Table 1 were obtained by inspection of the experimental data previous to the structure determination. The employment of the averages of Table 1 facilitated the solution of the problem to be published at a future date. It is of interest that, in this case, the structural origin for the renormalization depends upon the presence of six rationally dependent atoms. Their position vectors, $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_6$ satisfy the following relations approximately

$$\mathbf{r}_2-\mathbf{r}_1 \approx \mathbf{r}_4-\mathbf{r}_3 \approx \mathbf{r}_6-\mathbf{r}_5 \approx (\tfrac{1}{3}, 0, \tfrac{1}{3})\ , \qquad (4\cdot2)$$

$$\mathbf{r}_1-\mathbf{r}_3 \approx (0, \tfrac{1}{2}, 0)\ , \qquad (4\cdot3)$$

and

$$\mathbf{r}_1-\mathbf{r}_5 \approx (0, \tfrac{1}{4}, \tfrac{1}{4})\ . \qquad (4\cdot4)$$

5. Concluding remarks

As may be seen from the foregoing sections the treatment of the problem of rational dependence does not require a previous knowledge of structure. The renormalization procedure is based merely upon inspection of the averages of subsets. This process should be readily amenable to programming on automatic computing facilities.*

More general effects of rational dependence, which are included in $(2\cdot1)$ when $\nu=2$ and $m_1 \neq -m_2$ or $\nu>2$, change only the higher order terms in the phase determining formulas and therefore do not usually have a significant effect.

In general the average $\overline{E_{\mathbf{h}}^2}$ over all vectors in reciprocal space is unity, even for the case of rationally dependent atoms. However, when atomic coordinates overlap in projection, $\mathbf{E}_{\mathbf{h}}^2>1$ in that projection. With the finite number of data available from experiment this may cause a deviation from unity of the over-all average.

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* Since this paper was written, a program for renormalization has been developed by Dr Stanley Block of the National Bureau of Standards for the IBM 704.

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The Crystal Structure of Iron(II) Chloride Tetrahydrate

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The crystal structure of iron(II) chloride tetrahydrate has been determined by means of electron-density projections down the three crystallographic axes. Atomic coordinates have been refined by three-dimensional least-squares treatment of the diffraction data of the three equatorial zones. The crystals are monoclinic, space group $P2_1/c$ with $a=5\cdot91$, $b=7\cdot17$, $c=8\cdot44$ Å, $\beta=112° 10'$. The structure consists of discrete $Fe(H_2O)_4Cl_2$ groups, two per unit cell. They are distorted octahedra and it is suggested that they are held together by O–H · · · Cl hydrogen bonds. Bond distances within a group are Fe–Cl, 2·38; Fe–O(1), 2·09; Fe–O(2), 2.59 Å.

1. Introduction

The available crystal structural data on hydrated metallic halides are extremely limited (e.g. see Wells, 1954). There are only about ten detailed structure determinations reported in the literature and of these, only three, namely cobalt(II) chloride dihydrate ($Co(H_2O)_2Cl_2$) (Vajnštejn, 1949), copper(II) chloride dihydrate ($Cu(H_2O)_2Cl_2$) (Harker, 1936 and Petersen & Levy, 1957), and copper(II) fluoride dihydrate ($Cu(H_2O)_2F_2$) (Geller & Bond, 1958) refer to simple salts of transition metals. Of general interest in such crystals are (*a*) the nature of the metal–halogen bonds, (*b*) the stereochemical requirements of the water molecule, and (*c*) the nature of the hydrogen bonding. We propose to undertake a study of the crystal structures of a series of hydrated iron(II) halides as a contribution to the crystal chemistry of hydrated halides generally. The tetrahydrates of the chloride and fluoride of iron(II) are both readily available and, as such

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pairs of hydrates are few in number, a comparison of these two structures is useful. The structure analysis of the fluoride is described in a later paper (Penfold & Taylor).

