of a large portion of the molecule. The least-squares plane $0{\cdot}5030X+0{\cdot}4808Y+0{\cdot}7182Z=5{\cdot}934$, calculated including the dinitrobenzoate group and the bridgehead carbon atoms (17 atoms out of 23) has only three atoms with deviation of 0·2 Å from the plane, but no others more than 0·1 Å from the plane; the coefficients in the above equation are the direction cosines of the normal to the plane relative to **a**, **b** and **c***.

The structure contains no unusually short intermolecular contact distances. Fig. 4 shows a stereoscopic drawing of a packing diagram. The direction of view is approximately along the y axis, with the x axis across the Figure. The box indicates the volume of one unit cell ($0 \leq x \leq a$, $0 \leq y \leq b$, $0 \leq z \leq c$); the sixteen molecules which extend into this unit cell are shown.

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The Crystal Structure of Zinc Guanidinium Sulfate

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The crystal structure of zinc guanidinium sulfate, $Zn[C(NH_2)_3]_2(SO_4)_2$, has been determined by a three-dimensional X-ray analysis. The crystals are tetragonal, space group $I\bar{4}2d$, with cell dimensions of $a=9{\cdot}515$ and $c=14{\cdot}351$ Å. There are four formula units in the unit cell, with density calculated to be 1·929 g.cm^{-3} in agreement with the measured density (1·93 g.cm^{-3}). The structure has been determined by Patterson and Fourier methods from 741 reflections collected by counter and refined by least-squares to a conventional R index of 0·017. A network of zinc and sulfate ions constitutes the main feature of the structure; the sulfate ions are arranged tetrahedrally around the zinc ions with the Zn–O distance being 1·94 Å. The sulfate ion, on a twofold axis, has one pair of oxygen atoms coordinated to zinc ions, resulting in an S–O bond distance of 1·49 Å, which is significantly longer than the S–O distance of 1·44 Å for the second pair of sulfate oxygen atoms.

Introduction

The synthesis of a series of hexahydrated double salts between guanidinium sulfate and bivalent metal sulfates was reported by Canneri (1925). It was of interest to investigate the metal ion coordination in the bivalent metal guanidinium sulfate hexahydrates (M(II)GSH from here on), $M(II)[C(NH_2)_3]_2(SO_4)_2.6H_2O$, for comparison with the ammonium Tutton salts, $M(II)(NH_4)_2(SO_4)_2.6H_2O$, which have been studied extensively (see Montgomery, Chastain, Natt, Witkowska & Lingafelter, 1967). In an attempt to prepare ZnGSH by room temperature evaporation of the aqueous solution of the mixed salts, crystals were obtained which appeared to be monoclinic as reported for M(II)GSH (Canneri, 1925). Although there was no evidence to indicate that these crystals were the desired complex, the structure determination by X-ray diffraction was undertaken. Later the crystal was identified as tetragonal and anhydrous instead of monoclinic and hexahydrate. Efforts to prepare crystals of ZnGSH in this laboratory have been so far unsuccessful; however we have since then been able to prepare NiGSH and solve its structure (Morimoto & Lingafelter, paper in preparation). This paper reports the structure determination of anhydrous zinc guanidinium sulfate.

Experimental

The crystals, later identified as zinc guanidinium sulfate, $Zn[C(NH_2)_3]_2(SO_4)_2$, (analysis: Zn, 0·1725 found, 0·1731 calculated; N, 0·218 found, 0·2225 calculated) were obtained by the method described by Canneri (1925) for the series of M(II)GSH. Stoichiometric (1:1) proportions of $[C(NH_2)_3]_2SO_4$ and $ZnSO_4.7H_2O$ were dissolved in a minimum amount of water and the resulting aqueous solution, left to evaporate at room temperature, produced colorless crystals with rather poorly developed faces. Identical crystals were obtained at several temperatures between 0 and 60°C. Although the crystals were later recognized to be tetragonal, bounded by $\{1\ 0\ 1\}$, and often elongated along $[1\ 1\ 1]$, the tetragonal symmetry was not apparent. One of the elongated crystals was mounted for rotation about the elongation direction, and a set of oscillation and equi-inclination Weissenberg photographs were taken. These suggested that the axis of rotation was the *c* axis of a monoclinic crystal with space group *Ic* or *I*2/*c* (*i.e.* *hkl* absent for $h+k+l$ odd and *h*0*l* absent for *l* odd) and cell dimensions $a=9·84$, $b=13·45$, $c=9·84$ Å, $\beta=93·7°$. The Donnay–Takeda program (Stewart, 1964) for carrying out the Delaunay reduction indicated this cell to be the reduced monoclinic cell. (Later we found that this program, given the triclinic primitive cell, reduced it to a primitive cell with $a=9·52$, $b=9·84$, $c=9·52$ Å, $\alpha=118·9$, $\beta=90·0$ and $\gamma=118·9°$. We now recognize that the relationships, $a=c$, $\alpha=\gamma$, $\beta=\pi/2$, and $2b=a|\cos\alpha|$ suggest a body-centered tetragonal lattice.)

