Acta Cryst. (1967). **23**, 630

An X-ray Diffraction Study on Nickel(II) Chloride Dihydrate*

BY B. MOROSIN

Sandia Laboratory, Albuquerque, New Mexico, U.S.A.

(*Received* 8 *March* 1967)

The crystal structure of nickel(II) chloride dihydrate has been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data. The space group is $I2/m$ with lattice constants $a_0=6{\cdot}9093$, $b_0=6{\cdot}8858$, $c_0=8{\cdot}8298$ Å and $\beta=92{\cdot}246°$. The nickel ion is octahedrally coordinated by two water molecules (2·089 Å) and by four halide ions (2·387 and 2·410 Å) in a shared manner so as to form an extended linear chain. These strongly bonded chains are held together by weak bi- and trifurcated hydrogen bonds.

Introduction

Current interest in the magnetic properties of iron-group halide dihydrates (Narath, 1965) has prompted detailed structure determinations of several of these materials (Morosin & Graeber, 1965; Morosin, 1966*a*, *b*). Despite the different symmetries of the lattices, in all of these materials the metal ion is surrounded by four halide ions in a shared manner so as to form a strongly chemically bonded (polymeric) linear chain and by water molecules which fill the two remaining octahedral sites about the metal ions. The symmetry of the lattice is determined by the manner in which these polymeric chains are held together by hydrogen bonds.

Among the earlier studies which indicated the existence of various packing arrangements for these materials are the morphological investigations of Neuhaus (1938), the X-ray study on $CuCl_2.2H_2O$ by Harker (1936) and the electron diffraction studies of Vainshtein (1949, 1952*a*,*b*). These studies established that $CoCl_2.2H_2O$ and $NiCl_2.2H_2O$ are not isomorphous, contrary to the usual case for most divalent nickel and cobalt compounds. The room-temperature X-ray diffraction study on $NiCl_2.2H_2O$ reported here is part of a program to gain an understanding of the detailed relationship between these packing arrangements.

Experimental

The lattice constants for $NiCl_2.2H_2O$ ($a_0=6{\cdot}9093(5)$, $b_0=6{\cdot}8858(6)$, $c_0=8{\cdot}8298(4)$ Å and $\beta=92{\cdot}246(2)°$) were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1=1{\cdot}54050$ Å) by least-squares fit of 70 high 2θ values measured on films taken with a 115 mm diameter Weissenberg camera utilizing Straumanis film loading. Systematic absences of hkl for $h+k+l$ odd indicate a body-centered lattice, the statistics of the normal structure factors calculated from the intensity data indicate a centrosymmetric crystal structure, and therefore the most probable space group is $I2/m$. The experimentally determined density by the flotation technique is 2·622(2) g.cm^{-3}, compared with the value of 2·621 g.cm^{-3} calculated from the above lattice constants and four formula weights of $NiCl_2.2H_2O$ per cell.

Three-dimensional Mo $K\alpha$ intensity data were measured with the θ-2θ scan technique on a Picker diffractometer equipped with a Datex automatic control module for setting the angles on an E & A full circle Eulerian orienter and with a scintillation counter employing pulse-height discrimination. A unique set of 860 reflections (37 were considered unobserved) were obtained by averaging three sets of reflections (a unique set collected twice plus a symmetry-related set) after absorption corrections ranging from 3·42 to 4·70 had been applied ($\mu=57$ cm^{-1}; crystal bound by 7 faces of the type (010), (101) and (001) and of approximate size $0{\cdot}27\times0{\cdot}30\times0{\cdot}36$ mm).

Lorentz and polarization factors were applied and structure factors calculated with Ni^{2+}, Cl^- and O scattering factors from Table 3.3.1A and dispersion corrections for nickel and chlorine from Table 3.3.2C of *International Tables for X-ray Crystallography*.

