1970 observed reflections- Coghi *et al.* do not list the atomic parameters, but the over-all structure, including the bond distances and angles, is in reasonable agreement with our results.

Ward *et al.* describe their structure in a unit cell that is slightly more convenient than the one we have chosen ($a=6\cdot905(5)$, $b=11\cdot680(4)$, $c=17\cdot993(23)$ Å, $\beta=100\cdot68(10)°$; space group, $P2_1/n$).

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Refinement of the Crystal Structure of Iron Oxychloride

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The lattice constants and the positional parameters of crystals of the compound FeOCl, the crystal structure of which was reported more than 35 years ago, have been redetermined from single-crystal X-ray diffraction data. Except for corrections to the lattice constants and positional parameters, the previous description of the structure remains valid. The most probable space group is *Pmnm*. The revised lattice constants, one of which differs substantially from those previously reported, are $a=3\cdot780\pm0\cdot005$, $b=7\cdot917\pm0\cdot005$, and $c=3\cdot302\pm0\cdot005$ Å. The positional and anisotropic thermal parameters were refined by the method of least-squares, with 294 non-zero diffractometer data, to a conventional $R=0\cdot055$. Based on the refined parameters, the $Fe^{3+}-O^{2-}$ bond distances are $1\cdot964\pm0\cdot008$ and $2\cdot100\pm0\cdot010$ Å, and the $Fe^{3+}-Cl^-$ bond distance is $2\cdot368\pm0\cdot007$ Å.

Introduction

The crystal structure of the compound FeOCl, determined many years ago (Goldsztaub, 1934, 1935), was refined because a more accurate description of the structure was required for a proposed (Muir & Wiedersich, 1967*a*) redetermination of the nuclear quadrupole moment of the 14·4 keV level of ^{57}Fe ($Q^{57m}Fe$) from FeOCl data.

This investigation may be expected to aid in resolving the large discrepancies among values of $Q_{57m}Fe$ determined from data for other compounds [see discussions by Grant (1966) and by Artman, Muir & Wiedersich (1968)] because FeOCl has certain features which make it especially suitable for determining this constant. An unusually large ferric ion nuclear quadrupole interaction is observed in the ^{57}Fe Mössbauer spectrum of FeOCl (Muir & Wiedersich, 1967*a*). Furthermore, evaluation of the electric field gradient tensor at the ferric ion sites in the crystal, which is required in the analysis, is greatly facilitated by the small number of variable positional parameters in the FeOCl crystal structure and by the constraints imposed by the crystal symmetry and ferric ion site symmetry (see below).

In the proposed analysis, the particular step that requires very accurate structural data is a lattice sum calculation of the electric field gradient tensor components. The high sensitivity of such calculations to small variations in structural parameters has been discussed previously (Grant, 1966; Muir & Wiedersich, 1967*b*; Artman *et al.*, 1968).

Experimental

Crystals of FeOCl were grown by G. P. Espinosa of this Laboratory by a procedure similar to that reported

by Goldsztaub (1935). A mixture of $FeCl_3$ and Fe_2O_3 in one end of an evacuated and sealed glass tube was maintained at 350°, and the other end of the tube about 25° cooler, for two weeks. The FeOCl crystals, which grew in the cooler end of the tube, were similar in their thin blade-like habit and red color to those described by Goldsztaub.

From Buerger precession photographs taken at 23°C, the most probable space group, $Pmnm-D_{2h}^{13}$, reported by Goldsztaub (1934, 1935), was confirmed, and the lattice constants were measured. The crystallographic data are summarized in Table 1. The presently reported values of a and c agree satisfactorily with the values, 3·75 and 3·3 Å respectively, given by Goldsztaub (1934, 1935). The presently reported value of b agrees reasonably well with the value of 7·95 Å in the first of Goldsztaub's two papers on the FeOCl structure, but differs substantially from his subsequently revised value, in the second paper, of 7·65 Å, which must be concluded to be erroneous. As Goldsztaub (1935) pointed out, the thinness of the crystals in the b direction causes difficulty in determining b from b-axis rotation photographs. However, there is no such difficulty in the case of the Buerger precession photographs, from which the value of b appeared to be determinable with about the same accuracy as a and c. The presently reported values of the lattice constants were confirmed during the course of diffractometer measurement of the intensities.