2. Experimental

Pale green crystals of $FeCl_2.4\,H_2O$ were obtained following the directions given by King (1950), and the composition confirmed by chloride analysis. Fragments of suitable shape and size for X-ray examination were cut from larger crystals and sealed inside Lindemann glass capillary tubes in contact with a little concentrated hydrochloric acid. Under these conditions, they remained stable for several months.

Crystallographic data

In 'The Barker Index of Crystals' Vol. II (Porter & Spiller, 1956) the following data are given for monoclinic $FeCl_2.4\,H_2O$. The axial ratios a:b:c are 1·184:1:1·636 with $\beta = 111°\,25'$ and the density 1·96 g.cm.$^{-3}$. The unit-cell parameters, measured from our X-ray data are

$$a = 5{\cdot}91 \pm 0{\cdot}03,\ b = 7{\cdot}17 \pm 0{\cdot}03,\ c = 8{\cdot}44 \pm 0{\cdot}04\ \text{Å},\ \beta = 112°\ 10' \pm 20'.$$

These were obtained using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). They give axial ratios 0·825:1:1·177, which agree satisfactorily with those reported above if the 'Barker' a and c axes are interchanged and then a is halved. Density observed (by flotation) 1·93 g.cm.$^{-3}$; calculated 1·976 for two formula units per unit cell. Linear absorption coefficient for Mo $K\alpha$ radiation 30·5 cm.$^{-1}$. Absent spectra: $0k0$ for k odd and $h0l$ for l odd, indicating $P2_1/c$ as the probable space group, which was confirmed by the structure analysis.

Relative intensities of 164 $hk0$, $h0l$ and $0kl$ reflections were determined by visual estimation of Weissenberg photographs. Mo $K\alpha$ radiation was used and the crystals measured not more than 0·4 mm. normal to the X-ray beam.

3. The structure determination

The two iron atoms in the unit cell must lie on centers of symmetry, one of which may be chosen for the origin. The rest of the asymmetric unit is then made up of one chlorine atom and two water molecules. As the dominating interatomic vectors (apart from Fe–Fe vectors on special positions) will be those between Fe at the origin and Cl in a general position, the chlorine position was found readily from axial projections of the Patterson function. Then, with the assumption made that the signs of structure factors for all but the weakest reflections were those of the sum of Fe and Cl contributions, $0kl$, $h0l$ and $hk0$ Fourier syntheses were evaluated and gave approximate representations of the electron density viewed down a, b and c axes, respectively. Oxygen atoms of water molecules proved to be resolved only in the a axis projection which was refined by difference syntheses. The x coordinate of O(1) was determined from the b axis projection, in which two such atoms, related by a screw axis, overlap. The x coordinate of O(2) was found by trial from b and c axis projections which were also refined by difference syntheses. Subsequently all atomic coordinates and isotropic thermal parameters were refined by a three-dimensional least-squares treatment of all $0kl$, $h0l$ and $hk0$ data using the Remington Rand UNIVAC 1103 digital computer, non-diagonal terms in the matrix of the normal equations being ignored. Atomic scattering factors used for iron were those listed for Fe^{++} by Thomas & Umeda (1957), and for chlorine (Cl^-) and oxygen those of Berghuis *et al.* (1955). At the end of the preliminary refinement, O(1) appeared to lie on a screw axis at 0, 0, $\frac{1}{4}$. Prior to the least-squares treatment, it was moved slightly away and remained slightly displaced (0·15 Å) when refinement ceased. However, in view of the lack of resolution of this atom in both b and c axis projections, its x coordinate 0·024 must remain somewhat in doubt. This uncertainty does not significantly affect the observed Fe–O(1) separation.