Another crystal, having dimensions of 0·41 × 0·20 × 0·28 mm in the directions normal to (1 0 1), (0 1 1), and $(0\ 1\ \bar{1})$, respectively (tetragonal indices), was mounted in the same manner, but tilted so that the rotation axis was the monoclinic *c** axis, and used for data collection on a Picker automated four-angle diffractometer, with Mo-target tube ($\lambda=0·71069$ Å for $K\alpha$) set for a take-off angle of 3·5°, and equipped with a scintillation counter and pulse-height discriminator. The radiation was filtered through 0·001 inch niobium foil. Bragg angles were measured for 18 reflections using the $+2\theta$, -2θ technique, and cell dimensions calculated by least squares. The final cell dimensions are:

Monoclinic	Tetragonal
$a=9·838(2)$ Å	$a=9·515(1)$ Å
$b=13·454(2)$	$c=14·351(3)$
$c=9·836(2)$	
$\beta=93·68(2)°$	
$V=1299·1$ Å^3	$V=1299·7$ Å^3
$Z=4$	$Z=4$
$d_{\text{calc}}=1·929$ g.cm^{-3}	$d_{\text{obs}}=1·93(1)$ g.cm^{-3}

Transformation of the monoclinic cell axes into the tetragonal set is accomplished by

$$\begin{pmatrix} \mathbf{a}_t \\ \mathbf{b}_t \\ \mathbf{c}_t \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_m \\ \mathbf{b}_m \\ \mathbf{c}_m \end{pmatrix}.$$

Assuming the crystal to be monoclinic, intensity data were collected by the ω–2θ scan method (Furnas, 1957) with scan speed of two degrees per minute using Nb-filtered Mo $K\alpha$ ($\lambda=0·71069$ Å) radiation. A scan range for each reflection was calculated by the formula (Alexander & Smith, 1964) scan range $=(0·9+1·0\times\tan\theta)$ degrees. Background counts were obtained from the sum of two counts, taken at the beginning and end of

Table 1. *Positional parameters* (× 10^4) *and thermal parameters* (× 10^2) *with estimated standard deviations in parentheses**

Anisotropic thermal parameters are of the form $\exp\,[(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0	0	0	119 (2)	119 (2)	143 (1)	0	0	0
S	−306 (1)	2500	1250	117 (2)	133 (2)	165 (2)	0	0	−30 (2)
O(1)	647 (1)	1684 (1)	636 (1)	183 (5)	270 (6)	320 (6)	−44 (5)	78 (5)	−192 (5)
O(2)	−1168 (2)	1557 (2)	1788 (1)	445 (9)	329 (8)	448 (8)	−128 (7)	250 (7)	−1 (7)
C	2500	52 (3)	3750	430 (14)	185 (9)	284 (10)	0	−100 (11)	0
N(1)	2500	−1333 (3)	3750	682 (20)	173 (9)	410 (14)	0	−218 (16)	0
N(2)	3150 (3)	734 (3)	4422 (2)	832 (18)	235 (9)	462 (12)	2 (10)	−353 (12)	−55 (8)

Hydrogen positional parameters (× 10^3) and isotropic thermal parameters (× 10)

	x/a	y/b	z/c	B
H(11)	293 (4)	−175 (4)	423 (3)	58 (9)
H(21)	321 (4)	159 (5)	435 (3)	74 (13)
H(22)	349 (3)	25 (3)	491 (2)	54 (7)

* Those parameters without standard deviations are fixed by symmetry.

the scan range with the instrument stationary, and corrected for the time factor. A total of 1474 reflections were examined, out to $2\theta = 55°$. Reflections with intensities (I) less than two times their empirical standard deviations [$\sigma(I)$] were considered unobserved and assigned intensities of $I + 2\sigma(I)$. The intensities of the observed reflections ranged from 1 to 11000. A set of four standard reflections was remeasured periodically and was used to normalize the intensities to a common basis, correcting for any systematic change in the instrument or the crystal. The normalization factor was essentially constant with time, with an overall

Table 2. *Observed and calculated structure factors* (*corrected for dispersion*)

Columns are h, $10F_o$, $10|F_c|$, and phase angle in millicycles. Unobserved reflections are marked * and those assumed affected by secondary extinction with an E.