Table 1. *Crystallographic data for* FeOCl

Space group: $Pmnm-D_{2h}^{13}$
Lattice constants: $a = 3\cdot780 \pm 0\cdot005$ Å
                               $b = 7\cdot917 \pm 0\cdot005$
                               $c = 3\cdot302 \pm 0\cdot005$
Unit-cell volume = 98·82 Å³
Unit cell contains 2FeOCl
Formula weight = 107·3
Calculated density = 3·606 g.cm⁻³
Measured density = 3·55 g.cm⁻³ (Goldsztaub, 1935)
Systematic absences: $h0l$ with $h+l$ odd

Intensities were measured with a Buerger–Supper–Pace–Picker automatic diffractometer, Mo $K\alpha$ radiation, and balanced Zr and Y filters. The crystal was rotated about the c axis. The continuous scan mode was used, with a scan rate of 1° per minute, scan interval of 2° or more, and background counts of 60 seconds or more at the beginning and at the end of the scan interval. All independent $I(hkl)$ with $(\sin\theta)/\lambda \leq 0\cdot99$, a total of 500, were measured. Of these, 308 were greater than the background intensity. One reflection, 010, partially cut off by the beam stop, was estimated visually from a precession photograph. Unfortunately, it was found during the course of the refinement that the scan interval had not been made wide enough for the reflections 112, 113, 114, 204, 115, 225, 016, 116, 046, and 206, causing their measured intensities to be lower than their true intensities. It was decided to omit these ten reflections from the refine-

ment calculations, rather than to remeasure them, because the remaining data were more than adequate to solve the problem.

The crystal used for the intensity measurements was a thin rectangular plate with dimensions 0·42 (parallel to rotation axis, c) × 0·10 × 0·005 mm. The intensities were corrected for absorption by the method of Burnham (1966). The linear absorption coefficient for Mo $K\alpha$ radiation is 86·6 cm⁻¹. The correction factors were between 1·04 and 1·79.

The intensities were reduced to relative $|F_o(hkl)|^2$ by application of the usual Lorentz–polarization and Tunell factors.

Refinement of the structural parameters

All the atoms are in twofold mm special positions of space group $Pmnm$: the two Fe^{3+} ions are in the positions (b) with coordinates $0,y,\frac{1}{2}$ and $\frac{1}{2},\bar{y},0$; the two O^{2-} and two Cl^- ions are in two sets of positions (a) with coordinates $0,y,0$ and $\frac{1}{2},\bar{y},\frac{1}{2}$. Thus there are three variable positional parameters, one for each of the three atoms comprising the asymmetric unit. There are nine anisotropic thermal parameters, three for each of the three atoms.

The positional parameter values given by Goldsztaub (1934, 1935), $y_{Fe} = 0\cdot097$, $y_O = -0\cdot083$, and $y_{Cl} = 0\cdot305$, were taken as the starting values for the refinement.

The parameters were refined by the method of least-squares with the Busing, Martin & Levy (1962) computer program *ORFLS*. The function minimized was $\sum w(|F_o| - (1/k)|F_c|)^2$, in which k is a scale factor and w is a weighting function (for $|F_o| \geq 14$, $w = 200/|F_o|^2$; for $14| > |F_o \geq |F_{o,min}|$, $w = 1$). Only the $|F_o|$ above background were included in the least-squares calculations. Fourteen non-zero reflections were omitted from the least-squares calculations: 010, which was estimated visually; 002, 004, and 006, for which peak-heights rather than integrated intensities were measured; and the ten reflections mentioned earlier. However, during all refinement cycles, structure factors were calculated for the unobserved data and for the omitted non-zero reflections.

Scattering factors and dispersion corrections for Fe^{3+} and Cl^- were taken from *International Tables for X-ray Crystallography* (1962); for O^{2-}, the scattering factors given by Tokonami (1965) were used.

The refinement was carried out first with isotropic and finally with anisotropic thermal parameters. The procedure was repeated with atomic, rather than ionic, scattering factors, but this did not produce any significant changes in the parameter values or in the final value of the agreement index $R = \sum ||F_o| - |F_c||/\sum|F_o|$. The final parameter values are given in Table 2. All three positional parameters differ substantially from the previously reported values. Comparison of the $|F_o|$ with the $|F_c|$ calculated from the final parameter values is shown in Table 3. The final value of R is 0·055

for the data included in the least-squares calculations. For the unobserved reflections and the other reflections omitted from the least-squares calculations, Table 3 shows the agreement of $|F_o|$ and $|F_c|$ to be satisfactory.