Final coordinates and also thermal parameters B from the expression $\exp(-B \sin^2 \theta/\lambda^2)$ are listed in Table 1 for all atoms, together with mean standard deviations derived from the least-squares data as set out by Hughes & Lipscomb (1946). Standard deviations in interatomic distances which involve iron are those listed for chlorine and oxygen coordinates. Standard deviations for other distances are given in Table 3 and all angles are assumed to have the mean standard deviation of 1·3°. A list of observed and calculated structure factors is given in Table 2. Final values of

$$R = \Sigma \big| |F_o| - |F_c| \big| \div \Sigma |F_o| \quad \text{and} \quad r = \Sigma w (F_o^2 - F_c^2)^2 \div \Sigma w F_o^4$$

were 0·126 and 0·040, respectively, unobserved reflections being included in the calculation as one third of the minimum observable value in each case. No direct indication of hydrogen atoms was obtained from difference syntheses, random fluctuations in the (100) difference map being as much as 1·5 e.Å^{-2}.

Table 1. *Atomic coordinates and thermal parameters with their standard deviations*

	x	y	z	X (Å)	Y (Å)	Z (Å)	σX_i (Å)	B (Å^2)
Fe	0	0	0	0	0	0		1·64 ± 0·01
Cl	0·309	0·233	0·075	1·83	1·67	0·63	0·008	1·80 ± 0·01
O(1)	0·024	0·004	0·253	0·14	0·03	2·14	0·036	2·35 ± 0·03
O(2)	−0·274	0·294	−0·073	−1·62	2·11	−0·62	0·024	3·95 ± 0·05

Table 2. *Observed and calculated structure factors* (*scaled by* 10)

h k l	F_o	F_c
0 0 0	—	2000
2	664	662
4	398	358
6	209	−197
8	*	27
10	96	83
12	213	179
0 1 1	487	435
2	278	−243
3	434	389
4	221	−211
5	314	267
6	*	−53
7	221	203
8	145	96
9	165	129
10	112	122
0 2 0	72	−60
1	125	−121
2	253	−224
3	169	−170
4	600	592
5	109	−92
6	431	428
7	*	12
8	382	385
9	*	40
10	*	86
0 3 1	294	357
2	233	209
3	302	318
4	229	205
5	253	249
6	*	56
7	205	217
8	112	−88
9	145	134
10	117	−110
0 4 0	817	819
1	100	100
2	366	350
3	229	220
4	262	250
5	96	105
6	92	−81
7	*	−8
8	*	44
9	*	−69
0 5 1	266	291
2	205	−172
3	229	232
4	193	−179
5	209	127
6	*	−48
7	165	86
8	*	69
9	117	75
0 6 0	129	98
1	*	−99
2	*	23
3	129	−161
4	278	267
5	72	−108
6	225	219
7	*	19
8	213	208
0 7 1	185	76
2	137	119
3	149	138
4	137	123
5	153	184
6	*	35
0 8 0	233	256
1	*	55
2	141	142
3	96	133
4	112	119
1 0 0	398	482
2	559	−512
4	100	61
6	169	131
8	358	367
10	217	212
12	117	109
$\bar{1}$ 0 2	543	662
4	853	1151
6	386	381
8	197	178
10	92	−74
12	*	9
2 0 0	85	41
2	266	149
4	640	657
6	350	371
8	237	214
$\bar{2}$ 0 2	547	−509
4	439	350
6	386	365
8	467	525
10	185	217
12	*	87
3 0 0	772	875
2	539	535
4	398	363
6	*	−17
8	*	−13
10	*	10
$\bar{3}$ 0 2	262	160
4	60	74
6	209	−194
8	197	152
10	185	190
12	233	243
4 0 0	463	454
2	*	−32
4	*	−11
6	*	17
8	173	152
10	145	121
$\bar{4}$ 0 2	539	536
4	624	661
6	141	164
8	*	51
10	92	−75
12	109	58
5 0 0	*	−7
2	*	22
4	246	233
6	241	206
8	141	138
$\bar{5}$ 0 2	*	−29
4	358	345
6	394	366
8	358	378
10	100	121
12	*	30
6 0 0	298	274
2	302	270
4	233	201
$\bar{6}$ 0 2	*	33
4	*	−5
6	*	−21
8	225	183
10	185	203
12	189	190
7 0 0	241	227
2	*	54
$\bar{7}$ 0 2	290	272
4	237	245
6	*	48
8	*	−3
10	*	−14
12	117	84
8 0 0	*	−5
2	173	184
$\bar{8}$ 0 4	205	189
6	233	212
8	157	170
10	*	41
$\bar{9}$ 0 8	161	123
10	145	129
1 1 0	318	−281
2	793	848
3	282	240
4	358	316
5	237	−204
6	338	334
7	165	139
8	117	130
2 1 0	282	250
2	877	994
3	270	−198
4	161	138
5	185	138
6	374	365
7	117	−93
8	96	94
3 1 0	*	31
2	112	88
3	72	−69
4	539	535
5	89	74
6	89	73
7	*	−64
8	185	209
4 1 0	266	−228
2	270	236
3	237	202
4	322	285
5	193	−166
6	181	164
7	141	103
8	105	116
5 1 0	141	98
2	459	467
3	109	−74
4	*	21
5	*	38
6	237	248
7	*	−23
6 1 0	129	118
2	112	87
3	121	−113
4	225	220
5	105	86
7 1 0	153	−128
2	*	43
3	112	106
4	165	168