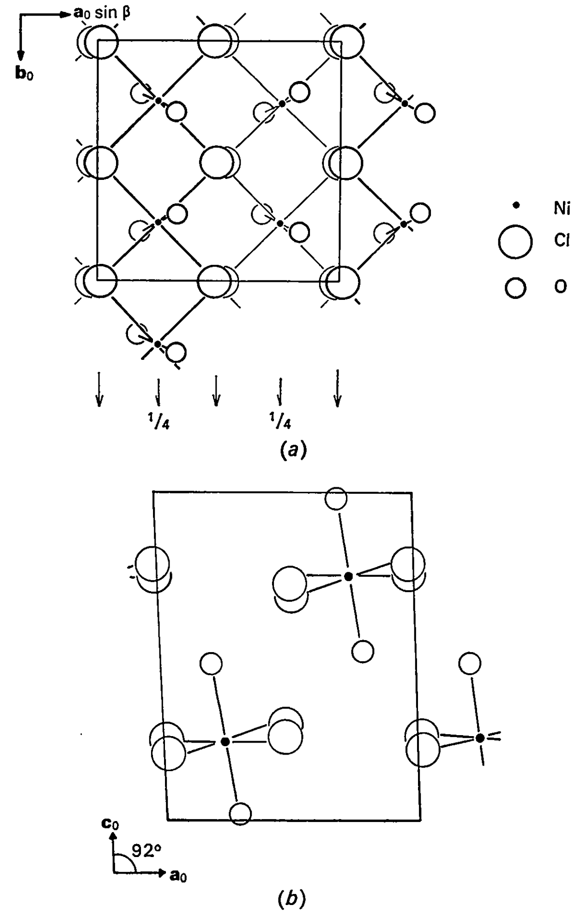
Structure determination

A three-dimensional Patterson function verified the relative positions suggested both by the mechanical behavior of crystals (when crushed or cut perpendicular to the **b** direction, collinear fibers are obtained suggesting presence of polymeric chains) and Vainshtein's (1952*b*) electron diffraction study. In the most general case, there are three choices for the position of the nickel atom in space group $I2/m$; these are special positions of the type (*e*), (*g*), or (*i*) which would place the nickel atom on an inversion center (case I), two-fold axis (case II), or mirror plane (case III), respectively. Geometrical consideration of the chains determine the positions of the chlorine atoms relative to the metal atom to be in mirror sites (special position (*i*) for cases I and II) or in general positions (case III); the oxygen atom would be in general positions (case I and II) or in a mirror site (case III). The Patterson

---

* This work was supported by the U.S. Atomic Energy Commission.

function clearly eliminates case III since the peak associated with the nickel–oxygen vector is not located on the mirror. This identical peak also suggests case II to be an unlikely candidate since the O–Ni–O angle would be about 164°; however, such a distorted octahedral environment about the nickel, though unusual, might be possible. Case II was eliminated from further consideration when the subsequent Fourier syntheses contained ghost peaks, and least-squares refinement resulted in higher isotropic thermal parameters than expected (5 cycles yielded $R = 0{\cdot}21$ for case II *versus* 0·09 for case I). Full-matrix least-squares refinement of positional and anisotropic thermal parameters was continued to a final reliability index, $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$, equal to 0·049. The function, $\Sigma w(F_o - F_c)^2$, was minimized; weights were assigned from counting statistics, the unobserved and the 002, 004 and 220 reflections being assigned zero weight. The final atomic positional and anisotropic thermal parameters are given in Table 1 and the list of observed and calculated structure factors appear in Table 2. The average and maximum parameter shifts as parts of the estimated standard deviation are both less than 0·01; the value for the standard error of an observation of unit weight is 0·91, indicating that the average value of the weights was somewhat underestimated. Final Fourier and difference syntheses verified the correctness of the structure. The latter indicated diffuse regions of positive density located about 0·9 Å from the oxygen atom which might have been interpreted as hydrogen positions; however, since only one electron density peak (0·29, 0·27, 0·54) is as well defined as the peaks found in other iron-group chloride dihydrates (Morosin & Graeber, 1965), no positions were assigned for the hydrogen atoms and their contribution is not included in Table 2.



(*a*)

(*b*)

Fig. 1. (*a*) A representation of the crystal structure of $NiCl_2.2H_2O$ viewed along the *c* axis. The infinite polymeric chains parallel the **b** direction in this packing arrangement. The nickel atoms are situated at inversion centers and the chlorine atoms are on the mirror planes at 0 and ½ along b_0. Oxygen atoms are misplaced (shifted along *x* away from the nickel atoms) from positions given in Table 1. (*b*) A representation viewed along the *b* axis. The two crystallographically different chlorine atoms are not coincident with each other as one views down the chain length. Symmetry axes (parallel to **b** and not shown) consist of four twofold rotation axes located at the origin, edge and face centers and four twofold inversion axes at (±¼, ±¼). Black dots: nickel; large open circles: chlorine; small open circles: oxygen.

Discussion

The prominent feature of the structures of the iron-group halide dihydrates is the polymeric chains as illustrated in Fig. 1(*a*) (in bold face) and in Fig. 2. In $NiCl_2.2H_2O$, these chains parallel the twofold axis of the monoclinic lattice in contrast to the arrangement (parallel to the **c** direction and, therefore, perpendicular to the twofold axis) found in the manganese, iron and cobalt compounds (hereafter MIC). In $NiCl_2.2H_2O$, the nickel atom is surrounded by four chlorine atoms in a near-square planar arrangement; however, such a plane (described by the five atoms) is tipped with respect to that plane about an adjacent nickel atom (Fig. 2) so as to form an angle of 167·94° between the two planes. The 87·6° Cl–Ni–Cl intrachain angle is similar to that found in MIC. In the case for MIC, the metal and chlorine atoms all coincide with the mirror plane of symmetry in space group $C2/m$. The