H,0,0			
2	643	634	14
4	867	897	12
6	691	673	11
8	694	687	12
10	60	37	796
12	460	461	13
H,1,0			
3	387	375	2
5	360	356	2
7	152	143	8
9	145	135	5
11	246	243	3
H,2,0			
2	795	811	991
4	1056	1074	8
6	554	550	12
8	728	723	11
10	273	274	23
12	533	549	12
H,3,0			
5	493	484	3
7	165	156	2
9	293	299	4
11	44	50	5
H,4,0			
4	1444E	1551	6
6	572	562	13
8	756	757	10
10	241	234	24
H,5,0			
7	696	736	2
9	49	36	995
11	133	127	10
H,6,0			
6	125	102	932
8	419	426	16
10	277	243	21
H,7,0			
9	266	272	5
H,8,0			
8	502	516	12
H,0,1			
1	1325E	1531	130
3	816	803	134
5	641	642	135
7	358	351	142
9	227	226	147
11	133	142	153
H,1,1			
2	681	672	957
-2	639	646	807
4	663	654	796
-4	713	716	968
6	563	536	829
-6	587	568	935
8	621	614	981
-8	585	573	788
10	385	346	117
-10	337	337	138
12	430	448	960
-12	474	430	821
H,2,1			
3	163	156	108
-3	172	172	206
5	583	563	192
-5	559	550	76
7	522	520	63
-7	548	545	205
9	436	433	197
-9	411	412	75
11	393	382	105
-11	392	391	169
H,3,1			
4	885	899	851
-4	887	906	914
6	337	337	777
-6	374	367	907
8	670	655	833
-8	697	677	734
10	274	286	243
-10	308	318	27
H,4,1			
5	881	885	199
-5	856	860	64
7	525	517	20
-7	559	553	239
9	273	268	753
-9	245	235	28
11	149	148	79
-11	163	163	218
H,5,1			
6	419	415	89
-6	362	358	171
8	428	431	980
-8	397	402	794
10	216	217	939
-10	208	213	848
H,6,1			
7	396	402	26
-7	429	432	244
9	353	359	207
-9	340	343	68
H,7,1			
8	286	293	792
-8	311	319	987
10	204	210	841
-10	218	214	946
H,8,1			
9	261	262	218
-9	245	246	62
H,0,2			
2	2009E	2561	750
4	383	374	750
6	29*	3	25
8	220	215	754
10	236	210	752
12	296	300	754
H,1,2			
1	891	908	69
-1	875	871	951
3	1267E	1308	54
-3	1217E	1279	959
5	882	868	36
-5	869	865	984
7	620	618	66
-7	591	595	959
9	492	483	103
-9	458	447	925
11	410	407	78
-11	383	382	952
H,2,2			
4	941	911	74
-4	942	932	927
6	88	86	799
-6	88	84	213
8	316	316	949
-8	316	309	155
10	294	290	753
-10	293	290	754
12	83	80	822
-12	86	80	180
H,3,2			
3	579	598	936
-3	621	636	90
5	733	725	949
-5	770	761	71
7	787	790	917
-7	828	827	100
9	466	468	0
-9	473	470	29
11	392	407	934
-11	425	432	93
H,4,2			
6	623	609	228
-6	622	610	775
8	91	82	827
-8	87	79	196
10	118	111	765
-10	110	107	54
H,5,2			
5	1078	1102	149
-5	1010	1016	862
7	509	513	23
-7	502	507	5
9	479	479	120
-9	439	442	906
11	261	266	73
-11	264	266	70
H,6,2			
8	239	233	234
-8	232	233	768
10	63	67	760
-10	60	67	757
H,7,2			
7	547	560	353
-7	606	620	164
9	341	341	28
-9	338	336	7
H,0,3			
1	472	500	385
5	761	752	882
7	441	433	847
9	359	361	949
11	474	416	886
H,1,3			
2	1160E	1202	147
-2	1114E	1138	114
4	729	698	173
-4	707	671	31
6	500	492	174
-6	494	485	104
8	221	213	843
-8	171	153	920
10	553	555	236
-10	526	522	34
12	164	163	798
-12	119	131	383
H,2,3			
3	833	822	765
-3	868	890	998
5	846	834	913
-5	824	823	852
7	403	391	850
-7	416	404	928
9	199	198	993
-9	168	166	802
11	182	189	936
-11	198	201	752
H,3,3			
4	92	88	127
-4	98	101	233
6	897	900	113
-6	896	897	151
8	565	569	13
-8	600	596	249
10	468	481	94
-10	482	488	177
H,4,3			
5	434	425	18
-5	381	382	741
7	521	525	815
-7	541	544	952
9	371	369	956
-9	355	350	819
11	282	292	851
-11	293	300	929
H,5,3			
6	532	525	227
-6	495	474	44
8	220	215	808
-8	177	172	972
10	297	294	716
-10	285	275	66
H,6,3			
7	393	393	776
-7	421	427	995
9	264	258	947
-9	253	247	836
H,7,3			
8	234	242	62
-8	257	260	221
H,8,3			
9	364	362	960
-9	341	346	812
H,0,4			
0	807	801	991
2	1155E	1269	7
4	284	251	27
6	805	793	11
8	71	70	99
10	684	687	11
12	230	222	25
H,1,4			
3	70	81	995
-3	76	82	25
5	352	338	983
-5	348	340	50
7	299	300	24
-7	296	298	983
9	184	185	31
-9	195	183	976
11	197	200	50
-11	196	197	987
H,2,4			
2	1953E	2319	889
-2	1974E	2417	118
4	646	634	25
-4	622	624	998
6	1185	1195	7
-6	1185	1196	8
8	375	370	980
-8	396	389	53
10	554	558	56
-10	534	533	968
H,3,4			
5	508	490	934
-5	499	498	70
7	188	180	23
-7	194	179	981
9	321	329	93
-9	318	319	907
11	61	61	19
-11	45	61	988
H,4,4			
4	701	774	714
-4	706	691	789
6	619	609	17
-6	605	606	9
8	243	240	922
-8	288	288	117
10	435	496	12
-10	493	497	17
H,5,4			
7	480	474	25
-7	473	471	991
9	36*	14	236
-9	49*	12	762
H,6,4			
6	753	758	993
-6	757	770	30
8	346	349	12
-8	341	351	23
10	333	329	24
-10	324	321	2
H,7,4			
9	311	308	931
-9	310	317	77
H,8,4			
8	277	286	63
-8	265	267	979
H,0,5			
1	405	392	138
3	520	519	135
5	222	191	153
7	465	463	135
9	464	460	136
11	241	240	144
H,1,5			
2	951	937	753
-2	1006	1051	7
4	287	295	765
-4	327	331	9
6	825	814	842
-6	829	824	923
8	440	445	240
-8	483	479	24
10	452	455	846
-10	465	462	927
H,2,5			
3	1105	1117	133
-3	1082	1121	128
5	543	539	85
-5	560	560	187
7	337	325	201
-7	312	305	82
9	295	276	107
-9	309	304	173
11	139	131	226
-11	115	113	81
H,3,5			
4	630	604	19
-4	571	562	244
6	575	564	975
-6	531	531	795
8	149	140	758
-8	109	100	939
10	393	389	977
-10	373	362	798
H,4,5			
5	362	362	75
-5	378	378	201
7	372	361	177
-7	352	355	100
9	395	396	117
-9	393	397	157
11	280	289	189
-11	281	279	92
H,5,5			
6	573	568	845
-6	574	575	924
8	337	341	800
-8	353	360	972
10	347	349	816
-10	356	366	958
H,6,5			
7	271	265	178
-7	259	261	110
9	157	160	6
-9	197	195	781
H,7,5			
8	384	378	977
-8	356	358	794
H,0,6			
2	331	355	796
4	254	250	751
6	1007	1005	751
8	135	140	755
10	162	164	753
H,1,6			
1	1028	1036	43
-1	971	1005	972
3	603	617	1
-3	602	620	26
5	710	712	919
-5	752	757	100
7	687	673	928
-7	717	711	91
9	512	513	565
-9	534	537	90
11	292	298	969
-11	314	315	68
H,2,6			
4	901	874	138
-4	901	889	856
6	98	93	772
-6	99	83	235
8	520	494	817
-8	452	490	185
10	152	136	763
-10	198	195	247
H,3,6			
3	1136	1152	22
-3	1117	1146	975
5	703	696	48
-5	670	677	974
7	527	511	137
-7	457	459	888
9	401	397	58
-9	374	379	975
11	378	373	132
-11	345	337	906
H,4,6			
6	240	237	774
-6	237	234	230
8	105	97	856
-8	105	92	154
10	114	113	841
-10	111	110	142
H,5,6			
5	631	644	514
-5	672	692	107
7	436	424	6
-7	429	426	26
9	437	444	507
-9	473	443	117
H,6,6			
8	70	62	136
-8	63	64	170
H,7,6			
7	571	573	98
-7	553	542	524
9	285	283	16