Table 2. Positional and thermal parameters and their estimated standard errors*

	$10^5 y$	$10^5 \beta_{11}$†	$10^5 \beta_{22}$	$10^5 \beta_{33}$
Fe^{3+}	11568 (13)	791 (35)	362 (11)	2481 (64)
O^{2-}	−4832 (61)	1113 (189)	293 (46)	2432 (324)
Cl^-	33003 (22)	3649 (105)	392 (17)	2403 (119)

* The estimated standard errors ($\times 10^5$) are given in parentheses.

† The β_{ii} are for the temperature factor expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; for all three ions the site symmetry requires $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

Discussion of the structure

The structure is illustrated in Fig. 1. Bond distances, bond angles, and other interatomic distances, computed with the Busing, Martin & Levy (1964) computer program ORFFE, are given in Table 4.

Except for the corrections to the lattice constants and positional parameters found in the present investigation, Goldsztaub's (1934, 1935) description of the structure remains valid. The structure consists of neutral layers, of composition FeOCl, oriented perpendic-

Table 4. Interatomic distances and angles*

Bond distances	$Fe^{3+}-O^{2-}$	$1\cdot964 \pm 0\cdot008$ Å
	$Fe^{3+}-O^{2-}$	$2\cdot100 \pm 0\cdot010$
	$Fe^{3+}-Cl^-$	$2\cdot368 \pm 0\cdot007$
Edges of octahedra	$O^{2-}-O^{2-}$	$2\cdot624 \pm 0\cdot011$
	$O^{2-}-O^{2-}$	$3\cdot302 \pm 0\cdot005$
	$O^{2-}-Cl^-$	$2\cdot995 \pm 0\cdot017$
	$O^{2-}-Cl^-$	$3\cdot357 \pm 0\cdot012$
	Cl^--Cl^-	$3\cdot302 \pm 0\cdot005$
Intralayer distance	Cl^--Cl^-	$3\cdot680 \pm 0\cdot006$
Intralayer distance	$Fe^{3+}-Fe^{3+}$	$3\cdot107 \pm 0\cdot008$
Bond angles	$O^{2-}-Fe^{3+}-O^{2-}$	$80\cdot34 \pm 0\cdot21°$
	$O^{2-}-Fe^{3+}-O^{2-}$	$103\cdot64 \pm 0\cdot66$
	$O^{2-}-Fe^{3+}-Cl^-$	$83\cdot97 \pm 0\cdot43$
	$O^{2-}-Fe^{3+}-Cl^-$	$101\cdot22 \pm 0\cdot31$
	$Cl^--Fe^{3+}-Cl^-$	$88\cdot42 \pm 0\cdot35$
	$O^{2-}-Fe^{3+}-O^{2-}$	$148\cdot48 \pm 0\cdot88$
	$O^{2-}-Fe^{3+}-Cl^-$	$172\cdot39 \pm 0\cdot30$

* The limits of error are $3 \times$ the estimated standard errors computed by the program ORFFE.

ular to the b direction. The translational period along b contains two layers. The layers are formed by the sharing of O–O and O–Cl edges of cis-FeCl₂O₄ octahedra. The outermost atoms on each side of the layers are the Cl⁻ ions. The Cl⁻ ions of adjacent layers are approximately close packed. As Goldsztaub (1934, 1935) pointed out, the arrangement accounts very

Table 3. Comparison of $10 \times |F_o|$ with $10 \times |F_c|$ calculated from final parameter values

Also listed are the calculated values of $10 \times \alpha = 10 \times \tan^{-1}(B/A)$. Within each reciprocal lattice level l the data are in the order of increasing detector angle. The 14 non-zero data omitted from the least-squares calculations are indicated by asterisks.

well for the perfect cleavage plane perpendicular to **b** and for the flexibility of the crystals, which allows them easily to be bent and then returned to their original shape.