Table 1. *Atomic positional and thermal parameters in* $NiCl_2.2H_2O$

Anisotropic temperature factors are of the form $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{i=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\right)$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	¼	¼	¼	0·97 (2)	0·85 (2)	0·99 (2)	−0·03 (2)	0·02 (1)	0·01 (2)
Cl(1)	0·0109 (2)	0	0·2034 (1)	1·13 (4)	1·07 (4)	1·30 (4)	0	−0·16 (3)	0
Cl(2)	0·4896 (2)	0	0·2554 (1)	1·01 (4)	1·05 (4)	1·71 (4)	0	−0·03 (3)	0
O	0·2106 (4)	0·2121 (4)	0·4815 (3)	1·86 (9)	1·39 (9)	1·17 (9)	0·15 (7)	0·04 (6)	0·02 (7)

Table 2. *Observed and calculated structure factors for* $NiCl_2.2H_2O$

H	10FO	10FC
K= 0 L= 0		
2	365	-281
4	1463	1522
6	36	-25
8	667	634
10*	7	8
K= 0 L= 1		
1	948	-1070
-1	1197	1200
3	1005	1036
-3	338	-284
5	982	-965
-5	727	659
7	419	381
-7	60	-39
9	493	-464
-9	470	444
K= 0 L= 2		
0	1360	-1509
2	437	-365
-2	453	-412
4	1175	-1196
-4	936	-991
6	14	5
-6	82	69
8	771	-730
-8	614	-582
10*	31	40
-10	156	131
K= 0 L= 3		
1	338	237
-1	1297	-1279
3	695	-615
-3	452	401
5	327	259
-5	1003	-1039
7	324	-298
-7	201	186
9	276	267
-9	604	-571
K= 0 L= 4		
0	1707	1700
2	422	-340
-2	597	-602
4	1051	1046
-4	1102	1084
6*	4	8
-6	343	-308
8	582	541
-8	434	428
10	63	38
-10	143	-147
K= 0 L= 5		
1	586	-514
-1	1213	1200
3	1098	1083
-3	155	-153
5	438	-404
-5	706	707
7	517	507
-7*	8	7
9	208	-211
-9	408	393
K= 0 L= 6		
0	672	-638
2	303	218
-2	214	177
4	800	-733
-4	428	-425
6	198	188
-6	257	246
8	539	-512
-8	280	-274
K= 0 L= 7		
1	117	61
-1	749	-712
3	598	-544
-3	207	182
5	79	89
-5	642	-686
7	402	-374
-7	186	180
-9	426	-398
K= 0 L= 8		
0	637	604
2	411	-386
-2	589	-564
4	435	418
-4	504	497
6	148	-148
-6	415	-404
8	258	254
-8	242	237
K= 0 L= 9		
1	383	-367
-1	664	649
3	636	611
-3	261	-267
5	235	-241
-5	407	405
7	362	348
-7	111	-123
K= 0 L= 10		
0	286	-280
2	373	359
-2	294	289
4	341	-331
-4	186	-180
6	294	289
-6	217	216
K= 0 L= 11		
1	151	170
-1	284	-257
3	247	-241
-3	198	212
5	148	137
-5	280	-282
K= 0 L= 12		
0	244	258
2	247	-253
-2	327	-323
4	138	151
-4	277	281
K= 0 L= 13		
1	308	-323
-1	274	283
-3	270	-283
K= 1 L= 0		
1*	10	33
3	55	-63
5	54	40
7	39	-33
9*	31	2
K= 1 L= 1		
0*	9	25
2	243	215
-2	258	227
4	64	56
-4	44	42
6	67	58
-6	69	59
8	65	53
-8	46	42
10*	31	20
-10*	31	8
K= 1 L= 2		
1	99	120
-1	88	106
3	62	-44
-3	63	62
5	54	44
-5	152	136
7	44	-36
-7	59	59
9*	29	-7
-9	87	85
K= 1 L= 3		
0	478	-420
2	246	-232
-2	176	-166
4	261	-235
-4	235	-214
6	200	-184
-6	99	-94
8	127	-116
-8	67	-61
10	109	-101
-10	38	-35
K= 1 L= 4		
1	163	-149
-1	298	-260
3	208	-187
-3	285	-258
5	39	-36
-5	197	-183
7	47	-48
-7	208	-197
9*	33	-1
-9	128	-121
K= 1 L= 5		
0	262	228
2	354	386
-2	310	286
4	290	272
-4	112	107
6	231	218
-6	102	97
8	204	194
-8	43	33
-10*	28	-1
K= 1 L= 6		
1	389	358
-1	352	322
3	216	202
-3	340	327
5	211	199
-5	314	303
7	102	96
-7	215	209
9	68	61
-9	186	179
K= 1 L= 7		
0	247	-208
2	210	-203
-2	78	-76
4	226	-214
-4	93	-88
6	229	-222
-6*	27	11
8	169	-160
-8	30	18
K= 1 L= 8		
1	340	-322
-1	418	-393
3	351	-338
-3	344	-336
5	230	-223
-5	282	-281
7	183	-176
-7	240	-232
K= 1 L= 9		
0	45	28
2	92	89
-2*	25	20
4	128	129
-4	69	-60
6	113	115
-6	84	-55
-8	90	-83
K= 1 L= 10		
1	357	345
-1	309	295
3	274	273
-3	292	289
5	257	256
-5	230	228
-7	162	158
K= 1 L= 11		
0	77	54
2	38	17
-2	115	107
4	40	-2
-4	98	92
-6	128	123
K= 1 L= 12		
1	209	-209
-1	236	-230
3	229	-234
-3	165	-168
-5	137	-138
K= 1 L= 13		
0	121	-107
2	96	-68
-2	108	-113
K= 2 L= 0		
0	419	-283
2	1808	2041
4	164	-123
6	959	920
8	3	10
10	410	395
K= 2 L= 1		
1	990	1118
-1	640	-598
3	951	-956
-3	846	816
5	649	596
-5	194	-123
7	651	-602
-7	579	538
9	176	184
-9	34	-21
K= 2 L= 2		
0	493	-411
2	1149	-1301
-2	1127	-1168
4	60	-75
-4	35	-46
6	948	-915
-6	788	-748
8	29	24
-8	122	114
10	517	-487
-10	405	-382
K= 2 L= 3		