-9	280	285	25
H,0,7			
1	562	567	867
3	755	773	883
5	710	729	893
7	275	298	837
9	251	241	894
11	141	139	901
H,1,7			
2	466	454	45
-2	491	443	223
4	317	339	56
-4	346	371	227
6	380	388	934
-6	431	439	826
8	615	598	32
-8	622	626	177
10	168	170	73
-10	186	182	219
H,2,7			
3	586	573	28
-3	535	526	233
5	321	322	816
-5	347	346	961
7	344	331	893
-7	336	334	886
9	401	400	822
-9	397	392	901
11	244	251	976
-11	240	242	647
H,3,7			
4	784	772	165
-4	753	762	97
6	230	141	779
-6	148	141	932
8	456	443	236
-8	410	412	39
10	193	186	792
-10	158	154	930
H,4,7			
5	434	422	846
-5	417	424	512
7	216	209	908
-7	217	212	871
9	214	222	843
-9	231	232	944
H,5,7			
6	331	335	124
-6	326	329	152
8	417	407	64
-8	433	426	209
10	177	186	968
-10	214	223	821
H,6,7			
7	375	366	974
-7	362	364	850
9	266	263	874
-9	276	273	956
H,7,7			
8	325	316	210
-8	301	300	47
H,0,8			
0	418	428	25
2	667	673	12
4	1537E	1672	6
6	347	352	10
8	965	956	8
10	189	180	24
H,1,8			
3	63	67	937
-3	74	72	82
5	319	320	999
-5	316	319	4
7	394	390	13
-7	390	390	991
9	145	150	27
-9	154	148	991
11	109	102	968
-11	95	105	45
H,2,8			
2	407	398	116
-2	345	350	911
4	728	742	1
-4	728	748	20
6	169	160	35
-6	209	213	855
8	535	535	30
-8	521	525	998
10	212	214	64
-10	205	206	9
H,3,8			
5	376	375	6
-5	372	375	0
7	151	141	15
-7	147	140	930
9	227	227	32
-9	225	225	978
H,4,8			
4	767	766	31
-4	750	749	992
6	468	455	14
-6	458	456	15
8	545	546	16
-8	538	542	10
10	104	117	34
-10	108	121	51
H,5,8			
7	249	225	24
-7	243	228	999
9	60*	29	345
-9	46*	30	142
H,6,8			
6	427	427	3
-6	420	433	24
8	403	396	20
-8	390	394	12
H,0,9			
1	369	370	143
3	852	875	132
5	475	476	137
7	381	394	138
9	186	171	150
H,1,9			
2	472	461	940
-2	431	432	737
4	816	828	751
-4	793	802	914
6	337	322	132
-6	286	270	157
8	495	487	357
-8	467	471	825
10	199	193	744
-10	182	188	942
H,2,9			
3	336	334	42
-3	361	364	331
5	142	157	222
-5	150	146	86
7	404	399	117
-7	406	403	154
9	298	300	173
-9	296	293	110
H,3,9			
4	555	570	439
-4	570	586	332
6	203	209	730
-6	233	234	395
8	474	415	913
-8	468	435	960
10	100	101	185
-10	134	141	92
H,4,9			
5	395	379	159
-5	393	378	123
7	254	254	132
-7	249	250	155
9	188	195	217
-9	169	178	74
H,5,9			
6	318	309	313
-6	303	312	864
8	404	395	937
-8	386	385	437
H,6,9			
7	237	235	111
-7	241	238	174
H,7,9			
8	242	234	766
-8	270	264	12
H,0,10			
2	441	436	754
4	182	192	751
6	723	736	751
8	148	145	755
10	62	48	759
H,1,10			
1	651	646	987
-1	668	656	36
3	584	582	29
-3	572	577	337
5	643	647	171
-5	591	597	393
7	495	490	99
-7	454	454	977
9	395	404	65
-9	390	391	954
H,2,10			
4	619	635	924
-4	613	626	179
6	125	124	226
-6	125	125	790
8	276	269	204
-8	278	271	930
10	148	141	755
-10	144	141	757
H,3,10			
3	641	656	349
-3	654	680	73
5	437	500	995
-5	498	513	42
7	487	479	919
-7	508	512	106
9	277	265	987
-9	285	277	56
H,4,10			
6	147	144	899
-6	142	144	118
8	78	83	758
-8	86	83	754
H,5,10			
5	451	446	101
-5	431	418	928
7	376	366	23
-7	364	365	10
9	451	442	133
-9	401	404	990
H,6,10			
8	86	87	197
-8	85	87	810
H,7,10			
7	350	355	992
-7	388	393	135
H,0,11			
1	320	312	889
3	307	312	889
5	22	29	138
7	362	356	887
9	225	302	889
H,1,11			
2	530	493	187
-2	472	473	98
4	337	321	780
-4	131	185	1
6	566	570	190
-6	556	555	79
8	261	253	760
-8	233	236	14
H,2,11			
3	657	687	880
-3	678	684	886
5	386	394	944
-5	371	374	833
7	285	249	834
-7	301	306	946
9	195	196	968
-9	127	183	841
H,3,11			
4	249	257	38
-4	280	283	239
6	352	361	82
-6	360	375	196
8	68	73	911
-8	114	117	966
H,4,11			
5	241	247	910
-5	240	244	975
7	237	239	860
-7	251	243	335
9	231	223	263
-9	261	257	815
H,5,11			
6	376	353	151
-6	355	356	126
8	302	305	272
-8	270	276	997
H,6,11			
7	225	220	928
-7	235	234	958
H,0,12			
0	45	34	757
2	560	569	13
4	137	138	959
6	573	572	12
8	172	176	29
H,1,12			
3	139	133	35
-3	141	137	974
5	201	236	21
-5	208	204	983
7	228	224	993
-7	232	226	15
9	60	69	961
-9	68	61	57
H,2,12			
2	1131	1130	47
-2	1076	1095	957
4	360	373	27
-4	362	365	0
6	642	657	14
-6	639	656	8
8	218	213	50
-8	176	202	399
H,3,12			
5	248	207	51
-5	206	204	955
7	73	75	932
-7	77	77	75
H,4,12			
4	316	323	868
-4	355	377	150
6	360	367	6
-6	367	373	29
8	216	216	132
-8	172	174	998
H,5,12			
7	268	267	981
-7	267	270	27
H,6,12			
6	476	466	20
-6	467	459	7
H,0,13			
1	260	258	141
3	35	29	792
5	265	264	142
7	240	251	141
H,1,13			
2	518	509	896
-2	530	501	878
4	202	209	793
-4	232	221	980
6	358	361	838
-6	375	373	940
8	96	97	245
-8	130	126	49
H,2,13			
3	438	434	196
-3	415	412	78
5	418	422	104
-5	435	431	169
7	235	239	199
-7	222	223	86
H,3,13			
4	125	121	914
-4	131	134	899
6	403	396	914
-6	402	394	860
8	300	302	16
-8	272	277	757
H,4,13			
5	182	186	58
-5	205	203	220
7	265	268	237
-7	242	246	19
H,5,13			
6	272	277	816
-6	291	295	963
H,0,14			
2	628	613	752
4	106	93	752
6	139	145	757
8	126	119	755
H,1,14			
1	421	411	5
-1	422	413	27
3	441	440	987
-3	446	450	41
5	407	411	938
-5	440	438	89
7	271	276	965
-7	288	293	73
H,2,14			
4	332	337	827
-4	325	329	179
6	93	90	174
-6	91	87	834
H,3,14			
3	345	334	139
-3	301	300	927
5	339	344	47
-5	335	332	789
7	429	423	104
-7	401	396	971
H,4,14			
6	214	209	219
-6	209	202	797
H,5,14			
5	379	382	898
-5	413	413	127
H,0,15			
1	456	451	886
3	392	389	887
5	286	283	891
7	160	164	899
H,1,15			
2	150	152	70
-2	168	170	221
4	358	358	135
-4	352	357	142
6	128	127	82
-6	144	138	218
H,2,15			
3	80	80	931
-3	75	81	911
5	170	171	819
-5	192	190	969
H,3,15			
4	332	336	192
-4	325	322	85
6	187	186	756
-6	164	165	27
H,4,15			
5	324	316	817
-5	340	334	958
H,0,16			
0	1001	998	7
2	313	317	18
4	517	520	13
6	198	200	25
H,1,16			
3	92	89	26
-3	85	89	385
5	96	93	13
-5	89	93	994
H,2,16			
2	98	76	76
-2	118	115	850
4	334	327	15
-4	332	328	20
H,3,16			
5	188	182	18
-5	188	182	992
H,4,16			
4	513	496	994
-4	512	504	31
H,0,17			
1	398	384	137
3	287	287	140
H,1,17			
2	97	93	962
-2	85	83	861
4	272	273	328
-4	269	266	855
H,2,17			
3	95	103	39
-3	127	128	757
H,0,18			
2	334	336	753
H,1,18			
1	291	283	40
-1	282	277	987