Each Fe^{3+} ion is bonded to two O^{2-} ions at a distance of $1 \cdot 964 \pm 0 \cdot 008$ Å and to two others at a distance of $2 \cdot 100 \pm 0 \cdot 010$ Å. The average of these distances is $2 \cdot 03$ Å. These distances are nearly the same as the $Fe^{3+}-O^{2-}$ bond distances in α-Fe_2O_3 (hematite), the structure of which was recently refined by Blake, Hessevick, Zoltai & Finger (1966). In α-Fe_2O_3 each Fe^{3+} ion is bonded to three O^{2-} ions at a distance of $1 \cdot 945$ Å and to three others at a distance of $2 \cdot 116$ Å, in an octahedral arrangement. These distances also average to $2 \cdot 03$ Å. The $Fe^{3+}-O^{2-}$ bond distances in FeOCl are also nearly the same as the $Fe^{3+}-O^{2-}$ bond distances reported for γ-FeOOH (lepidocrocite), the structure of which is closely related to that of FeOCl. In γ-FeOOH there are layers similar to those in FeOCl, with OH^- ions instead of Cl^- ions. The $Fe^{3+}-O^{2-}$ bond distances in γ-FeOOH, $1 \cdot 94$ and $2 \cdot 14$ Å, which average to $2 \cdot 04$ Å, were reported by Goldsztaub (1935) at the same time as his results on FeOCl. These average $Fe^{3+}-O^{2-}$ distances are all somewhat longer than the octahedral $Fe^{3+}-O^{2-}$ distances in garnets (Lind &

Geller, 1969, and references cited therein) and in perovskite-like structures (Coppens & Eibschütz, 1965).

The $Fe^{3+}-Cl^-$ bond distance, $2 \cdot 368 \pm 0 \cdot 007$ Å, is practically the same as the $Fe^{3+}-Cl^-$ bond distance, $2 \cdot 39$ Å, in $FeCl_3$ (Wooster, 1932). It is substantially greater than the $Fe^{3+}-Cl^-$ bond distance of $2 \cdot 30$ Å found in the trans-$[FeCl_2(H_2O)_4]^+$ ion (Lind, 1967). Interference between Cl^- ions in cis positions is probably the reason for the longer $Fe^{3+}-Cl^-$ distances in FeOCl and $FeCl_3$.

The $FeCl_2O_4$ octahedron in FeOCl is considerably distorted. The edge lengths vary from $2 \cdot 624$ to $3 \cdot 357$ Å. (The edge lengths not given in Fig. 1 are those of the Cl^--Cl^- and $O^{2-}-O^{2-}$ edges parallel to **c**, which are equal to the lattice constant c.) The shortest $O^{2-}-O^{2-}$ and $O^{2-}-Cl^-$ edges of the octahedron, $2 \cdot 624$ Å and $2 \cdot 995$ Å respectively, are those which are shared with other octahedra. The packing of the four O^{2-} and two Cl^- ions about the Fe^{3+} ion is such that the centers of all the O^{2-} ions are well within one hemisphere about the Fe^{3+} ion, opposite to the Cl^- ions. The $O^{2-}-Fe^{3+}-O^{2-}$ and $O^{2-}-Fe^{3+}-Cl^-$ angles between bonds directed toward opposite corners of the octahedron are $148 \cdot 48$ and $172 \cdot 39°$ respectively. These may be compared with an $O^{2-}-Fe^{3+}-O^{2-}$ angle of $162 \cdot 21°$ in the α-Fe_2O_3
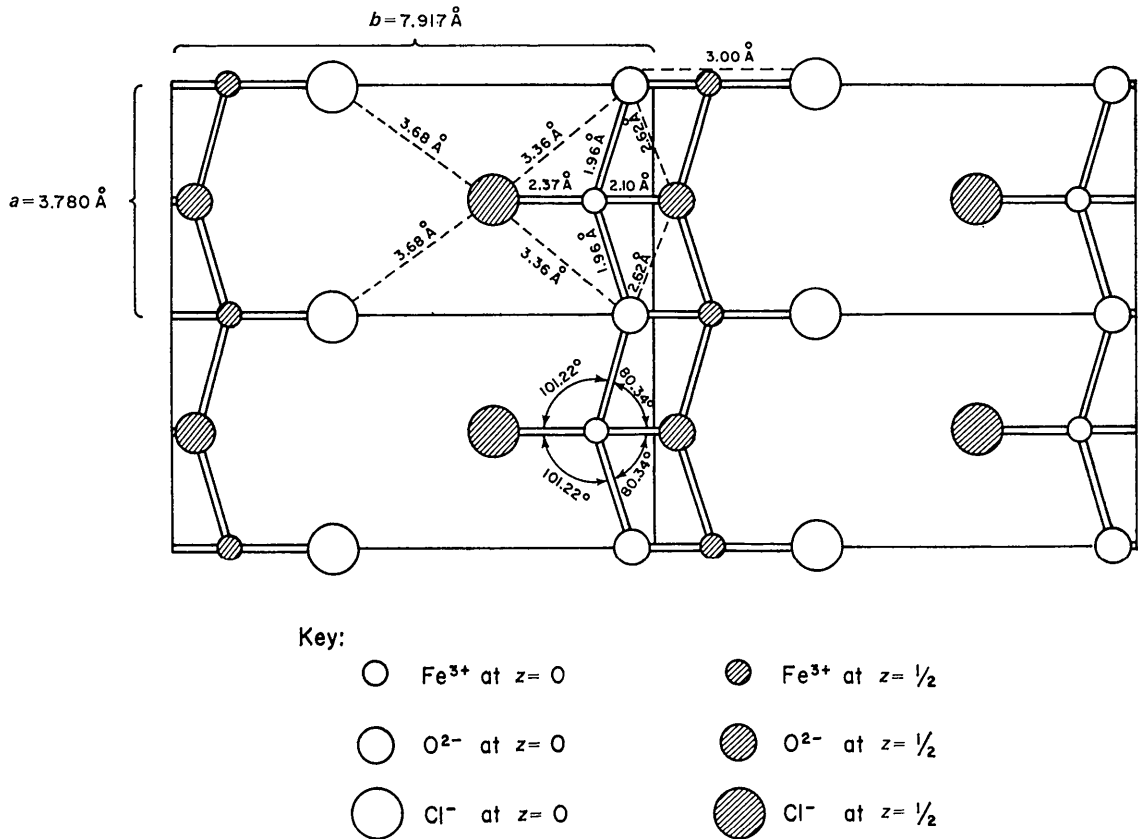