1	902	-893
-1	453	338
3	318	254
-3	1059	-1136
5	485	-422
-5	314	260
7	299	279
-7	777	-749
9	202	-199
-9	76	87
K= 2 L= 4		
0	592	-472
2	1277	1293
-2	1288	1323
4	193	-105
-4	473	-403
6	759	728
-6	680	651
8	57	38
-8	202	-200
-10	251	248
K= 2 L= 5		
1	1083	1136
-1	404	-315
3	501	-447
-3	863	890
5	755	715
-5	65	-44
7	280	-276
-7	345	322
9	302	298
-9	24	-1
K= 2 L= 6		
0	263	196
2	764	-701
-2	570	-516
4	246	211
-4	280	225
6	645	-612
-6	359	-344
8	121	124
-8	248	235
K= 2 L= 7		
1	682	-622
-1	183	124
3	84	76
-3	705	-698
5	488	-454
-5	195	187
7	124	115
-7	538	-511
-9	133	131
K= 2 L= 8		
0	544	-477
2	532	498
-2	584	550
4	244	-243
-4	487	-474
6	327	321
-6	349	338
8	79	-94
-8	294	-279
K= 2 L= 9		
1	677	633
-1	345	-316
3	298	-295
-3	531	512
5	478	458
-5	186	-179
7	142	-156
-7	295	283
K= 2 L= 10		
0	363	326
2	330	-311
-2	231	-224
4	336	384
-4	255	249
6	290	-279
-6	148	-155
K= 2 L= 11		
1	275	-248
-1	187	191
3	147	163
-3	274	-262
5	239	-229
-5	205	212
K= 2 L= 12		
0	313	-299
2	192	198
-2	273	272
4	195	-200
-4	290	-287
K= 2 L= 13		
1	260	244
-1	307	-305
K= 3 L= 0		
1	65	-62
3	110	119
5	119	-107
7	61	53
9	37	-38
K= 3 L= 1		
0	417	361
2	85	-79
-2	116	-103
4	145	134
-4	173	156
6	70	57
-6	41	38
8	31	15
-8*	27	13
10	52	51
-10	47	41
K= 3 L= 2		
1	76	-57
-1	84	70
3	186	157
-3	197	172
5	118	-104
-5*	25	-6
7	52	46
-7	155	145
9	44	-39
-9	36	29
K= 3 L= 3		
0	24	-47
2	384	-350
-2	428	-386
4	196	-176
-4	60	-48
6	145	-136
-6	145	-131
8	169	-154
-8	67	-60
-10*	32	-12
K= 3 L= 4		
1	331	-283
-1	194	-168
3*	23	8
-3	197	-172
5	163	-190
-5	277	-254
7*	29	12
-7	114	-108
9*	32	-17
-9	165	-156
K= 3 L= 5		
0	423	373
2	221	199
-2	70	60
4	256	245
-4	241	222
6	258	242
-6	39	38
8	141	133
-8	34	35
K= 3 L= 6		
1	200	178
-1	403	380
3	344	321
-3	328	308
5	99	92
-5	231	220
7	132	131
-7	260	256
-9	122	119
K= 3 L= 7		
0	94	-85
2	230	-217
-2	220	-201
4	234	-224
-4*	26	27
6	160	-134
-6	55	-50
8	203	-195
-8	36	38
K= 3 L= 8		
1	444	-408
-1	306	-281
3	217	-211
-3	346	-329
5	276	-266
-5	293	-282
7	141	-141
-7	178	-174
K= 3 L= 9		
0	91	77
2	81	80
-2	78	-65
4	77	83
-4	32	13
6	156	153
-6	111	-103
K= 3 L= 10		
1	248	253
-1	386	340
3	330	323
-3	242	237
5	198	197
-5	208	202
K= 3 L= 11		
0	79	72
2	36	31
-2	60	46
4	54	-42
-4	155	147
K= 3 L= 12		
1	280	-257
-1	162	-152
3	166	-168
-3	200	-193
K= 3 L= 13		
0	104	-96
K= 4 L= 0		
0	1583	1567
2	160	-120
4	1085	1096
6	27	-13
8	572	555
K= 4 L= 1		
1	658	-653
-1	877	797
3	712	640
-3	363	-294
5	654	-610
-5	661	607
7	280	278
-7	65	-76
9	401	-383
-9	420	401
K= 4 L= 2		
0	1103	-1107
2	81	-91
-2	71	-86
4	989	-982
-4	887	-842
6	19	-13
-6	70	68
8	626	-601
-8	509	-487
K= 4 L= 3		
1	381	280
-1	964	-880
3	642	-575
-3	318	254
5	306	282
-5	828	-785
7	293	-285
-7	110	114
9	249	241
-9	489	-469
K= 4 L= 4		
0	1098	1080
2	228	-188
-2	306	-321
4	857	838
-4	819	773
6	24	-11
-6	248	-230
8	499	486
-8	362	366
K= 4 L= 5		
1	380	-303
-1	932	873
3	802	782
-3	153	-135
5	287	-280
-5	863	827
7	418	408
-7	28	-28
-9	380	381
K= 4 L= 6		
0	657	-582
2	244	203
-2	271	229
4	638	-600
-4	448	-413
6	133	135
-6	250	235
8	433	-419
-8	250	-242
K= 4 L= 7		
1	151	115
-1	887	-825
3	549	-515
-3	155	151
5	109	111
-5	576	-542
7	349	-335
-7	129	131
K= 4 L= 8		
0	513	481
2	334	-314
-2	450	-413
4	378	371
-4	393	373
6	147	-152
-6	338	-319
K= 4 L= 9		
1	284	-258
-1	563	509
3	500	477
-3	213	-213
5	174	-185
-5	374	354
-7	116	-125
K= 4 L= 10		
0	273	-255
2	319	302
-2	298	279
4	274	-288
-4	184	-188
-6	218	211
K= 4 L= 11		
1	181	181
-1	277	-251
3	247	-235
-3	191	199
-5	242	-229
K= 4 L= 12		
0	222	217
2	238	-230
-2	277	-281
K= 5 L= 0		
1	63	48
3	123	-109
5	101	97
7	74	-74
9*	33	26
K= 5 L= 1		
0	137	-127
2	233	219
-2	256	238
4*	27	-1
-4	28	-25
6	44	45
-6	49	55
8	76	80
-8	50	48
K= 5 L= 2		
1	148	123
-1	67	80
3	130	-112
-3	28	-10
5	113	107
-5	180	186
7	79	-76