variation of 1·1% in intensity. The intensities were corrected for coincidence loss (6×10^{-8} count^{-1}) and for Lorentz and polarization factors but not for absorption ($\mu=23$ cm^{-1}). Empirical standard deviations of the intensities were calculated by the relationship $\sigma(I)^2=\sigma^2+(kC_T)^2$, where σ is the standard deviation in intensity due to counting statistics, C_T is total counts, and k is a stability constant, set at 0·01 for the present data from examination of the variance of the standard reflections.

Determination and refinement of the structure

All calculations were carried out on an IBM 7040/7094 DCS using programs adapted or developed at the University of Washington (Stewart, 1964). Scattering factors for Zn, S, O, C, and N atoms were taken from Doyle & Turner (1968) and for H from Table II of Stewart, Davidson & Simpson (1965). Dispersion corrections were not applied in the early refinements but were included for the final tetragonal refinement cycles.

The structure was solved on the basis of the monoclinic cell, using 1474 measured intensities. A three-dimensional Patterson synthesis and Fourier syntheses were used to determine the structure in the space group *Ic*. The refinement of the structure was carried out by the full-matrix least-squares method to a conventional R of 0·022, where $R=\sum||F_o|-|F_c||/\sum|F_o|$, excluding unobserved reflections and reflections which were considered affected by secondary extinction.