* Unobserved reflection.

4. Discussion

From views of the crystal structure down *a* and *b* axes as shown in Fig. 1 it can be seen that there are discrete $Fe(H_2O)_4Cl_2$ units in the sense that every water molecule and every chlorine atom is associated with one and only one iron atom. The units are distorted octahedra, the dimensions of which are shown in Fig. 2. The difference of 0·50 Å in the two Fe–O distances is highly significant and we conclude that $H_2O(2)$ molecules are very weakly held in each group. The shorter distance of 2·09 Å does not differ significantly

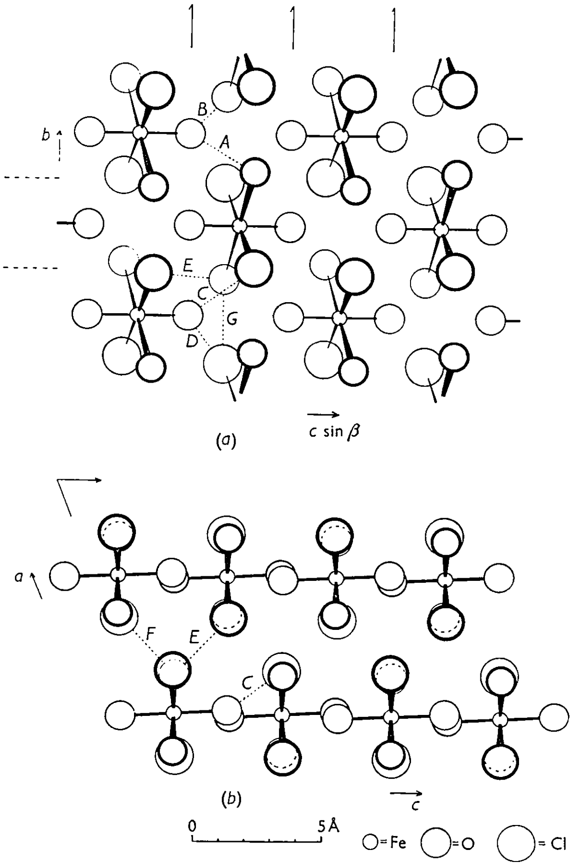


Fig. 1. Views of the crystal structure (*a*) down the *a* axis and (*b*) down the *b* axis. Broken lines indicate the short intergroup distances listed in Table 3.