-7*	33	-7
9	35	17
-9	106	100
K= 5 L= 3		
0	365	-351
2	100	-79
-2*	9	3
4	199	-188
-4	239	-222
6	174	-161
-6	51	-46
8	66	-61
-8	52	-47
K= 5 L= 4		
1	24	-30
-1	231	-197
3	238	-213
-3	224	-205
5	42	34
-5	109	-96
7	77	-73
-7	211	-197
K= 5 L= 5		
0	80	78
2	294	276
-2	313	290
4	223	206
-4	25	18
6	147	147
-6	106	106
8	191	181
-8	33	22
K= 5 L= 6		
1	369	331
-1	221	201
3	87	82
-3	265	242
5	214	209
-5	284	268
7	51	48
-7	129	125
K= 5 L= 7		
0	221	-210
2	153	-138
-2*	28	12
4	154	-152
-4	144	-130
6	210	-206
-6	57	48
K= 5 L= 8		
1	200	-187
-1	370	-347
3	336	-321
-3	260	-248
5	142	-137
-5	218	-207
-7	216	-207
K= 5 L= 9		
0	33	-8
2	68	71
-2	75	63
4	128	123
-4	113	-103
-6*	30	-10
K= 5 L= 10		
1	340	323
-1	196	190
3	174	170
-3	257	243
-5	190	185
K= 5 L= 11		
0	45	28
2	32	4
-2	134	119
-4	37	32
K= 6 L= 0		
0*	5	-6
2	1040	971
4	17	-3
6	651	647
8	30	-18
K= 6 L= 1		
1	613	537
-1	430	-368
3	516	-465
-3	641	588
5	314	306
-5	168	-169
7	386	-379
-7	462	446
K= 6 L= 2		
0	15	3
2	945	-882
-2	905	-840
4	29	-22
-4	48	48
6	645	-636
-6	564	-549
8*	3	-8
-8	72	76
K= 6 L= 3		
1	682	-680
-1	272	281
3	299	279
-3	718	-688
5	388	-378
-5	108	108
7	242	248
-7	513	-487
K= 6 L= 4		
0	172	-145
2	808	746
-2	764	683
4	47	-56
-4	192	-179
6	548	550
-6	449	434
8	28	-11
-8	149	-151
K= 6 L= 5		
1	684	638
-1	186	-153
3	206	-196
-3	658	622
5	447	440
-5	61	-76
7	163	-174
-7	445	427
K= 6 L= 6		
0	230	215
2	563	-517
-2	498	-456
4	133	135
-4	243	233
6	421	-414
-6	297	-288
K= 6 L= 7		
1	550	-516
-1	151	133
3	121	130
-3	535	-498
5	386	-379
-5	107	109
-7	366	-345
K= 6 L= 8		
0	305	-287
2	371	346
-2	348	321
4	194	-200
-4	298	-282
-6	219	216
K= 6 L= 9		
1	421	392
-1	179	-179
3	157	-162
-3	379	356
-5	137	-148
K= 6 L= 10		
0	268	262
2	235	-224
-2	213	-211
-4	240	233
K= 6 L= 11		
1	247	-235
-1	180	187
K= 7 L= 0		
1	47	-31
3	82	67
5	83	-78
7	58	48
K= 7 L= 1		
0	193	181
2	44	-44
-2	57	-54
4	96	91
-4	107	101
6	45	34
-6*	29	22
-8*	31	4
K= 7 L= 2		
1	37	-28
-1	45	39
3	108	99
-3	115	106
5	89	-81
-5	32	-15
7	62	48
-7	123	113
K= 7 L= 3		
0	41	-28
2	223	-210
-2	245	-231
4	120	-110
-4	40	-20
6	97	-87
-6	100	-97
K= 7 L= 4		
1	186	-172
-1	103	-99
3*	30	12
-3	121	-110
5	116	-113
-5	183	-174
7*	33	20
-7	68	-61
K= 7 L= 5		
0	235	236
2	130	121
-2	46	31
4	168	164
-4	166	156
6	170	166
-6	33	16
K= 7 L= 6		
1	112	106
-1	246	236
3	257	228
-3	214	202
5	52	44
-5	146	138
K= 7 L= 7		
0	65	-45
2	158	-148
-2	153	-148
4	157	-152
-4	40	37
-6	44	-49
K= 7 L= 8		
1	292	-286
-1	180	-174
3	129	-123
-3	234	-225
-5	200	-192
K= 7 L= 9		
0	63	60
2	62	52
-2	61	-57
-4	38	26
K= 7 L= 10		
1	137	138
-1	242	242
K= 8 L= 0		
0	732	700
2	58	43
4	619	598
6	21	-8
K= 8 L= 1		
1	326	-302
-1	456	439
3	294	285
-3	220	-221
5	311	-299
-5	441	431
K= 8 L= 2		
0	725	-712
2	28	19
-2	47	58
4	619	-598
-4	579	-557
6	19	-14
-6	34	62
K= 8 L= 3		
1	218	216
-1	526	-504
3	420	-414
-3	110	106
5	236	239
-5	449	-426
K= 8 L= 4		
0	549	523
2	44	-50
-2	87	-86
4	519	501
-4	425	403
6	34	-34
-6	118	-121
K= 8 L= 5		
1	112	-107
-1	497	482
3	401	386
-3	86	-92
5	120	-123
-5	444	427
K= 8 L= 6		
0	419	-411
2	145	149
-2	212	212
4	377	-365
-4	385	-317
K= 8 L= 7		
1	130	134
-1	430	-420
3	388	-383
-3	96	100
K= 8 L= 8		
0	252	250
2	195	-191
-2	213	-204
K= 9 L= 0		
1*	30	14
3*	31	-39
5	51	38
K= 9 L= 1		
0	47	-26
2	91	92
-2	97	95
4*	26	5
-4*	28	-1
K= 9 L= 2		
1	56	49
-1	33	32
3	41	-39
-3	31	9
5	46	49
-5	80	83
K= 9 L= 3		
0	164	-159
2	63	-61
-2	40	-26
4	108	-104
-4	113	-113
K= 9 L= 4		
1	45	-36
-1	105	-104
3	101	-101
-3	112	-107
K= 9 L= 5		
0	65	63
2	147	148
-2	144	141
-4	35	22
K= 9 L= 6		
1	171	173
-1	122	122
-3	136	138
K= 9 L= 7		
0	115	-111
K= 10 L= 0		
0	67	56
2	458	454
K= 10 L= 1		
1	253	256
-1	188	-197
3	207	-207
-3	332	340
K= 10 L= 2		
0	54	57
2	490	-501
-2	476	-480
K= 10 L= 3		
1	347	-355
-1	118	123
K= 10 L= 4		
0	30	-32