During the examination of the structure, it was noticed that the structure conformed almost exactly to the tetragonal space group $I\bar{4}2d$. This led us to examine the correlation coefficients. Correlation coefficients between parameters of atoms related by the tetragonal symmetry ranged from below 0·1 to 0·64, so that the monoclinic matrix was at no time near to singularity. The original 1474 reflections were then reduced to a unique set of tetragonal reflections by taking weighted averages of intensities of symmetry-equivalent reflections using $1/\sigma(I)^2$ as the weights, and the systematic absences corresponding to $I\bar{4}2d$ were found. A substantial number of these pairs of equivalent reflections were noticed to differ by more than five times the standard deviation in intensities, and all of these large differences could be accounted for on the basis of anomalous dispersion effects. Therefore, 741 reflections (including 5 reflections which were considered unobserved), making up a complete octant of the limiting sphere to $2\theta=55°$, were considered and dispersion corrections were applied, with $\Delta f'=0·3$ and 0·1 and $\Delta f''=1·5$ and 0·2 for zinc and sulfur respectively.

The refinement of the structure was reinitiated from the atom parameters (with isotropic temperature factors) of the monoclinic refinement, and was carried out by the full-matrix least-squares method. The function minimized was $\sum w(F_o-F_c)^2$, first with $w=1$ and then with $\sqrt{w}=1/\sigma(F)$. Using individual isotropic temperature factors, refinement of the structure proceeded from $R=0·070$ to $R=0·058$ in one cycle. A plot of $\ln(F_o/F_c)$ *vs.* I_c (Housty & Clastre, 1957) was made which disclosed 11 reflections possibly suffering from large secondary extinction effects, and these reflections were given zero weights in subsequent refinements. Anisotropic temperature factors of the form,

$$\exp\left\{-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}\,h_i\,h_j\,a_i^*\,a_j^*\right\},$$

were assigned, and two successive cycles of refinement reduced R to 0·024. Hydrogen atoms were located on a difference Fourier synthesis and were refined isotropically. Refinement was continued with all $w=1$ on all atoms to $R=0·019$ and was followed by three final cycles with $\sqrt{w}=1/\sigma(F)$.

The final R values were $R=0·017$ and weighted $R=0·020$ with the standard deviation of an observation of unit weight, $\{\sum w(F_o-F_c)^2/(n-p)\}^{1/2}$, of 2·70, where n and p are the number of observed reflections and of parameters respectively. During the last cycle of refinement, the average and maximum parameter shifts were $0·105\sigma$ and $0·768\sigma$ respectively. The final atom parameters are listed in Table 1. A three-dimensional difference Fourier synthesis, calculated at the

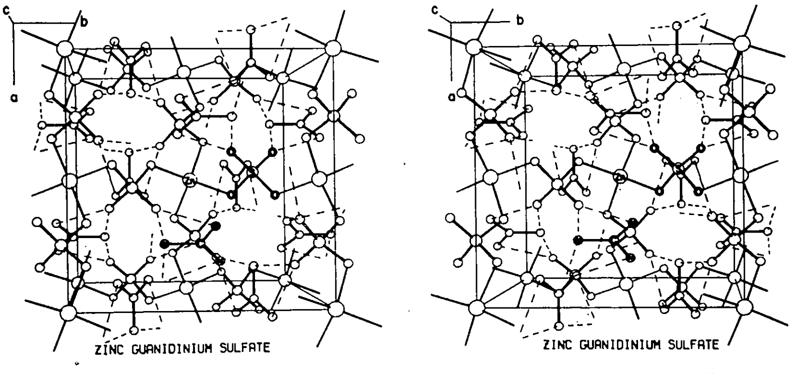

Fig. 1. A stereoscopic pair of drawings of the unit cell viewed along the *c* axis. Dashed lines represent hydrogen bonds.

conclusion of the refinement, showed no region of density greater than 0·33 e.Å^{-3} or less than −0·38 e.Å^{-3} (with 0·16 e.Å^{-3} the estimated error in electron density). The final structure factors are given in Table 2.

Discussion

The structure consists of an interconnected network of zinc and sulfate ions, extending in three dimensions in a fashion resembling the diamond structure. Sulfate ions are arranged in tetrahedral coordination around the zinc ion, which is on a $\bar{4}$ axis, and form Zn–O–S–O–Zn bridges between zinc ions. The guanidinium ions are not involved in metal coordination but form hydrogen bonds with the sulfate groups. A stereoscopic view of the arrangement of the ions in the unit cell is shown in Fig. 1.

Bond lengths and angles, calculated from the final atom parameters, are shown in Fig. 2 and Table 3. Root-mean-square components of the thermal displacements of the atoms, presented graphically in Fig. 2, are given in Table 4. Values for the bond lengths and angles of the guanidinium groups are not significantly different from those reported for $[C(NH_2)_3]Cl$, in which C–N distances are 1·318(6), 1·325(5) and 1·325(6) Å, and N–C–N angles are 120·8(8), 119·3(8) and 119·7(8)° (Haas, Harris & Mills, 1965). The zinc–oxygen bond length, 1·944(1) Å, is slightly shorter than the distances for tetrahedrally coordinated zinc reported by others: 1·986(30) Å and 1·978(10) Å in $Zn_2Mo_3O_8$ (Ansell & Katz, 1966); 1·962(7) Å in bis(dipivaloylmethanido)-zinc(II) (Cotton & Wood, 1964); 1·94, 1·99, 1·99 and 2·06 Å in $Na_2Zn_2Si_2O_7$ (Amirov, Nikitin, Iliukhin & Belov, 1967). The coordination tetrahedron of the zinc ion is significantly distorted. Two angles, O(1)–Zn–O(1‴) and O(1″)–Zn-O(1⁗), are considerably larger than the regular tetrahedral angle, and the rest of the angles of the tetrahedron are much smaller. The cause of this distortion of the tetrahedron, a compression along the $\bar{4}$ symmetry axis, is not clear. The sulfate groups display two distinctly different S–O distances depending upon metal ion coordination. The longer S–O bond length of 1·485(1) Å to the oxygen atoms involved in coordination to the zinc ion, compared