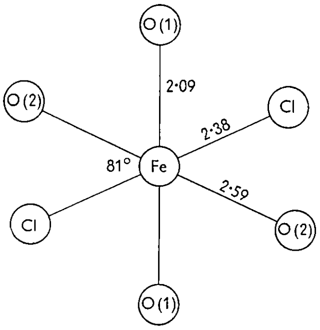
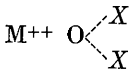


Fig. 2. Dimensions of $Fe(H_2O)_4Cl_2$ unit. Angles other than O(2)–Fe–Cl do not differ significantly from 90°.

from 2·17 Å, the shortest observed Fe–H_2O distance in $Fe_3(PO_4)_2.4\,H_2O$ (Ito & Mori, 1951), apparently the only other structure in which this length has been measured. Neither of these distances differs significantly from the sum of the ionic radii of iron and oxygen (2·16 Å). The observed Fe–Cl bond length of 2·38 Å is significantly shorter than the sum of ionic radii (0·76+1·80). However, as similar shortening is observed in the tetrahydrate of iron(II) fluoride (Penfold & Taylor), no conclusions should be drawn from this evidence alone regarding the possible covalent character of the Fe–Cl bonds. In anhydrous $FeCl_2$ (Ferrari *et al.*, 1929) the corresponding distance is not known with precision because of a large uncertainty in the chlorine parameter.

Environment of water molecules and chlorine atoms

In most hydrates of oxy-salts and in the hexahydrates of $MgCl_2$ and $AlCl_3$, water molecules have a tetrahedral charge environment as in ice (Wells, 1954). Even in the dihydrates of $CuCl_2$ (Petersen & Levy, 1957), CuF_2 (Geller & Bond, 1958) and $CoCl_2$ (Vajnštejn *et al.*, 1949) where departure from pure ionic bonding is expected, this simple situation still exists. The doubly charged metal ion provides the positive region opposite the lone pairs of the water oxygen, and this oxygen also forms two hydrogen bonds with neighboring halogens, the whole



$$\mathrm{M}^{++}\ \mathrm{O}\genfrac{}{}{0pt}{}{\cdot\cdot X}{\cdot\cdot X}$$

groupings being planar or nearly so.

In this structure, the key to the exact nature of the charge environment of the water molecule is the hydrogen bonding scheme. This will be considered with the aid of the list of seven intergroup distances given in Table 3, all of which are well under the sums of the relevant van der Waals radii (3·96 for $R_{\mathrm{OH}}+R_{\mathrm{Cl}}$ and 3·56 for $R_{\mathrm{OH}}+R_{\mathrm{O}}$) but not sufficiently short (with the possible exception of the O–Cl bond *E* of 3·07 Å) to be necessarily hydrogen bonds. Assuming that all four hydrogen atoms in the asymmetric unit are used for bonding, a maximum of eight different O–H · · · O bonds but only four O–H · · · Cl bonds could be formed. We shall now consider the angles subtended at the oxygen atoms by pairs of close atoms. The most likely hydrogen bond formation will occur for values closest to the angle H–O–H in water, i.e. 105°. Further, the angle distribution is most unfavorable for the oxygen atoms to form one bond of each type, O–H · · · O and

Table 3. *Interatomic distances and bond angles external to the discrete groups*

Bond or angle	Magnitude	Designation on Fig. 1
O(1)–O(2)	2·96 ± 0·04 Å	*A*
O(1)–O(2)	3·05 ± 0·04	*B*
O(1)–Cl*	3·22 ± 0·04	*C*
O(1)–Cl*	3·45 ± 0·04	*D*
O(2)–Cl(*a*)*	3·07 ± 0·025	*E*
O(2)–Cl(*b*)*	3·18 ± 0·025	*F*
O(2)–Cl(*c*)*	3·40 ± 0·025	*G*
∠ O(2)–O(1)–O(2)	89°	
∠ O(1)–O(2)–O(1)	91°	
∠ Cl–O(1)–Cl	103°	
∠ Cl(*a*)–O(2)–Cl(*b*)	85°	
∠ Cl(*a*)–O(2)–Cl(*c*)	91°	
∠ Cl(*b*)–O(2)–Cl(*c*)	94·5°	

* Suggested hydrogen bond.