polymeric chains differ in one other aspect; in $NiCl_2.2H_2O$, the oxygen atoms are not equally spaced (see Fig. 2; 2·921 and 3·965 Å) while in MIC the oxygen atoms are equally spaced (and equal to the c_0 axis length). The manner in which the polymeric chains are held together by hydrogen bonds also differs; whereas in MIC, these bonds are between the oxygen and one neighboring chlorine atom, in $NiCl_2.2H_2O$ these bonds appear to be the weak bi- and trifurcated type as have been found in several other hydrates: $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, Morosin (1966*b*), Dance & Freeman (1965); $[Mg(H_2O)_6]_3.[Ce(NO_3)_6]_2.6H_2O$, Zalkin, Forrester & Templeton (1963); $[Co(H_2O)_4Cl_2].2H_2O$, Mizuno (1960); and $[Ni(H_2O)_4Cl_2].2H_2O$, Mizuno (1961). The diffuse positive density on the final difference synthesis suggests that one of these hydrogen bonds is located along the bisector of the Cl–O–Cl angle (with Cl–O separations of 3·428 and 3·383 Å, Table 3) while the other is located so that the oxygen–hydrogen vector points towards the center of a triangle defined by an oxygen atom and a chlorine atom on an adjacent chain (2·941 and 3·542 Å, respectively) and the nearer oxygen atom on the same chain (2·921 Å; see Fig. 3). A neutron diffraction study is planned to clarify these hydrogen locations.