Fig. 1. Projection of structure on (001) showing four complete unit cells.

structure (Blake, *et al.*, 1966). The other bond angles at the Fe^{3+} ion are in the range 80·34 to 103·64°, which is about the same as that reported for α-Fe_2O_3 (Blake, *et al.*, 1966).

The interlayer Cl^-–Cl^- distance, 3·680 Å, closely approximates twice the van der Waals radius of chlorine.

The principal axes of the thermal motion probability ellipsoids are required by the crystal symmetry to be parallel to the crystallographic axes (as are the principal axes of the electric field gradient tensors, which were discussed in the *Introduction*). The root-mean-square components of thermal displacement along the three principal axes of the thermal motion probability ellipsoids are given in Table 5; these were computed with the Busing, Martin & Levy (1964) computer program *ORFFE*.

Table 5. *Thermal motion probability ellipsoids*

Root-mean-square component of thermal displacement* along principal axis parallel to

	a	b	c
Fe^{3+}	0·076±0·005 Å	0·107±0·005 Å	0·117±0·005 Å
O^{2-}	0·090±0·023	0·097±0·023	0·116±0·023
Cl^-	0·163±0·007	0·112±0·007	0·115±0·008

* The limits of error are 3 × the estimated standard errors computed by the program *ORFFE*.

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The Relation Between γ- and α-Chymotrypsin. II.*
Direct Comparison of the Electron Densities at 5·5 Å Resolution

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Extensive comparisons have been made between 5·5 Å resolution electron density maps of the two molecules in the asymmetric unit of α-chymotrypsin, and between the α-chymotrypsin electron density and a 5·5 Å electron density map of γ-chymotrypsin. The transformations describing the relation between the respective pairs of molecules have been refined by a least-squares method. On the basis of these comparisons the respective electron density maps are shown to be identical, within experimental error. It is concluded that at this resolution there is no significant evidence of any conformational difference between the two α-chymotrypsin molecules or between α- and γ-chymotrypsin.

Introduction

α-Chymotrypsin (αCHT) and γ-chymotrypsin (γCHT) are the end products of the activation of chymotryp-

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* The first paper of this series is Matthews, Cohen, Silverton, Braxton & Davies (1968).

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sinogen A and are distinguished by their respective crystal forms (Kunitz, 1938; Desnuelle, 1960). αCHT crystallizes at pH 4·4 in a monoclinic space group with two molecules per asymmetric unit and the structure has been determined to atomic resolution (Matthews, Sigler, Henderson & Blow, 1967; Sigler, Blow, Matthews & Henderson, 1968). γCHT crystallizes at pH 5·6 in a tetragonal space group and a 5·5 Å resolution elec-