O–H · · · Cl. Therefore O(1) must form a pair of bonds either with two O(2) atoms or with two Cl atoms, the pair being repeated across a center of symmetry (see Fig. 3). If we assume that the bonds are made to Cl atoms on account of the favorable angle Cl–O(1)–Cl of 103°, then O(2) must also form its bonds with Cl atoms. As all the angles of type Cl–O(2)–Cl are closely similar, it is likely that there is in fact a disordered arrangement of hydrogen bonds about O(2), two hydrogen atoms being used to form three bonds, *E*, *F*, *G*.

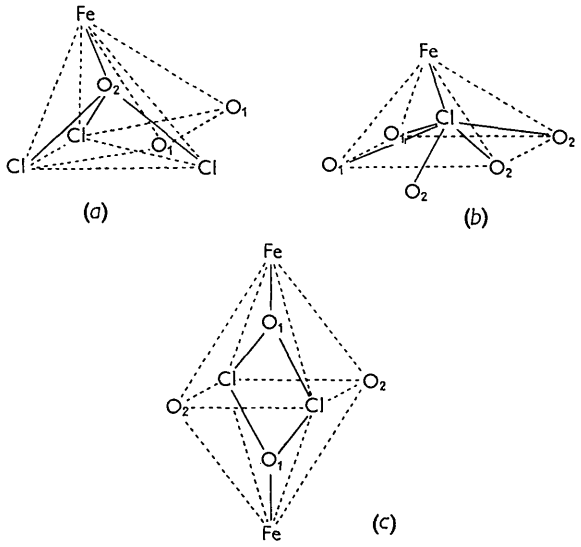


Fig. 3. Atomic environments of (*a*) O(2), (*b*) Cl and (*c*) O(1). Full lines denote suggested hydrogen bonds and bonds to Fe within a group. Broken lines show the coordination polyhedra.

Fig. 3 shows the nature of the environment of $H_2O(1)$, $H_2O(2)$ and Cl, non-bonding neighbors within a group being ignored as they are in the following discussion. Type (1) water molecules have two chlorine nearest neighbors to which they are hydrogen bonded, and two water nearest neighbors of type (2) at van der Waals distances in addition to an ion Fe^{++} at a distance of 2·11 Å. Both the FeO(1)ClCl and FeO(1)O(2)O(2) groups are approximately planar and the complete environment approximates to a square-based pyramid. Type (2) water molecules have three chlorine nearest neighbors, to any two of which they are hydrogen bonded, and two water nearest neighbors of type (1) at van der Waals distances in addition to an ion Fe^{++} at a distance of 2·59 Å. $H_2O(2)$ would then be in the center of a distorted tetrahedron made up of FeClClCl, the two negative regions of the water environment being distributed over three chloride ions. Chlorine nearest neighbors are five water molecules, two of type (1) and three of type (2), any four of which are hydrogen bonding, and in addition an ion Fe^{++} at a distance of 2·38 Å which forms the apex of a pyramid with a roughly square base of four of the water molecules. It is of interest to note that the hydroxyl ion (of comparable size to Cl) in hydrates of NaOH (Wunderlich, 1959) has also a square-based pyramidal coordination polyhedron but with the OH^- ion lying in the square base.

It may be observed in conclusion that the tetrahedral environment rule holds for the water molecules to a good approximation. The main cohesive forces between groups appear to be hydrogen bonds of type O–H · · · Cl. There is no evidence to conflict with magnetic susceptibility data reported by Pauling (1940) which show this hydrate to have four unpaired electrons per iron atom and hence that the iron to chlorine bonding is not strongly covalent. It would appear that water molecules of type (2) have their positions determined more by the packing requirements of the large Cl^- ions than by a strong attachment to Fe^{++}.

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