Table 3. *Interatomic separations and angles in* $NiCl_2.2H_2O$

Intrachain separations and angles

Ni–Cl(1)	2·410 (2) Å	Cl(1)–Ni–Cl(2)	87·63 (7)°
Ni–Cl(2)	2·387 (2)	Cl(1)–Ni–O	87·89 (14)
Ni–O	2·089 (5)	Cl(2)–Ni–O	89·59 (14)
Cl(1)–Cl(2)	3·322 (2)		
Cl(1)–Cl(2)	3·462 (2)		
Cl(1)–O	3·131 (5)		
Cl(1)–O	3·247 (5)		
Cl(2)–O	3·161 (5)		
Cl(2)–O	3·184 (5)		
O–O	2·921 (7)		
O–O	3·965 (7)		

Interchain separations

Cl(1)–O	3·428 (5) Å	Cl(1)–Cl(1)	3·589 (2)
Cl(1)–O	3·542 (5)	Cl(2)–Cl(2)	4·316 (2)
Cl(2)–O	3·383 (5)	O–O	2·941 (7)
Cl(2)–O	3·521 (5)	O–O	3·999 (7)
		O–O	4·146 (7)

The octahedral environment about the nickel atom (Fig. 2 and Table 3) is slightly distorted, and the nickel–chlorine and nickel–oxygen separations are similar to those found in $[Ni(H_2O)_4Cl_2].2H_2O$ (2·38 and 2·10 Å). The 2·40 Å average value for the nickel–chlorine separation indicates that the nature of these bonds is more covalent (1·39+0·99 Å; Pauling, 1960) than ionic (0·72+1·81 Å). Such a trend of increasing covalency as one proceeds along the iron-group elements can be noted in Table 4. It also appears that as one increases the covalent character of the metal–chlorine bonds, the difference in length of the two metal–chlorine separations become smaller. (In MIC, two additional trends which were not previously pointed out and which result from covalency or a 'charge transfer effect' can be seen; the two different near-neighbor contact separations between chains decrease in the same manner from the manganese to the cobalt compound). The smaller amount of ionic character in the bonds allows a tighter packing of the chains in the cobalt and nickel compounds (molar volumes obtained from lattice constants are 119·0, 113·2, 110·1, and 104·9 Å^3 for the Mn, Fe, Co and Ni compounds, respectively).

The anisotropic thermal parameters are in agreement with the strong bonding or close contact separations found in this compound in a manner similar to that which had been noted in MIC. For example, the magnitude of the Cl(2) thermal parameter along $\mathbf{c}_0$ (perpendicular to the nickel–chlorine bonds) is significantly larger than along the chain or bonding direction; the identical parameter for Cl(1) is not as large as found for Cl(2) and this is probably due to the shorter (3·589 *versus* 4·316 Å) interchain interaction involving this atom. Similarily the larger thermal parameter for the

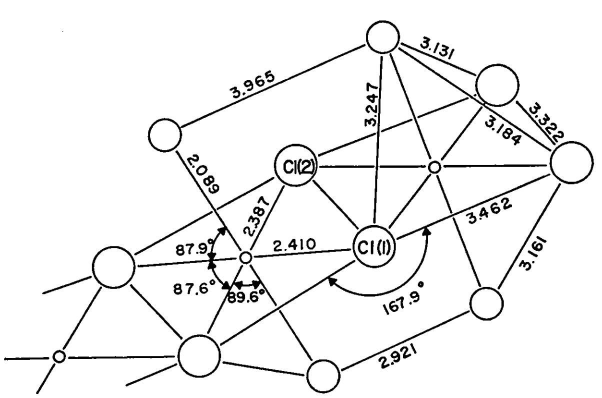


Fig. 2. A sketch of the polymeric chain as well as the coordination about the nickel atom. The edge of the nickel octahedron formed by the two chlorine atoms is shared by an adjacent octahedron; the two octahedrons are tipped with respect to one another. This results in a close and a more distant oxygen–oxygen near-neighbor along the chain in contrast to that found in other iron-group chloride dihydrates.