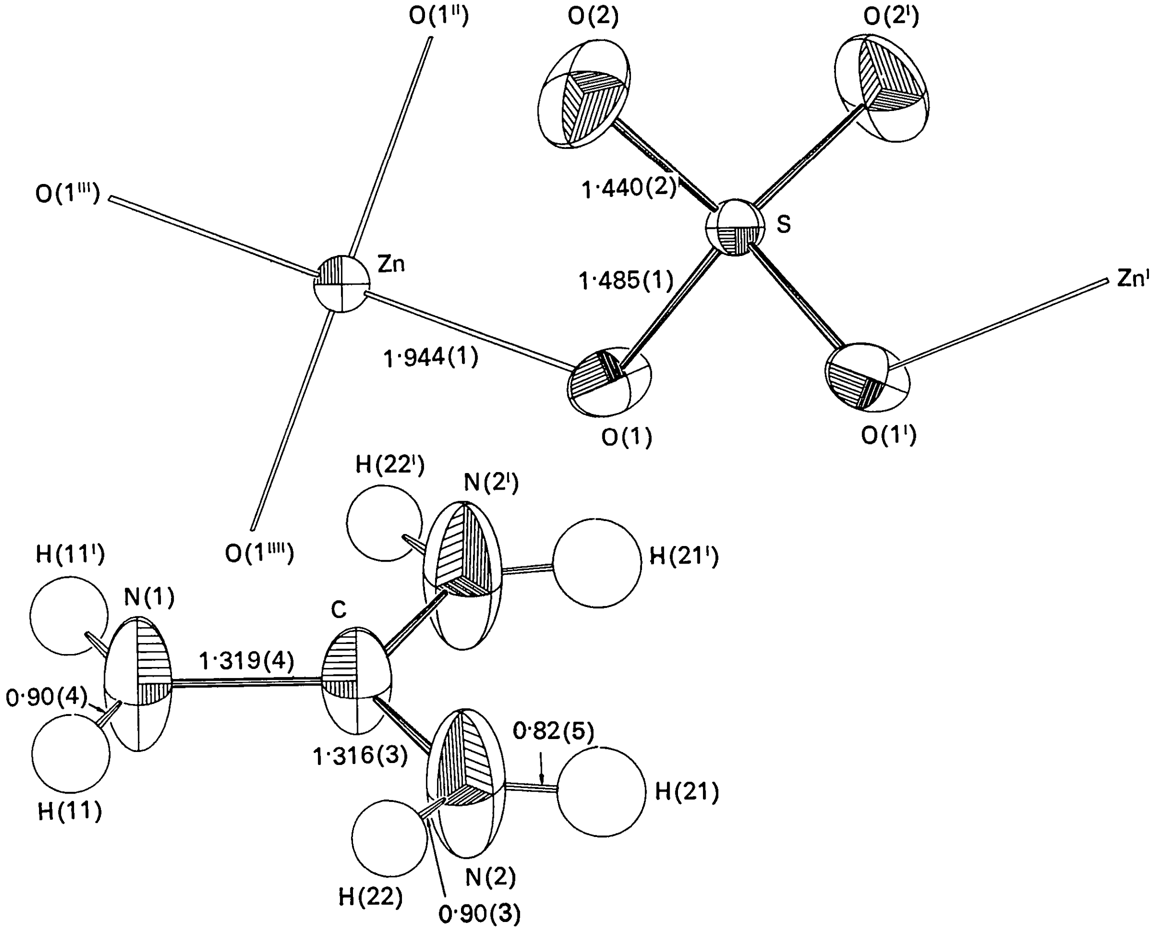

Fig. 2. Bond lengths (Å) and thermal motions of atoms in zinc guanidinium sulfate.

with that of 1·440(2) Å for the non-coordinated oxygen atoms, may be attributed to a smaller double-bond character of this S–O bond due to the zinc–oxygen interaction. The O(1) atoms are further characterized by an O(1)–S–O(1′) angle of 104·6(1)°, which is noticeably smaller than the 109·9°–110·8° for the other bond angles of the sulfate ion. The oxygen–oxygen distances within the sulfate tetrahedron are presented in Table 3. The O(2) atoms, which are not involved in coordination, are hydrogen bonded to the guanidinium ions. Hydrogen bond distances are: N(1)–H(11)–O(2″), 3·090(2) Å; and N(2)–(H22)–O(2″), 2·934(3) Å, where O(2″) is generated from O(2) by the transformation of ($\frac{1}{2}+x$, $-y$, $\frac{3}{4}-z$). The hydrogen bondings, which are represented by dashed lines in Fig. 1, create a helical arrangement of guanidinium and sulfate ions extending parallel to the *c* axis. H(21), which is not involved in any hydrogen bonding, has a higher temperature factor than the other hydrogen atoms as expected.

The guanidinium ion is planar due to the twofold symmetry along the C–N(1) vector. The equation of the plane calculated for the CN_3 group is

$$0{\cdot}8416\,X-0{\cdot}0000\,Y-0{\cdot}5402\,Z=-0{\cdot}9053\,,$$

where X, Y, Z are orthogonal Ångström space coordinates referred to **a**, **b**, **c**. The distances of the hydrogen atoms from this plane are as follows; H(11), 0·026 Å; H(21), −0·106 Å; H(22), 0·111 Å.

