 2/3, \pm z)$. The relatively high errors in F_o for the weak reflections may explain why it was not possible to locate the rest of the hydrogen atoms.

The final values of the atomic parameters and their standard deviations are presented in Tables 2 and 3. These values are based on a least squares refinement using atomic scattering factors for ammonium ion.[8] The observed and calculated structure factors are listed in Table 4.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $(NH_4)_9[Fe(SO_3)_6]$ can be described as being built of $Fe(SO_3)_6$ groups linked together by ammonium ions (*cf.* Fig. 1). The iron atom is octahedrally surrounded by six oxygen atoms, $O(3)$, belonging to six different sulphite groups. The FeO_6 octahedron thus formed is rather regular
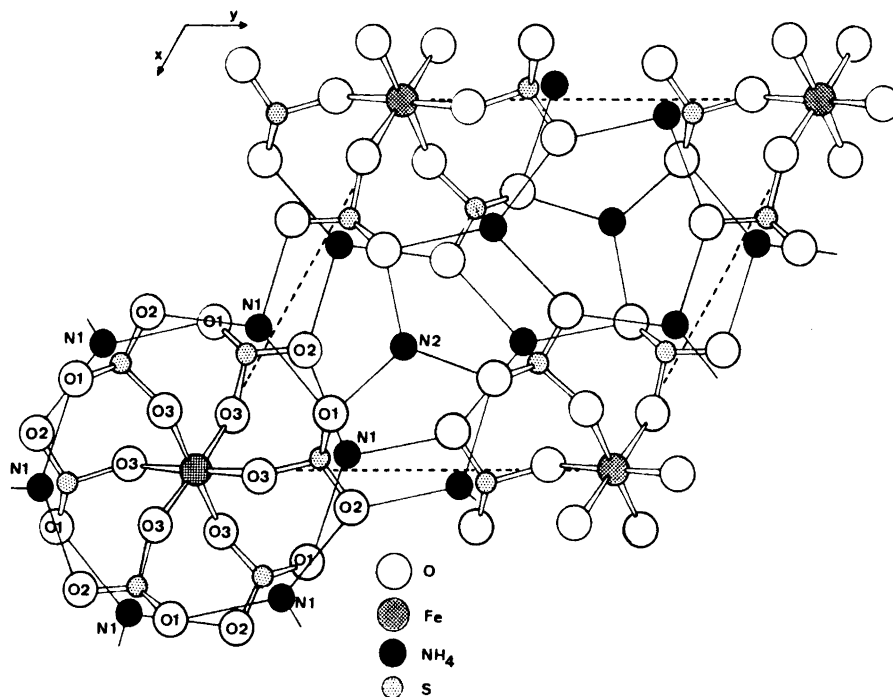
Fig. 1. The structure of $(NH_4)_9[Fe(SO_3)_6]$. The ammonium ions N(3) at position $(0,0,\frac{1}{2})$ are not shown in the figure. A possible hydrogen bond scheme is indicated by solid lines.

(*cf.* Table 5 for interatomic distances and angles), and the Fe−O distance is 2.028 Å. This value is in good agreement with Fe−O distances of 1.993 Å, 2.00 Å and 2.02 Å found for six-coordinated iron in $FeNH_4(SO_4)_3.3H_2O$,[9] $FeOHSO_4$,[10] and in $Na_3Fe_5O_9$,[11] as well as with the sum, 2.04 Å,[12] of the ionic radii of Fe^{3+} (0.64 Å) and O^{2-} (1.40 Å).

Table 5. Interatomic distances (Å) and angles (°) with their standard deviations. The distances are uncorrected for thermal motion.

Fe	−O(3)	2.028(6)	N(1)−O(2)	2.786(11)
	−S	3.257(2)	−O(1)	2.868(11)
S	−O(2)	1.488(7)	−O(1)	2.888(11)
	−O(1)	1.512(6)	−O(2)	2.893(11)
	−O(3)	1.551(6)	−O(3)	3.240(10)
O(1)−O(2)		2.391(9)	N(2)−O(1)	2.860(10)
−O(3)		2.401(8)	−O(2)	3.060(11)
O(2)−O(3)		2.404(9)	N(3)−O(3)	2.873(6)
O(1)−S−O(2)		105.7(4)		
O(1)−S−O(3)		103.2(3)		
O(2)−S−O(3)		104.5(4)		
O(3)−Fe−O(3)		87.2(2)		
O(3)−Fe−O(3)		92.8(2)		

The sulphite group coordinates to the iron atom through O(3) only. The difference between the length of the $S-O(3)$ bond 1.551 ± 0.006 Å and the average value, 1.500 Å, of the two other $S-O$ bond lengths (1.512(6) and 1.488(7) Å, respectively) is 0.051 Å, or eight times the standard deviation. If the sulphite oxygen atoms have metal ions as ligands, the $S-O$ bond will be longer than it is in the free anion. The O(1) and O(2) atoms have no metal ligands, and the corresponding average $S-O$ bond distance of 1.500 Å is in good agreement with the value of 1.504 Å found for the free anion.[13]

The effect exerted by the Fe^{3+} ion on the $S-O(3)$ bond is very pronounced due to the high polarizing power of the ferric ion. The same effect has been observed in $ZnSO_3.2\frac{1}{2}H_2O$ where the sulphite oxygen atoms have zinc ions as ligands and the $S-O$ mean distance is 1.54 Å.[14] In $Tl[Cu(SO_3)_2]$[15] close contacts exist between copper and two of the sulphite oxygen atoms. The $Cu-O$ distance is 1.99 Å, and the corresponding $S-O$ bond length is 1.550 ± 0.005 Å. The third $S-O$ bond length is 1.515 ± 0.006 Å, so that there is a difference between the two bonds lengths of 6σ.

The ammonium ions may form hydrogen bonds between the $Fe(SO_3)_6$ groups as well as within the groups. A possible hydrogen bond scheme is indicated in Fig. 1. The ammonium ion N(3) in position $(0,0,\frac{1}{2})$ is situated inside a distorted octahedron. There are six $N-O$ distances of equal length, and thus the ammonium ion might have several equivalent orientations.

The average distances in the sulphite group, i.e. the $S-O$ distance (1.517 Å) and the $O-O$ distance (2.399 Å) are approximately the same as in other sulphites of type $SO_3{}^{2-}\cdots X$, where X is nitrogen, oxygen, and/or metal ion. In $(NH_4)_2SO_3.2H_2O$ the $S-O$ and $O-O$ distances are 1.524 Å and 2.408 Å.[16] The average $O\cdots(H)-N$ distances in $(NH_4)_9[Fe(SO_3)_6]$ are 2.872 Å, 2.913 Å, and 3.057 Å for O(1), O(2), and O(3), respectively; and in $(NH_4)_2SO_3.2H_2O$, the corresponding values are 2.85 Å, 2.83 Å, and 2.84 Å.

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