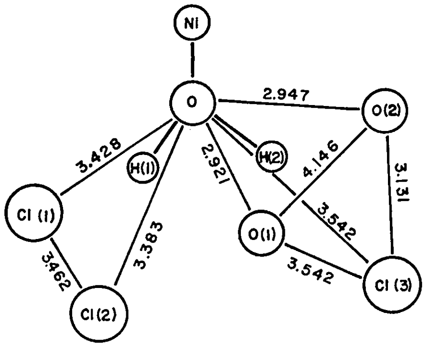


Fig. 3. A sketch of the oxygen near-neighbors. The separations of the atoms which are believed to be involved in the weak bi- and trifurcated hydrogen bonds are shown. Hydrogen labeled H(1) appears to be located along the bisector of Cl(1) and Cl(2) while H(2) would be between O(1), O(2) and Cl(3).

Table 4. *A comparison of interatomic separations* (Å) *found in iron-group chloride dihydrates*

	Mn	Fe	Co	Ni
Expected*				
Ionic M–Cl	2·61	2·57	2·55	2·53
Covalent M–Cl		2·22	2·31	2·38
Experimental				
M–Cl	2·515	2·488	2·459 (3)†	2·387 (2)
M–Cl′	2·592	2·542	2·487 (3)	2·410 (2)
M–O	2·150	2·074	2·034 (5)	2·089 (5)
Cl–O	3·767	3·713	3·695 (6)	3·542 (5)‡
				3·521 (5)
Cl–Cl	3·992	3·989	3·958 (4)	3·589 (2)
				4·316 (2)
Difference in M–Cl and M–Cl′ separation	0·077	0·054	0·028	0·023

* The radii used to obtain the expected ionic and covalent separations are taken from Pauling (1960); no value is given for the six-coordinated covalent manganese(II) radius.

† The errors in MIC are all similar.

‡ These separations in $NiCl_2.2H_2O$ are believed to be influenced by hydrogen interactions.

oxygen atom is associated with a direction perpendicular to the chain as well as to the 2·921 Å oxygen–oxygen separation.

The assistance of Mr R.A.Trudo is gratefully acknowledged.

References

Dance, I. G. & Freeman, H. C. (1965). *J. Inorg. Chem.* **4**, 1555.

Harker, D. (1936). *Z. Kristallogr.* **93**, 136.

International Tables for X-ray Crystallography (1962). Vol.III, p.202. Birmingham: Kynoch Press.

Mizuno, J. (1960). *J. Phys. Soc. Japan*, **15**, 1412.

Mizuno, J. (1961). *J. Phys. Soc. Japan*, **16**, 1574.

Morosin, B. & Graeber, E. J. (1965). *J. Chem. Phys.* **42**, 898; and reference therein.

Morosin, B. (1966*a*). *J. Chem. Phys.* **44**, 252.

Morosin, B. (1966*b*). *Acta Cryst.* **21**, 280.

Narath, A. (1965). *Phys. Rev.* **136**, A766; and references therein.

Neuhaus, A. (1938). *Z. Kristallogr.* **98**, 113.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd edn. Ithaca: (Cornell Univ. Press).

Vainshtein, B. K. (1949). *Dokl. Adak. Nauk SSSR*, **68**, 301.

Vainshtein, B. K. (1952*a*). *Dokl. Akad. Nauk SSSR*, **83**, 227.

Vainshtein, B. K. (1952*b*). *Zh. Fiz. Khim.* **26**, 1774.

Zalkin, A., Forrester, J. D. & Templeton, D. H. (1963). *J. Chem. Phys.* **39**, 2881.

Acta Cryst. (1967). **23**, 634

Complex Sulphur Compounds. I. The Crystal Structure of $MgGa_2S_4$

By C. Romers, Beatrijs A. Blaisse and D. J. W. IJdo
Laboratory of Inorganic Chemistry, University of Leiden, The Netherlands

(*Received* 6 *February* 1967)

Single monoclinic crystals of $MgGa_2S_4$ are obtained by heating the elements in appropriate amounts *in vacuo* at 1200°C. The space group is $C2/c$, $Z=12$ and the unit-cell dimensions are $a=12{\cdot}74$, $b=22{\cdot}54$, $c=6{\cdot}43$ Å and $\beta=108{\cdot}8°$. Comparison with analogous $M^{II}M_2^{III}S_4$ compounds and consideration of lattice dimensions lead to a cubic close-packed array of sulphur ions. Initial parameters were derived from a Patterson analysis and the structure was refined by Fourier and least-squares methods using 1310 observed reflexions. Three double layers of anions with Ga in tetrahedral interstices in the first and third double layer and with Mg in octahedral interstices in the second one are succeeded by an empty double layer. The interspacing of the empty layers is larger than that of the filled layers and results in a distortion of the array of sulphur ions.

Introduction

Structures of complex sulphides with composition $M^{II}M_2^{III}S_4$ have been reported by several authors. M^{II} and M^{III} being metals of the first transition period, spinel (Lotgering, 1956; Koerts, 1965; Bouchard & Wold, 1966; Holt, Bouchard & Wold, 1966) or defect NiAs-structure types (Jellinek, 1957) usually occur. We have extended the investigations to compounds in which M^{II} is Mg, Mn, Fe, Co, Ni and M^{III} is Al, Ga, Nb or Ta.