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Table 3. *Bond angles (in degrees) and some non-bonding distances (in* Å)

O(1)–Zn–O(1″)	102·74 (4)	O(1)–O(1″)	3·038 (2)
O(1)–Zn–O(1‴)	123·98 (9)	O(1)–O(1‴)	3·433 (3)
Zn—O(1)–S	121·08 (8)		
O(1)–S–O(2)	109·9 (1)	O(1)–O(2)	2·394 (2)
O(1)–S–O(2′)	110·9 (1)	O(1)–O(2′)	2·409 (2)
O(1)–S–O(1′)	104·6 (1)	O(1)–O(1′)	2·349 (3)
O(2)–S–O(2′)	110·5 (2)	O(2)–O(2′)	2·366 (4)
N(1)–C–N(2)	119·5 (2)		
N(2)–C–N(2′)	121·0 (3)		
C —N(1)–H(11)	117 (3)		
H(11)–N(1)–H(11′)	126 (5)		
C —N(2)–H(21)	116 (3)		
C —N(2)–H(22)	119 (2)		
H(21)–N(2)–H(22)	126 (4)		

Table 4. *R.m.s. components of thermal displacements of atoms*

$\alpha,\beta.\sigma$, are the angles between the crystal axes a,b,c, and principal axes of thermal ellipsoids.

			Orientation of axis		
	Axis	R.m.s. displacement	α	β	σ
Zn	1	0·123 (1) Å	0°	90°	90°
	2	0·123 (1)	90	0	90
	3	0·134 (1)	90	90	0
S	1	0·121 (1)	90	31 (1)	59 (1)
	2	0·122 (1)	0	90	90
	3	0·153 (1)	90	59 (1)	31 (1)
O(1)	1	0·110 (3)	75 (3)	47 (2)	47 (1)
	2	0·144 (2)	22 (2)	64 (3)	89 (2)
	3	0·255 (2)	75 (1)	50 (1)	43 (1)
O(2)	1	0·137 (3)	47 (1)	62 (1)	56 (1)
	2	0·212 (2)	80 (1)	32 (1)	60 (1)
	3	0·302 (3)	45 (1)	76 (1)	49 (1)
C	1	0·153 (4)	90	0	90
	2	0·172 (4)	63 (2)	90	27 (2)
	3	0·247 (4)	27 (2)	90	63 (2)
N(1)	1	0·148 (4)	90	0	90
	2	0·191 (4)	61 (1)	90	29 (1)
	3	0·319 (5)	29 (1)	90	61 (1)
N(2)	1	0·157 (3)	72 (2)	41 (4)	55 (3)
	2	0·191 (3)	66 (2)	49 (4)	51 (3)
	3	0·364 (4)	31 (1)	88 (1)	59 (1)

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Investigations of Dithienylglycollic Esters. II. The Crystal and Molecular Structure of Quinuclidinyl Di-α,α′-thienylglycollate

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Crystals of quinuclidinyl di-α,α′-thienylglycollate are monoclinic, space group $P2_1$ with two formula units in a cell having the dimensions $a=9{\cdot}762$, $b=11{\cdot}348$, $c=8{\cdot}556$ Å, $\beta=118{\cdot}405°$. The crystal structure was solved by a three-dimensional Patterson synthesis and refined by three-dimensional least-squares to a final R value of 0·042. The two thiophene rings make an angle of 96° to each other. The glycollic bridge connecting the thiophene rings with the quinuclidine is almost planar. The quinuclidine skeleton is twisted 5° around its threefold axis. An intermolecular hydrogen bond is present between the hydroxyl hydrogen atom of the glycollic bridge and the nitrogen atom in the quinuclidine.

Introduction

The crystal structure of the anticholinergic drug, quinuclidinyl di-α,α′-thienylglycollate,

$$(C_4H_3S)_2C(OH)CO_2C_7H_{12}N,$$

has been solved as part of our programme on the correlation between molecular configuration and pharmacological action of psychotomimetic compounds. The crystal structure of the closely related quinuclidinyl benzilate has been determined in the hydrobromide salt (Meyerhöffer & Carlström, 1969). As one of the important factors in psychotomimetic drugs is probably the availability of a free electron pair on a nitrogen atom (Gabel & Abood, 1965), it was regarded as important to solve the structure of a psychoactive base. All attempts to determine the structure of the base of the benzilate proved unsuccessful. For this reason the equally active thiophene compound was chosen as it could be analyzed directly by the 'heavy-atom' method. Another advantage was that the hydrogen positions could be determined, which was not possible in the case of the hydrobromide salt because of the strong interference of the heavy bromine atoms.

Experimental

The synthesis of quinuclidinyl di-α,α′-thienylglycollate has been described by Nyberg, Östman & Wallerberg (1970). Large, colourless, optically perfect crystals were prepared through recrystallization in acetone during slow cooling. The unit-cell dimensions were determined from Weissenberg photographs and from diffractometer measurements. The density of single crystals was established by flotation in mixed solvents.

Crystal data

Quinuclidinyl di-α,α′-thienylglycollate, $C_{17}H_{19}NO_3S_2$ F.W. 349·47

$a=9{\cdot}762\pm0{\cdot}005$ Å
$b=11{\cdot}348\pm0{\cdot}005$ Å
$c=8{\cdot}556\pm0{\cdot}005$ Å
$\beta=118{\cdot}405°\pm0{\cdot}010°$
$V=833{\cdot}72$ Å^3
D_m $1{\cdot}393\pm0{\cdot}005$ g.cm^{-3}
D_x $(Z=2)$ $1{\cdot}392\pm0{\cdot}002$ g.cm^{-3}

The only systematic absences were $0k0$ when k is odd. Since the molecule is asymmetric and the unit cell contains two molecules the space group can only be $P2_1$.

Intensity data were collected with a Philips automatic single-crystal diffractometer (PAILRED) using monochromatic Mo $K\alpha$ radiation. The crystal, having the dimensions $0{\cdot}42\times0{\cdot}62\times0{\cdot}41$ mm, was oriented about the b axis and 15 layers corresponding to the entire Cu sphere were recorded. There were 2171 independent reflexions of which 146 were too weak to be